



ł

This is to certify that the

thesis entitled

DE HAAS-VAN ALPHEN STUDY OF THE AuGa<sub>2</sub> ALLOY PHASE presented by

John Jesse Higgins

has been accepted towards fulfillment of the requirements for

Physics

roed Major professor

Date 18 November 1977

**O**-7639

....

# DE HAAS-VAN ALPHEN STUDY OF AuGa ALLOY PHASE

By

John J. Higgins

.

A DISSERTATION

Submitted to

Michigan State University

in partial fulfillment of the requirements

for the degree of

DOCTOR OF PHILOSOPHY

Department of Physics

City, the Dir (ER) of the from the top, parazeters va structure exis hiigman metho ercess Au (.23 at.2). F rang of the rigid b. about stoichio: Record the second secon tage of F. Ar <sup>Gates</sup> a concent ¥≑les. Stoic Mat. The day. Tatled from 55 t

The de .

#### ABSTRACT

# DE HAAS-VAN ALPHEN STUDY OF THE AuGa, ALLOY PHASE

BY

John J. Higgins

The de Haas-van Alphen frequency (F) of the third zone neck orbit (C<sub>3</sub>), the Dingle temperature  $(T_D)$ , and the residual resistance ratio (RRR) of the intermetallic compound  $AuGa_2$  were measured on samples cut from the top, middle, and bottom of three single crystals to see if these parameters vary over the range of composition in which the fluorite structure exists. The three crystals, 4 to 6 cm long, were grown by the Bridgman method from melts that deviated from stoichiometry by having excess Au (.287 at.% from stoichiometry) and excess Ga (.203 and .549 at.%). F ranged from 3388 kG to 3384.2 kG to 3405.7 kG. Assumption of the rigid band model implies for these samples a concentration range about stoichiometry less than .06 at.% Ga. But analogy to the case of Pd impurity associates a value between .22 and .43 at.% Ga with the range of F. An independent analysis of uncertain reproducibility indicates a concentration difference of .35+.10 at.% between two groups of samples. Stoichiometry does not coincide exactly with the congruent point. The dHvA phase constant was found to be .46  $\pm$  .09. RRR and T<sub>D</sub> varied from 55 to 1800 and from 5.0 K to 1.1 K, respectively.

I wish to t assistance durin for his counsel Frent Blumenstoc resistance ratio preparing sample: the physics depar apparatus and to Edunds, who dona system. Vivian S Bigelow of the Un Suzio Ono were ze Probe experiment -I am indebt. and inked in mantion for the intr a special copy E The support ećgeć,

#### ACKNOWLEDGMENTS

I wish to thank Professor Peter A. Schroeder for his guidance and assistance during the course of this research; and Professor F. J. Blatt, for his counsel in preparing a preliminary report. I am grateful to Brent Blumenstock for his diligent assistance in measuring the residual resistance ratios, and to Boyd Shumaker, for growing the crystals and preparing samples for analysis. I wish to express my appreciation to the physics department machinists, who manufactured much of the cryogenic apparatus and to the people in the electronics shop, especially Dan Edmunds, who donated several overtime evenings towards improving the NMR system. Vivian Shull, MSU microprobe specialist, and Professor W. C. Bigelow of the University of Michigan, and his students Jerry Hoffman and Sumio Ono were generous with their time in guiding and running the microprobe experiments.

I am indebted to my wife, Debbie, who typed most of the first draft and inked in many of the drawings, and for whom, in partial indemnification for the intrusion of this work into nearly every aspect of her life, a special copy has been reserved for her to tear apart.

The support of the National Science Foundation is gratefully acknowledged.

**ii** 

LIST OF TABLES . LIST OF FIGURES. EPER I. MOTIVATION 1.1 I: 1.2 Hy 1.3 Pr H. FERMI SURFA 2.1 Pr 2.2 Fer 2.3 Cr 2.4 Fe 2.5 Or II. BASIC THEO; 3.1 T.

# TABLE OF CONTENTS

LIST OF	TABLES	• • • • • • • • • • • • • • • • • • • •	vi
LIST OF	FIGURES	5	viii
CHAPTER	Ł		
I.	MOTIVATI	ION AND PURPOSE	1
	1.1	Introduction	1
	1.2	A metallurgical question	2 8 8
	1.3	Phase diagrams and crystal growth	9 9
II.	FERMI SU	JRFACE OF AuGa <sub>2</sub>	11
	2.1	Preliminary Definitions.   Ideal crystal   Perfect crystal   Static crystal.   Real crystal.   Free electron model   Coordinate systems.   Magnetic field nomenclature   Sign of charge carriers   Fermi Surface of an Ideal Crystal.	11 11 12 12 12 13 15 17
		Empty lattice model	17 18 19
	2.3 2.4	Crystalline Structure of AuGa <sub>2</sub>	20 21 21 26
	2.5	Orbits on the Fermi Surface	26
III.	BASIC TH	HEORY OF THE DE HAAS-VAN ALPHEN EFFECT	30
	3.1	Two Aspects of Electronic Magnetization Moving charges	31 31 33 34

EL2 TER
3.2 H 3.3 L
<b>३.</b> ७ ्
3.5 T.
3.6 S;
3.8 J: 3.9 C:
IV. DE HAAS-VAN
4.1 De
4.2 D:
4.3 Cc 7. EVPER
J.I Te
5.0
5.2 Fi
DE HAAS-TAT
6.1 Pr

#### . CHAPTER

	3.2	History of the de Haas-van Alphen Effect	34
	3.3	Landau Levels	37
		Free electron model	37
		Degeneracy	38
		Periodicity	40
		Real crystals	40
	3 /	Augustization of Arbita	42
	5.4		42
			42
		Cylinders of orbits	43
		Periodicity and dHvA frequency	44
		Degeneracy	47
	3.5	Temperature and Scattering Effects	50
		Nonzero temperature	50
		Scattering	51
	3.6	Spin-splitting	53
	3.7	Lifshitz-Kosevich Theory	54
	3.8	Justification of Semiclassical Theory.	59
	3.9	Corrections to Semiclassical Theory	62
	5.5	Magnetic interaction (Many-body affects)	62
		Demonstration	64
			04
		Magnetic Dreakdown	64
IV.	DE HAAS-	VAN ALPHEN EFFECT AS A PROBE OF CRYSTAL COMPOSITION	69
	. 1	De Vege-yen Alphon Erequency	60
	4.1	De naas-van Alphen Frequency	09
			/1
		Relation to AuGa $_2$	72
	4.2	Dingle Temperature	74
	4.3	Considerations for Precision	76
v.	EXPERIME	NTAL TECHNIQUE FOR THE DE HAAS-VAN ALPHEN EFFECT	78
	5 1	Toobadayog Avoilable	70
	5.1		70
			/8
		Pulsed fields	80
		Field modulation	80
		Other techniques	82
	5.2	Field Modulation Technique	82
		Magnetic field variable	83
		Voltage	83
		Spectral analysis	90
		Data reduction.	94
VI.	DE HAAS-	VAN ALPHEN APPARATUS	97
	6.1	Probe.	98
		Flange and support tube	102
		Mohila haca	102
		$\begin{array}{c} \text{routile Dabe } \cdot $	103
			104
		Sample nolder assembly	106
		dHvA coils	108
		Coil winding and specifications	110
		Electrical lines; Heat Leaks	118

=

CLOTER	
6.2 E 6.3 S 6.4 M	
WI. EXPERIMENT.	
7.1 G 7.2 O 7.3 S 7.4 D	
THE GROWTH AND	
8.1 Ti.	
8.2 <u>M</u> e	
8.3 <u>M</u> e	
II. CHARACTERIZ.	
9.1 An 9.2 Di	
9.3 <sub>Re</sub>	
Ĭ	
" UISCESSION	
10.1 C 10.2 d 10.3 d 10.4 p	
·····	
IST OF REFERENCES	

CHAPTER

	6.2	Electronics
	6.3	Superconducting Solenoid and Dewar
	6.4	Magnetic Field Measurement
		Nuclear magnetic resonance
		Calibrated resistors
VII.	EXPERIME	NTAL PROCEDURE AND DE HAAS-VAN ALPHEN DATA 127
	7.1	General Procedure 127
	7 2	Orientation 128
	73	Skin Effect
	7.5	Data Reduction
	/.4	
VIII.	GROWTH A	ND PREPARATION OF SAMPLES
	8.1	Theory of Freezing for Solid Solutions 142
		Phase equilibria
		Homogeneity
		Growth kenetics
		Hybrid approach
	8.2	Methods.
		Growing
		Cutting 160
		$\mathbf{Y}_{\mathbf{Paying}} = \mathbf{Y}_{\mathbf{Paying}} = \mathbf{Y}_{Pay$
	8 2	$\mathbf{A} = \mathbf{A} \mathbf{y} 1 \mathbf{n} \mathbf{g} \cdot \mathbf{n} \cdot \mathbf$
	0.5	
IX.	CHARACTE	RIZATION OF SAMPLES
	9.1	Anticipated Difficulties
	9.2	Direct Analysis.
	<i></i>	Chemical analysis 170
		Microprobe 175
		Other methods considered 204
	0.2	Desidual Desistance Datia
	9.3	
		Relation to concentration and Dingle tempera-
		ture
		AC method
		DC method
х.	DISCUSSI	ON OF THE RESULTS
	10.1	Concentration
	10.2	dHvA Phase Constant.
	10 3	dHvA Frequency 220
	10.5	Possible Phase Width 202
	10.4	
•••	• • • •	
LIST O	F REFEREN	CES AND NOTES

131 1. RRR and Impus 1. Comparison e 3. Structure Fa 4. Specification XMR Modul 5. Thermal Leak (Room T) 6. Superconduct 7. Characterist conductin 8. Sample Char; Melt Con: 9. Data on the Method . 13. Dimensions ll. Chemical And 12. Microprobe / lj. Typical Sta: Reproducibil li. Tentative C Gallium <sup>16</sup>. Error in Cc. Deviatic: Concentra D. Comparing V

# LIST OF TABLES

TABLE		
1.	RRR and Impurity Concentration of $AuX_2$ Crystals	6
2.	Comparison of Vacancy Concentrations and RRR in $AuAl_2$	6
3.	Structure Factors of $AuGa_2$	22
4.	Specifications for de Haas-van Alphen Coils N5 and N6 and NMR Modulation Coil NMR-M	112
5.	Thermal Leaks: Conductive Heat Flow from Top of Probe (Room T) to LHe Level (10' Above Sample)	120
6.	Superconducting Solenoid	123
7.	Characteristics of the Standard Resistors for the Super- conducting Solenoid	126
8.	Sample Characteristics by Position and Parent Crystal's Melt Concentration	140
9.	Data on the Three AuGa <sub>2</sub> Crystals Grown by the Bridgman Method	158
10.	Dimensions of dHvA and RRR Samples	162
11.	Chemical Analysis of Slug A (AuGa <sub>2</sub> +.204 at.% Ga)	174
12.	Microprobe Analysis of Slugs A and B	183
13.	Typical Statistics Used to Compute Table 12	184
14.	Reproducibility and Resolution Tests of the MSU Microprobe.	188
15.	Tentative Conclusions for the Relative Change in the Gallium Concentration with Respect to the Bottom of Slug	191
16.	Error in Concentration Differences ∆c Due to Hypothetical Deviations from Linearity in the X-ray Count versus Concentration	195
17.	Comparing Variances in Mocroprobe Data	201

1431E

18. Scattering

19. Results of

# TABLE

18.	Scattering	Rates	from	dHvA	and	RRR	in	Cu	and	Au.	•	•	•	•	•	•	210
19.	Results of	Compar	ing l	RRR f	rom	DC a	nd /	AC N	letho	ods.	•	•	•	•	•	•	215

FIGTRE 1. RER of AuGa2 2. Coordinate s 3. The four axe orientati 4. Crystal stru j. Holes in the in the re 6. Holes in the in the re 7. Fourth zone AuGa<sub>2</sub> in 8. Some extrem. surface (110) pl 9. Energy bands 10. Intersectio: C'4 (star ll. Orbits on a ll, The relatic-E<sub>F</sub>··· 13. A slice in Fermi su: l4. Changes in : an ellip <u>B = H</u>. 13. Former k-st onto the

# LIST OF FIGURES

#### FIGURE

1.	RRR of AuGa $_2$ crystals versus excess Ga in the melt	5
2.	Coordinate systems in real and reciprocal spaces	14
3.	The four axes in <u>k</u> -space: $k_x$ , $k_y$ , $k_z$ , and $k_H$ , and their orientation with respect to the magnetic field	16
4.	Crystal structure of $AuGa_2$	23
5.	Holes in the third zone of the empty lattice model of AuGa <sub>2</sub> in the reduced zone scheme	23
6.	Holes in the third zone of the empty lattice model of AuGa <sub>2</sub> in the repeated zone scheme	24
7.	Fourth zone sheet of the empty lattice Fermi surface of AuGa <sub>2</sub> in the repeated zone scheme	24
8.	Some extremal cross-sections of the empty lattice Fermi surface of AuGa <sub>2</sub> when the magnetic field is scanned in a {110} plane	25
9.	Energy bands of AuGa <sub>2</sub> by a non-relativistic APW calculation.	27
10.	Intersection of the path Q with the orbits $C'_3$ (hexagon) and $C'_4$ (star)	27
11.	Orbits on a hypothetical Fermi surface	29
12.	The relation between the Landau levels and the Fermi level ${}^{E}_{F}$	41
13.	A slice in <u>k</u> -space showing quantized orbits superposed on a Fermi surface of arbitrary shape, at some value of $k_{\rm H}$ .	45
14.	Changes in the quantization scheme as the principal axes of an ellipsoidal Fermi surface vary their orientation in $\underline{B} = \underline{H} \dots \dots$	45
15.	Former <u>k</u> -states lying between quantized orbits are swept onto the orbits	49

TRE 16. Theoretical upon the 17. Hypothetical B. Cross-secti (clear) = for B 19. Orbits cent-10. Typical dat ll. The constru: + h(t). 11. Modulation harmonic tion Mos voltage 13. Plan view cu 2. Plan view co 25. Exploded via assembly. 26. Angle map c: 27. Dimensions 18. Ceil windin across a 19. Coil windin. across a <sup>30</sup>. Block diagr 31. Theoretical graphs f 2. Typical exp. 3. identificat <sup>by</sup> (1) r <sup>34. Skin</sup> effect

.

# FIGURE

16.	Theoretical dependences of magnetization and free energy upon the inverse field, $1/B$ for $T = T_D = 0$	58
17.	Hypothetical orbits to illustrate magnetic breakdown	66
18.	Cross-section of the enpty lattice surfaces in the third (clear) and fourth (black) zones at the k values given for <u>B</u>    <111>	66
19.	Orbits centered on point L on the Brillouin zone	68
20.	Typical data for the C' (Third zone neck) orbit of $AuGa_2$	87
21.	The construction of $M(H_0,t)$ from $M(H)$ and $h(t)$ , with $H = H_0 + h(t) \dots \dots$	89
22.	Modulation of the steady field $\underline{H}_{o}$ by $\underline{h}$ cos $\omega_{m}$ t causes each harmonic component $\underline{M}_{r}$ (H) of the oscillatory magnetiza- tion $\underline{M}_{osc}$ of equation (71) to induce an alternating voltage v(t) $\propto d\underline{M}_{r}(\underline{H}_{o},t)/dt$	92
23.	Plan view of the de Haas-van Alphen probe (top)	99
24.	Plan view of the de Haas-van Alphen probe	100
25.	Exploded view of the probe's coil former and sample holder assembly	101
26.	Angle map of mobile base tilt angle	107
27.	Dimensions of coil formers	111
28.	Coil winding contour map of coil strength in Gauss per volt across a coil on half of Former CF2. T = 20 <sup>0</sup> C	116
29.	Coil winding contour map of coil strength in Gauss per volt across a coil on half of Former CF2. T = 4.2K	117
30.	Block diagram of dHvA and NMR electronics	121
31.	Theoretical curves of constant phase and dHvA rotation graphs for orbit $C'_3$	130
32.	Typical experimental rotation graphs	131
33.	Identification of positive peaks in a dHvA rotation graph by (1) rotation, (2) reset field, (3) rotation	132
34.	Skin effect test on Sample 12	135

:::RE 35. Skin effect 36. Selected dat 37. Summary of c 38. Simplified e 39. Hypothetical nonzero ; 40. Gradient for in the z. 41. Gallium conc and liqui 42. Concentrati fractiona 43. De Haas-van samples f 4. Location of 45. Error introd ences by 46. Display of t line ver-47. Display of t line vers, <sup>46.</sup> Display of t line vers 9. Theoretical 9. Histograms c Run 2 on <sup>31.</sup> Apparatus fc: <sup>11. Possible Aug</sup> continuou 3. Hypothetical continuou concentra. 5. An expansion. grammed i.

# FIGURE

35.	Skin effect test on Sample 30	136
36.	Selected data for AuGa <sub>2</sub>	139
37.	Summary of dHvA and RRR data	141
38.	Simplified equilibrium phase diagram for Au-Ga	143
39.	Hypothetical intermetallic compound (solid phase S) with a nonzero phase width and c <sub>m</sub> not at stoichiometry	147
40.	Gradient for a dilute concentration of an alloying element in the melt	147
41.	Gallium concentration of the melt at the interface of solid and liquid is lower than for an equilibrium system	153
42.	Concentration of melt at solid-liquid interface versus fractional distance along crystal	156
43.	De Haas-van Alphen and RRR samples (circled numbers) and samples for microprobe analysis (not circled)	161
44.	Location of samples cut from Slug A	171
45.	Error introduced into measurements of concentration differ- ences by deviations from linearity in x-ray count	194
46.	Display of the data: 10 second x-ray count N for the Ga K line versus trial number in Run 2	196
47.	Display of the data: 10 second x-ray count N for the Ga L line versus trial number in Run 2	197
48.	Display of the data: 10 second x-ray count N for the Au M line versus trial number in Run 2	198
49.	Theoretical frequency distributions of x-ray count N	202
50.	Histograms of x-ray count N for three x-ray lines of AuGa <sub>2</sub> , Run 2 on Slug A	203
51.	Apparatus for residual resistance ratio measurements	211
52.	Possible AuGa <sub>2</sub> phase boundary. Based on assuming T <sub>D</sub> varies continuously with position	225
53.	Hypothetical phase boundaries for AuGa <sub>2</sub> consistent with continuous Dingle temperature and the prepared melt concentrations	227
54.	An expansion of the first phase boundary in Figure 53, dia- grammed in the manner of Figure 52	228

1.1 Introduction

De Haas-van of a nonferromagn The local atomic between these more of the lower ener ay contribute t the susceptibili: electrons in motif tental conditions adis two componen increasing diama Parallel and ant the presence of agnetic field, N. j. de Haas ; reasuring the m liquid hydrogen essily observed The drive eff their such infor *a the p*ast few y Sarity concent.

#### CHAPTER I

#### MOTIVATION AND PURPOSE

#### 1.1 Introduction

De Haas-van Alphen effect in studies of metals. The magnetization of a nonferromagnetic substance arises from various physical phenomena. The local atomic or ionic magnetic moments, the exchange interaction between these moments and the electrons, and the preferential occupation of the lower energy, spin-up electronic states (Pauli spin magnetism) may contribute to the total paramagnetism. The diamagnetic component of the susceptibility arises from the quantum mechanical response of electrons in motion to an applied magnetic field. Under certain experimental conditions this response of the conduction electrons in metals adds two components to the magnetization, one of which is a steadily increasing diamagnetism, while the other oscillates, becoming alternately parallel and anti-parallel to the applied field. The last phenomenon, the presence of oscillation in the magnetic susceptibility with increasing magnetic field, is called the de Haas-van Alphen (dHvA) effect, after W. J. de Haas and P. M. van Alphen,<sup>1</sup> who observed it in 1930 when measuring the magnetic susceptibility of a single crystal of bismuth at liquid hydrogen temperatures. At low temperatures and big fields it is easily observed in most metals.

The dHvA effect has been used since the middle of the 1950's to obtain much information about the shapes and sizes of Fermi surfaces. In the past few years quantitative research into the effect of the impurity concentration on the dHvA measurements has led to the investigation

of the dHvA effe their concentrat. This development the course of a series of intermto investigate s by the Bridgman ( empounds used i tell how these q. then. The last izvestigation of A zetalling corpound, also c. of fluorite and allim within s. each two Ga ator. issoribed in Char Eigure 38, the p sition AuGa<sub>2</sub> ind. it lies within a the long range of to the tendency tally by Au atoand the tendency attice of an or  $\alpha_{\text{tending throug}}$ <sup>by one species of</sup> The residual

of the dHvA effect as a probe of scattering potentials of impurities, their concentrations, and their effect on the Fermi surface of the host. This development combined with speculations and questions that arose in the course of a study of the galvanomagnetic properties of an homologous series of intermetallic compounds to suggest the use of the dHvA effect to investigate some phenomena that apparently occur during the growth, by the Bridgman technique, of the single crystal AuGa<sub>2</sub>, one of the compounds used in the galvanomagnetic study. The next two subsections tell how these questions arose and describe the hypotheses suggested by them. The last section of this chapter outlines the program for the investigation of the hypotheses.

<u>A metallurgical question</u>.  $AuGa_2$  is an example of an intermetallic compound, also called an ordered alloy. Its crystal structure is that of fluorite and is shown in Figure 4. It is grown by mixing gold and gallium within several atomic percent of stoichiometry (one Au atom for each two Ga atoms), melting this charge, and slowly cooling it, as described in Chapter VIII. According to the equilibrium phase diagram Figure 38, the precipitate, at least initially, will be of fixed composition AuGa, independently of the prepared melt concentration, so long as it lies within a rather broad range about stoichiometry. In particular, the long range order should be the same. The long range order relates to the tendency of the Au-sites of the lattice to be occupied preferentially by Au atoms rather than by Ga atoms, impurities, or vacancies, and the tendency of the Ga-sites to be occupied by Ga atoms.<sup>2</sup> The lattice of an ordered alloy is divided into two or more sublattices extending throughout the whole crystal, and each preferentially occupied by one species of atom.

The residual resistance ratio (RRR) is an experimental measure of

long range order. ferent scatterin crystalline symm sees the site of species as a scat me atmosphere: ity, which conse rom temperature tesperature the tions in the lon resistance ratio. <u>.</u> increases monote From the at  $\frac{Au_{a}}{2}$  to have a all near stoich: We to vary wide <sup>centration</sup> and t pared AuGa and g percies as AuGa 2 <sup>steichiometric.</sup> (1) Crystal elezent prepared <sup>ad for AuGa</sup>2, (2) a maxim differe: long range order. Because the Au and Ga ions in the crystal have different scattering potentials, randomly intermixing them destroys crystalline symmetry. The Bloch wave of the conduction electron thus sees the site of a sublattice containing anything other than its correct species as a scatterer. At low temperatures (normally in liquid He at one atmosphere: 4.2 K) such scattering dominates the crystal's resistivity, which consequently varies with the amount of long range order. At room temperature the phonons dominate the resistivity. Because at room temperature the phonon spectrum is much less sensitive to small variations in the long range order the resistivity is, too. Thus the residual resistance ratio,

$$RRR = \rho_{RT} / \rho_{4.2} = R_{RT} / R_{4.2}, \text{ fixed geometry} \qquad [1]$$

increases monotonically with long range order.

From the above discussion one would expect a single crystal of  $AuGa_2$  to have a uniform RRR, and crystals grown from different melts, all near stoichiometry, to have the same RRR. But it is not unusual for RRR to vary widely in crystals grown from melts of nearly the same concentration and the same purities. Specifically, in 1968 J. Longo<sup>3</sup> prepared  $AuGa_2$  and  $AuAl_2$  (with the same fluorite structure and similar properties as  $AuGa_2$ ) from melts that were within  $\pm 0.5$  wt% Al or Ga of being stoichiometric. He found (see Table 1 and Figure 1) for both alloys,

 Crystals grown from melts prepared rich in the Group III element had much higher RRR than crystals grown from melts prepared stoichiometric;

and for AuGa,,

(2) a maximum in the RRR of the most pure samples taken from different AuGa<sub>2</sub> crystals (plotted against the prepared melt

concent

(3) within

average

also e:

(4) traces

concent

lengo concluded :

Straumanis and K.

78.18 to 78.94 w:

tange 300 to 401

Stramanis and Co

Al-site vacancie

giving a vacancy

inther maintain

Al-sites are comp

Al-rich melt havi

However, Lo-

<sup>be consistent</sup> wit

⇔irical relati

where I = impurit <sup>describes</sup> many m. Some binary allow

(Table 2) from h ( Cable 2) from h ( Concentration in Speculated that ( concentration);

- (3) within a given AuGa<sub>2</sub> crystal, a big spread of RRR about the average value. The average RRR versus melt concentration also exhibits a clear maximum;
- (4) traces of Ga on the surface of crystals grown from melts of concentration > 0.5 wt% Ga.

Longo concluded that these data are consistent with a report by M. E. Straumanis and K. S. Chopra<sup>4</sup> that AuAl<sub>2</sub> has a homogeneity range from 78.18 to 78.94 wt% Au (32.92 to 33.92 at.% Au) in the temperature range 300 to 400 °C, with the phase being fcc, fluorite structure. Straumanis and Chopra also said that at stoichiometry there are 0.152 Al-site vacancies per cell and 0.076 Au-site vacancies per cell, giving a vacancy concentration of 1.9 at.% on each sublattice. They further maintained that at the Al-rich end of the homogeneity range the Al-sites are completely filled, resulting in a crystal grown from an Al-rich melt having a higher RRR.

However, Longo reported that his values for RRR seemed too high to be consistent with Straumanis and Chopra's vacancy concentration. The empirical relation

$$(RRR)(I) \approx 1,$$
 [2]

where I = impurity (or vacancy) concentration in percent, describes many metals as well as the intermetallic compound AuSn.<sup>5</sup> Some binary alloys are more nearly described by

Assuming either one of these relations holds for  $AuAl_2$ , Longo calculated (Table 2) from his measured RRR a much lower impurity (including vacancy) concentration in AuAl\_than that reported by Straumanis and Chopra. Longo speculated that if such a concentration of vacancies exists the vacancies





Table 1. RRR an (Adaps Me ] exa 147 a. Lon b. Tak Tat Stoic: Al-ri homoge (0.56 Al)

Table 1. RRR and Impurity Concentration of AuX<sub>2</sub> Crystals.

(Adapted from Longo, Ref. 3) RRR of AuX<sub>2</sub> Crystals AuGa2 AuA12 Melt Prepared Melt Prepared exact Al-rich exact Ga-rich 140<sup>a</sup> 550 1. 250 904 2. 190<sup>b</sup> 950b

a. Longo (Ref. 3) cites JPSST (Ref. 10).b. Taken from graph in Ref. 3.

Table 2. Comparison of Vacancy Concentrations and RRR in AuAl<sub>2</sub>

	Straumanis <sup>4</sup> and Chopra	(RRR)(I)=1	(RRR)(I)=10		
Stoichiometry	1.9 at.%	0.0071 at.%	0.071 at.%		
Al-rich end of homogeneity range (0.56 at.% excess Al)	0.634 at.%	0.0018 at.%	0.018 at.%		

ray coalesce to He states that t Another possibil and big RRR value Te<sub>0.575</sub>S.<sup>6</sup> Howe which were not o Impurities, itom stoichiometric iescription of the Intay pictures, ieviations from

techanists. Som

variation in the

components). The to a range of RRI

.10 to .053 at .3

detect by metho

this marrow cours. The fact t

telts prepared .

arise from oth

tangruent poin.

di stoichiomet

is 19225, which

Magruest point.

ase of the const

may coalesce to form small voids dispersed throughout a macroscopic region. He states that the variation of RRR over one crystal supports this belief.<sup>3</sup> Another possibility consistent with a high concentration of vacancies and big RRR values is that the vacancies are ordered, as in Al<sub>3</sub>Ni<sub>2</sub> and in Fe<sub>0.875</sub>S.<sup>6</sup> However, such crystals would exhibit x-ray superlattice lines, which were not observed by Straumanis and Chopra.<sup>7</sup>

Impurities, dislocations, crystallites, and deviations from stoichiometry could account for Longo's RRR observations. His description of the care taken in the growing of the crystals, the good x-ray pictures, and the regular pattern of the RRR values suggest deviations from stoichiometry may be more important than the other mechanisms. Some binary alloys have equilibrium phases with a wide variation in the range of homogeneities (in atomic percent of one of the components). The range of concentration for Longo's samples corresponding to a range of RRR from 190 to 950, obtained from the relation (3), is .10 to .053 at.% deviation from stoichiometry, a range difficult to detect by methods of compositional analysis. Consequently, a phase this narrow could be reported as nominally fixed composition.

The fact that AuGa crystals with the biggest RRR must be grown from melts prepared off stoichiometry is not unusual.<sup>8</sup> This phenomenon may arise from other phases existing near the phase of interest, from the congruent point (the maximum in the liquidus curve) lying slightly off stoichiometry, and other conditions. An example of another condition is  $Mg_2Pb$ , which has a peritectic point that looks very much like a congruent point.<sup>9</sup> See Figure 39 and discussion there for a hypothetical case of the congruent point lying off stoichiometry.
# 1.2 Hypotheses The hypothe of the use of the tions. They are (1) when a compos varies (2) The Au exactl (3) The dH concer on hew and so If these hypothinternetallic co dHvA effec: dëva signals, w <sup>dur primary</sup> obję dava signal and study of Fermi a <sup>gous</sup>, but slight: the samples is the concentrati avaluation of t <sup>22</sup>tion. These r discussion of the

The hypotheses of this thesis are suggested by the above discussions of the use of the dHvA effect in the study of metals and the RRR variations. They are:

- (1) When a AuGa crystal is grown from a melt of given initial composition by the Bridgman technique the crystal's composition varies along the direction of solidification.
- (2) The AuGa line of the equilibrium phase diagram is not
   exactly vertical, but slanted, and crosses stoichiometry.
- (3) The dHvA effect is capable of detecting the above range of concentration. Furthermore, dHvA studies may yield information on how Au, Ga, and vacancy impurities affect the Fermi surface and scattering of electrons.

If these hypotheses are correct for AuGa<sub>2</sub>, they may extend to other intermetallic compounds which are of nominally fixed composition.

<u>dHvA effect and concentration.</u> AuGa<sub>2</sub> yields moderately strong dHvA signals, which have provided Fermi surface information since 1965.<sup>10</sup> Our primary objective is to see if there is a correlation between the dHvA signal and RRR of samples all nominally AuGa<sub>2</sub>, and thus extend the study of Fermi surface dependence upon impurity concentration to an analogous, but slightly different condition. Some method of characterizing the samples is desirable, and much work went toward a direct analysis of the concentration. The results were only partially intelligible, so the evaluation of the data relies mostly on indirect methods of characterization. These results are discussed in Chapters IX and X. Further discussion of the dHvA effect is deferred until Chapter III.

Phase d dation of the an alloy may growth. The samples are d Having c the suitabili the dEvA effe tion, and the appropriate t 1.3 Proposed Grow sin. telt with inioff stoichione leasure dHvA and concentra: <sup>Chapter</sup> ; VII gives the <sup>locations</sup> of t <sup>the data</sup> for t the residual r tese data and (1) The se dHvA f resist (2) The  $v_a$ simple are con to inc <u>Phase diagrams and crystal growth</u>. A secondary objective is elucidation of the growth pattern of the AuGa<sub>2</sub> crystal. The concentration of an alloy may depend upon both the equilibrium phases and the kinetics of growth. The data presented later indicate that the variations among the samples are due to both effects.

Having considered the puzzle (the range of RRR values in AuGa<sub>2</sub>), the suitability of this alloy for an extension of the study by means of the dHvA effect of the dependence of the Fermi surface upon concentration, and the influence of the method of growing the crystal, it is appropriate to outline the experimental program.

#### 1.3 Proposed Program and Summary of Results

Grow single crystals of AuGa<sub>2</sub> by the Bridgman method, each from a melt with initial concentration slightly (less than one atomic percent) off stoichiometry. Cut samples from along the axis of each crystal and measure dHvA frequency, Dingle temperature, residual resistance ratio, and concentration.

Chapter VII contains the dHvA and Dingle temperature data; Chapter VIII gives the melt concentrations for growing the crystals and the locations of the samples cut from the crystals; Chapter IX gives both the data for the direct analysis for concentration in the crystals and the residual resistance ratios for the samples. Chapter X discusses these data and draws conclusions, an epitome of which follows:

- The samples exhibit a definite and non-random variation in dHvA frequency (F), Dingle temperature (T<sub>D</sub>), and residual resistance ratio (RRR).
- (2) The variation in RRR correlates with that in  $T_D$  according to simple models. That is, samples ordered by increasing RRR are consequently ordered by decreasing  $T_D$ , both corresponding to increasing long range crystalline order.

- (3) The same the cr centra stoich
- (4) Direct partia being method cussed

- (3) The samples of lowest T and highest RRR came from regions of the crystals which solidified at a time when the average concentration of the remaining melt was gallium rich (compared to stoichiometry).
- (4) Direct analysis of the concentration of the crystals was only partially successful due to the differences in concentration being of the same order as the resolution of the available methods of analysis. Some trends were evident and are discussed in Chapter IX.

The Fermi s ignamical proper Before mentionin it is useful to of crystals. To citen ignored i: <u>11 Preliminar</u> Discussion physical models <u>lieal crus</u>: <sup>atozic</sup> basis th: it is seen that up the content of are no phonons; Xiat. Perfect cr titoughout a fir are no impuritie presence of phon <sup>the</sup> ideal crysta

#### CHAPTER II

FERMI SURFACE OF AuGa<sub>2</sub>

The Fermi surface is a mathematical construction related to the dynamical properties of the conduction electrons of a crystal.<sup>11</sup> Before mentioning some of the methods used to calculate the Fermi surface it is useful to list some important, well-known terms from the physics of crystals. Their enumeration here will highlight several distinctions often ignored in general use but important in dHvA theory.

#### 2.1 Preliminary Definitions

Discussion of the theory refers from time to time to the following physical models of a real, crystalline solid:

Ideal crystal. A perfectly periodic and static repetition of an atomic basis throughout all space. From the formal relation,

crystal structure = lattice + basis, [4]

it is seen that the cluster of ions and atoms forming each basis makes up the content of each primitive cell. A static repetition means there are no phonons; each basis is rigidly fixed with respect to its lattice point.

<u>Perfect crystal.</u> A perfectly periodic repetition of an atomic basis throughout a finite region of space. As with the ideal crystal there are no impurities, vacancies, cracks, or other imperfections. The presence of phonons gives this model different properties from those of the ideal crystal.

Static cry-

static repetiti.

of space. This

or of imperfect.

Real cryst

arrangement of .

phonons and imp-

and depends on t

Free elect

region of space

crude model of

being free to  $\pi$ 

structure, whose

calculations of

A-states when p-

with the Pauli .

energy surfaces

where m<sub>o</sub> is the real materials w effective mass r and m<sub>3</sub>. Importa first derived ar is then made to Extrison construexply lattice man [11]. <u>Static crystal.</u> An imperfect, but approximately periodic and static repetition of an atomic basis throughout a possibly finite region of space. This is a model for calculations of the effects of alloying or of imperfection on physical properties when phonons are ignored.

<u>Real crystal.</u> The physically obtainable, approximately periodic arrangement of atoms assumed by numerous elements and compounds. Both phonons and imperfections are present to a degree that varies widely and depends on the crystal's history and environment.

<u>Free electron model.</u> Non-interacting electrons confined to finite region of space throughout which the potential energy is constant. This crude model of a crystal includes the idea of the conduction electrons being free to move throughout the crystal, but ignores the crystalline structure, whose potential varies periodically. It is useful for rough calculations of physical properties because it does lead to discrete <u>k</u>-states when periodic boundary conditions are imposed and, in conjunction with the Pauli exclusion principle, to the idea of a Fermi surface. The energy surfaces in k-space are given by

$$E = \frac{\hbar^2 k^2}{2m_0} , \qquad [5]$$

where  $m_0$  is the free electron mass. Often this model is extended to real materials with ellipsoidal Fermi surfaces by replacing  $m_0$  with an effective mass m\* or with an effective mass tensor with elements  $m_1$ ,  $m_2$ , and  $m_3$ . Important concepts of the dHvA theory for real metals were first derived and are most easily understood using this model. Extension is then made to more complicated cases. Such is the case for the Harrison construction for the Fermi surface (see the description of the empty lattice model in the next section) and the Landau levels (Chapter III).

Coordinate 🗧 systems need to b Figure 2 illustra this thesis has a lattice. Hence t 1, also called t blique. The axe all, etc., cont of the correspond minitive basis i  $\hat{z} = \hat{\mathbf{n}}_1 \hat{\underline{A}}_1 + \cdots + \hat{\mathbf{y}}_n$ lanes. The zone brillouin zone in labeled k<sub>1</sub>, k<sub>2</sub>, k teferred to as k-1 $\frac{1}{2}$ , the orientati ubic systems a to <sup>la zero</sup> field thi Espace because s attic planes and <sup>2 are chosen for d</sup> ≭:ai apparatus, i Dot be paralle:

Coordinate systems. Some conventions of notation for coordinate systems need to be established for later use in presenting the theory. Figure 2 illustrates these. The intermetallic compound AuGa<sub>2</sub> studied in this thesis has a cubic conventional cell and a face centered cubic lattice. Hence the conventional basis is the orthogonal triad  $\underline{a}_1$ ,  $\underline{a}_2$ ,  $\underline{a}_3$ , also called the crystalline axes. The primitive basis  $\underline{p}_1$ ,  $\underline{p}_2$ ,  $\underline{p}_3$ , is oblique. The axes along  $\underline{a}_1$ ,  $\underline{a}_2$ ,  $\underline{a}_3$  are also denoted by [100], [010], [001], etc., concisely represented by <100>, called a form. The lattice of the corresponding reciprocal space is body centered cubic, and its primitive basis is  $\underline{A}_1$ ,  $\underline{A}_2$ ,  $\underline{A}_3$ . The bisector planes of the vectors  $\underline{G} = n_1 \underline{A}_1 + \dots$  yield the zone planes, which are parallel to the atomic planes. The zone planes closest to the origin define the first Brillouin zone in reciprocal space. Axes in reciprocal space are usually labeled  $k_1$ ,  $k_2$ ,  $k_3$  in the literature, so reciprocal space is often referred to as <u>k</u>-space. For a given orientation of the  $\underline{a}_i$  and hence the  $\underline{G}_{i}$ , the orientations of the <u>k</u>-axes may be chosen for convenience. In cubic systems a triad that coincides with the crystalline axes is used. In zero field this is the most convenient choice for coordinates in k-space because spatial directions in the crystal are defined by the atomic planes and their intersections. Spatial axes x, y, and z are chosen for convenience in representing the geometry of the experimental apparatus, and convenience may require that their unit vectors  $\mathbf{\hat{1}}_{i}$  not be parallel to the  $\underline{\mathbf{a}}_{i}$ , as for a crystal at arbitrary orientation



Figure 2. Coordinate systems in real and reciprocal spaces.

- (a) Basis vectors <u>a</u> (conventional) and <u>p</u> (primitive) of the fcc lattice.
- (b) The primitive reciprocal basis vectors  $\underline{A}_{i}$  and their relation to the Brillouin zone. The reciprocal lattice is body centered cubic.
- (c) The perpendicular axes in reciprocal space (also <u>k</u>-space) and their orientation with the Brillouin zone.
- (d) External conditions (e.g. field direction) may be used to define spatial axes x, y, and z not necessarily parallel to the  $\underline{k}_{i}$  axes.

DE EN

The de Ha

 $(C_j^t)$ , the Dingle (RER) of the inte from the top, mid parameters vary o <sup>structure</sup> exists. Midgan method f excess Au (.287 a at.). Franged of the rigid band bout stoichiozet <sup>2</sup> inpurity assoc <sup>tange</sup> of F. An i <sup>istes</sup> a concentrá ≋≂ies. Stoichi Mint. The dHvA . <sup>Tatiad</sup> from 55 to

#### ABSTRACT

DE HAAS-VAN ALPHEN STUDY OF THE AuGa<sub>2</sub> ALLOY PHASE

By

John J. Higgins

The de Haas-van Alphen frequency (F) of the third zone neck orbit (C<sub>3</sub>), the Dingle temperature  $(T_{D})$ , and the residual resistance ratio (RRR) of the intermetallic compound AuGa<sub>2</sub> were measured on samples cut from the top, middle, and bottom of three single crystals to see if these parameters vary over the range of composition in which the fluorite structure exists. The three crystals, 4 to 6 cm long, were grown by the Bridgman method from melts that deviated from stoichiometry by having excess Au (.287 at.% from stoichiometry) and excess Ga (.203 and .549 at.%). F ranged from 3388 kG to 3384.2 kG to 3405.7 kG. Assumption of the rigid band model implies for these samples a concentration range about stoichiometry less than .06 at.% Ga. But analogy to the case of Pd impurity associates a value between .22 and .43 at.% Ga with the range of F. An independent analysis of uncertain reproducibility indicates a concentration difference of .35+.10 at.% between two groups of samples. Stoichiometry does not coincide exactly with the congruent point. The dHvA phase constant was found to be .46  $\pm$  .09. RRR and T<sub>D</sub> varied from 55 to 1800 and from 5.0 K to 1.1 K, respectively.

in a uniform

Magneti

also called

include the :

intensity of

"magnetic fi

rean H or B,

Correct inte

E and <u>B</u>, eve

significant.

The ori

surface is i

expressions

are zaintai:

axes for the

field, plus

axes are al.

Eis also co

reader the a

end z. The

axes and he:

and azimutha

Figure 3 11: angles of the in a uniform field.

<u>Magnetic field nomenclature.</u> The vector <u>B</u> is the magnetic induction, also called the flux density. <u>H</u> is the magnetic intensity and does not include the magnetic contributions of the material medium. <u>M</u> is the intensity of the magnetization, or simply the magnetization. The term "magnetic field" and its abbreviation, "field," are used variously to mean <u>H</u> or <u>B</u>, depending on the context, when distinction is not important. Correct interpretation of dHvA data can require one to distinguish <u>H</u> and <u>B</u>, even in nonmagnetic media, when magnetic interaction is significant. (See section 3.9)

The orientation of the magnetic field with respect to the Fermi surface is important because the topology of the Fermi surface enters the expressions in the dHvA theory. Thus two coordinate systems in <u>k</u>-space are maintained: the former  $k_1$ ,  $k_2$ ,  $k_3$ , which are parallel to the crystalline axes for the cubic structure, and a new direction  $k_H$  parallel to the field, plus two axes normal to it (Figure 3). In this thesis the spatial axes are always chosen so that <u>B</u> is parallel to the z-axis. (Normally <u>H</u> is also considered parallel.) General crystal orientation will thus render the crystalline axes noncongruent with the spatial axes, x, y, and z. The orientation of the field with respect to the crystalline axes and hence with respect to the Fermi surface is given by the polar and azimuthal angles,  $\theta$  and  $\phi$ , and a gradient operator is defined:

$$\nabla_{\rm H} = {\bf i}_{\rm H\overline{\partial}H} + {\bf i}_{\theta} \frac{1}{{\rm H}} \frac{\partial}{\partial \theta} + {\bf i}_{\phi} \frac{1}{{\rm H}\sin\theta} \frac{\partial}{\partial \phi}.$$
 [6]

Figure 3 illustrates the relations among the <u>k</u>-axes,  $k_{H}$ , and the angles of the field direction.



Figure 3. The four axes in <u>k</u>-space:  $k_x$ ,  $k_y$ ,  $k_z$ , and  $k_H$ , and their orientation with respect to the magnetic field.

Sign of e0. Most eq holes by chan, in the flux qu distinction th q is used for negative. 2.2 Fermi Su The eige for the single quantum numbe distribution energy surfac directions in The energy fu the metal de Fermi energy Permi surfac thus primari is used depe Detal requi: <sup>and</sup> the acc: ere given b. Epty crystalline electron to Sign of charge carriers. The charge of the electron is -e, where e>0. Most equations are written for electrons and can be changed for holes by changing the sign. (When e appears as a universal constant, as in the flux quantum  $\hbar c/e$ , no sign is implied.) When necessary for distinction the positive electronic charge is written p or |e|. Sometimes q is used for general charge, and may be implicitly positive or negative.

### 2.2 Fermi Surface of an Ideal Crystal

The eigenfunctions of the conduction electrons in an ideal crystal for the single-particle approximation are Bloch waves,  $\psi_{\underline{k}}$ , indexed by the quantum numbers  $\underline{k}$ , called the wave-vector. The quasi-continuous distribution of eigenenergies  $\underline{E}_{\underline{b}}(\underline{k})$  in k-space gives rise to constant energy surfaces in each Brillouin zone b of  $\underline{k}$ -space. Along given directions in k-space the functions  $\underline{E}_{\underline{b}}(\underline{k})$  correspond to the energy bands. The energy functions and the number n of electrons per unit volume of the metal determine the maximum energy of occupied states at 0 K (the Fermi energy  $\underline{E}_{\underline{F}}$ ). The continuum of states  $\underline{k}$  belonging to  $\underline{E}_{\underline{F}}$  form the Fermi surface in k-space. The problem of calculating the Fermi surface is thus primarily the evaluation of  $\underline{E}_{\underline{F}}(\underline{k})$ . Which of various methods available is used depends on the properties of the metal (e.g., a transition metal requires more sophisticated methods than does a simple metal) and the accuracy required. Some methods of calculating the Fermi surfaces are given below. Results of applying two of these to AuGa<sub>2</sub> then follow.

<u>Empty lattice model.</u> This combines zone theory, which uses the crystalline structure to derive the Brillouin zone, and the free electron model. The spherical energy surfaces  $E = \hbar^2 k^2 / 2m_0$  are divided

into sheet:

are examine

may use th

zone, empt

struction,

features

This model

Harrison co

Section 2.

## Limita

model usual

the free e

corrections

with exper:

cant error.

space latt:

ionic Pote:

The ionic :

empty latt:

changes ca:

The well k:

<sup>lodel</sup>, are

Furthe

the free s

after crys (

of the crys

Spin-c

into sheets by the zone boundaries. The sheets of the Fermi surface are examined in various ways, depending on the problem at hand. Thus one may use the extended, reduced, or repeated zone schemes. The reduced zone, empty lattice model is obtained most easily by the Harrison construction,<sup>12</sup> which is extensively used to explain and predict gross features of the Fermi surfaces of metals and properties related to it. This model is also frequently referred to as 1-OPW and free electron. The Harrison construction of the Fermi surface of AuGa<sub>2</sub> is discussed in Section 2.4.

Limitations of the empty lattice model. Although the empty lattice model usually gives reasonable accurate first order results (considering the free electron sphere as the zeroth approximation), second order corrections are almost always needed to obtain good qualitative agreement with experiment, and occasionally first order predictions have significant error. This is because, although the model reflects the primitive space lattice of the crystal, the influence of the atomic basis (the ionic potentials) enters the model only through the effective valence. The ionic potential usually causes changes in the topology of the empty lattice Fermi surface where it approaches zone boundaries, and these changes can be significant with regard to some of the metal's properties. The well known necks of the noble metals, absent in the empty lattice model, are examples of this effect.

Further, if the atoms forming the metal have occupied d orbitals inthe free state whose energies are close to those of the valence states after crystallization, both the band structure and the effective valence of the crystal may differ from those of this model.

Spin-orbit interactions, an important cause of the lifting of

degeneraci In sp: adequate fo a reference some of the mentioned b <u>Method</u> In the near expansion i energies fo thought, th. (this refere peints: (1) components V Would be exp the ions als (3) Simple p which is inv Reglect of t But it now a of the pseud <sup>directly</sup> for illustrating The orth <sup>due to</sup> Herrir It can be use the augmented degeneracies in crystals of heavy atoms, are not included in this model.

In spite of these limitations, the empty lattice Fermi surface is adequate for this study of AuGa<sub>2</sub>. But for completeness, and also because a reference to a band structure calculation for AuGa<sub>2</sub> will be given, some of the standard methods of band structure calculations are briefly mentioned below.

Methods to include the ionic potentials and spin-orbit interactions. In the nearly free electron (NFE) model Bloch waves are treated as an expansion in plane waves. The expansion coefficients and the eigenenergies for given k are obtained from perturbation theory. At first thought, the NFE method appears to have fundamental defects. J. M. Ziman $^{13}$ (this reference is hereafter referred to as Ziman) lists the following points: (1) The deep potential well at each ion means the Fourier components  $V_{\sigma}$  of very short wavelength are important, so that the series would be expected to converge slowly. (2) Rapid oscillation of  $\psi_k$  near the ions also requires short wavelengths and implies slow convergence. (3) Simple perturbation theory effectively uses the Born approximation, which is invalid for deep atomic potentials. These arguments led to the neglect of this method as a practical scheme for band structure calculations. But it now appears that it can be made formally valid by the introduction of the pseudopotential (Ziman, p. 76). The NFE model is not used directly for band structure calculation, but remains useful as a means of illustrating the periodicity of E(k) and its gaps at zone boundaries.

The orthogonalized plane waves (OPW), or pseudopotential method is due to Herring,<sup>14</sup> and is important in the calculation of band structures. It can be used when the ions lack spherical symmetry, a requirement for the augmented plane waves method (see below). After the ionic potentials

are replaced Bloch function made orthogon functions, w<sup>2</sup>

wave function

needed even :

Ferzi surface

models are of

sozewhat inte

conduction el

transition z.

as Au.

The met:

Slater.<sup>16</sup> Th.

the ions and

potential is

are augmente.

are matched .

leaves its o

Similarly, a

Valences are

<sup>to be applie</sup>

2.3 Crystal

AuGa<sub>2</sub> ha Bravais latt <sup>4)</sup>. The str are replaced by pseudopotentials an iterative process approximates the Bloch functions by summing orthogonalized plane waves (plane waves made orthogonal to the core states). The first step yields the 1-OPW functions, which are often quite sufficient to represent the electronic wave functions over large regions of k-space; only 3 or 4 terms may be needed even in the corners of the Brillouin zone (Ziman, p. 94). The Fermi surfaces given by the free electron, the empty lattice, and the 1-OPW models are often equal or nearly equal, so that these names are used somewhat interchangeably. OPW assumes a distinction between core and conduction electrons.<sup>15</sup> This condition may not be well satisfied for transition metals and other elements with high level d orbitals, such as Au.

The method of augmented plane waves (APW) was suggested by J. C. Slater.<sup>16</sup> The space of the crystal is divided into spheres centered on the ions and interstitial regions of constant potential. The ionic potential is assumed spherical. Plane waves in the interstitial regions are augmented by spherical harmonic waves in the cores, and the two waves are matched at the surface of the sphere. Assuming a valence 1 for Au leaves its outer subshell 5d<sup>10</sup> filled and hence spherically symmetrical. Similarly, assuming a valence 3 for Ga leaves outer subshell 3d<sup>10</sup>. These valences are supported by experiment and theory, and allow the APW method to be applied to AuGa<sub>2</sub>, with results to be given in Section 2.4.

## 2.3 Crystalline Structure of AuGa,

AuGa<sub>2</sub> has the fluorite structure.<sup>10</sup> The face centered cubic (fcc) Bravais lattice has an atomic basis of one Au and two Ga atoms (Figure 4). The structure factor

is obtained by positions and form fact conventional : interference monatomic fee scattering pow direction (hkd Table 3. Because t lattice is body Brillouin zone 2.4 Fermi Sur-Espty lat: Tecpleton<sup>10</sup> det the method of H lone for Au and <sup>the dBvA</sup> data, others.17-20 <sup>Codel</sup> is the pr tereas extens only to that z supported also

$$S(hkl) = \sum_{i} f_{i} \exp(-2\pi i(hx_{i}+ky_{i}+lz_{i}))$$
[7]

is obtained by using the cubic conventional cell and summing over the positions

$$\frac{r_{i}}{1} = x_{i} \frac{a_{1}}{1} + y_{i} \frac{a_{2}}{2} + z_{i} \frac{a_{3}}{3}$$
[8]

and form factors  $f_i$  of the ions in the cell, expressed with respect to the conventional cubic axes  $\underline{a}_i$ . This structure factor predicts constructive interference of diffracted x-rays in the same directions as for a monatomic fcc crystal, but with different intensities due to the unequal scattering power of Au and Ga. Structure factors associated with the direction (hkl), that is, diffraction from planes (hkl), are given in Table 3.

Because the primitive Bravais lattice is fcc, the primitive reciprocal lattice is body centered cubic (bcc), and the first (and each reduced) Brillouin zone is the polyhedron of Figure 5.

## 2.4 Fermi Surface of AuGa2

Empty lattice Fermi surface. Jan, Pearson, Saito, Springford, and Templeton<sup>10</sup> determined the empty lattice Fermi surface of  $AuGa_2$  by the method of Harrison<sup>12</sup> in 1965, assuming a valence of seven electrons (one for Au and three for each Ga). It is in fair agreement with most of the dHvA data, reported first by them<sup>10</sup> and confirmed and extended by others.<sup>17-20</sup> The first zone is full. The most notable failure of the model is the prediction of a big octahedron of holes in the second zone, whereas extensive experiments have not shown a signal that could belong only to that zone. The conclusion that the second zone is full is supported also by a band structure calculation.<sup>21,22</sup> The third and

fourth z resistan predicte Prevente of the e evidence The Sectional Figures are from <sup>tur</sup>e. A, dayA data about the a pipiput <sup>area</sup> here "Piached ,

Cha	ara	cter of Diffraction Plane, (hkl)	Structure Factor S(hkl)
h,	k,	and l are all even	$4f_{Au} + 8f_{Ga}(-1)^{(h+k+l)/2}$
h,	k,	and 1 are all odd	4f <sub>Au</sub>
h,	k,	l mixed even and odd	zero

fourth zone sheets have been generally verified by the dHvA, magnetoresistance,<sup>23</sup> and a few other types of measurements.<sup>24</sup> Tiny pockets predicted in zones five and six by the model are expected to be prevented by the effect of the crystal potential's rounding off corners of the empty lattice Fermi surface. No experiments give definite evidence of occupation of zone five.<sup>19</sup> Zone six is certainly empty.<sup>19,22</sup>

The third zone sheet, the fourth zone sheet, and the extremal crosssectional areas for all sheets for directions <100> are shown in Figures 5, 6, 7, and 8, all for the empty lattice model. (The figures are from Ref. 10; its notation for cross sections is used in the literature. A, B, and C refer to directions <100>, <110>, and <111>.) The dHvA data of this thesis all pertains to the necks of the third zone, about the point L on the zone boundary, where the cross-sectional area is a minimum and the charge carriers are holes. The measured cross-sectional area here is .32 times that given by Figure 5, so that the necks are more "pinched off" than the figure suggests.

22

TABLE 3. Structure Factors of AuGa,

Figure 4. Cryst circ

Heure 5. Holes in t Bril

.



Figure 4. Crystal structure of AuGa<sub>2</sub>. Open circles are Au and filled circles are Ga. (Ref. 10)



Figure 5. Holes in the third zone of the empty lattice model of AuGa<sub>2</sub> in the reduced zone scheme. The polyhedron is the Brillouin zone. (Ref. 10)



Figure 6. H i

Rure 7.



Figure 6. Holes in the third zone of the empty lattice model of AuGa2 in the repeated zone scheme. Extremal cross sections are shown at right. (Ref. 10)



Figure 7. Fourth zone sheet of the empty lattice Fermi surface of AuGa2 in the repeated zone scheme. It has both electron and hole character. Extremal cross sections are shown at right. (Ref. 10)

EXTREMAL SECTION OF FERMI SUBJACE IN UNITS OF (27/6)<sup>2</sup>

Heure 8. Som. Surg (11) bang the sphe



Figure 8. Some extremal cross-sections of the empty lattice Fermi surface of  $AuGa_2$  when the magnetic field is scanned in a {110} plane. Sections corresponding to the 5th and 6th bands are shown by dotted lines. The top line framing the graph (7.02) refers to a great circle of the Fermi sphere. (Ref. 10)
Band		
structure		
ure 10 sh		
gon forme		
the star		
2.5 Orbi		
Cond		
generated		
paths. S		
the Ferni		
Where E		
charge q		
the condu		
crystal m		
valid dyn		
Then it i		
<sup>lagne</sup> tic		
While rep.		
Section of		
called an		
effect :		
13		

<u>Band structure</u>. Switendick  $^{21,22}$  calculated the nonrelativistic band structure (Figure 9) by the method of augmented plane waves (APW). Figure 10 shows the path Q, between points L and W, intersecting the hexagon formed by the third zone neck sheet (labeled '+' in Figure 10) and the star formed by the fourth zone sheet (labeled '-').

#### 2.5 Orbits on the Fermi Surface

Conduction electrons subjected to a magnetic field and the forces generated by the crystalline potential move in real space on complicated paths. Semi-classical theory relates this to the motion of <u>k</u>-states on the Fermi surface. The Lorentz force is

$$\underline{F} = \underline{\dot{p}} = q(\underline{E}_{t} + \frac{1}{c} \underline{v} \times \underline{B}_{t}) , \qquad [9]$$

where  $\underline{E}_t$  and  $\underline{B}_t$  are the total electric and magnetic fields seen by signed charge q of velocity  $\underline{v}$  and canonical momentum p. Assume (9) holds for the conduction electrons, and assume that replacement of p,  $\underline{E}$ , and  $\underline{B}$  by crystal momentum hk, and applied fields  $\underline{E}_a$  and  $\underline{B}_a$  respectively leaves a valid dynamical equation,

$$\underline{\mathbf{F}} = \mathbf{\hat{\mathbf{R}}} = \mathbf{q}(\underline{\mathbf{E}}_{a} + \frac{1}{c} \underline{\mathbf{v}} \times \underline{\mathbf{B}}_{a}) \quad . \tag{10}$$

Then it is easy to show that the application of a constant, uniform magnetic field causes electrons to undergo a continuous change of state while remaining at constant energy: the electron moves along the intersection of its energy surface and a plane normal to <u>B</u>. Such a path is called an orbit, whether or not it is closed. For a given Fermi surface and field direction there may be a continuum of orbits. The dHvA effect is dominated by closed orbits having extremal cross-sectional

Figure 9. Ener (Ref

/

Egure 10. Int C4 re: Pap



Figure 9. Energy bands of AuGa<sub>2</sub> by a non-relativistic APW calculation. (Ref. 22)



Figure 10. Intersection of the path Q with the orbits  $C_3'$  (hexagon) and  $C_4'$  (star). The empty lattice orbits have been modified to reflect the gap shown in Figure 9. Plane {111} lies in the paper.

areas. Figure

surface at two

<u>B</u> along the z-

surface of Au

The appli

to move along

area, in accor

is the origin

areas. Figure 11 illustrates such orbits on a hypothetical Fermi surface at two different orientations with respect to the applied field <u>B</u> along the z-axis, and Figures 6 and 7 show extremal orbits on the Fermi surface of  $AuGa_2$  when the field is along symmetry directions.

The applied magnetic field does more than cause the electron states to move along orbits. It turns out that closed orbits are quantized in area, in accordance with the Bohr-Sommerfeld quantum condition, and this is the origin of the dHvA effect. The theory is described in Section 3.4.

Reare 11.

(a)

(b)



Figure 11. Orbits on a hypothetical Fermi surface.

- (a) All extremal orbits (M = maximal area, m = minimal area) and one general orbit (G) for <u>B</u> along a symmetry direction.
- (b) The same types of orbits for the Fermi surface at an arbitrary orientation with field.

(or equiva

The d

zanifestei

(usually a

field 1/B

sectional

upon the c

and scatt.

a scatter

either T<sub>D</sub>

arises as

applied =

approach,

bility fo

<sup>in</sup> classi

equations

<sup>any</sup> Point

each Poin

Fortunate

cl<sub>assical</sub>

<sup>enclog</sup>ica

<sup>lechanics</sup>

orly small

### CHAPTER III

## BASIC THEORY OF THE DE HAAS-VAN ALPHEN EFFECT

The de Haas-van Alphen effect is the oscillatory magnetization (or equivalently, susceptibility) of crystals with free charge carriers manifested at low temperatures (usually below 20 K) and big fields (usually above 1 kG). The oscillations are periodic in reciprocal field 1/B with a period that is directly related to the extremal crosssectional areas of the Fermi surface. Their amplitudes are dependent upon the curvature of the Fermi surface, the cyclotron effective mass m\*, and scattering. The amplitudes yield density of states information and a scattering parameter, called the Dingle temperature and denoted either  $T_{D}$  or x, related to crystal imperfections. The dHvA effect arises as part of the response of band state electrons and holes to an applied magnetic field. The theory requires a quantum mechanical approach, as can be seen from calculations<sup>25</sup> of zero diamagnetic susceptibility for a classical gas of free electrons. Paraphrasing Dingle,<sup>35</sup> in classical theory the electrons pursue any path consistent with Maxwell's equations. Under such lax conditions the average electronic current at any point vanishes. Quantum theory restricts the orbits; the current at each point no longer averages out, and magnetic behavior becomes possible. Fortunately the gross features of the dHvA effect are predicted by semiclassical theory, and the important deviations can be expressed in phenomenological relations. Calculations using the full panoply of quantum mechanics and many body theory justify these results and generally give only small corrections, if any.<sup>26</sup> The basic semiclassical theory will

be given i dicted so The looking a field: t and the s Then are sketch o correcti <u>3.1 Two</u> <u>Xo</u> Lorentz field a Where k constan Thus cl follows form a Initipl: the k-s Equ <sup>Carri</sup>ers k:setati be given in this chapter, with mention when appropriate of features predicted solely by more complete methods.

The plan of this chapter is first to compare briefly two ways of looking at the magnetization of the conduction electrons in a magnetic field: the first involves the dynamics of electrons moving in a field, and the second is a thermodynamic approach. These give equivalent results. Then are presented a brief history of the dHvA effect, basic concepts, a sketch of the standard semiclassical theory, and finally some of the corrections to the semiclassical theory that are relevant to this study.

## 3.1 Two Aspects of Electronic Magnetization

Moving charges. This discussion follows Pippard.<sup>26</sup> The effective Lorentz force (10), with no applied electric field and with the magnetic field along the z-axis, can be integrated to yield

$$\underline{\mathbf{k}} - \underline{\mathbf{k}}_{\mathbf{O}} = \underline{\mathbf{s}} \times (\underline{\mathbf{r}} - \underline{\mathbf{r}}_{\mathbf{O}}), \qquad [11]$$

where  $\underline{k}_0$  and  $\underline{r}_0$  are constants of integration (which can be written as one constant), and s is a scaling factor,

$$\underline{s} = \frac{\underline{B}}{\hbar c/e}$$
 [12]

Thus closed orbits in <u>k</u>-space are related to the path in real space as follows: Project the real space path onto a plane normal to <u>B</u>; it will form a closed path. Rotate this path by a positive angle  $\pi/2$  about <u>B</u> and multiply its area by the scaling factor s<sup>2</sup>. The result is congruent with the k-space orbit. (This is Onsager's theorem.)

Equation (10) is sometimes called the dynamical expression for charge carriers in crystals. The velocity  $\underline{v}$  it contains is given by the kinematical expression,

These lead  $4^2$ charge carrie where defines the  $\epsilon$ area of the c The real essarily clos. with a pitch : motion in <u>k-sp</u> For reasons t <sup>iccinated</sup> by a <sup>vhose</sup> areas A Pippard<sup>26</sup> sho: is the same a where A is the

$$\underline{\mathbf{v}} = \frac{1}{h} \nabla_{\underline{k}} E(\underline{k}) \quad .$$
 [13]

These lead<sup>42</sup> to the following expression for the cyclotron frequency of a charge carrier on a closed orbit on the Fermi surface:

$$\omega^{\star} = \frac{eB}{m^{\star}c} , \qquad [14]$$

where

$$m^* = \frac{\hbar^2}{2\pi} \frac{\partial A_k}{\partial E}$$
 [15]

defines the effective mass for the orbit, and A is the cross-sectional k area of the orbit in <u>k</u>-space.

The real space path corresponding to an orbit in <u>k</u>-space is not necessarily closed. But the field does render the path periodic along <u>B</u>, with a pitch Z in real space. An analysis of the electron's corresponding motion in <u>k</u>-space, as was done for (15), leads to<sup>26</sup>

$$sZ = \partial A_k / \partial k_z$$
 [16]

For reasons that will become apparent in Section 3.4, the dHvA signal is dominated by charge carriers on extremal orbits, that is, closed orbits whose areas  $A_k$  in <u>k</u>-space are extremal. For these the pitch is zero. Pippard<sup>26</sup> shows that the magnetization due to electrons on extremal orbits is the same as for the equivalent current loop:

$$M = e\omega A/2\pi , \qquad [17]$$

where  $\underline{A}$  is the vector area of the closed, real space path, with components

$$A_{\mathbf{x}} = \frac{1}{s^2} \frac{\partial A_{\mathbf{k}}}{\partial \Theta_{\mathbf{y}}}, \qquad [18a]$$

$$A_{y} = \frac{1}{s^{2}} \frac{\partial A_{k}}{\partial \theta_{x}} , \qquad [18b]$$

where  $\frac{\partial}{\partial y}$  re f to rotat tion of equ the extrem. shows <u>M</u> an M parallel this is us Therm the depend through t This can of a Lagn correspon intensity ael-holtz cianges a Special c <sup>calculati</sup> on strain <sup>az</sup> electr.

Where n is the Fermi-

$$A_{z} = \frac{1}{2} A_{k}$$
, [18c]

where  $\theta_y$  refers to rotation of B about the y-axis (coincident with  $k_y$ ),  $\theta_x$  to rotation about the x-axis, and equation (18c) follows from integration of equation (11) about the orbit. The derivatives are evaluated at the extremal cross sections for the given field direction. Equation (18) shows <u>M</u> and <u>B</u> are not generally parallel. However, from (18) one expects <u>M</u> parallel to <u>B</u> when along symmetry directions of the Fermi surface, and this is usually the case.

<u>Thermodynamic approach</u>. The magnetization of a system is related to the dependence of its Gibbs free energy G on the magnetic intensity H through the thermodynamic relation

$$\underline{\mathbf{M}} = -(\nabla_{\mathbf{H}}\mathbf{G})_{\mathbf{T}}.$$
 [19]

This can be demonstrated by considering the work and heat energy changes of a magnetic system. It is analogous to  $V = -(\partial G/\partial P)$ , where volume V corresponds to magnetization M, and pressure P corresponds to magnetic intensity H.<sup>27</sup> Frequently no distinction is made between the Gibbs and Helmholtz free energies in a solid system, since the effects of volume changes are negligible and reference is made simply to the free energy  $\Omega$ . Special cases are considered separately. For example, magnetostriction calculations require that the free energy explicitly include the dependence on strain. The general expression for the free energy per unit volume of an electron gas is<sup>28</sup>

$$\Omega = nE_F + k_B T \Sigma \ln[1-f_o(E)], \qquad [20]$$
states

where n is the total number of conduction electrons per unit volume,  $f_0$  is the Fermi-Dirac function, and the summation is over all conduction states.

Equation (19

Implicat

sufficiently

sufficiently

this region a

can make sev

be carried f

moving char

with equal

occupied or

given cross

dynamics, t

an amount :

are relate

A bri

these basi

in inverse

3.2 Histo

The d The d The observ year anoth by de Haas Indep Landau<sup>30</sup>

steady magn

Equation (19) then is rewritten as

$$\underline{\mathbf{M}} = -(\nabla_{\underline{\mathbf{H}}}\Omega)_{\mathrm{T}}.$$
 [21]

Implications for the dHvA effect. When a region of the sample is sufficiently extensive that it can contain the electronic motion and sufficiently crystalline, pure, and cold that there is associated with this region a well defined Fermi surface on which the electronic states can make several orbits before scattering, then both approaches above can be carried further to yield the dHvA effect. From the point of view of moving charges and orbits on the Fermi surface, the orbits become quantized, with equal increments of area  $A_k$  between orbits and some finite number of occupied orbits (i.e. the number of quantized orbits that fit within the given cross section of Fermi surface). From the point of view of thermodynamics, the conduction electrons contribute to the total free energy an amount  $\Omega_{osc}$ , which oscillates with field. Of course, these two approaches are related, as demonstrated at the end of Section 3.7.

A brief history of the dHvA effect is followed by definitions of these basic concepts: Landau levels, quantization of orbits, periodicity in inverse field, and dHvA frequency.

# 3.2 History of the de Haas-van Alphen Effect

The dHvA effect is named after W. J. de Haas and P. M. van Alphen,<sup>1</sup> who observed it in 1930 in a single crystal of bismuth. Later that same year another quantum oscillation effect, in magnetoresistance, was observed by de Haas and Shubnikov.<sup>29</sup>

Independently of de Haas and van Alphen, but in the same year, 1930, Landau<sup>30</sup> considered the quantum mechanical problem of free electrons in a steady magnetic field and remarked that the magnetization of a metal would

be expe the orb called effect ic ene have c name i was Pr Landa odic Blac. rest àić for Kos, cal ear the Ie fo Cą t be expected to exhibit periodic variations because of the quantization of the orbits of the conduction electrons. The energy levels of this system, called Landau levels, enter directly into the calculation for the dHvA effect. Although calculations from first principles are limited to quadratic energy surfaces, the concept is extended to real metals, most of which have complicated Fermi surfaces not resembling ellipsoids. Thus Landau's name is associated with the early development of the dHvA theory. But it was Peierls<sup>31</sup> who in 1933 first addressed the dHvA effect, by showing that Landau's quantization extends to conduction electrons in systems with periodic potentials. Between the years 1933 and 1939 Landau, <sup>30</sup> Peierls, <sup>31</sup> 32 Blackman, and Shoenberg developed the theory of Landau levels, still restricted to ellipsoidal energy surfaces. Not until the years 1952-56 did Onsager, Dingle and Lifshitz and Kosevich develop the theory for Fermi surfaces of general shape, usually referred to as the Lifshitz-Kosevich (LK) semiclassical theory. As the name suggests, this was not a calculation directly from the Schrodinger equation, but concepts from the earlier theory were incorporated. This raised the question of whether all the results of the LK semiclassical theory were generally applicable. In recent years full quantum mechanical calculations have given this theory a formal foundation and extended many of the important results to the general (See Ref. 38, hereafter called Gold, for examples and references to case. these calculations.)

The dHvA effect was thought to be a peculiarity of bismuth until observed in zinc in 1947 and shortly afterwards in a number of other metals.<sup>39,54</sup> Its importance as a tool to study the Fermi surface was perhaps not fully appreciated until Onsager<sup>34</sup> in 1952 showed that the frequencies of the oscillations (with respect to inverse field) are directly proportional to the extremal cross-sectional areas of the Fermi surface perpendicular to

the field. crystals. Within were done or. early work w characterize. day. For a ipurities h of theories much more qu Chapter IV. Meanwhij types of cry; (PbTe) and a: possess both their Fermi s <sup>of</sup> pure metal In recer <sup>access</sup> the d: <sup>derivatives,</sup> The rela <sup>and</sup> the fundena other tha ield is char Properties (-<sup>capacity</sup>, mag thermal con-<sup>constant</sup>). -

the field. It is now extensively used to study the Fermi surface of crystals.

Within a few years of the discovery of the dHvA effect, experiments were done on dilute alloys of bismuth.<sup>69</sup> In fact, some feel that all the early work was on samples that were effectively alloys, albeit poorly characterized ones, when compared with the highly purified metals used today. For a number of years the goal of dHvA studies on samples to which impurities had been added was the study of the scattering and the testing of theories predicting amplitude dependence. These studies have now become much more quantitative and have increased their scope, as mentioned in Chapter IV.

Meanwhile, experimentalists were looking for dHvA signals in other types of crystals. In 1961 they were first observed in a semiconductor<sup>40</sup> (PbTe) and an intermetallic compound<sup>41</sup> (InBi). Intermetallic compounds possess both long range order and a high density of charge carriers, so their Fermi surfaces have been studied in nearly as much detail as those of pure metals.

In recent years other investigations have profited by the direct access the dHvA effect gives to the Fermi surface. One example is pressure derivatives, the effect of pressure on the band structure.

The relation of the free energy to the dHvA effect (see Section 3.1) and the fundamental importance of the electronic energy suggest that phenomena other than magnetic susceptibility will exhibit oscillations as the field is changed, and these are observed in abundance, in both equilibrium properties (magnetic susceptibility, quasi-adiabatic temperature, heat capacity, magnetostriction, and contact potential) and transport properties (thermal conductivity, magnetoresistance, thermo-electric power and Hall constant). The generic term for these phenomena is quantum oscillations.

Because
informa
orbit
and cy
to det
tion t
Measur
or pre
condi
3.3
a vol
bound
(5).
chang
Waves
ت=:e
ener
stet <sup>e</sup> . پور
arg 1
their
equati

Because quantum oscillations involve orbits on the Fermi surface they yield information about its topology and various parameters, such as extremal orbit areas, energy levels, level widths (related to crystalline perfection), and cyclotron effective masses. The dHvA oscillations are usually easier to detect than the other oscillations, and have made the biggest contribution to the measurement of the cross-sectional areas of Fermi surfaces. Measurements of the other quantum oscillations sometimes give more accurate or precise values for the other parameters, depending on the substance and conditions.

### 3.3 Landau Levels

<u>Free electron model.</u> Free, non-interacting electrons constrained to a volume V of dimensions  $l_x$ ,  $l_y$ ,  $l_z$  satisfying periodic (Born-von Kármán) boundary conditions have single particle energy levels given by Equation (5). Application of a magnetic induction

$$\underline{B} = B\hat{z}$$
[22]

changes the quantization scheme: new wave functions replace the plane waves,  $k_x$  and  $k_y$  are no longer good quantum indices, and two new quantum numbers arise, one of which is n = 0, 1, 2, ... and appears in the new energy,

$$E_n(k_z) = h\omega_0(n + 1/2) + \frac{h^2k_z^2}{2m_0}$$
, [23]

where  $m_0$  is the free electron mass, the cyclotron frequency is

$$\omega_{\rm O} = \frac{\rm eB}{\rm m_{\rm O}C} , \qquad [24]$$

and 1/2 is a phase constant. These levels are called Landau levels, after their first calculation by Landau,<sup>30</sup> who started from the Schrödinger equation for magnetic field,

where the kin He used the L for flux dens <u>H</u> is substitu given simply because one i

of energy wit

The abse

the Landau le

crystalline p

<sup>existence</sup> of of the Landau

D.

Degenera

274) shows (2

and

<sup>there</sup> u(x) sat <sup>bar</sup>lonic oscil

n.

$$\frac{\left(\underline{p}-\underline{e}_{A}\right)^{2}}{2m_{o}} \psi = E\psi , \qquad [25a]$$

where the kinetic momentum operator is

$$\underline{\mathbf{p}} = \frac{\mathbf{h}}{\mathbf{i}} \nabla \cdot \mathbf{i}$$
 [25b]

He used the Landau (also, linear) gauge for the vector magnetic potential

$$A = B(0,x,0)$$
 [25c]

for flux density <u>B</u> parallel to the z-axis. (Frequently magnetic intensity <u>H</u> is substituted for <u>B</u> in the literature.) Usually the Landau level is given simply as

$$E_n = h_{\omega_0}(n + 1/2)$$
, [26]

because one is usually interested in a fixed value of  $k_z$ , so the variation of energy with  $k_z$  can be ignored.

The absence of the second new quantum number in (23) and (26) renders the Landau levels of higher degeneracy than the energy levels of the crystalline potential, a characteristic which is intimately related to the existence of the dHvA effect. In view of this, a sketch of the derivation of the Landau levels and their degeneracies is warranted.

Degeneracy. A standard derivation (see, for example, Ziman, pp. 269-274) shows (25) is satisfied by

$$E = E' + \frac{h^2 k_z^2}{2m_0}$$
 [27]

and

$$\psi(\mathbf{x},\mathbf{y},\mathbf{z}) = \mathbf{u}(\mathbf{x}) \exp(\mathbf{i}(\beta \mathbf{y} + \mathbf{k}_{\mathbf{z}}\mathbf{z})), \qquad [28]$$

where u(x) satisfies the one-dimensional Schrödinger equation for a simple harmonic oscillator,

of frequency \_ The eigenvalue Equations (27) 9 quantizes k z of k is unres by (30) if one whose orbits 1 them for macro giving Thus the numbe <sup>making</sup> each le <sup>So that</sup> the de <sup>threading</sup> the All these <sup>but are direct:</sup>

$$-\frac{\hbar^2}{2m_o}\frac{d^2u(x)}{dx^2} + \frac{m_o}{2}(\omega_o x - \frac{\hbar\beta}{m_o})^2 u(x) = E'u(x) , \qquad [29]$$

of frequency  $\omega_{O}$  and centered at the point

$$x_{o} = \frac{1}{\omega_{o}} \frac{\hbar\beta}{m_{o}}$$
[30]

The eigenvalue problem (29) has eigenvalues

$$E' = \hbar \omega_0 (n + 1/2)$$
 [31]

Equations (27) and (31) give the final result (23). Single-valuedness of  $\psi$  quantizes  $k_z$  and  $\beta$  in units of  $2\pi/\ell_z$  and  $2\pi/\ell_y$  respectively. The range of  $k_z$  is unrestricted, as in zero field, but the range of  $\beta$  is restricted by (30) if one considers only those states corresponding to electrons whose orbits lie completely within volume V (which is practically all of them for macroscopic V). Thus

$$0 \leq x_{0} \leq \ell_{x} , \qquad [32]$$

giving

$$0 \leq \beta \leq \frac{m_0 \omega_0^{\ell} x}{\hbar} = \frac{eB}{\hbar c} \ell_x .$$
 [33]

Thus the number of distinct values of  $\beta$  is

$$p_{o} = \frac{m_{o}\omega_{o}}{h} \ell_{x}\ell_{y} , \qquad [34]$$

making each level (23) p-fold degenerate. Note that

$$p_{o} = \frac{B^{l} x^{l} y}{hc/e} = \frac{total \ flux}{flux \ quantum} , \qquad [35]$$

so that the degeneracy of each level equals the number of flux quanta threading the specimen.

All these derivations are for a right parallelpiped and for  $\underline{B} || \hat{z}$ , but are directly extendible to a specimen of general shape and for general

field orien
Period
the field,
the levels
occupied le
(E.g., n <sub>o</sub> =
at which le
B <sub>2</sub> > B <sub>1</sub> be
visida
STELETING
·#-:
which is in
lion of the
<sup>1/b</sup> , with a
Each denor
k <sub>n</sub> tenlaa
field in the second sec
chanze in 1
tth mer
is sate
$\frac{\operatorname{Satisfie}}{\operatorname{S}(k)}$
l"H, wit the c:
- <sup>sign</sup> al.

field orientation,  $k_z$  becoming  $k_H$  for the latter case.

<u>Periodicity.</u> Figure 12 shows the relation between the Landau levels, the field, and the Fermi level. Equation (26) shows the spacing between the levels increases in proportion to the field so that the highest occupied level  $n_0$  suddenly depopulates as its energy value rises above  $E_F$ . (E.g.,  $n_0 = 7$  at  $B = B_1$  and  $n_0 = 6$  over  $B_1 < B \leq B_2$ .) Let  $B_1$  be the field at which level  $E_n = E_F$  for some specific quantum number  $n = n_0$  and let  $B_2 > B_1$  be the field at which level  $n_0$ -1 equals  $E_F$ . From (26) this gives

$$\frac{E_F}{(\hbar e/m_0 c)} = B_1(n_0 + 1/2) = B_2(n_0 - 1/2) , \qquad [36]$$

yielding

$$\frac{1}{B_1} - \frac{1}{B_2} = \frac{1}{B_1(n_0 + 1/2)} = \frac{\hbar e/m_0 c}{E_F}$$
[37]

which is independent of the quantum numbers at the Fermi level; depopulation of the levels occurs at equally spaced intervals in inverse field, 1/B, with a period

$$P = \frac{1}{B_n} - \frac{1}{B_{n-1}} = \frac{(he/m_oc)}{E_F} .$$
 [38]

Each depopulation means a sudden change in the energy (23),  $E_n(k_H)$ , where  $k_H$  replaces  $k_z$  to allow for a general orientation of the crystal in the field, in line with the definitions in Section 2.1. This sudden energy change implies, by Section 3.1, a consequent pulse in magnetization, with pulses from different  $k_H$  generally out of phase because  $E_n(k_H) = E_F$  is satisfied at different fields B (through  $\omega_0$ ). Near extremal values of  $E_n(k_H)$ , with respect to  $k_H$ , the pulses are in phase, and these dominate the signal.



Hgure 12. The r E<sub>F</sub>. an ar highe value



Figure 12. The relation between the Landau levels and the Fermi level  $E_F$ . At any field B the Landau levels are equally spaced by an amount that is proportional to B. As B increases the highest occupied level  $n_o$  suddenly depopulates as its energy value rises above  $E_F$ .

Real		
depopulati		
electron m		
of state o		
holes as t		
the Fermi		
with quadra		
replaced by		
ture masses		
plicated Fe		
talline im:		
hibit simil		
tion		
for the Lan		
is not nece		
very near :		
3.4 Quanti		
Derivat		
<sup>de Haas-van</sup>	•	
<sup>shape</sup> by cor		
<sup>tronic</sup> orbit		
<sup>electrons</sup> as		
<sup>Scommerfeld</sup> q		
Viere _		

**.**....

<u>Real crystals.</u> The existence of Landau levels and the periodic depopulation occur in systems far more complicated than the simple free electron model. All quantum oscillations arise from the sudden change of state of a non-negligible fraction of the conduction electrons and holes as the magnetic field causes successive Landau levels to exceed the Fermi level  $E_F$ . The quantitative theory can be extended to crystals with quadratic energy surfaces by generalizing to the effective mass,  $m_o$ replaced by  $m^* = (m_1m_2)^{1/2}$  in equation (23), where  $m_i$  are the band structure masses (elements of the effective mass tensor). But even for complicated Fermi surfaces in the presence of finite temperatures and crystalline imperfections the properties of the band states continue to exhibit similar periodicities, governed by the slightly more general equation

$$E_{n} = \hbar \omega * (n + \gamma)$$
 [39]

for the Landau levels, where  $\omega^*$  is given by (14) and the phase constant  $\gamma$  is not necessarily 1/2. But full quantum theory and experiments give  $\gamma$  very near 1/2 for most metals (Gold, pp. 45 and 85).

## 3.4 Quantization of Orbits

<u>Derivation.</u> In 1952 Onsager<sup>34</sup> was able to extend the theory of the de Haas-van Alphen effect in crystals with Fermi surfaces of arbitrary shape by considering the effect of the applied magnetic field on the electronic orbits, rather than the electronic energy levels. In a field the electrons assume orbital motion, which is quantized according to the Bohr-Sommerfeld quantum condition

$$\$P_{n} dq = \hbar(n + \gamma) , \qquad [40]$$

where q is the generalized coordinate, p is the canonical momentum

<u>A</u> is the
of the e
force (1
orbits a
Where p.
Landau 1.
to be un
$\gamma = 1/\gamma$
Ret
to obtain
From the
<sup>the</sup> Path
<sup>By</sup> Stokes
Substitut
Show -
is a
uanti 🤍
Cyli
<sup>of</sup> arbitr
cross-sect
musber the

$$\underline{\mathbf{p}}_{\mathbf{c}} = \hbar \underline{\mathbf{k}} + \frac{\mathbf{q}}{\mathbf{c}\underline{\mathbf{A}}} , \qquad [41]$$

<u>A</u> is the vector potential, and  $\gamma$  is a phase constant. This quantization of the electron motion in real space leads, by the semiclassical Lorentz force (10), to the quantization of orbits in <u>k</u>-space, so that only those orbits are allowed whose area is given by

$$A_n = 2\pi s(n + \gamma) , \qquad [42]$$

where n and  $\gamma$  are the same quantum number and phase constant as in the Landau levels (39), s is the scaling factor (12), and <u>B</u> (in s) is assumed to be uniform over the electron's orbit. For quadratic energy surfaces  $\gamma = 1/2$ .

Returning to (40), combine it with equations (11), (12), and (41) to obtain

$$\underline{B} \cdot \underline{\$r} \times d\underline{r} - \underline{\$A} \cdot d\underline{r} = 2\pi s(n + \gamma).$$
[43]

From the definition of flux  $\Phi$  through the area  $A_{\text{H}}$  defined by projecting the path onto a plane normal to <u>B</u>,

$$\underline{\mathbf{B}} \cdot \underline{\mathbf{s}} \underline{\mathbf{r}} \times \mathbf{d} \underline{\mathbf{r}} = 2\Phi \quad . \tag{44}$$

By Stokes's theorem

$$\$A \cdot dr = \int curl A \cdot da = \Phi .$$
 [45]

Substitution into (43) gives

$$2\pi s(n + \gamma) = \Phi = BA_{H}, \qquad [46]$$

showing that the flux in the projected real space area  $A_H$  of the orbit is quantized. Onsager's theorem transforms (46) directly into (42).

<u>Cylinders of orbits.</u> Figure 13 shows orbits at  $k_H$  on a Fermi surface of arbitrary shape. This is referred to as a slice of <u>k</u>-space.  $A_F$  is the cross-sectional area at the Fermi surface. Because  $k_H$  is a good quantum number the orbits are quasi-continuous along the field direction and form
tubes of parallel tube is n quadratic in which c As th face in Fi depopulate level (39) causes a pu of moving c slices alor next subsec Period between the sizilar to  $\frac{A_{f}(k_{H})}{E}$  be the <sup>nor</sup>⊒al to <u>B</u> <sup>surface</sup> cont the discussi âŊ <sup>are equivale</sup> <sup>the</sup> period in tubes of constant cross-sectional area with a common axis, not necessarily parallel to <u>B</u>, unless <u>B</u> is parallel to a symmetry axis. The shape of a tube is not necessarily constant along  $k_{\text{H}}$  unless the energy surfaces are quadratic,

$$E(\underline{k}) = \frac{\hbar^2}{2m^*} \underline{k} \cdot \underline{A} \cdot \underline{k} , \qquad [47]$$

in which case they are elliptic cylinders (Gold, p. 44). See Figure 14.

As the field increases and a given orbit passes beyond the Fermi surface in Figure 13 the Fermi-Dirac distribution requires that it suddenly depopulate. Each orbit (42) corresponds to a highly degenerate Landau level (39), and the sudden change in the distribution of orbit states causes a pulse in the magnetization, as expected from the point of view of moving charges, Section 3.1. The way in which pulses from different slices along k contribute to the total dHvA signal is discussed in the  $_{\rm H}$  next subsection.

<u>Periodicity and dHvA frequency.</u> The period in inverse field 1/Bbetween the pulses coming from a given slice can be found by an analysis similar to that made for Landau levels. For a fixed field direction let  $A_F(k_H)$  be the area of the intersection of the Fermi surface with the plane, normal to <u>B</u> at  $k_H$ , that defines the slice of <u>k</u>-space. (Note that the Fermi surface contains an orbit only for discrete values of B.) As suggested by the discussions of pulses in the magnetization, the conditions

$$E_n(k_H) = E_F$$
 [48]

and

$$A_{n} = A_{F}(k_{H})$$
[49]

are equivalent. Comparison of equations (39) and (42) gives immediately the period in inverse field for the orbits breaking through the Fermi surface:



Figure 13. A slice in <u>k</u>-space showing quantized orbits superposed on a Fermi surface of arbitrary shape, at some value of  $k_H$ . This is not necessarily an extremal cross-section. <u>B</u> is parallel to  $k_H$ .



Figure 14. Changes in the quantization scheme as the principal axes of an ellipsoidal Fermi surface vary their orientation in <u>B</u> = <u>H</u>. The number of cylinders (levels) increases as the maximal cross-sectional area of the ellipsoid increases. (From Gold, p. 44)

I t **L**á wł Fi s: () coi Whe the den har: for cons sign Dexia field The t <sup>add</sup>it

$$P = \frac{1}{B_{n}} - \frac{1}{B_{n-1}} = \frac{2\pi e}{\hbar c} \frac{1}{A_{F}(k_{H})}$$
 [50]

43

It can be shown that magnetization from each slice versus 1/B is a sawtooth wave (Figure 16(a)), with a period that varies with  $k_H$ , so that signals tend to cancel except those from that part of the Fermi surface for which  $A_F(k_H)$  is stationary with respect to  $k_H$ : the extremal orbits. Figures 16(c) and 16(d) show the net magnetization after summing over slices in the vicinity of a maximum and minimum in cross-sectional area. (One figure is for no spin, and the other for spin 1/2 electrons.)

The inverse of the grouping in (50) occurs often enough that it is convenient to define the dHvA frequency

$$F(\Theta,\phi) = \frac{hc}{2\pi e} A_{F,ext} .$$
 [51]

where the dHvA frequency F depends on the field direction  $(\Theta, \phi)$  through the extremal cross-sectional area  $A_{F,ext}$  of the Fermi surface, hereafter denoted A<sub>F</sub>. The dHvA signals (Figures 16(c) and (d)) can be resolved into harmonic components, each having a distinct period when plotted against 1/B:

$$M_{osc,r} \propto \sin[2\pi r(\frac{F}{B} - \gamma) + \frac{\pi}{4}], \qquad [52]$$

for the r-th dHvA harmonic, where the positive sign in the second phase constant is for orbits of minimal cross-sectional area, and the negative sign, for maximal. Figure 16(e) shows the fundamental harmonic for both maxima and minima. There may be more than one value of  $A_F$  for a given field orientation; then there are terms like (52) for each dHvA frequency. The total magnetization will also have a non-oscillatory term, due to additional magnetism from the electrons and from the lattice.

Equation (52) shows the dHvA signal is directly related to the Fermi

surface can giv and in As orbits the net occurri Fermi su Deg each orb degenera <u>k</u>-states area betw the semic. <sup>here</sup> a ca the free. In z energies <sup>com</sup>es H : E' given g <sup>energy</sup> of set (n, K<sub>H</sub>) çuantum nu classical Assuming t in what reg <sup>for any</sup> fie surface's extremal cross-section in each direction, information that can give good clues about the shape and dimensions of the Fermi surface, and in simple cases allows direct calculation.

As outlined above, the sum of pulses in magnetization from all orbits passing through the Fermi surface generates the oscillations in the net dHvA signal. Equivalently, the oscillations can be imagined as occurring when each cylinder (Figure 13) or tube of orbits bursts the Fermi surface, which can occur only at extremal cross-sections.

<u>Degeneracy</u>. As mentioned in the subsection on cylinders of orbits, each orbit represents a degenerate energy level. It turns out that the degeneracy is the same for each level and equals the number of former <u>k</u>-states that lie between the orbits, a result known as sweeping out the area between orbits. Although a rigorous proof of degeneracy is beyond the semiclassical arguments presented so far in this section, we present here a calculation showing the validity of this heuristic concept for the free electron model.

In zero magnetic field the free electron model has discrete eigenenergies  $E = h^2 k^2 / 2m_o$ . In magnetic fields the Schrodinger equation becomes H = E', where H is given in (25a), with discrete eigenenergies E' given by (23). The energy difference  $U_n = E' - E$  is the change in energy of the state <u>k</u> as it is transformed into one of the states of the set  $(n, k_H)$ . By the correspondence principle, in the limit of big quantum numbers we expect both systems to have the same energy, since classical charge carriers do not gain energy in a steady magnetic field. Assuming this carries over to each slice of <u>k</u>-space, the question is, in what region can an orbit "sweep out" the <u>k</u>-states so that U = 0 for any field? This is answered by summing over

47

states w:

orbit (F

where

and

Using the

<u>k</u>-space

in

Bives

The limits

states within a slice of unit thickness over a trial region for the n-th orbit (Figure 15). Consider

$$U_{n} = (E'-E)_{one} = \hbar_{\omega_{0}}(n+1/2) + \frac{\hbar^{2}k_{p}^{2}}{2m_{0}}$$
[53a]

$$= \frac{\hbar^2}{2m_o} \left( 2s(n + 1/2) - k_p^2 \right)$$
 [53b]

$$= \frac{\hbar^2}{2\pi m_0} \left( A_n - A_k \right) , \qquad [53c]$$

where

$$k_p^2 = k_x^2 + k_y^2$$
 [54]

and

$$A_{k} = \pi k_{p}^{2} .$$
 [55]

$$w_{k} = \frac{\ell_{x}\ell_{y}}{(2\pi)^{2}}$$
[56]

in

$$U_{\text{slice}} = \int_{A_{k,1}}^{A_{k,2}} U_n(A_k) w_k dA_k, \qquad [57]$$

gives

$$U_{\text{slice}} = \int_{A_{k,1}}^{A_{k,2}} \left( \frac{\ell_{x} \ell_{y} \hbar^{2}}{4\pi^{2} m_{0}} \right) \left( A_{n} - \pi k_{p}^{2} \right) k_{p} dk_{p} .$$
 [58]

The limits shown in Figure 15(a),

$$A_{k,1} = \left(\frac{A_n - \Delta A/2}{\pi}\right)^{0.5}$$
 [59a]

Assi of <u>k</u> to le (a)

(b)

Pigure 15.



Figure 15. Former <u>k</u>-states lying between quantized orbits are swept onto the orbits. Alternative schemes (a) and (b) for circular orbits in a slice from a spherical Fermi surface.

and where is the ce a result o in Figure and give the re which is no of Figure 1 3.5 Tempera The eff <sup>the latter</sup> r <sup>Dingle</sup> tempe The higher ha Nonzero <sup>the sharp</sup> Fer and

$$A_{k,2} = \left(\frac{A_n + \Delta A/2}{\pi}\right)^{0.5}$$
, [59b]

where

$$\Delta A = 2\pi s$$
 [59c]

is the center area associated with the phase constant 1/2, give

$$U_{slice} = 0$$
, [60]

a result consistent with the correspondence principle. The limits shown in Figure 15(b),

$$A_{k,1} = \left(\frac{A_n}{\pi}\right)^{0.5}$$
 [61a]

and

$$A_{k,2} = \left(\frac{A_{n+1}}{\pi}\right)^{0.5}$$
, [61b]

give the result

$$U_{\text{slice}} = - \left( \frac{e^{2\ell_{x}\ell_{y}}}{4\pi m_{o}c^{2}} \right) B^{2} , \qquad [62]$$

which is not consistent with the correspondence principle. Thus the scheme of Figure 15(a) is the one to use.

# 3.5 Temperature and Scattering Effects

The effect of both temperature T and scattering on the Fermi surface, the latter represented by the scattering parameter X, or equivalently, Dingle temperature  $T_D$ , is to reduce the amplitudes of the dHvA signal (52). The higher harmonics of  $M_{\rm osc}$  are reduced the most.

Nonzero temperature. The equations of Sections 3.3 and 3.4 assume the sharp Fermi surface and Fermi energy obtaining at zero absolute

v G of le eχ dH: are are fin Pas ter atur

Where

temperature. At temperatures above zero both of these quantities are "smeared out," the Fermi level  $E_F$  by an amount  $k_B^T$  and the Fermi surface by an equivalent amount in <u>k</u>-space. Hence from the points of view of either Landau levels passing through  $E_F$  or orbits passing through the Fermi surface, depopulation of states occurs over a broader field range, with a consequent attenuation of magnetization.

The existence of quantum oscillations requires

$$\hbar\omega^* \geq k_B^T$$
, [63]

where  $h\omega^*$  is the quantum of energy for the system with magnetic field. In Gaussian units this is equivalent to

$$B(kG) \ge 7.45 \frac{m^*}{m_o} T(K).$$
 [64]

Another consequence of finite temperature is in increased scattering of the electrons by phonons. This increases the width of the energy levels, with an effect on  $M_{OSC}$  amplitude that goes approximately as exp(-const. T/B).

<u>Scattering.</u> Impurities and strains in the crystal also attenuate the dHvA signal. A nonrigorous approach is to argue that the Landau levels are given a finite width as the electron lifetimes in the orbital states are reduced from infinity to finite values by scattering, and that this finite width further decreases the rate of level depletion as the level passes  $E_F$ . Dingle<sup>36</sup> first modified the dHvA theory for the effect of scattering, expressing it in terms of an increase  $T_D$  in the effective temperature, which appears in an attenuation factor added to (40):

$$M_{\rm osc} \propto e^{-r\alpha T_{\rm D}/B} \sin[2\pi r(\frac{F}{B} - \gamma) + \frac{\pi}{4}], \qquad [65]$$

where

and k lifet these These (Gold, D the am real m slight] (67). However theory d5vA ef pcint a real sp shows t <sup>and</sup> ana <sup>Ch</sup>apter Two <sup>nitude</sup> c dence on the Ferm <sup>field</sup> is

$$\alpha = 2\pi^2 k_{\rm B} m^* c/\hbar e , \qquad [66]$$

and  $k_{p}$  is Boltzmann's constant.

Dingle also investigated the relations among  $T_D$ , the mean inverse lifetime  $1/\tau$  on the orbit, and the level width  $\Gamma$ . The present forms for these relations are

$$\exp(-\pi/\omega^*\tau) = \exp(-2\pi\Gamma/\hbar\omega^*) = \exp(-2\pi^2k_BT_D/\hbar\omega^*) . \qquad [67]$$

These relations assume a Lorentzian line shape for the energy levels (Gold, pp. 57-58).

Dingle assumed the free electron model, but the field dependence of the amplitude of M as given in (65) is observed to hold very well for osc real metals, and a Green's function calculation by Brailsford <sup>44</sup> only slightly modified Dingle's results, with a factor 2 in lifetime, giving (67). Others <sup>45</sup> extended these expressions to general Fermi surfaces. However, accurate numbers for T must be found experimentally, and the theory is not clear on just how disordered a crystal may be before the 46,47 dHvA effect can no longer exist. It used to be thought that if point and line defects approached a density of one per electron orbit in 48 real space that no dHvA oscillations would be observed, but recent work shows that even in this limit the signal is strong enough for measurement and analysis, and the theory is still under development, as described in Chapter IV.

Two important characteristics of T are its independence of the magnitude of magnetic field in nonmagnetic media,  $^{60}$  and its noticeable dependence on field orientation. The latter effect arises because scatter on the Fermi surface is generally anisotropic, and as the orientation of the field is changed different regions of the Fermi surface make the dominant

conti 3.6 į the i: shitz effect throug shifte and sh S = <u>+1</u> transf upon re signals the tot a trigo: <sup>shews</sup> th <sup>splittin</sup> it <sub>can a</sub>

. .

contribution to the dHvA signal.

## 3.6 Spin Splitting

Dingle<sup>35</sup> first considered the effect on electronic magnetization of the interaction of the electron's spin with the magnetic field. Lif-<sup>37</sup> shitz and Kosevich<sup>37</sup> extended his result to arbitrary effective mass. The effect of Zeeman splitting of each Landau level is to give, for any slice through the Fermi surface, two sets of levels with the same spacing but shifted in phase, giving rise to two signals of half the original amplitude and shifted in phase. The field's interactions with the electron spin  $S = \pm 1/2$  perturbs the spinless Landau levels (39) by the amount  $Sg\mu_B^B$ , transforming (39) into

$$E_n = \hbar\omega * (n + \gamma) + \frac{1}{2}g\mu_B \qquad [68a]$$

$$= \hbar \omega * (n + \gamma + gm * / 4m_{2})$$
 [68b]

upon removing common factors. Thus the phase constants in the two dHvA signals  $M_{OSC,r}^{(+)}$  analogous to (52) should be replaced by  $\gamma \pm gm^*/4m_o$ , so that the total signal is

$$M_{osc,r} = M_{osc,r}^{(+)} + M_{osc,r}^{(-)}$$
 [69a]

$$= A_{r} \sin[2\pi r(F/B - \gamma - gm^{*}/4m_{o}) + \pi/4] + A_{r} \sin[2\pi r(F/B - \gamma + gm^{*}/4m_{o}) + \pi/4]$$
[69b]

= 
$$A_r \sin[2\pi r(F/B - \gamma) + \pi/4] \cos\left(r \frac{\pi}{2} g \frac{m^*}{m_o}\right)$$
, [69c]

a trigonometric relation giving the Dingle cosine factor in (69c), which shows that some values of gm\* can give zero signal, called a spinsplitting zero. By multiplying the phase shift  $gm*/4m_0$  by the dHvA period it can also be expressed in terms of 1/B, giving the total splitting

bet hav the ly ; 3.7 the tron under part cept the i full densi Poiss assur curve deriva butior tory p between peaks (see Figure 16(d)):

$$\delta[1/B] = gm^{*}/2m_{o}F.$$
 [69d]

In magnetic media the signals from the two spin systems generally have different amplitudes, so this simple relation no longer holds because the  $A_r^{(+)}$  are not equal and the energy of perturbation is no longer directly proportional to field.<sup>60</sup>

### 3.7 Lifshitz-Kosevich Theory

In 1956 Lifshitz and Kosevich<sup>37</sup> started with the expression (20) for the free energy of a gas of nearly free electrons, assumed that the electrons do not interact (i.e.,  $\underline{B} = \underline{H}$ ), and showed that summing over states under the condition of the Onsager relation (42) yields an oscillatory part for the free energy, from which the oscillatory magnetization and susceptibility are easily obtained by differentiation. In succeeding years the important results of this semiclassical theory have been validated by full quantum theory.

The free energy summation in (20) can be evaluated by expressing the density of states in terms of the coordinates (E,  $k_H$ , H), and using the Poisson summation formula. The perfectly sharp Landau levels are then assumed to be replaced in the real crystal by a series of Lorentzian curves of half-width  $\Gamma$  to reflect the effects of crystal impurities. The derivation also includes non-zero temperature in the Fermi-Dirac distribution. After including the Zeeman splitting the result for the oscillatory part of the free energy is (see Gold, pp. 55-67 for a derivation):

$$\Omega_{\rm osc} = \sum_{r=1}^{r=\infty} \Omega_r , \qquad [70a]$$

where

where =

and

evaluat

Th

cosine

field.

where

<u>M</u>r

where

$$\Omega_{\mathbf{r}} = \frac{1}{\sqrt{2}} \left(\frac{\mathrm{He}}{\mathrm{rhc}}\right)^{3/2} \frac{\mathbf{k}_{\mathrm{B}} \mathrm{T}}{|\mathbf{A}_{\mathrm{ext}}''|^{\frac{1}{2}}} \frac{\exp(-\mathrm{r\alpha}\mathrm{T}_{\mathrm{D}}/\mathrm{H})}{\sinh(\mathrm{r\alpha}\mathrm{T}/\mathrm{H})} \cos\left(\frac{\pi}{2} \mathrm{rg} \frac{\mathrm{m}^{*}}{\mathrm{m}_{\mathrm{o}}}\right)$$
$$\times \cos\left[2\pi\mathrm{r}\left(\frac{\mathrm{F}}{\mathrm{H}} - \gamma\right) + \frac{\pi}{4}\right], \quad [70b]$$

where  $\propto$  is from (66), H is the magnetic intensity, F is the dHvA frequency, and

$$A_{ext}'' = \frac{\partial^2 A_F}{\partial k_H^2} , \qquad [70c]$$

evaluated at the  ${\bf k}_{\rm H}$  corresponding to the extremal cross-sectional area.

The magnetization is given by (21), taking the derivative of only the cosine term since the other factors are comparatively independent of field. Using (6) gives

$$\underline{\underline{M}}_{osc} = \sum_{r=1}^{r=\infty} \underline{\underline{M}}_{osc,r} = \sum_{r=1}^{r=\infty} \underline{\underline{M}}_{r}(\underline{\underline{H}}) \sin \psi_{r}(\underline{\underline{H}}) , \qquad [71a]$$

where

$$\psi_{\mathbf{r}} = 2\pi \mathbf{r} \left[ \frac{\mathbf{F}(\theta, \phi)}{\mathbf{H}} - \gamma \right] + \frac{\pi}{4} , \qquad [71b]$$

$$\underline{M}_{r} = -\left(\frac{2}{\pi r}\right)^{\frac{1}{2}} \underline{G} \left(\frac{\mathbf{e}}{\hbar c}\right)^{\frac{3}{2}} \frac{k_{B}T}{\sqrt{H}} \frac{\exp(-r_{\alpha}T_{D}/H)}{\sinh(r_{\alpha}T/H)} \cos\left(\frac{\pi}{2} rg \frac{m^{\star}(\theta,\phi)}{m_{o}}\right)$$

$$x \frac{F(\theta,\phi)}{|A_{ext}''|^{\frac{1}{2}}}, \quad [71c]$$

$$\underline{G} = \hat{\imath}_{H} - \hat{\imath}_{\theta} \frac{1}{F} \frac{\partial F}{\partial \theta} - \hat{\imath}_{\phi} \frac{1}{F \sin \theta} \frac{\partial F}{\partial \phi} , \qquad [71d]$$

an Th an SU ⊐e th ne il te to (f î H (o do fro fo sh Fi tuo fir the att req ren obs. and

$$\alpha = 2\pi^2 k_B m^* c/e\hbar$$
, (146.9 kG/K for  $m^* = m_O$ ). [71e]

The term  $\gamma$  is generally ignored or taken to be a constant in both direction and magnitude of field; hence it is called the phase constant here. Measurement of its angular variation requires a series of precision measurements of phase, and apparently has not been made for any metals, although the values of  $\gamma$  at symmetry directions has been reported for the noble metals.<sup>49</sup> The total free energy (70) and the magnetization (71) are best illustrated graphically by first taking the limit as T and T<sub>D</sub> (i.e. scattering) go to zero (the ideal crystal condition) and then setting g = 0, to give spinless states. The resulting waveforms are shown in Figure 16(b) (free energy) and Figure 16(c) (the component of the magnetization along  $\hat{i}$ ). In Figure 16(c) the solid line is for a maximal cross-sectional area H (of either an electron or a hole sheet of the Fermi surface), and the dotted line is for a minimum (again either electron or hole).

Now "turn on" spin. As discussed in Section 3.6 the signal arising from each spin sheet will be identical in nonferromagnetic crystals except for a phase shift downward in 1/B for the spin-up electrons and an equal shift upward for the spin-down electrons, giving a waveform like that in Figure 16(d).

The above ideal crystal condition gives the maximum relative amplitudes for the harmonics in  $\Omega_{\rm osc}$  and  $M_{\rm osc}$ . As evident from (65) and 71(c), finite T and T<sub>D</sub> tend to wash out the oscillations in each harmonic, with the higher harmonics being attenuated the most. Because of this rapid attenuation of the harmonics, their detection beyond the third normally requires very pure samples and very low temperatures, and for many experiments only the fundamental harmonic, illustrated in Figure 16(e), is observed. For such a case Zeeman splitting of the levels attenuates the

Figure 16.	Thec the	pretical dependences of magnetization and free energy upon inverse field, $1/B$ for T = $T_D$ = 0.	(b)
	(Fig	gures (a), (c), and (e) are from Gold, p. 48)	
	(a)	Magnetization of a single slice of the Fermi surface.	
	(b)	Oscillatory part of the <u>free energy</u> contributed by spinless electrons near an extremal section of the Fermi surface of an ideal crystal. All harmonics are present.	(c)
	(c)	Magnetization, summed over slices, conditions as in (b), for a maximal cross-section (solid) and a minimal one (dotted). All harmonics are present.	
	(d)	Magnetization from a Fermi surface maximum, conditions as in (c) except electrons have spin $\frac{1}{2}$ with consequent level splitting.	
	(e)	Fundamental component of each of the two curves in (c). Figure (e) could also represent the two fundamentals of each of the two spin signals of (d), coming from a single extremal orbit, in which case the amplitude of the sum is reduced by the factor $\cos(\pi gm^*/2m_o)$ .	(d)

(a)

(e)

57



Figure 16

8		
:		
3		
S		
٥d		
5		
ar		
ar		
00		
סנ		
la		
di		
erı		
vil		
bee		
'er		

signal amplitude by the cosine factor in 71(c), but does not change the shape of the wave from a sinusoid.

Important properties of crystals can be inferred from measurements of the fundamental (or from any one harmonic). These are 1) the extremal cross-sectional areas of the Fermi surface (given by dHvA F), 2) cyclotron mass m\* (obtained from the dependence of amplitude  $M_r(\underline{H})$  upon the temperature), 3) T (from the dependence of  $M_r$  upon field), and 4) the effective g-factor (from extrapolation to the infinite field phase). The g-factor is more commonly measured directly from a quantum oscillation waveform rich in harmonics, as shown in Figure 16(d).

#### 3.8 Justification of Semiclassical Theory

Early theory rigorously developed applied only to single-particle states of independent electrons, and most of the present theory easily compared with experimental data is either semiclassical or has been extended by analogy from its free electron origins to real crystals. The concept most important to Fermiology, quantization of orbits, has two vulnerable areas, as pointed out by its originator, L. Onsager, in 1952. These are the ambiguity of the connection between E(k) and the Bohr-Sommerfeld condition due to the fact that the components of the kinetic momentum do not commute, and the implicit assumption of wave packets. Onsager speculated that it was "reasonable to hope that neither previous theories of diamagnetism nor the present generalization will be invalidated by the error involved...or at least that the error in the computed susceptibility will not vary rapidly with the field intensity." 34 So far his hope has been upheld, with subsequent rigorous calculations tending to support various elements of the theory. Let us consider the theoretical support

f P с e ť t 01 Th ti re fu an Su: f (j ele eig tiz cia Pas fund Jore area radi well for three important semi-classical features: firstly, the concept of wave packets representing the orbiting electron; secondly, the relation between width of the energy levels and electronic lifetime; and thirdly, the concept of independent electrons. (See References 26 and 38 for more references and details than are given below.)

Regarding wavepackets and the use of the dynamical relation (10) and the kinematical relation (13), when the field can be considered a perturbation of the total crystal potential one may write the wave function of an orbiting electron as (Ziman, pp. 147-157)

$$\phi(\underline{\mathbf{r}}, t) = \sum_{n \ \ell} \int_{\ell} f(\underline{\ell}, t) \ W_{n}(\underline{\mathbf{r}}-\underline{\ell}).$$
[72]

The  $W_n(\underline{r} - \underline{l})$  are Wannier functions, obtained from a unitary transformation of the Bloch waves and so are a suitable set of basis function for a representation of the electron wave functions. The f(r,t) is an envelope function obtained by solving an equation with the equivalent Hamiltonian and very similar to the Schrödinger time dependent wave equation, and the sum is over all energy bands n and sites l in the sample. As time passes, f(l,t) peaks at successive sites along the real space path of the orbiting electron, picking up wave functions centered on the sites. The various eigenfunctions that have been calculated this way suggest the idea of a time-dependent mixing of states: the uniform, static perturbation associated with the magnetic field generates a mixing of k-states. As time passes the k-state that most nearly characterizes the oscillatory wave function moves around the orbit. Increasing the field intensity draws more k-states into the mixing, corresponding to an increased increment of area,  $\Delta A_{k} = 2\pi s$ . It is to be noted that as B increases so that orbit radius decreases,  $\Delta A_k$  increases, so that k at any instant of time is less well defined, illustrating the well known relationship between quantization and the uncertainty principle.

Regarding the width of the energy levels, considerations by Falicov and Stachowiak<sup>50</sup> present the wave packet as a superposition of many orbital functions which spread in all directions, coming together periodically after one cyclotron period, thus forming a series of pulses. They show that the density of states about the center of a level is a Fourier transform of the total, time dependent wave packet, energy being conjugate to time in quantum mechanics. So long as the pulses continue unchanged indefinitely in time they add to give a sharp energy level. Scattering of individual orbital functions attenuates the pulse more and more as time passes, with a consequent increase in the width of the energy level. This is the theoretical foundation of the relation (67) between level width  $\Gamma$ and mean inverse lifetime  $1/\tau$ .

The problem of the electron-electron interaction has been approached from many directions. This sketch follows Cracknell and Wong (pp. 416-420 of Ref. 15, hereafter called CW). It is assumed that the behavior of the electrons lies between the two extremes of completely independent and completely correlated (plasma wave) motion. To a first approximation the interactions can be put into the crystal potential through a screening parameter  $\lambda$ :

$$V(\underline{\mathbf{r}}) = \sum_{\ell} \frac{Q_{ion}}{|\underline{\mathbf{r}}-\underline{\ell}|} e^{-\lambda |\underline{\mathbf{r}}-\underline{\ell}|} .$$
[73]

This still assumes the system can be described by single-particle states. <sup>51</sup> Landau's phenomenological theory of the Fermi liquid, originated for liquid <sup>3</sup>He, can apply to the conduction electrons as the interaction is turned on, and the Coulomb repulsion between electrons becomes partially balanced by the attractive force due to the exchange of virtual phonons, thereby generating the eigenstates of the interacting system by a continuous

61

transformation from the old eigenstates. The entities associated with the new eigenstates are called quasi-particles. They are independent modes that can replace the electrons, a replacement justified by perturbation  $^{52}$  A finite discontinuity in momentum space at zero temperature remains, leaving the concept of the Fermi surface intact. Implications of the theory for T<sub>D</sub> and dHvA F are not clear. Experiment shows that deviations from predictions of the semiclassical theory are negligible, if observable at all (Gold, pp. 96-97). The LK amplitude 71(c) agrees (within an experimental uncertainty of 5% to 20%) with the data on the noble metals. <sup>53</sup> Also, because the measured Fermi volume of copper lies within 3% of that predicted by the single-particle LK theory, <sup>61</sup> effects due to electron-electron interaction should change dHvA F less than 2% (Gold, p. 97).

#### 3.9 Corrections to Semiclassical Theory

As stated above, full quantum calculations have supported most results in the semiclassical theory, with minor adjustments of energy levels or dHvA frequency usually smaller than the experimental resolutions. But two intrinsic effects not predicted by semiclassical theory, magnetic interaction and magnetic breakdown, are easily observed. A third observed deviation is due to the demagnetization in a sample of finite size.

<u>Magnetic interaction (Many-body effects).</u> Each electron sees the flux density <u>B</u> and not just the applied magnetic intensity <u>H</u>, which Lifshitz and Kosevich assumed in their derivation. Replacement of <u>H</u> by <u>54</u> <u>54</u> <u>54</u> in (70) and (71) was first suggested by Shoenberg, in order to explain an abnormally rich harmonic content in certain samples giving a strong

62

dHvA signal and subsequently justified by theory.<sup>55,56</sup> He referred to this as the B-H effect. The reason that the very small magnetization of non-ferromagnetic samples can alter the dHvA signals is that the field appears in the phase  $\psi_r$  of M<sub>r</sub>. This gives

$$\underline{\mathbf{M}}_{\text{osc}} = \sum_{r=1}^{r=\infty} \underline{\mathbf{M}}_{r}(\underline{\mathbf{H}}) \sin \psi_{r}(\underline{\mathbf{B}}) , \qquad [74a]$$

where

$$\psi_{\mathbf{r}}(\underline{B}) = 2\pi \mathbf{r} \left( \frac{\mathbf{F}(\theta, \phi)}{\mathbf{B}} - \gamma \right) + \frac{\pi}{4} , \qquad [74b]$$

and H is retained in  $M_r$  because these functions are not measurably changed by magnetic interaction. The flux density is given by

$$\underline{\mathbf{B}} = \underline{\mathbf{H}} + 4\pi \underline{\mathbf{M}} , \qquad [75a]$$

with the total magnetization  $\underline{M}$  of the electrons the sum of the oscillatory part due to quantization of the orbits and a steady part,

$$\underline{M} = \underline{M}_{steady} + \underline{M}_{osc} .$$
 [75b]

Because  $\underline{M}_{OSC}$  is the dominant part of  $\underline{M}$  at the fields and temperatures used to study the dHvA effect, one normally approximates  $\underline{M}$  in 75(a) by  $\underline{M}_{OSC}$ . Equation (74) is thus an implicit equation for  $\underline{M}_{OSC}$ . A calculation by Gold (pp. 69-78) shows that 74(a) has additional, nonharmonic frequencies arising from extremal orbits labeled a and b, truncating 74(a) to the fundamental term for both orbits and adding the two signals gives, after solving the implicit equation to first order in the harmonics, the following frequencies:  $F_a$  and  $F_b$  normally the strongest,  $2F_a$ ,  $2F_b$ ,  $F_a - F_b$ , and  $F_a + F_b$  the next strongest, and additional frequencies of smaller amplitudes.

The magnetic interaction effect is strongly field dependent. Thus the character of the oscillations may rapidly change with field to a more complex pattern, sometimes exhibiting beats. Demagnetization. When the dHvA amplitudes and the magnetic susceptibility are big enough that magnetic interaction is observable, then demagnetization produced by the shape of the sample may also be important, entering the dHvA phase through

$$\underline{\mathbf{B}}_{\text{internal}} = \underline{\mathbf{H}}_{\text{applied}} + \underline{\mathbf{H}}_{\text{demag}} + 4\pi \underline{\mathbf{M}} .$$
 [76]

This can increase the difficulty of calculating the relative amplitudes of the harmonics in 1/H. If

$$\frac{M_{\rm osc}}{H^2/8\pi^2 F} \stackrel{\geq}{=} 1 , \qquad [77]$$

then the magnetic response for a sample of arbitrary shape will be exceedingly complicated, and the only simple fact is that it will oscillate with the same period as for the LK theory (Gold, p. 75).

<u>Magnetic breakdown.</u> Cohen and Falicov<sup>57</sup> were the first to point out the possibility of an electron's jumping between adjacent semiclassical orbits on the Fermi surface (an interband transition by the magnetic potential). Under the influence of a moderate magnetic field states will move along arc C to arc D of the hypothetical orbits of Figure 17 to form orbit  $A^{(2)}$ . A stronger field may cause a transition from one zone to the other, so that the state moves from arc C to arc E. By Onsager's theorem, such orbits correspond to real space orbits, with resultant quantization.

The sign of the area was ignored in the derivation of Onsager's relation (42), with no distinction between hole and electron orbits. Breakdown orbits require explicit consideration of the sign which arises in step (43), where  $\underline{r} \times d\underline{r}$  may be negative on some arcs and positive on other arcs. It is obvious that the integral of  $\underline{r} \times d\underline{r}$  about an orbit that intersects itself is equal to the algebraic sum of areas from each simple loop of the orbit if one assigns negative value to hole orbits and positive value to electron orbits. Magnetic breakdown thus generates new dHvA frequencies which are sums and differences of the old ones, and proportional through (51) to such areas as  $A^{(3)}$  and  $A^{(4)}$  of Figure 17.

Blount showed that the condition for significant probability of magnetic breakdown is

$$\left(E_{F} \hbar \omega^{*}\right)^{\frac{1}{2}} \stackrel{\geq}{=} E_{g}, \qquad [78]$$

where  $E_g$  is the energy gap between bands at the point in <u>k</u>-space where breakdown occurs. The breakdown parameter B<sub>o</sub> gives the probability of a jump as<sup>59</sup>

$$P = \exp(-B_0/B)$$
, [79a]

where

$$B_{o} = \frac{E_{g}^{2}}{2\hbar^{2}G\omega^{2}K}$$
, [79b]

where G is the reciprocal basis length, and K is the distance in  $\underline{k}$ -space from the center of the orbit to the breakdown point.

These conditions are so strong that almost all experimentally observed breakdown occurs across the small energy gaps due solely to the spin-orbit interaction, which may lift degeneracies allowed by the crystal field. Breakdown across the basal planes of the hexagonal close packed structures is the most common example.

However, breakdown across energy gaps generated by the crystal field does occur, although rarely, with the needles of Zn being the oft-quoted example. So investigation of the possibility of breakdown on orbit  $C_3'$  is justified. Consider the only two zones containing sheets of the Fermi surface of AuGa<sub>2</sub>, namely the third and fourth zones, and superpose them, with <u>B</u> || (111). All the extremal orbits labeled C shown in Figures 6 and


Figure 17. Hypothetical orbits to illustrate magnetic breakdown. Original orbits and new orbits created by magnetic breakdown (arrows MB). The areas of electron and hole orbits have different signs. B into the paper.





Figure 18. Cross-section of the empty lattice surfaces in the third (clear) and fourth (black) zones at the  $k_z$  values given for <u>B</u> || <111>. Height of the unit cell is 2.0. (From Refs. 3 and 23)

7 can exist on the Fermi surface. Orbits  $C'_3$  and  $C'_4$  have the same  $k_{\rm H}$ . A construction by Longo<sup>3,23</sup> (given here as Figure 18) clearly shows this property (as well as the origin of some of the other extremal orbits that lie in the {111} planes). The last diagram of Figure 18 is in the plane of the hexagonal zone boundary of Figure 5. (Half the distance from a corner to the center of a cube of edge 2 is .866). This is redrawn in Figure 19(a) and (b), showing the two orbits concerned. Figures 19(c) and (d) show hypothetical breakdown orbits, with the points of breakdown circled. Orbit (d) is self-intersecting. To calculate the magnetic fields required for significant breakdown probability, take  $E_g = 0.54 \text{ eV}$  from Figure 9, and m\* = .175 m<sub>o</sub> from Ref. 10. Condition (78) requires

$$B \stackrel{>}{=} 479 \ kG$$
 . [80]

This value is only an estimate because a bandstructure calculation is not absolutely accurate. The parameter B can be calculated if one knows G and K. The lattice constant <sup>10</sup> a = 6.055 Å at 4.2 K gives G, and an estimate of K can be obtained from either the empty lattice diagram Figure 5 or the band structure of Figure 9, by calculating ratios of distances on the Brillouin zone. The empty lattice Fermi surface figure gives K = .11G and the band structure graph gives K = .061G. These give B as 1.6 x 10<sup>6</sup> Gauss and 2.8 x 10<sup>6</sup> Gauss, respectively, with corresponding transition probabilities at the highest field used (5 x 10<sup>4</sup> Gauss) of 10<sup>-14</sup> and 10<sup>-25</sup>. Even assuming the true value of K is twice that of the empty lattice calculation (an unlikely event since the lattice potential tends to reduce small cross sections near zones), P = 10<sup>-7</sup>. The "significant" P associated with the field (80) is between .2% (for K = .061) and 4% (for K = .11). These models show magnetic breakdown should have negligible effect on the dHvA oscillations of the C<sup>1</sup>/<sub>3</sub> orbit of AuGa<sub>2</sub>.



A (III) zone boundary lies in the paper.



Orbits in zones 3 and 4. The crystal field smooths the sharp corners of the free electron orbits.



Orbits possible by magnetic breakdown. O=breakdown point. Orbit(d) self-intersects.

Figure 19. Orbits centered on point L on the Brillouin zone.

- (a) Intersection of <111> plane with Fermi spheres.
- (b) Neighboring hole orbits:  $C'_3$  (hexagon) and  $C'_4$  (star).
- (c) and (d) Two examples of many possible hypothetical breakdown orbits. However, all have essentially zero probability.

#### CHAPTER IV

## DE HAAS-VAN ALPHEN EFFECT AS A PROBE OF CRYSTAL COMPOSITION

Within a few years of the discovery of the dHvA effect, experiments were done on dilute alloys of Bi.<sup>33,69</sup> For a number of years the goal of dHvA studies on samples to which impurities had been added was to study the scattering effect and test theories predicting amplitude dependence. But quantitative measurements on even dilute alloys were hindered by the strong dependence of the signal's amplitude on crystalline purity. Typically, the amplitude is attenuated by factors of 100 to 1000 per atomic percent of concentration of impurity. The development of sensitive and precise measurement techniques<sup>49,62-68</sup> has made possible recent and continuing use of the dHvA effect to study the effect of composition on the topology of the Fermi surface, the scattering of conduction electrons, and the contribution of the impurity atoms to the density of conduction electrons. Such studies are still limited to dilute alloys, however.

## 4.1 De Haas-van Alphen Frequency

The introduction of impurities changes the topology of the Fermi surface of a metal. In the case of impurities having a valence different from that of the host, the consequent change in the electron to

atom ratio causes coarse changes in the Fermi surface. Finer changes are caused by the alteration of the band structure, due to the different atomic potential of the impurity. The biggest change in dHvA F occur usually for big valence difference Z, small pockets of the Fermi surface, and the highest concentrations of impurity allowing observable dHvA signals. The maximum concentrations of impurity useable have been about one atomic percent. The changes in dHvA F are typically less than 0.1%. Although early work on alloys, summarized by Heine, <sup>70</sup> was valuable in showing alloy experiments to be feasible, it did not allow significant comparison with the theory. As referenced above, the development of methods for precise measurements of dHvA F allowed more quantitative experiments. One result was the determination of the average number of conduction electrons contributed by each impurity atom in some alloys of the noble metals.<sup>71,72</sup> Various other alloy systems have yielded a range of results, from no change in F (ZnGe in  $A1^{73}$ ) to a modification in the Fermi surface sufficient to produce new dHvA F (In in Pt<sup>74</sup>).

Derivation of a theory began in 1956 with Heine's<sup>70</sup> interpretation of much of the published data using the theory of primary solid solutions and Friedel's<sup>75,76</sup> rigid band structure model. This model assumes that the band structure of the host does not change upon adding impurities, the only effect being a change in  $E_F$ . It was later extensively developed by Stern.<sup>77</sup> A theory to allow band structure and density of states to change upon alloying was put forward in 1958 by Cohen and Heine<sup>78</sup> for monovalent metals. Coleridge<sup>79</sup> has introduced partial wave analysis into the theory.

Quantitative correlation of the data with the more complete theory requires accurate knowledge of composition. Such knowledge is not obtainable for our samples, as will be described in Chapter IX.

Furthermore, it turns out that the compositional variations in our samples have only a slight effect on dHvA F. Thus only a general, qualitative description of the simpler theory, i.e. the rigid band model, is pertinent.

<u>Rigid band model</u>. Following Stern<sup>77</sup> and Coleridge and Templeton,<sup>71</sup> the addition of impurities is assumed to have no effect on the electronic band structure of the host, and the only basic change is in the density of conduction electrons, i.e. the number per unit sample volume, if the relative valence of impurity to host is not zero. Secondary changes follow in the density of states at the Fermi level and in the topology of the Fermi surface, specifically in cross sectional areas. The rigid band (RB) model can be used for cubic systems even when alloying changes the lattice parameter because the relative dimensions in reciprocal space remain unchanged.

Let N be the density (number/volume) of atoms in the alloy,  $N_i$  the density of impurity atoms,  $a_i$  their fractional concentration,

$$a_{i} = \frac{N_{i}}{N}, \qquad [81]$$

and Z their valence difference relative to the valence of the host atoms. Then the increase in the density of conduction electrons is

$$dn = Za_{i}N.$$
 [82]

For small a, the change in Fermi level is

$$dE_{F} = \frac{Za_{i}N}{D(E_{F})},$$
[83]

where  $D(E_F)$  is the density of states evaluated at the Fermi level. The RB model then predicts a relative change in the dHvA F;

V.

t Ē6 C.V. tha

$$\frac{\mathrm{dF}}{\mathrm{F}} = \frac{1}{\mathrm{A}_{\mathrm{F}}} \left(\frac{\mathrm{dA}_{\mathrm{F}}}{\mathrm{dE}}\right)_{\mathrm{E}_{\mathrm{F}}} \mathrm{dE}_{\mathrm{F}} = \frac{\mathrm{m}^{*}\mathrm{cNZ}}{\mathrm{\hbar}\mathrm{eF} \mathrm{D}(\mathrm{E}_{\mathrm{F}})} a_{\mathrm{i}}.$$
[84]

Thus changes in F are directly proportional to both impurity concentration and to valence difference. Coleridge and Templeton<sup>71,72</sup> observed this behavior for Cu alloys with  $|Z| \leq 2$ . But Si and Ge did not fit the RB predictions. The behavior of the transition metal impurities varied. For example Ni fit the model approximately,<sup>72</sup> by others showed no simple correlation with Z. Furthermore, the rate of change of F with  $a_i$  did not agree quantitatively with the rate measured for Cu necks. A parameter sometimes used to characterize the change in the Fermi surface is

$$S = \frac{dF/F}{dn/n}$$
[85a]

$$= \frac{dF/F}{NZ a_{i}/n}$$
[85b]

$$= \frac{m*cn}{\hbar eF D(E_F)}.$$
 [85c]

The empty lattice model gives S = 2/3. The measured<sup>71</sup> values for Cu are S = 0.69 for the belly orbit and S = 6.2 for the neck orbit.

RB theory has limitations when applied to metals with more complicated Fermi surfaces and structures than those of the noble metals. For example, RB depends on an unambiguous valence assignment, not possible when d bands lie close to the Fermi level. Experiment also shows that the alloy band structure is not really independent of the lattice parameter, even for a cubic lattice. For a discussion of RB failure, see CW, pp. 499-501.

Relation to AuGa<sub>2</sub>. The observation by Coleridge and Templeton<sup>71</sup> that RB fails for |Z| > 2 in noble metal hosts suggests that a reliable

prediction for the response of the C'\_3 (neck) orbit of  $AuGa_2$  to a variation in vacancy concentration requires either theoretical calculation more sophisticated than RB or experimental evidence. (For Ga-site vacancies, Z = 3.) The calculated S for this orbit is 27.33, and by equation (85c) is independent of the relative valence Z and concentration  $a_i$ . Both  $E_F = 9.19$  eV and  $D(E_F) = 2.06 \times 10^{22}$  eV<sup>-1</sup> were calculated from the free electron equations. The lattice constant and the assumed valences of Au and Ga give n =  $1.26 \times 10^{23}$  cm<sup>-3</sup>. Two data points for dF of C'\_3 versus concentration of Pd, taken from work of Schirber,<sup>20</sup> give

$$dF/F = 7.14 a_{\star}$$
 [86]

(with large uncertainty) near  $a_1 = .005$  atomic fraction of Pd). The Pd substitutes for Au in Au<sub>1-x</sub>Pd<sub>x</sub>Ga<sub>2</sub>. Substitution of (86) and (82) into (85a), using the lattice constant to get N = 5.41 x 10<sup>22</sup>, and assuming the valence of Pd is zero (i.e., Z = -1) give S = 3.8, a much slower change in F than the RB model predicts.

This discrepancy could arise three ways: (1) the use of a free electron value for  $D(E_F)$ , (2) Z is not -1 for Pd, and (3) the RB model fails, so that dF/F is not due entirely to changes in n. It is difficult even to estimate the effect of (1). As for (2), taking Pd valence to be zero may be unreliable for quantitative work, but probably gives a good idea of the direction of changes, and has been found acceptable in the interpretation of dHvA data on some intermetallic compounds containing Pd. Finally, part of the discrepancy is certainly due to (3), the inappropriateness of applying pure RB theory to the C'\_3 orbit, which is clearly demonstrated by measurement of the pressure derivative:  $d(\ln F)/dP$ . Schirber and Switendick<sup>18</sup> and Schirber<sup>20</sup> measured  $d(\ln F)/dP = (-13\pm4) \times 10^{-4} \text{ kbar}^{-1}$ . (There was a rapid decrease in the derivative above 6 kbar.) The pressures used correspond to volume changes about 1%.<sup>20</sup> The result of APW band structure calculations<sup>18</sup> using a lattice parameter reduced 1% below that used previously (Reference 22 and Figure 9) agree with the sign of the pressure derivative. These show that the second zone begins to empty and the third zone neck region begins to fill.<sup>20</sup> Both these investigations show RB fails to the extent that band structure depends on the average lattice parameter a.

It is not clear how much change in a is caused by the Pd impurity, but the direction of the discrepancy in S (i.e. the fact that measured dF/F is smaller than that predicted) requires a decrease of a in view of the reports of Schirber and Switendick. A decrease in a is suggested by the smaller a of pure Pd (3.88 Å versus 4.07 Å in pure Au; Reference 42, p. 29), while both elements have the fcc structure. Also, the ionic radius of Pd (.80 Å) is smaller than for Au (1.37 Å) (Reference 156, p. F-117).

Vacancies would give a smaller a. They also have zero valence. If the deviation of the composition of AuGa<sub>2</sub> from stoichiometry is due to vacant lattice sites, the opposing tendencies for increasing and decreasing F could give a very small change.

## 4.2 Dingle Temperature

In contrast to dHvA frequency F, the Dingle temperature  $T_D$ , also called the scattering temperature, or scattering parameter, is unaffected by ordered changes of composition. However, disorder strongly increases  $T_D$ , and the most important cause is lattice dislocations, due

to the fact that small angle scatter (any angle greater than 1/n, where n is the dHvA phase) is sufficient to eliminate the contribution of the scattered electron.  $^{48,80,81,82}$  Dislocations have strain fields that fall off very slowly (1/r) in comparison to those of impurities  $(1/r^3)$ .  $^{80,81}$  The scattering of an electron through the strain field can be treated equivalently as successive small angle scattering and as dispersion of a wave by a medium of variable refractive index.  $^{48}$ 

Impurities act almost as point scatterers, and the strain field is usually ignored.<sup>80,81,83,84</sup> Most of the measurements of scattering anisotropy, i.e. obtaining  $\tau_k$  by inverting  $T_D$ , have been done for impurity scattering.<sup>85,86,87,88</sup> Such inversion requires thorough knowledge of both the Fermi surface topology and the electron velocities.<sup>87</sup> There is appreciable anisotropy in the noble metals, depending upon the impurity.<sup>87</sup> See Section 9.3 and Table 18 for further comparison of the types of scattering.

Scattering by vacancies has received little attention. Lengeler and Uelhoff<sup>89</sup> reported  $T_D/a_i$  for various orbits in Au, obtained by quenching and extrapolating the vacancy concentration from its value (720 ppm) at the melting temperature. The range of  $T_D/a_i$  was 35 to 51 K/at.%, and 40 K/at.% on the neck orbit. For comparison, Lowndes <u>et al</u>.<sup>87</sup> found  $T_D/a_i = 9.1$  K/at.% for Au(Ag). They also verified the linear dependence on concentration.

The theory has been developed by Soven<sup>90</sup> and Coleridge <u>et al</u>.<sup>91</sup> Using multiple scattering theory, Soven<sup>90</sup> computed the oscillatory density of states when a dilute, random distribution of atomic scattering potentials is put into a free electron gas in a uniform magnetic field. The shifts in dHvA F can then be calculated. Coleridge <u>et al</u>.<sup>91</sup> based

their theory on partial wave analysis, extracting from anisotropy measurements the relative amount of interaction with s, p, and d waves.

#### 4.3 Considerations for Precision

In their discussion of experimental technique, Coleridge <u>et al</u>.<sup>68</sup> and Coleridge and Templeton<sup>49</sup> emphasize the need for highly controlled experimental conditions. Coleridge and Templeton<sup>49</sup> used magnetic fields with homogeneities of 10 ppm over the sample diameter (a few millimeters), angular resolution of .03° (corresponding to a resolution in dHvA F of 5 in  $10^7$ ) by using the dHvA signal's symmetry to align the probe, and dHvA signals with little noise, yielding a maximal resolution in phase of .002 cycles and an assured resolution of .01 cycles. Their field was measured with an uncertainty of less than one Gauss by the use of <u>in</u> situ NMR.

Our superconductive solenoid had a resolution of about .02% over 4 cm between 30 and 50 kG, or 5 ppm over 1 mm. Our NMR probe could measure the field with 5 significant digits easily, but stability of the oscillator was not quite good enough for 6 digits. Thus the resolution was between 0.1 and 1 Gauss. Angular setting was achieved by a sample holder copied after that of Coleridge and Templeton, <sup>49</sup> that would be tilted with the probe in place and recording a dHvA signal.

The experimental apparatus being of suitable sensitivity, it remained to choose one orbit to examine. Since our intent was to see the relation between the dHvA effect and the composition of our samples, rather than a general study of the Fermi surface, our experiments measure the dHvA signal from only one extremal orbit, that of the third zone neck,  $C_3'$ . The reasons for choosing this orbit are as follows. Previous experiments  $^{10,45}$  on AuGa<sub>2</sub> showed that the signal from C'<sub>3</sub>, the third zone neck orbit, w is a strong one. It has even symmetry about <111>, and varies fast enough with angle to allow precise orientation of the probe. As a small orbit, its greater sensitivity to impurities is suspected, an assumption consistent with the more rapid increase (by a factor of two to three) of  $T_{D}$  of Cu neck with respect to Cu belly orbits when dislocations are introduced. 48,82 And equation (84) shows the relative change may be greater for small F. The sensitivity of the neck region of AuGa $_2$  to structural changes was also implied by Schirber's  $^{20}$  work: the magnitude of the pressure derivative of orbit  $C_3'$  was among the biggest. Some of the other orbits with comparable pressure derivatives had weaker signals. In the <111> direction and at 4.2 K, the easiest temperature to maintain, the signal from  $C'_3$  was completely dominant. This frequency is also isolated, of help in obtaining accurate phase measurements. On the other hand, after much of this thesis data was collected, Templeton and Coleridge<sup>72</sup> reported  $dF/a_i$  to be three to six times greater for Cu belly than for Cu neck when Ni and Al are the impurities. However, due to the plotting methods of obtaining precision F, it isn't clear whether greater precision is obtained from an orbit with bigger absolute change in F, or bigger relative change. Detecting the signal from a AuGa, orbit of greater area would have been difficult in the presence of the dominant neck signal.

#### CHAPTER V

# EXPERIMENTAL TECHNIQUE FOR THE DE HAAS-VAN ALPHEN EFFECT

### 5.1 Techniques Available

Measurement of the frequency and amplitude of the oscillatory magnetization (equation 71) of the dHvA effect yields extremal cross-sectional areas, cyclotron masses, lifetimes of the charge carriers, effective g-factors, and other properties of electrons on the Fermi surface. By recording the magnetization as a function of the magnitude of the field and of the temperature, with angle of orientation as a parameter, the angular dependence of the quantities can be mapped, and also the shape of the Fermi surface determined.

Three techniques are commonly employed to measure  $\underline{M}_{osc}$ . One measures  $\underline{M}$ , the total magnetization, directly by its torque in a uniform field, and the other two measure differential magnetization through the voltage induced in a coil by the response of M to a time dependent field.

<u>Torque.</u> The original observations made by de Haas and van Alphen<sup>1</sup> used Faraday's method of measuring magnetic susceptibility,<sup>92</sup> which requires a non-uniform field. Shoenberg<sup>69</sup> devised a method specifically for the dHvA effect: mechanical linkage to the torque couple of samples suspended in a uniform magnetic field. The couple is a measure of the differences of magnetic susceptibilities along the principal axes. A uniform field increases resolution and simplifies analysis of the effect.

A major advantage of the torque method over the induction methods is that it is a more direct measure of the amplitudes of the dHvA harmonics of 71(a), allowing comparison with LK theory. (See D. Shoenberg and J. Vanderkooy<sup>53</sup> and references therein.) As will be seen, the induction methods further resolve each dHvA harmonic into time harmonics, with each amplitude weighted by additional functions. Summing the time harmonics to obtain the dHvA harmonic is uncertain because the gains and phase shifts imposed by the apparatus vary with each harmonic and are usually difficult to determine.

Two major disadvantages of the torque method are that  $\underline{M} \times \underline{B}$  is zero when  $\underline{B}$  is parallel to a symmetry axis of the sheet of the Fermi surface being measured, since  $\partial F/\partial \theta$  and  $\partial F/\partial \phi$  in 71(d) are then zero, and that the apparatus requires more access room and less freedom of orientation. This latter difficulty has been ameliorated by new designs, including measurement of the torque by the counter torque provided by a small coil about the sample. <sup>53</sup>

A non-ferromagnetic sample may experience a torque because  $\underline{M}$  and  $\underline{B}$ are not parallel for a general direction in a metal with a non-spherical Fermi surface. Whether the field is swept or rotated, the sample must not be permitted to move in response to the torque  $\underline{M} \times \underline{B}$  acting on it if relatively uncomplicated signals are desired. Otherwise  $F(\theta, \phi)$  will oscillate about its mean with a frequency F and amplitude proportional to  $\underline{M}$ , giving rise to sum and difference frequencies. (Sum and difference frequencies also arise from magnetic interaction. The cause is the same: oscillations in the phase (74b), although in one case F oscillates and in the other case B oscillates.) For this reason counter torques are applied during the experiment. The induced voltage methods are also subject to this distortion, although it is not as inherently as big a problem since

with them the sample is rigidly mounted. The mounting of easily deformed crystals for both low stress and low compliance presents some difficulties at times, but these difficulties are small for AuGa<sub>2</sub>, which is a hard, brittle alloy.

<u>Pulsed fields.</u> Banks of capacitors repeatedly drive big currents through solenoids, each pulse enduring for times of the order of microseconds. Fields to 300 kG may be generated easily. An oscilloscope displays the voltage

$$\mathbf{v}(t) = \frac{\mathrm{d}\Phi}{\mathrm{d}t} \propto \frac{\mathrm{d}H}{\mathrm{d}t} + 4\pi \frac{\mathrm{d}M}{\mathrm{d}t} . \qquad [87]$$

The second term is isolated and recorded by photography or digital storage.

The pulsed field technique was also originated by D. Shoenberg and extensively used by him and his collaborators to first observe many of the high dHvA frequencies.<sup>93</sup> It remains the only method for observing the dHvA signals of very low amplitude (usually those with  $m^* > m_0$ , although recently the use of very strong solenoids permits the measurement of dHvA signals corresponding to  $m^*$  two or three times  $m_0$ ).

Limitations of the pulsed field technique include the limited resolution, noise, and eddy currents. The last both complicate the analysis of the signal and create temperature instabilities. High speed collection and analysis of the data by digital electronics has recently improved both sensitivity and signal-to-noise ratio, but for most metals the field modulation technique, to be discussed next, remains the best method.

Field modulation. The field modulation technique was frequently called the Shoenberg-Stiles method, after its inventors, D. Shoenberg and P. J. Stiles, but the basic idea has been so extensively modified by so many others 95-101 that it is now usually known by its acronym, FMT. The field modulation technique induces v(t) in (87) by superposing an alternating magnetic field  $\underline{h}(t)$  on the steady field  $\underline{H}_{0}$ . The use of a steady field gives better control of the field and more time for removal of the noise in the dHvA signal. (Here, steady means the  $\underline{H}_{0}$  is considered fixed in time for the purposes of calculation. To analyze the dHvA signal obtained during a field sweep, the sweep rate must be slow enough that the time dependence of  $\underline{H}_{0}$  affects the results by a negligible amount. This condition is easily satisfied in practice.) The modulation field  $\underline{h}(t)$  is usually sinusoidal.

Shoenberg and Stiles used modulation frequencies in the megahertz range, perhaps a carry-over from the microsecond electronics used in the pulsed field work previously. Skin effect in normal metals and alloys is significant at these frequencies. A. B. Pippard analyzed the extreme case (anomalous skin effect), and much Fermi surface information was obtained on various metals.<sup>93</sup> However, the intermediate regime of strong, but not anomalous, skin effect is exceedingly difficult to analyze, and even in the anomalous regime the complications caused by the eddy currents prevent the extraction of the full wealth and precision of information about the Fermi surface contained in the dHvA signal.<sup>94,102</sup>

Shoenberg and Stiles also used small amplitude modulation, so their version of FMT could be described as high frequency, small amplitude. The low frequency, large amplitude version developed subsequently 95-101 is the one most often used today. It offers numerous advantages: a more straight-forward analysis of the data, higher resolution, more convenient signal processing, less noise in the signals, and the availability of an internal spectrometer action of the sample to discriminate against strongly interfering dHvA signals and to enhance weak ones. The theory of FMT will be further developed in the next section.

Other techniques. The three techniques described above are the most useful ones. For special conditions other techniques may be better, or they may be usable when none of the primary three is. One of these is a vibrating sample method, which is useful for semi-metals and semiconductors, which have low conductivity and small cross-sections. It is rarely used for studies of the high frequency oscillations one ordinarily finds in metals and alloys. There are also methods which combine or modify the primary three. Field modulation with two modulation frequencies, one high and one low (the dHvA signal appearing as a pair of side bands of the modulation frequency), field modulation in combination with torque, and field modulation in combination with pulsed field (to utilize the maximum in field, where the induced voltage would otherwise be zero) have all been used. See Gold, pages 112-120, for references.

### 5.2 Field Modulation Technique

The dHvA data of this thesis was obtained with the low frequency, large amplitude FMT because it is the most convenient, an electromagnet and solenoids to provide steady fields were readily available, and the types of measurements desired were suitable for FMT. Because the dHvA signal from the C' orbit is strong and  $m^* = .175m$  the main advantage of the pulsed field, its ability to measure small signals, was not needed. Rather, since high precision was sought, it is doubtful that the pulsed field method could have been used; the development of high precision measurements has been done using the low frequency, large amplitude FMT. Furthermore, the torque method could not have been used because the field was in the symmetry direction <111>.

The remainder of this chapter gives the theory of FMT and shows how to determine the quantities of interest from the theoretical expressions

describing the sample's interaction with the detection system. Chapter VI examines our apparatus in detail. Chapter VII outlines the experimental procedure, and comments on some problems to be aware of when applying this theory to real measurements.

<u>Magnetic field variable.</u> The fundamental field quantity is flux density (or magnetic induction) <u>B</u>, both in its microscopic (i.e., at points within a crystalline cell) and macroscopic (i.e., averaged over a small number of cells) forms. But as usual when dealing with macroscopic media, the magnetic intensity, defined as <u>H</u> = <u>B</u> -  $4\pi\underline{M}$ , is more convenient to use in measurement and calculation. In this chapter manipulations of the LK equations (71) and (74) for <u>M</u> use <u>H</u> because LK theory was first derived assuming <u>B</u> = <u>H</u>, the calculations in the literature use <u>H</u>, and it is easier to compare fields measured with different devices, since <u>H</u> discounts variations due to different media. Clearly there is no difference between using <u>H</u> and using <u>B</u> when magnetic interaction is negligible. The data of this thesis were taken under this condition. (Recordings in which magnetic interaction is visible were not analyzed.)

<u>Voltage.</u> Let the steady field  $\underline{H}_{o}$  be modulated by a small, parallel, alternating field h(t) so that the total field magnitude is

$$H(t) = H_{o} + h(t)$$
, [88a]

with modulation field

$$h(t) = h \cos(\omega_m t) , \qquad [88b]$$

where

$$\omega_{\rm m} = 2\pi f_{\rm m} \qquad [88c]$$

is the modulation frequency, and h is the amplitude of the modulation

field. An oblique geometry ( $\underline{H}_{0}$  not parallel to  $\underline{h}$ ) can be used to enhance different dHvA frequencies of the spectrum,  $9^{8-101}$  but the data of this thesis were taken using condition (88). The only significant changes in the spectrum  $\underline{M}_{osc}$  (71a) arising from the field modulation come through the phase (71b), which now depends explicitly on time as well as on the steady field  $\underline{H}_{osc}$ :

$$\Psi_{r}(t) = 2\pi r \left( \frac{F}{H_{o} + h \cos(\omega_{m} t)} - \gamma \right) + \frac{\pi}{4},$$
 [89]

where F is  $F(\theta, \phi)$  evaluated for the direction  $(\theta, \phi)$  of  $\underline{H}_{o}$  (see Figure 3) and is a constant in time due to  $\underline{h} \mid \mid \underline{H}_{o}$ . The skin effect is negligible because

$$\omega_{\rm m} < \frac{c^2}{2\pi\sigma d^2} , \qquad [90]$$

permitting <u>h</u> to uniformly penetrate the sample. For h << H<sub>o</sub> an approximate treatment<sup>97</sup> obviates the work of Fourier analyzing  $M(H_o,t)$ :

$$\frac{F}{H_{o} + h \cos(\omega_{m}t)} \stackrel{:}{\stackrel{:}{\stackrel{\:}{\:}} \frac{F}{H_{o}} [1 - \frac{h}{H_{o}} \cos(\omega_{m}t)]$$
[91]

so that

$$\sin \psi_{r}(t) = \sin \left( 2\pi r \left[ \frac{F}{H_{o}} - \frac{Fh}{H_{o}^{2}} \cos(\omega_{m} t - \gamma) + \frac{\pi}{4} \right]. \qquad [92]$$

Let

$$\lambda = 2\pi \frac{Fh}{H_o^2} .$$
 [93]

Trigonometric relations transform (92) into

$$\sin\psi_{r}(t) = \sin\psi_{r} \cos[\lambda r \cos(\omega_{m} t)] + \cos\psi_{r} \sin[\lambda r \cos(\omega_{m} t)], \quad [94]$$

7 a 0 fj 0U

:s d or

the

har

where  $\psi_{\mathbf{r}}$  is now (and for the rest of this chapter) the phase (71b) evaluated at the steady field H<sub>o</sub>, and is to be distinguished from the time dependent  $\psi_{\mathbf{r}}(t)$  of (89). The Fourier series for the time dependent function involves the Bessel functions of the first kind:

$$\cos[\lambda \mathbf{r} \cos(\omega_{\mathrm{m}} \mathbf{t})] = 2 \sum_{n=0}^{\infty} (-1)^{n} J_{2n}(\lambda \mathbf{r}) \cos(2n\omega_{\mathrm{m}} \mathbf{t}), \qquad [95a]$$

$$\sin[\lambda r \cos(\omega_{m} t)] = 2 \sum_{n=0}^{\infty} (-1)^{n} J_{2n+1}(\lambda r) \cos[(2n+1)\omega_{m} t], \qquad [95b]$$

where the first term of the primed sum has a factor  $\frac{1}{2}$ . Substitution of (94) and (95) into (71a) yields the following expression for the time dependent magnetization. It has been generalized for the case of more than one dHvA signal (i.e., more than one extremal orbit on the Fermi surface for the given field orientation) by summing over orbit index i.

$$\underline{\underline{M}}_{osc}(t) \stackrel{:}{:} 2 \sum_{i} \sum_{r=1}^{\infty} \underline{\underline{M}}_{r}^{(i)}(\underline{\underline{H}}_{o})$$

$$x \left\{ sin\psi_{r}^{(i)} \left( \frac{1}{2} J_{o}(\lambda_{r}^{(i)}) + \sum_{n=0}^{\infty} (-1)^{n} J_{2n}(\lambda_{r}^{(i)}) \cos(2n\omega_{m}t) \right) - \cos\psi_{r}^{(i)} \left( \sum_{n=0}^{\infty} (-1)^{n} J_{2n+1}(\lambda_{r}^{(i)}) \cos[(2n+1)\omega_{m}t] \right) \right\}.$$
[96]

Note that  $\underline{H}_{0}$  has been substituted for the correct value  $\underline{H}$  in  $\underline{M}_{T}$ . This approximation introduces less error than the previous approximation (91), of the order of 0 to  $\frac{1}{4}$ % compared with 0 to 4% of the amplitude for the field and temperature ranges we used. To particularize this equation to our experiment, put  $\underline{H}_{0}$  || [111] so that only the first component of (71d) is not zero. The fundamental (r = 1) signal from orbit C'\_3 completely dominates, so only that term survives. The orbit area is a minimum, so the phase constant is  $+\frac{\pi}{4}$ . Finally, detection is at the second time harmonic, so only the J<sub>2</sub> (n = 1) term, in the first Bessel series of (96) is recorded by the signal processing equipment. Thus

$$\underline{M}_{osc}(t) = -2\hat{i}_{H}M_{1}(\underline{H}_{o}) (\sin\psi_{1}) J_{2}(\lambda) \cos(2\omega_{m}t).$$
[97]

This quantity is measured through the voltage induced in a small pick-up coil surrounding the sample and in close flux linkage with it. From (87) and (97) we get

$$\mathbf{v}(t) = \mathbf{V}_2 \cos(2\omega_m t), \qquad [98]$$

where  $V_2$  is the amplitude

$$V_{2} = 2_{\eta \omega_{m}} M_{1}(\underline{H}_{o}) J_{2}(2\pi Fh/H_{o}^{2}) \sin[2\pi(\frac{F}{H_{o}} -\gamma + \frac{1}{8})], \qquad [99]$$

where  $\eta > 0$  includes various numerical constants and the amount of coupling between the pick-up coil and the sample. Voltage polarity is important only for evaluating the phase constant  $\gamma$ .

Figure 20 shows a typical recording of the r.m.s. value of v(t) =  $V_2^2/\sqrt{2}$  (versus field rather than inverse field). The envelope function is  $M_1(\underline{H}_0)$ . Note that it is essentially a single sinusoid, in accordance with (99).

Equation (93) shows that the amplitudes in (96) depend upon the ratio  $h/H_0^2$  in the argument of the Bessel functions. The optimum modulation amplitude for the production of the second time harmonic when the dHvA magnetization is dominated by its fundamental component is given by

$$\lambda_{o} = \frac{2\pi Fh_{opt}}{H_{o}^{2}} = 3.05,$$
 [100a]

for which

$$J_2(\lambda_0) = \text{First Maximum} = 0.486. \qquad [100b]$$

Fi



Figure 20. Typical data for the  $C_3'$  (Third zone neck) orbit of AuGa<sub>2</sub>.  $m* = .175m_0$ , T = 4.2, T<sub>D</sub> ~ 1 to 2 K. Plot of r.m.s. second time harmonic of v(t) induced by the sample versus field.

The Bessel function also strongly affects the time harmonics of the induced voltage v  $\propto$  dM/dt. Figure 21 illustrates this graphically by showing the theoretical result of modulating the steady field H<sub>o</sub> with h(t) in (88b). At a fixed H<sub>o</sub> the instantaneous magnetization M(H<sub>o</sub>,t) may be a complicated function of time, even though the field dependence of the dHvA magnetization M(H) is sinusoidal, as shown in Figure 21. Further, the form of M(H<sub>o</sub>,t), and hence its harmonic content in time, varies with H<sub>o</sub> and h, with h measured as a proportion of the h<sub>opt</sub> corresponding to M<sub>o</sub>. Because the magnetization is shown over only a few oscillations, the amplitude is taken as constant in Figure 21. Note the distinction in this figure and in Figure 3 between the general variable H (a "dummy" variable for the function M<sub>osc</sub>) and H<sub>o</sub>, the steady field to which the modulation field is added.

Because it is easier to visualize changes with field rather than inverse field, the concept of the field period is useful.  $M_{osc,r}$  is not strictly periodic in field, but over four or five oscillations it is nearly sinusoidal. Let the phase  $\psi_r$  differ by  $2\pi$  radians at H and H' > H. Then the field period is

$$P_{H} = H' - H = \frac{HH'}{F} = \frac{H^{2}}{F-H} \div \frac{Havg}{F},$$
 [101a]

where the second and third steps follow directly from equations (50) and (51), and the fourth step is an approximation, with  $H_{avg} = \frac{1}{2}(H+H')$ .

For AuGa2,

$$P_{H}(C'_{3}) = \begin{cases} 739 \text{ Gauss at } H_{0} = 50 \text{ kG} \\ 185 \text{ Gauss at } H_{0} = 25 \text{ kG.} \end{cases}$$
 [101b]

Note that for  $C'_{3}$  (F = 3385 kG) and when  $H_{o}$  = 50.18 kG, equation (100a)



Figure 21. The construction of  $M(H_o,t)$  from M(H) and h(t), with  $H = H_o + h(t)$ . M(H) is assumed sinusoidal. Changing  $H_o$  or h changes  $J_n(\lambda)$  and hence the harmonic spectrum of  $M(H_o,t)$ . F = 3385 kG.

gives  $h_{opt} = 361$  Gauss, about half  $P_{H}$ . Figure 21 illustrates why this maximizes the second time harmonic generated by the fundamental dHvA harmonic: for the given conditions  $M(H_o, t)$  approximates cos  $2u_m t$ .

Figure 22 illustrates, in a slightly different format, the theoretical magnetization  $M(H_o,t)$  generated under the conditions discussed above. The field periods are given by (101b). The amplitude at H = 50 kG is 1 Gauss (close to a measured value), and it is adjusted for  $H_o = 25$  kG by (71c). Because the fundamental dHvA harmonic constitutes  $M_{osc}(H)$  illustrated in Figure 22,  $M(H_o,t)$  is designated by  $M_1(H_o,t)$ , abbreviated to  $M_1(t)$ . Each graph shows a possible  $M_1(t)$  and the h(t)and  $H_o$  which generate it. Together they show how the harmonic spectrum of  $M_1(t)$  depends on both parameters, h and  $H_o$ . Thus curves like that of Figure 20 are generated by the sample when  $H_o$  varies and one time harmonic is detected.

Comparison of Figures 22(d) and (e) illustrates the fact (see equation (96)) that the relative Fourier amplitudes remain constant if h changes with  $H_0$  to keep  $\lambda$  constant. Such diagrams are useful for estimating the harmonic content of M(t) and for establishing the relative phases of h(t) and v(t)  $\infty$  dM/dt.

Figures 21 and 22 assume no magnetic interaction.

<u>Spectral analysis.</u> From (87) and (96) it is clear that (98) is one of an infinite set of terms of the form

for the amplitude of the s-th time harmonic of the voltage induced by the

- Figure 22. Modulation of the steady field  $\underline{H}_{o}$  by  $\underline{h}$  cos  $\omega_{m}$ t causes each harmonic component  $\underline{M}_{r}(\underline{H})$  of the oscillatory magnetization  $\underline{M}_{osc}$  of equation (71) to induce an alternating voltage v(t)  $\infty \ d\underline{M}_{r}(\underline{H}_{o},t)/dt$ . Theoretical values of  $\underline{M}_{1}(\underline{H}_{o},t)$  are shown in (b) through (e). Assume  $\underline{B}_{internal} = \underline{H}_{applied}$  and that  $\underline{M}_{osc} = \underline{M}_{osc,1}$ .
  - (a)  $M_{osc,1}(H) = M_1(H) \sin 2\pi(F/H + \phi)$  around 25 kG and 50 kG. F = 3385 kG;  $\phi = 0.3$  is hypothetical.
  - (b) (e).  $M_1(H_0,t) = M_1(t)$ : solid line, scale -1 to +1 Gauss; h(t): dotted line, scale -360 to +360 Gauss. And  $h_{opt}$  is for  $J_2(\lambda)$ .
  - (b)  $M_1(t)$  at 50.00 kG, h =  $\frac{1}{2}h_{opt}$  = 179 Gauss. Fundamental dHvA harmonic dominates.
  - (c)  $M_1(t)$  at 50.18 kG, h = h<sub>opt</sub> = 361 Gauss. Second dHvA harmonic dominates.
  - (d)  $M_1(t)$  at 50.00 kG, h = h = 359 Gauss. Fundamental and third dHvA harmonics dominate.
  - (e) M<sub>1</sub>(t) at 25.13 kG, h = h<sub>opt</sub> = 76.7 Gauss. First and third dHvA harmonics dominate, as in (d). For both (d) and (e) H<sub>o</sub> is at the same relative phase of M<sub>1</sub>(H<sub>o</sub>), a downward zero crossing, and h = h<sub>opt</sub>.



Figure 22

r-th dHvA harmonic of the i-th extremal orbit, and that in the general case sophisticated spectral analysis is needed if the recorded signal voltage is to be resolved. This is especially true in metals, which may have up to a dozen frequencies in a given direction. The harmonic amplitudes from a single orbit decrease rapidly with order, so that detection of order four and above requires special effort, and usually only the fundamental and first overtone are easily detected. The wide range of frequency (usually  $10^6$  to  $10^9$  Gauss in metals  $10^1$ ) commonly present in complicated Fermi surfaces aids in separating the frequencies. Ordinarily the separate  $M_{ost,r}^{(i)'}$  must be known to determine the values of the various Fermi surface parameters contained in the dHvA effect. (But the g-factor for a given orbit is usually evaluated from the total signal,  $M_{osc}^{(1)}$ .) Stark and Windmiller<sup>101</sup> give a summary of techniques they and others have developed to exploit the spectrometer action of the crystal-coil system. These are the adjustment of the relative orientations of  $\underline{H}_{\alpha}$ ,  $\underline{h}$ , and the axis of the pick-up coil to nullify the entire signal  $M_{osc}^{(1)}$  from an orbit. It is possible to nullify as many as four orbit signals. They also analyze the choice of the magnititude of the modulation field to use the dependence of  $V_{r,n}^{(i)}$  on Bessel functions to nullify separate dHvA harmonics from additional orbits, a more practical technique, which is in common use.

External filtering is more extensively used than the orientations mentioned above becasue of various technical difficulties when general orientations are used. The most common method is an inverse-field-sweep; i.e.,  $1/H \propto time$ , so  $V_r \propto sin(r \omega_m t)$ , which can then be isolated by conventional electronic filters. Fourier transformation is currently the easiest method of spectral analysis when the data is recorded by digital equipment. The Fourier transform of the data is then found by computation.

If two signals to be resolved are close in frequency, neither external filtering nor Fourier transformation can separate them with much precision. If the design of the apparatus holding the sample does not allow nullifying the interfering signal by the relative orientation of the fields and sample, then about the best that can be done is graphical analysis: considering the shape of the recording in light of what other information one may have about the signal's components. We used this method. Although it was originally our intention to use 1/H filtering, we found the signals most troublesome to the precise measurement of F of C' lay very close to the signal of interest. Therefore, it was felt that external filtering could not improve the precision and plans to construct an 1/H sweep were canceled. Digital recording equipment was not readily available. The design of the sample holder precluded using the orientation method. The validity of using  $V_2$  of (99) (corresponding to the presence of only one dHvA component), the structure of the signal, and the resolution of the measured dHvA frequencies are discussed in section 7.2.

<u>Data reduction.</u> The procedure of typical dHvA experiments is (1) to record the r.m.s. voltage versus field magnitude and direction and temperature; (2) to resolve the voltage into its components  $V_{r,s}^{(1)}$ ; and (3) to evaluate the corresponding  $M_r^{(1)}$  as functions of H,0, $\phi$ , and T, and from those functions to obtain F, m\*, T<sub>D</sub>, etc. The previous two subsections discussed (1) and (2). This subsection gives the basic method of (3) for some parameters. The apparatus for voltage and field measurements are described in Chapter VI and the details of the data reduction for our conditions are given in Chapter VII.

Let the expression (71c) for  $M_r$  show m\* explicitly by writing

$$\alpha = \frac{m^{\star}}{m_{o}} \alpha_{o} = (2\pi^{2}k_{B}m_{o}c/e\hbar) \left(\frac{m^{\star}}{m_{o}}\right) = 146.9 \frac{m^{\star}}{m_{o}} \frac{kG}{Kelvin}, \quad [103]$$

analogous to (71e). When  $\sinh(r\alpha T/H)$  is close to  $\frac{1}{2}\exp(r\alpha T/H)$  for a given orbit and dHvA harmonic, then

$$\ln\left(\frac{r}{T}\right) = \ln(2A) - \frac{r\alpha}{H} \frac{m^{\star}}{m} T, \qquad [104]$$

where A includes the other factors of (71c). Thus the slope of  $\ln(\frac{n}{T})$  versus T and at fixed field gives the cyclotron mass m\* for the orbit, with separate measurements for the dHvA harmonics being a check on the measurements. Or having obtained m\*, one has another test of whether a detected signal is an overtone or from another orbit. An analysis of the error introduced by the sinh-exp approximation gives

Error = 
$$\left(\frac{m^{\star}}{m_{o}}\right)_{\text{graph}} - \left(\frac{m^{\star}}{m_{o}}\right)_{\text{true}} = \left(\frac{m^{\star}}{m_{o}}\right)_{\text{true}} \left(\frac{1}{\sinh(r\alpha T/H)} - 1\right),$$
 [105]

which results in

Error 
$$< \frac{1}{2}\%$$
 for  $\frac{r_{\alpha}}{H} \frac{m^{*}}{m_{o}} T < 2.1.$  [106]

Once m\* is known,  ${\bf T}_{\rm D}$  for the same orbit may be found by a similar plot:

$$\ln[M_r \sqrt{H} \sinh(r_\alpha T/H)] = \ln(A') - r_\alpha T_D(\frac{1}{H}) , \qquad [107]$$

where the slope of the left-hand side versus 1/H is  $-r\alpha T_D$ .

The dHvA frequency F may be obtained by counting cycles in the measured M of (71a) and plotting the number of cycles versus 1/H.

Another method reduces statistical error and gives more information: plot the phase  $\psi_r$  of (71b) versus 1/H; the slope is F and the intercept gives the phase constant  $-2\pi r\gamma + \frac{\pi}{4}$ .
### CHAPTER VI

#### DE HAAS-VAN ALPHEN APPARATUS

The work described in this thesis evolved from a preliminary attempt to find de Haas-van Alphen (dHvA) signals in various materials. The first probes were designed for a Harvey Wells iron core electromagnet with a maximum field of 22 kG. The first probe was designed to have the pick-up coil, that detects the voltage induced by the sample's magnetization, rotate over a wide angle with respect to the sample. The necessarily weak flux linkage, low electron density of the sample (PbSnTe) and low magnetic fields combined to give a null result. The next step was to improve flux linkage by using a rigidly fixed, solenoidal pick-up coil with a bore slightly bigger than the sample's diameter. There was still no signal from a sample of such low carrier density, so three metallic samples (Sn, Au<sub>2</sub>Pb, and AuGa) were used to test the apparatus. Tin gave very big signals with excellent signal-tonoise ratio in the fields available. The intermetallic compounds gave very small signals. About this time the decision was made to attempt to see if there was any relationship among the variation in RRR of  ${\rm AuGa}_2$ samples, possible changes in the Fermi surface (as exhibited by the dHvA effect), and possible very small changes in concentration. (These hypotheses have been detailed in Chapter I.) Therefore, a new probe was designed for a 50 kG superconducting solenoid that was available for our use.

This chapter shows the basic design and operating features of the probe used in the 50 kG solenoid, and describes the circuit diagram for the electrical connections, the electronic instruments, the superconducting solenoid and dewar, and two methods of measuring the magnetic field: nuclear magnetic resonance (NMR) for precision, and measurement of the current through the solenoid by the voltage across a standard resistor.

#### 6.1 Probe

Our objective of detecting very small changes in the Fermi surface would likely require very precise measurements of dHvA frequency F, where F is proportional to an extremal cross-sectional area of the Fermi surface. We wanted precise measurements of some part of the Fermi surface of AuGa, that gave big signals and might also be sensitive to small changes in concentration. Thus precise orientation of the crystal in the field is required. For this purpose a probe for measuring the dHvA effect using the field modulation technique (FMT) was constructed following the design of Templeton and Coleridge. 49 See Figures 23, 24, and 25. The basic construction is the usual one for cryostats used in cryogenic experiments: a long stainless steel tube with electrical and mechanical feedthroughs at the top, samples and detectors at the bottom, and in between a flange capable of sealing the top of a dewar holding the cryogenic fluid in which the bottom end of the tube is submerged. In our case the dewar also held the superconducting solenoid. The following are contained in a holder at the bottom end of the probe: the dHvA sample, the coils for detecting the dHvA signal, an NMR sample for



Figure 23. Plan view of the de Haas-van Alphen probe (top).





- (a) Bottom assemblies.
- (b) dHvA coil former, coils, and sample.
- (c) Probe, dewar, and solenoid placement.



Figure 25. Exploded view of the probe's coil former and sample holder assembly.

precise measurement of the magnetic field, and the associated coils, one for modulating the field for NMR and a radiofrequency (RF) coil. The holder is not attached rigidly to the tube, but is suspended from the bottom of it and pulled upward by one or more springs, to be held firmly against three pointed rods. Two of these are threaded and may be rotated to adjust their lengths and thus tilt the holder to allow a well controlled orientation of the sample inside.

Discussion of the probe falls naturally into a number of assemblies: flange and housing tube; mobile base, to which the holder is attached and which is able to tilt; control tubes and motor for tilting the mobile base and hence orientating the dHvA sample; a sample holder assembly consisting of the coil formers with their coils, places for the samples to be seated, and a spindle for attaching the holder to the mobile base; and lastly, electrical lines and feedthroughs for both dHvA and NMR. Letter codes in the following description correspond with those on the figures.

Flange and support tube. The main housing tube (HT) is stainless steel (s.s.), .020" wall, 1-3/8" OD, and 153 cm in length, with an overall length for the probe of 170 cm. A Quick-Seal (QS) soldered to a brass flange (SF) permits both a seal for the dewar of the cryostat sufficient for the bath vapor pressures we used and easy adjustment of the vertical position of the probe. Such adjustment allowed a check by NMR of the axial homogeneity of the solenoid, and a subsequent positioning of the sample in the flatest part of the field profile. The flange is bolted to a copper tee of 2" bore that provides access to the dewar. HT is sealed at the top by a lift ring (LR) and feedthrough box (FB).

On top of FB four 3/16" Quick seals (QS), of which the back two are hidden behind the front two, permit entry for two control tubes (CT) and the NMR RF coaxial line (RFL). The fourth seal was either blanked off or used for a tension wire (not shown; see below). The RFL is vacuum tight and terminates in a BNC connector on a copper elbow (E). The feedthrough box has four ports with o-ring seals for hermetic, electrical feedthroughs (EF), which have nine pins each. The sides of two are shown in Figure 23.

Three threaded tripod posts (TP) hold the probe at the desired height and also support the motor at the very top (not shown). The housing tube also has a lower flange (LF) at the bottom, for guiding and attaching the lower assemblies.

Mobile base. A brass disk (MB) has a small flange beneath for attaching the holder assembly and three smaller stainless steel disks (SS) seated on top to provide hard contact points for the three threaded, pointed, equidistant tripod legs (TL). One or more springs (SG) attached to the lower flange by a cross bar on two threaded spring posts (SP), hold the mobile base firmly against the tripod. A phosphor bronze wire leads from each spring, running close by TL and through small holes in LF and MB to beneath MB, where it is soldered to a small pivot cone, applying nearly vertical tension for the range of tilting angles used. One leg is a stud; the other two are rotated by means of control tubes (CT) extending beyond the top of the housing tube to tilt the mobile base and holder assembly. Threads 4-48 provided fine control. The arrangement of the springs changed from one central spring passing through center holes in the lower flange and in the mobile base (as in

Ref. 49), to the addition of three helper springs located symmetrically on the circumference of the lower flange, to two symmetrically positioned, off-axis springs (SG in Figure 24) near and parallel to the rotating tripod legs. This last provided greater and more uniform tension. Deterioration in the signal-to-noise (S/N) ratio when the axis of the modulation coils (coaxial with the mobile base) was more than about 2° from the direction of B of the solenoid (vertical) prompted the addition of a strong central wire (not shown) running from the center of the mobile base through the feedthrough. After the crystal was oriented much more tension could be applied through the wire than through the springs. Although the tension wire returned S/N to almost the value prevailing when the axes of the coils were parallel to B, it was marginally beneficial because the dHvA electrical signals obtained offaxis were used only for orienting the sample, and did not have to be especially clean. Clean signals were needed only from <111> || B, and except for Sample 6 this put the coil axis within  $2^{\circ}$  of <u>B</u>. Springs were of phosphor-bronze. Some were purchased from McMaster Supply; some were wound in the machine shop from wire of .020". Springs of (unstretched) lengths ranging 2 cm to 4 cm and of two diameters, .18 cm and .22 cm, were used. All had spring constants 2.65+.06 Nt/m.

<u>Control tubes and motor.</u> The control tubes (CT) are two 3/16" s.s. tubes, each soldered to a tripod leg at the bottom and to a shaft at the top. Each shaft has two thick spur gears (G) spaced slightly apart, but with teeth aligned, to enable continuous engagement with a spur gear (MG) on the shaft of a synchronous motor as CT turns and moves vertically over a range of about 2 cm. The motor is pivoted manually to engage one

CT at a time. Because the dHvA signal depends upon the vector <u>B</u>, continuous change of the crystal's orientation in a static field gives a dHvA rotation signal (a different signal from that obtained by a field sweep, but also oscillatory). The smooth change of orientation given by the synchronous motor (6 revolutions per minute) gives a signal much easier to interpret than those obtained from a hand rotation. However, unless S/N is very poor, the motor is a convenience, not a necessity.

It is desirable to know the relation between the number of turns  $C_1$  of  $CT_1$  and the polar angle and aximuthal angle of the mobile base. (The Euler angles are not appropriate because the mobile base has only two degrees of freedom, being unable independently to rotate about its axis. For the sample to realize a third degree of freedom it would have to be removed from the holder assembly and rotated about its long axis.) Knowledge of this relation permits a calculation of the angular resolution for the crystal's orientation and from  $F(\theta, \phi)$  calculation of the resolution in F. It is also a check on how closely aligned are <111> and the axis of the cylindrical sample. Finally, the angular variation can be converted to translation of the NMR sample to obtain information about the radial homogeneity of the field. The equations are

$$\tan \theta = \left[ \left( \frac{C_1^p}{s} \right)^2 + \left( \frac{p}{2h} \right)^2 \left( C_1 - 2C_2 \right)^2 \right]^{\frac{1}{2}}$$
[108a]

$$\tan \phi = \frac{(2C_2 - C_1)s}{2h C_1}$$
[108b]

where  $C_1$  is the number of turns of the first control tube, CT1, attached to tripod leg TL1; and similarly for  $C_2$ . The polar angles  $(\theta, \phi)$  are with respect to the axes defined by the probe axis (z-axis) and the line (x-axis) connecting the tips of TL fixed and TL1, where TL1 is chosen so TL2 lies in quadrant I of the xy-plane. (Axis z is vertical and plane xy is horizontal.) The TL form an equilateral triangle in or nearly parallel to the xy-plane. The parameters are triangle side s, height h, and pitch p of the 4-48 threads: s = .9544", h = .8265", and p = .0283". Figure 26 is a contour map of polar angle. The range of turns is roughly <u>+8</u> from the level, corresponding to maximal  $\theta$  of about 25°. The resolution in setting  $\theta$  at a value near zero is 0.4°, corresponding to a resolution in dHvA frequency F of 28 ppm when orienting the sample by the symmetry of the dHvA signal of the C<sub>3</sub> orbit of AuGa<sub>2</sub>. (This value was obtained from the equation of Ref. 10.) The orientation procedure is iterative: a theoretically infinite series of alternate adjustments of CT. (See Chapter VII for details.) It was normally carried through three steps (one step being an adjustment of each CT) to give an accuracy of orientation corresponding to an error of less than 1 kG in F, which is about the standard deviation of F for any one run.

Sample holder assembly. This consisted of the coil formers with their coils, the samples, and a spindle (SL) and cap (CP) that held the assembly together and affixed it to the mobile base. There were two types of coil formers, one (CF2) for the split NMR modulation coils (NMR-M) another (CF1) for all three FMT coils, with numerous editions of each. The three FMT coils are solenoids and may be grouped into a long modulation (M) coil (which could be considered two coils in series) and a signal (S) coil consisting of a pick-up (P) coil and a balance (B) coil in series opposition. With the exception of one of the formers for NMR, all formers and the spindle are plastic, laminated epoxy with paper filler, EP-22 manufactured by the Synthane Corp. This was found to



Figure 26. Angle map of mobile base tilt angle. The numbers in the body of the map give polar angle  $\theta$  (degrees) between the base's normal and the probe's axis. Rough contour lines are identified by angle. The numbers along the axes are revolutions of each control tube.

have excellent mechanical properties both for machining and for use at LHe temperatures. Plastic was used for lightness, to increase the force of contact between the mobile base and tripod. It was also felt that if the spindle (SL) passing through the center of the NMR sample and RF coil were metal, it would attenuate the NMR signal. In order to make an accurate measurement of field, the dHvA sample lies in the center of the NMR sample. The cap has a center access hole through which the leads exit. They are taped to the outside of the probe nearly its whole length from the cap to just under the flange (SF), where they pass into the interior of HT to the electrical feedthroughs (EF) in the feedthrough box (FB).

<u>dHvA coils.</u> Reference 49 used a coil similar to NMR-M but with half the diameter, for both NMR and dHvA modulation, but our larger ratio of magnetic moment to center modulation field h decreased our S/N by a factor of 40 when NMR-M was used to modulate the field for detection of the dHvA signal. Bigger h and S/N were possible from winding M directly over S.

The dHvA magnetization induces a voltage directly into the pick-up coil (P). The balance coil (B) has two jobs: to reduce the noise voltage and to reduce the voltage induced in the P coil directly by the M coil (transformer action). A large contribution to the noise in the final signal could come from vibration of the P coil in the slightly inhomogeneous magnetic field of the solenoid. (The vibration is due to the alternating magnetic moments of the M coil and the sample.) Cancelation of vibrational noise will occur if coils P and B have the same flux linkage to the steady field. This is approximated by having them physically close and with the same area-turns. The B coil sees

roughly the same field variation with time, and so tends to cancel the voltage induced in the S coil by this vibration. Although vibrational noise is greatly attenuated, as shown by comparing v(t) with and without the B coil at typical, fixed values of H and h, it remains the overwhelming contribution to the total noise in the final signal, as is shown by the fact that v(t) from a well balanced signal coil in high, constant field with typical modulation current is much noiser than v(t) recorded under the following test conditions (except for the indicated change conditions are as for recording dHvA signals): (1) H = 0, (2) h = 0, and (3) the input to the detector shunted by an impedance similar to that of the S coil.

Weak flux linkage between the B coil and the sample is required to prevent serious attenuation of the desired signal. The design of coils N5 and N6 used in these experiments satisfies the above requirements: P and B have the same dimensions, the same number of turns of wire, and they are close together. An alternative design is to wind the B coil over the P coil; this decreases their separation but also decreases the net signal from the sample. The proper choice probably depends upon the homogeneity of the field and the intensity of magnetization. The first design was found to have significantly lower S/N for our experimental conditions.

The second job of the B coil is to cancel the strong voltage induced directly in the P coil by the M coil, a voltage which is typically  $10^2$  to  $10^6$  times greater than the dHvA voltages.<sup>101</sup> When measuring the fundamental time harmonic of M(t) it is essential to reduce this overriding background signal, coming at the same frequency, to a level that enables the electronic amplifiers to properly process the small oscillatory component. Even when detecting at overtones, which is usually the case, filtering out such a strongly interfering signal electronically is impractical and leads to deterioration of S/N. A much improved signal results from reducing this interference at its source by having the P and B coils see the same modulation field. This is accomplished by the twin M coils shown. The balance ratio (the ratio of voltages from the S and P coils) depends upon the characteristics of the sample and coils; typical values<sup>101</sup> can range from  $10^{-2}$  to  $10^{-3}$  and the required effectiveness of balance depends upon the strength of the dHvA and the harmonic of detection. Most detection equipment has filters becasue the dHvA signal has strong time harmonics, so that reducing the balance ratio below the value necessary to allow optimal electronic filtering does not improve S/N. Very low ratios of the order of  $10^{-4}$  to  $10^{-5}$  cannot be maintained over wide field ranges because of magnetoresistance and diamagnetism of the sample and wire.<sup>97</sup>

<u>Coil winding and specifications.</u> The dimensions of the formers for coils NMR-M, M, P, and B are shown in Figure 27. Coil specifications are given in Table 4. The coil strength of the modulation coils was calculated from

$$S_{c} = \frac{BN}{I_{m}}$$

$$= \left(\frac{\mu_{o}}{4\pi}\right) \frac{1}{(r_{2}-r_{1})L} \left\{z_{2} \left(\sinh^{-1}(r_{2}/|z_{2}|)-\sinh^{-1}(r_{1}/|z_{2}|)\right) - z_{1} \left[\sinh^{-1}(r_{2}/|z_{1}|)-\sinh^{-1}(r_{1}/|z_{1}|)\right]\right\}, \quad [109]$$

where the units are mks, with the final answer for S in Gauss/Ampere-



- Figure 27. Dimensions of coil formers.
  - (a) Former CRl for dHvA coils N5 and N6. Each has windings P (pick-up), B (balance) and M (dHvA modulation). Dimensions in mils (thousandths of an inch).
  - (b) Former CF2 for coil NMR-M, for NMR modulation. Dimensions in inches.

Coil	Winding <sup>a</sup>	Wire <sup>b</sup> Size (AWG)	Number of Turns	DC Resis RT <sup>C</sup>	tance (Ω) 4.2 K zero kG
N5	P	41	250	14	_
	B	41	250	14	_
	M	43	1326	152	2.6
N6	P	50	2300	.99 k	12
	B	50	2300	(note d)	12
	M	50	6936	3.88 k	48
NMR-M		42	6240	2.66 k	33

TABLE 4. Specifications for de Haas-van Alphen Coils N5 and N6 and NMR Modulation Coil NMR-M

WINDINGS

## COMPLETE COILS

Coil	Balance <sup>e</sup> V <sub>S</sub> /V <sub>P</sub>	Input Impedance <sup>f</sup> at 100 Hz, 4.2 K, and zero kG	Coil ( (Gauss) Theory <sup>8</sup>	Strength S /milliAmp) <sup>C</sup> Experiment <sup>h</sup>
N5	10 <sup>-5</sup>	148 Ω at 1 <sup>0</sup> (note i)	1.25	1.28
N6	0.5% (note d)	63 $\Omega$ at 47 <sup>0</sup>	6.42	5.8-7.0

<sup>a</sup>P stands for pick-up; B for balance; M for modulation.

<sup>b</sup>Leads were usually AWG 36.

<sup>C</sup>Room temperature.

<sup>d</sup>As wound, balance was 0.5% and B resistance was .99 k $\Omega$ . Later the balance became 2.4% and resistance .96 k $\Omega$ , probably due to a few turns shorted on one winding.

<sup>e</sup>V<sub>S</sub> is voltage induced in the signal windings (P and B in series opposition). V<sub>P</sub> is for pick-up winding alone. At 4.2 K in zero field.

<sup>f</sup>The presence of the dHvA sample made no difference.

<sup>g</sup>From Equation (109).

<sup>h</sup>From fitting data to Bessel function of Equation (99).

<sup>1</sup>Additional data for room temperature and zero field: measured inductance of 4.3 mH and Q of .18, both at 1 kHz.

turn equal to  $10^{-4}$ S<sub>c</sub> in units of Tesla/Ampere-turn. L, r<sub>1</sub>, and r<sub>2</sub> are the solenoid's length and inner and outer radii (meters),  $\mu_0/4\pi =$  $10^{-7}$ (mks), z<sub>1</sub> and z<sub>2</sub> are signed distances from the field point to the left and right ends, respectively, of the solenoid (note the absolute values in the arguments of the inverse hyperbolic sine functions), and the field points lies on the long symmetry axis. Equation (109) comes from integrating the Biot-Savart expression, and its accuracy is about 2%. This was determined for dHvA formers N5 and N6 from the Bessel zeros of the dHvA signal and the roots of J<sub>2</sub> in (99), and for NMR former M by direct measurement with a Hewlett-Packard field/current meter.

For coil strength at the center (109) reduces to

$$S_{c} = \frac{B}{NI} = \frac{4 \times 10^{-7}}{D_{2}^{-D_{1}}} (\sinh^{-1}(\frac{D_{2}}{L}) - \sinh^{-1}(\frac{D_{1}}{L})), \qquad [110]$$

where D is diameter. It also reduces to the usual thin solenoid formula

$$\frac{B}{NI} = \frac{\mu_0}{2L} (\cos a_1 + \cos a_2),$$
 [111]

where a<sub>i</sub> are the angles subtended at the axial field point by the basal radii.

Estimates for the optimal values of the size of wire and number of turns were made as follows. Matching the impedance of the oscillator  $(50\Omega)$  permits the maximal power and the maximal modulation field. The desired maximum for second harmonic detection (see Figure 45) is one-half (amplitude 367 G) the field period (735 G) at the maximal field (50 kG). The available power of the oscillator is 0.5 W, which is lost to Joule heat and flux leakage in both the coils and the impedance matching transformer at the front end of the detector. Room temperature

DC resistance of the M coil is 2 k $\Omega$ , and the RRR of fine (AWG 42 to 50) Cu magnet wire is 95 to 100 (as measured). Assuming all power goes to the Joule heat, the maximal current into the cold coil is 35 mA<sub>rms</sub>. The maximal coil strength for fine wire on formers of the given dimensions is around 7 G/mA (1.25 G/mA for coil NS and 6.42 G/mA for coil N6), giving a maximum amplitude of 330 Gauss. This shows maximizing the power into the M coil is important. Flux leakage, less than optimal matching, and magnetoresistance of the Cu reduced the maximal modulation field so that equation (100a) could be satisfied only for H near 40 kG.

To wind the M coil to match impedance assume that the coil and input transformer truly reflect the infinite input impedance of the amplifier, ignore magnetoresistance, and wind the coil to have resistance  $R_c = R_s$  of the source (oscillator) when the coil is at liquid helium (LHe) temperature. For a constant voltage supply the useful parameter field per volt, and the equations are

$$B = \frac{S_{c}NV_{s}}{((R_{s} + R_{c})^{2} + X^{2})^{\frac{1}{2}}},$$
 [112a]

where V and R are the source voltage and resistance; R and X are the coil's resistance and impedance at frequency  $\omega = 2\pi f$ :

$$X = \omega S_{c} C N^{2}$$
 [112b]

where C is the cross-sectional area  $(m^2)$ 

$$C = \frac{\pi}{2}(r_1^2 + r_2^2). \qquad [112c]$$

The packing densities of fine wires of diameter  $d_w$  were both calculated and measured. Using them and (112) the field B(N,d<sub>w</sub>) per volt  $V_s$  was calculated for N windings of copper magnet wire of diameter  $d_w$  on one recess of former CF2 with our oscillator (R = 50 $\Omega$ , f = 100 Hz) as the source. The field point is on the coil's axis and at the center of the single recess. (Note that the two recesses of NMR-M are a modified Helmholtz pair.) Sketches of contours for  $B/V_s$  are shown in Figure 28 for 20°C and in Figure 29 for 4.2 K. Because fringing effects reduce the accuracy of (112b), the frequency was adjusted by a factor found experimentally. Spot checks of these calculations against measured values yielded 4% accuracy for frequencies near 100 Hz.

The contours of Figures 28 and 29 assume a length L and inner coil diameter ID. The third constraint, outer diameter, determines another boundary on the map: an OD line (dashed), the locus of the points  $(d_w, N_d)$ , where  $N_d$  is the maximal number of turns of wire of diameter  $d_w$ that the former has room for. Maximal field per volt for the former is given by the maximum within the accessible region defined by the two axes and the OD line. In Figure 29 the OD line happens to pass close by the absolute maximum. During collection of the data an unexpected problem arose that later appeared to be temperature rise of the sample, caused by the heating in the M coil of CF1. Thus choosing the best coil specifications is not as simple as described above. The maximal modulation field h that will be required, the combination of turns N and modulation current  ${\rm I}_{\rm m}$  necessary to establish it, the resulting coil resistance  $R_c$  and Joule heat, the rate of heat dissipation in the coil and holder, and the maximum temperature rise of the sample all are interrelated parameters that must be adjusted for optimum detection.

The coils were all wound on a Meteor coil winding machine. The wires had solderable insulation; it vaporized from the heat of soldering









with ordinary PbSn solder. The tips of heavy leads (AWG 36) were cleaned, tinned and anchored to the coil former by threading through small (drill No. 72) holes on the shank, with 1 mm left protruding. The former was put onto a mandrel with a drum on which the heavy leads were secured. The fine wire was wrapped about the tip, soldered, wound onto the former, cut, and that end soldered to the second heavy lead. Each layer was glued with very thin DuCo cement.

<u>Electrical lines; Heat Leaks.</u> The heavy (AWG 36 or 38) leads from CF1 led through the hole in the cap (CP) to above LF, where each was soldered to a separate probe lead (AWG 32) running to electrical feedthroughs (EF) on FB. Likewise for CF2 leads. All leads were rigidly taped, except for the last few inches at the top, either to the exterior side of HT or to a narrow aluminum bridge (not shown) to facilitate taping on the holder assembly. Coil leads were twisted pairs; probe leads ran parallel. Experience showed several centimeters of loosely dangling (but twisted) coil lead did not have noticeable effect on S/N. Taping also protected against mechanical damage.

Three NMR RF lines were used, one at a time. RFLO is a 3/16" s.s. tube (the outer conductor) with a 1/32" s.s. tube as the center conductor, spaced by three or four Teflon triangles and tension at each end. These sizes give an impedance close to that of the RG58 cables used ( $54\Omega$ ). The impedance changed slightly with the level of LHe. The major design consideration was low thermal leakage. An effort was made to improve NMR S/N in RFL1 by using as the center conductor a Cu magnet wire, size AWG 18 chosen for current coaxial impedance matching, spaced by Teflon triangles every 2 or 3 inches. S/N improvement was small but noticeable. Later REL2 was made vacuum tight by a hermetic BNC connector on a copper elbow because running procedure required frequent removal and reinsertion of the probe. Water of condensation collected inside the tube and absorbed the FR power, killing the signal. RFL2 is another 3/16" tube enclosing an RG58 cable with the insulation and ground braid removed, leaving the AWG20 Cu center plus foam insulation. S/N was about the same, perhaps lower. This RFL was used only when the probe was left in LHe during the entire run, so it was not vacuum tight. RFL1 was used most.

Because the sample and coils were in the LHe bath, thermal leaks were a concern only in conserving LHe. Heat flux down the probe, with the top at room temperature and the bottom in LHe to about 10" above the sample was calculated from tables of integrated thermal conductivities.<sup>103</sup> Results are given in Table 5. These are upper limits because the loss of heat to the rising cold He gas carries away much heat before it reaches the bottom of the probe.

#### 6.2 Electronics

The electronics were standard for the field modulation technique (FMT). See References 95 through 101 for typical circuits. Lower case v and i are time dependent variables, capital V and I are amplitudes or phasors.

In Figure 30 oscillator number 1 (OSC1) with voltage  $V_m$  generates a sinusoidal current  $I_m$  of frequency  $f_m$  and distortion less than .02%.  $I_m$  generates the dHvA modulation field h. A digital volt meter (DVM) measures  $I_m$  but sometimes an oscilloscope (S) was used. The dHvA

TABLE 5. Thermal leaks: Conductive heat flow from top of probe (room T) to LHe level (10" above sample).

Path	Heat Flow (Watts)
1 wire, 32 AWG	$2.88 \times 10^{-3}$
All probe leads except RFL (18 wires, 32 AWG each)	.052
RFLO (s.s. center)	.02
RFL1 (18 AWG Cu center + air space)	.073
Probe housing tube (HT) (s.s.)	.166
Control tube (CT) (s.s.) (each)	.025
Solenoid's (SCS) 3/8" suspension tubes (all three)	0.44
Total (Probe with RFL1 + SCS suspension; exclude dewar conduction, radiation leaks, gas thermal exchange)	.39

a. Assumes no heat given up to rising cold He gas (no exchange).

voltage  $v_S = v_P + v_B$  from the dHvA coils enters a lock-in amplifier (LA) via a switch box (SB), where connections are shielded.

In addition to the B coil and electrical filters, a null control is frequently employed. A phase coherent voltage, obtained from either the B coil or from a third coil in the probe, and available for external phase and amplitude control, is added in series to null the fundamental voltage from the S coil. During development of the apparatus a phase shifter and a voltage attenuator modified  $v_S$  before it entered LIA. But data presented in this thesis was taken either with  $v_S$  going directly to LIA or with a commercial ratio transformer (RT) improving the balance first. The inset at the top left of Figure 30



Figure 30. Block diagram of dHvA and NMR electronics.

shows the two cases. RT enables a variable, precise fraction of  $v_B$  to be added in opposition to  $v_B$ , but no phase change is possible. Coil N5 was balanced well enough that it needed no help; coil N6 had about  $2^{1}2^{\infty}$  imbalance which was reduced by RT (no phase shifting) enough that the bandpass filter of the LIA could handle it. The switch box (SB) had internal shields to prevent cross-over of the modulation and signal voltages.

The LIA input was a transformer, found to give much improved S/N compared to the other option, transistor input. The LIA output  $V_0$  was recorded against steady field  $H_0$  of the superconducting solenoid (SCS) on a chart recorder (CR).  $V_0$  was proportional to the n-th harmonic component (in time) of  $v_s$ . The component has amplitude  $V_n$  and frequency  $f_n = f_d$  (the detection frequency). Except for special measurements, n = 2 for the data. Thus the LIA effectively performed a Fourier analysis to  $v_s$ , recording  $V_2 \cos(\theta - \phi)$ , where  $\theta$  is the phase angle of  $V_2$  relative to  $V_1$  and  $\phi$  is the LIA phase.

The x-axis of CR was the steady magnetic field H . Field measureo . Field measure-

# 6.3 Superconducting Solenoid and Dewar

A cryostat was built to suspend the SCS. The superconducting solenoid (SCS) was a NbTi, filaments in a Cu matrix, 50 kG at 60 A and 4.2K, manufactured by Oxford Instruments, Cambridge. Hysteresis appeared to be negligible. The NMR field measurements are unaffected by hysteresis; when the calibrated resistors were used, field points  $H_0$  for dHvA frequency data were approached by one or two decreasing oscillations. Some of the dHvA phase plots show a small hysteresis effect. See Table 6. TABLE 6. Superconducting Solenoid

Design	Oxford Instruments, 50 kG, NbTi, 850 Gauss/Amp (Spec.)		
Hysteresis (from dHvA phase separation between up-field and down-field sweeps)	.022% lag at 37 kG .037 31 .11 21		
Maximum error in dHvA	(Normally avoided by cycling into the field point.)		
frequency F phase phase constant	<u>+</u> 7.5 kG <u>+</u> .04 cycles at 31 kG <u>+</u> .17 cycles		
Homogeneity (Specification) (Axial)	.1% over a 1" diameter volume, which gives an average of 40 ppm/mm. However, the profile may be jagged.		
(NMR)	Five or six points over 4 cm gave		
(Leads to negligible phase smearing)	jagged profiles. Either in field or poor NMR precision in reading line center.		
	Average Typical		
	Field over 4 cm Gradient Avg. (kG) ( <u>+</u> %) ( <u>+</u> ppm/mm) 4 cm		
	9.82 .1 92 25		
	26.76 .019 37 4.7		
	30.53 .029 28 7.4		
	35.42 .008 2.8 2.1		
Calibration (field measured	Across $R_W$ (water-cooled tube):		
by NMR versus voltage $V_W$ across standard resistor $R_W$ as measured by a 5 digit.	(141.433 <u>+</u> .055) kG/V <u>+</u> .001 kG ( <u>+</u> .044 accuracy)		
1 microvolt resolution DVM. Average and Standard Deviation of 22 points over	Across $R_{LN}$ (as given by above and $R_{LN}/R_W$ ):		
29 – 49 kG)	(850.825 <u>+</u> .331) kG/V <u>+</u> .001 kG		
Maximum error in duvA			
frequency F	+ 3.4 kG		
phase	+ .074 cycles at 20 kG		
phase constant	<u>+</u> .096 cycles		

## 6.4 Magnetic Field Measurement

The field was measured by NMR and a standard resistance  $R_w$  or  $R_{LN}$  in series with the solenoid's current. Later a precision calibration of these resistors by NMR while measuring SCS current I with a DVM (not shown) enabled their use for field measurements sufficiently precise and reproducible for our dHvA measurements of F, given the complications presented by the crystal itself. Calibration is given in Table 6.

Nuclear magnetic resonance. Precise measurements of magnetic field were made by NMR of <sup>27</sup>Al. A marginal oscillator (MO) put RF power into the sample through the electrical feedthrough (NMR-RF) on the probe. A detector in MO demodulated the RF signal, whose amplitude decreased at resonance, giving a dip in the demodulated voltage. This was seen on S after being cleaned by filters F. Filters were 60 Hz twin-T rejection plus sometimes a bandpass set close to the modulation frequency, which was 70 to several hundred Hz. For more precise field measurements, or for weak signals, another LIA replaced S. Frequency was measured by a Hewlett-Packard Frequency Counter (FC). The method of tuning was by changing the lengths of RG58 coaxial cables, as described in Ref. 104, which also gives the MO circuit diagram (ours was slightly modified).

The sample was made by mixing filings of shop grade Al alloy with epoxy. This paste was packed into a cylindrical shell into which the RF coil has previously been inserted. After the epoxy had set a transverse hole was drilled to allow insertion of the dHvA coil former and sample holder.

The S/N for the NMR signal was only fair. Below 30 kG the decreasing NMR signal amplitude and the difficulty in making the MO work at the required lower frequencies combined to make field measurements very difficult. Various sizes of wire and numbers of turns were tried for this type of  $^{27}$ Al sample in order to improve S/N. Solid Al metal and ruby were tried out of curiosity. Niobium in NbSn superconducting wire was also tried. The best NMR sample was  $^{27}$ Al with RF being about six turns of wire in the Al-epoxy. The size of the sample was 1.5 cm x 1.0 cm diameter, with a hole of diameter 0.57 cm at the center. The wire was AWG20 but size is apparently unimportant.

<u>Calibrated resistors.</u> Two low resistance, high current resistors were used, one at a time, to provide both a voltage for the  $H_0$  scale of the chart recorder and a precise measurement of field, the latter in conjunction with a 5½ digit DVM, with a sensitivity of 1 microvolt. Both resistors were calibrated and checked occasionally with NMR. See Table 6 for calibration data and Table 7 for characteristics. Temperature was monitored with a thermocouple meter. Note that  $R_{LN}$  may be more constant over 0 - 60A than  $R_W$ . The calibration ratio that was used was obtained by dividing that for  $R_W$  by the  $R_{LN}/R_W$  ratio at 60 Amperes.

# TABLE 7. Characteristics of the Standard Resistors for the Superconducting Solenoid

R —	lesistor R <sub>W</sub>
Design	Water-cooled 3/8" s.s. tube. Distance between potential leads = 5 cm.
Resistance (By $R_{LN}/R_W$ )	$(6.017 \pm .002) \times 10^{-3}$ Ohms
Temperature coefficient (ΔR/R/ΔT)	$1.77 \times 10^{-4} (^{\circ}C)^{-1}$ at 11 $^{\circ}C$
Joule heat: $\Delta T(I)$	$\Delta T = (.00145)I^{1.94} \circ C/A (at 20°C)$
T rise: At 60 A (Amp)	$\Delta T = 2.7^{\circ}C$ (By thermocouple on outer surface. But $\Delta T$ of cooling water = $0.2^{\circ}C \Rightarrow T$ gradient in s.s. shell.)
I-V <sub>W</sub> linearity over 60 A (from T coef. & T rise)	± .07% if uniform T in shell ± .035% if linear T grad in shell
Error by above effect in	2.49 kG error in field measurement
extrapolating the NMR calibration to 20 kG	.021 cycle error in dHvA phase at 20 kG field. The error in dHvA F and phase constant is variable. That in F would show as a curve in the phase plot.

Resistor R<sub>LN</sub>

Design	500 Ampere standard resistor by Leeds-Northrup. Air-cooled. Very big (about 40 pounds).
Resistance (specification)	$1 \times 10^{-3} \pm .04\%$
Temperature coefficient	Given as very low
$R_{LN}/R_{W}$ (by DVM)	.16617 at O Amp .16624 at 60 Amp (.04% increase)

B-V<sub>LN</sub> CALIBRATION (by  $R_{LN}/R_W$  ratio)=(850.825 ± .331) kG/V ± .008 kG

## · CHAPTER VII

## EXPERIMENTAL PROCEDURE AND DE HAAS-VAN ALPHEN DATA

# 7.1 General Procedure

The general procedure was to cool the superconducting solenoid (SCS) and probe, record the dHvA oscillations on a long field sweep to see their general form, coax the marginal oscillator into working, and record the data.

The dHvA frequency F and phase constant  $\gamma$  were obtained by measuring the dHvA phase as a function of a steady field H. The Dingle temperature T<sub>D</sub> is obtained from the measured variation of the signal amplitude with field H. Theoretically, the amplitude is M<sub>1</sub>(H) of (71a). The recorded voltage V<sub>2</sub> is really the r.m.s. value of (98), uniformly proportional to its amplitude (99).

Phase data was obtained by recording  $V_2$  while sweeping down in field, stopping every 5 to 10 oscillations to note the phase and measure the field with either NMR or by recording the voltage  $V_w$  across  $R_w$ , the solenoid's standard resistor. (W stands for both the standard resistors W and LN unless distinction is necessary.) In the first runs NMR was used mostly, but as it became evident that the physics of the crystal was complicating the signal so that the slightly lower precision of H measured by  $V_W$  across  $R_W$  was irrelevant,  $R_W$  was used exclusively to greatly speed up the collection of data.

Dingle data was recorded separately for convenience. At spaced field values the modulation current  $I_m$  was adjusted for constant Bessel factor, the amplitude of  $V_2$  was recorded, and H measured. Both  $V_W$  and the calibrated current dial of the SCS power supply were accurate and precise enough for Dingle data.

# 7.2 Orientation

The crystal was oriented by turning the control tubes (CT) while observing the symmetry in  $V_2$ . The concept of surfaces of constant dHvA phase<sup>101</sup> is useful in this method of orientation. Let the direction of H be fixed in real space (xyz) while both the crystalline and k-axes may undergo general angular displacement. Given a Fermi surface (FS) with cross-sectional area  $A(\Theta,\phi)$  corresponding to  $F(\theta,\phi)$ , the field's magnitude is varied to keep the dHvA phase of (71b) constant as the crystal undergoes general displacement in real space and the direction of <u>H</u> undergoes a corresponding displacement in <u>k</u>-space (see Figure 3). The constant phase surface is the locus of H vectors, and the family of surfaces is generated by varying the phase. A spherical FS gives a spherical surface of constant phase; a prolate ellipsoidal FS gives an oblate ellipsoid. Thus there are two types of dHvA signals: field sweep and rotation. In the latter, H remains constant in magnitude as its direction in the crystal changes, giving oscillations as it crosses the surfaces of constant phase.

Ref. 10 has shown that an hyperboloid of one sheet models the third zone neck of AuGa<sub>2</sub> very well, giving the extremal cross-sectional area as a function of the polar angle  $\theta$ :

$$A(\theta) = \frac{A(0)}{[(1+b) \cos^2 \theta - b]^{\frac{1}{2}}},$$
 [113]

where  $b = m_t/m_{\ell} = .16$ , the ratio of the transverse and longitudinal masses. H  $\propto$  A gives bowl-shaped surfaces whose axis is parallel to <111>. Figure 31(a) shows their intersection with a plane containing <111>. The solid lines are quarter phase and the dashed lines are three-quarter. The other two arcs are the paths in this plane of two <u>H</u> vectors as the crystal undergoes a small angular displacement about <111>. The arcs are distorted from being circular due to the unequal scales of the figure. The corresponding rotation signals are shown in Figure 31(b).

One peak does not correspond to quarter or three-quarter phase; it is a turning point (TP), where the field and <111> are exactly parallel, and may be a positive or negative peak, as shown in Figure 31(b). Typical rotation diagrams from our runs are shown in Figure 32. If the phase  $\psi_{\rm TP}$  at which the turning point occurs is close to  $\psi_{1/4,3/4}$  (as is most likely for arbitrary field), the two will be confused, and the rotation graph will show no obvious TP. The fact that the envelope function of the rotation graph can change greatly with angle and its being generally different from the sweep envelope further confuse the identification of TP. So frequently a rotation graph at fixed H does not identify TP clearly and each peak must be examined to see if it is due to  $\psi_{\text{TP}}$  or  $\psi_{1/4,3/4}$ . An example is shown in Figure 32(c). Figure 33 shows how to identify a positive rotation peak as a turning point, a peak preceding TP, or a peak following TP. This allows one to check only positive peaks (a similar analysis applies to negative peaks) and thus move over angle more rapidly. The method is as follows: the





- Arcs (negative axis) of constant field magnitude intersect curves of constant phase  $\psi_1$  (positive axis). Arcs would be circular for equal scales. (a)
  - Corresponding sin  $\theta$  versus angle (or equivalently, versus H ) at constant field magnitude. **(**9



- Figure 32. Typical experimental rotation graphs. Horizontal segments denote the limits of rotation.
  - (a) Positive turning point (TP).
  - (b) Negative turning point (TP).
  - (c) The same sample and angular range as in (a). A small change in  $\underline{H}$  obscures the turning point.
  - (d) Another example of an obscured TP. Numbers are revolutions of one control tube. TP identified by subsequent data.



- Identification of positive peaks in a dHvA rotation graph by (1) rotation, (2) reset field, (3) rotation. Figure 33.

  - (a) Peak is a turning point.(b) Peak precedes a turning point.
  - (c) Peak follows a turning point.
first peak reached in a rotation is examined by reducing H to put  $V_2$  at a positive going zero crossing and rotating slightly about the new position. The signal recorded is then compared against theoretical diagrams like those of Figure 33. If the peak precedes a TP, continue to rotate in the same direction; if it follows a TP rotate the other direction. Continue in this manner until either TP is found or the next peak examined is one that follows TP, in which case TP is the previously recorded negative peak.

Resolution in orientation and resulting error in F and was mentioned in Chapter VI.

#### 7.3 Skin Effect

When the absolute value of the volumetric magnetic susceptibility of the sample is less than 100 and the sample's conductivity and the modulation frequency are such that the skin depth  $\delta$ , where

$$\delta = \frac{c}{(2\pi\mu\omega\sigma)^{\frac{1}{2}}},$$
[114]

is several times the sample's greatest axial diameter D, then the combination of electrical filters and a moderately balanced S coil gives good S/N. The condition

$$\frac{\delta}{D} > 1$$
[115]

for most metal samples requires a modulation frequency less than 10 Hz if the sample diameter is one or two millimeters, RRR is greater than 500, and magnetoresistance is less than 100. A trade-off is made between increasing frequency and field inhomogeneity. Increased frequency has the advantages of increased voltage (until the skin effect becomes severe), improved electrical performance, and ease of adjusting the filters and detectors, decreased time constant on the final DC filter of the detector, and generally increased S/N and ease of operation.

Regarding improved performance of the filters, at very low frequencies finding the resonant frequency is difficult and time consuming. Voltage transients arise from turning the dHvA signal off to make an NMR measurement and then on, and from other adjustments. Each transient caused the filters to ring many minutes when a 10 Hz modulation frequency was attempted. The modulation frequency of 100 Hz we used permitted the slight eddy current arising from the skin effect to induce a fundamental component of several milliVolts. A null control (ratio transformer) divided this by more than 100 to give a level which the filters could easily reject, leaving S/N as high as when no sample was in the coil. The residual eddy current does not affect the results. Figure 34 and 35 show the results of two tests to check that the dHvA amplitude is not seriously affected by any residual skin effect at 100Hz. Figure 34 shows the amplitude is at least 96% of its zero frequency limit for Sample 12, with RRR = 205. Figure 35 shows a test for a sample of presumably lower RRR. Voltage has become independent of frequency at 100 Hz. The dashed line shows the phase of  $V_S$ . The theoretical value for a uniform field is zero.

## 7.4 Data Reduction

The dHvA frequency F and phase constant  $\gamma$  were obtained by plotting the number of recorded oscillations (starting with the highest field oscillation) against inverse field, a technique described in References 49



Figure 34. Skin effect test on Sample 12.



Figure 35. Skin effect test on Sample 30.

and 68. In accordance with equations (71a) and (87), a positive-going zero crossing of voltage with respect to decreasing field denoted the start of another cycle. Let m+r denote the relative phase (m whole cycles plus remainder r) as measured from the high field reference phase N, chosen to be integral (i.e., a positive-going zero crossing). Then

$$m+r = \psi_1(H) - N.$$
 [115b]

From (71), (87), and (115b), m+r clearly has slope F and intercept

$$INF = -\gamma + 1/8 - N + \xi$$
 [115c]

where INF stands for the infinite field intercept (i.e., at 1/H = 0) and  $\xi = 0$  if the Dingle factor is negative and the number of coildetector polarity reversals is even, and  $\xi = \frac{1}{2}$  if either the Dingle factor is positive or there is a polarity reversal. For our system  $v \propto +dM/dt$ . N is determined from the known field and the value of F from the slope. For evaluation of (115c), see Section 10.2.

The trick is to isolate the fundamental component of the extremal orbit desired. Ordinarily digital Fourier analysis, electronic filtering of a sweep signal made with time t  $\propto$  1/H, and the sample's own signal discrimination, all discussed in Chapter V, are used to separate frequencies differing by a big factor. Very close frequencies that must be precisely determined require graphical analysis and consideration of the phasors involved. The latter approach was made for this data, in which the C'\_3 signal dominated. The error introduced by residual oscillations in both the phase plots and Dingle plots is the same order as the effect of uncertainty in measurements from the instruments, the temperature rise in the sample, magnetic interaction, and the occasional presence of crystallites. Very small signals from crystallites could be tolerated, but several samples were discarded because of too much interference.

Figure 36 shows typical data. Table 8 and Figure 37 summarize the measurements of the dHvA frequencies and phase constants, Dingle temperatures, and residual resistance ratios. These results are discussed in Chapter X, after the presentation in the next two chapters of some data and theory on the growth and analysis of the samples.





1. H || <|||>. Unfiltered dHvA signal. Modulation at 100 Hz.

Figure 36. Selected data for AuGa<sub>2</sub>.

note a S		Sample No.	INF <sup>b</sup>	dHvA Freq. (kG)	Dingle Temp. (K)	RRR
Melt C +.549 at.%	60	- 30 - 27	90	3388 ±4	4.0 ±.5 2.75	
	$\bigvee$	26			1.88±.12	207 <sup>C</sup>
Melt A		- 6		c d	1.09 <sup>d</sup>	≥1800 <sup>e</sup>
+.204 at.%	a	16	82 94	3384.2±0.6 <sup>f</sup>	1.34	>1700 <sup>e</sup>
		5			1.47	<u>&gt;</u> 1000 <sup>e</sup>
	$\bigcirc$	10	90 75	3385.2±1.2 <sup>f</sup>	1.91	> 500 <sup>e</sup>
Melt B 288 at.%		/ <sup>12</sup>	83	3389.3±0.5 <sup>f</sup>	2.02±.10	205±20
	m	20	92	3396.4±0.3	2.55±.15	157
	E H	13	79 65	3391.8±1.4 <sup>f</sup> 3402.4±0.4 <sup>f</sup>	5.00±.14	56
		${14}$	75 88	3405.7±0.8		55

# TABLE 8. Sample Characteristics by Position and Parent Crystal's Melt Concentration<sup>a</sup>

<sup>a</sup>Deviation of Ga concentration from stoichiometry: positive (negative)  $\Delta c_c$  means Ga excess (deficit).

<sup>b</sup>INF = infinite field phase =  $-\gamma - 3/8$  cycles for orbit C<sup>'</sup><sub>3</sub> of AuGa<sub>2</sub>, where  $\gamma$  = phase constant of LK theory. (INF includes net  $-\frac{1}{2}$  voltage reversals.) Average INF =  $-.83\pm.09$ , giving  $\gamma$  =  $.46\pm.09$ .

<sup>C</sup>Axis || <111>.

<sup>d</sup>Axis 23<sup>0</sup> off <111>.

<sup>e</sup>Lower bound.

 $f_{\underline{In} \underline{situ}}$  NMR measurements for field.



Figure 37. Summary of dHvA and RRR data.



AuGa<sub>2</sub>

#### CHAPTER VIII

#### GROWTH AND PREPARATION OF SAMPLES

This chapter considers enough of the theory of growing alloys to give an idea of what to expect to find in an alloy grown from the melt, although reliable quantitative answers are difficult to obtain because of the scarcity of data and because making measurements on a freezing metal is a full project in itself. Next are given some of the details of growing, cutting, and x-raying our crystals, all of which used standard techniques. These crystals presented no special difficulties other than the usual uncertainties involved in growing single crystals. Questions regarding some of the samples are discussed in Chapter IX. The last section is an exposition of the melt concentrations we chose and why.

In this and the following chapters the big crystal taken from the crucible after growing is sometimes called a slug to distinguish it from the small crystals cut from the slug and used as samples in the dHvA and RRR experiments. Both are single crystals (unless something went wrong).

### 8.1 Theory of Freezing for Solid Solutions

<u>Phase equilibria</u>. Figure 38(a) shows a simplified equilibrium phase diagram for the Au-Ga system, omitting some details not





- Figure 38. Simplified equilibrium phase diagram for Au-Ga. (After Ref. 105)
  - (a) Full range of concentration.
  - (b) Sketch of the region near AuGa<sub>2</sub> stoichiometry expanded, illustrating reversible processes.

pertinent to AuGa<sub>2</sub>. Figure 38(b) shows the phases near AuGa<sub>2</sub> stoichiometry. The relevant phase boundaries are Ls=liquidus and the AuGa, AuGa, and Ga vertical boundaries. I=isothermal lines, and the phase regions are L=liquid, S=solid, S+L=solid + liquid, and E=eutectic. The concentration at the congruent point (the relative maximum in melting temperature) is  $\mathbf{c}_{\mathbf{m}},$  a value near, but not necessarily exactly at, stoichiometry. A melt of concentration  $c_1 < c_m$  and at temperature  $T_1$  may cool in a reversible manner (i.e., the system remains close to its equilibrium states) until at  $T_{2}$  a phase mixture starts to form: a nucleus of precipitate (solid AuGa, crystal) in the bulk of liquid melt remaining. After additional slow cooling the system, represented by the three points  $(c_1,T_3)$ ,  $(c_2,T_3)$ , and  $(AuGa_2,T_3)$ , still has two phases: liquid melt of concentration c<sub>2</sub> constituting the molar fraction b/(a+b) of the system (lever rule), and solid AuGa<sub>2</sub> of concentration 66.7 at.% Ga and constituting molar fraction a/(a+b) of the system. The average concentration of the whole system is c1. Phase separation continues with further cooling until the melt reaches  $c_e$  at  $T_e$ =451°C, the eutectic point. The temperature remains at  ${\tt T}$  upon further slow removal of heat, and the remaining melt freezes to form a eutectic alloy, an intimate mixture of AuGa and AuGa, in the proportion d/c. The eutectic forms inclusions in the pure AuGa2. As another example, if a melt of concentration  $c_4 > c_m$  is cooled reversibly to  $T_4$  phase separation into solid AuGa<sub>2</sub> and liquid melt again commences, but now the melt becomes richer in Ga as cooling continues, with the melt concentration following the liquidus line to the right, passing through  $c_5$ , and the system finally reaching a different isothermal line  $I_2$ , corresponding to the solidification of pure Ga. Again, the average concentration of the total system is constantly  ${\bf c}_4.$ 

<u>Homogeneity range</u>. In Figure 38(a) the phases Au, AuGa, AuGa<sub>2</sub>, and Ga are represented by vertical lines, indicating that these phases are of fixed composition, at least to the accuracy of measurement for the diagram. The phases labeled  $\beta$  and  $\gamma$  have a non-zero range of homogeneity, or width in concentration, even though they are singlephase systems (unlike the extended eutectic region E) and have been assigned specific formulas:<sup>105</sup> Au<sub>3</sub>Ga for the  $\beta$  phase, of maximum width 2.7 at.%, and Au<sub>7</sub>Ga<sub>3</sub> for the  $\gamma$  phase, of approximate width 1.0 at.%. An ordered alloy of fixed composition can be described in accordance with equation (4) by

alloy structure = 
$$\sum_{r}$$
 (sublattice + basis<sub>r</sub>), [116]

where, except for the most complicated structures, the basis is monatomic. A range of concentration for a fixed crystal structure implies some disorder in the occupation of the sites of each sublattice: substitutions, interstitials, or vacancies. In some crystal structures one sublattice represents ordered vacancies. Two examples are<sup>6</sup> Al<sub>3</sub>Ni<sub>2</sub> and  $Fe_{0.875}$ S. One way of characterizing the amount of order in an alloy system with ordered phases is by order parameters, a simple set being  $f_i$ , the fraction of atoms of species A on the i-th sublattice.<sup>2</sup> Thermal and x-ray measurements show the  $f_i$  change continuously with the temperature and concentration of the samples, corresponding to continuous transformations among states of relatively high order and states of relatively low order (with respect to separation of the atomic species onto their own sublattices). Furthermore, these transformations (i.e., changes of crystal structure) usually extend over non-zero ranges of concentration before arriving at the next well-defined phase, whether the transformations be homologous (a continuous transformation from one single-phase system to another) or heterogenous (passing through a two-phase stage). Both of these observations lead one to expect that most of the distinct phase boundaries of a phase diagram are in reality blurred, and that intermediate phases of nominally unique concentration (i.e., intermettalic compounds) will have some width.

Additionally, for intermetallic compounds having a congruent melting point, there is no a priori reason that it must lie at the point of stoichiometry for the compound, as attested by numerous phase diagrams for binary allows. Figure 39 shows a simple scheme, devised to resemble the AuGa, system of Figure 38(a), which could describe a real alloy with a homogeneous range of concentration and with the congruent point not at stoichiometry. Suppose that the solid is an intermetallic compound. Consider this figure in light of the quasistatic (reversible) process discussed earlier, so that the system is always in equilibrium. As it is cooled from  $T_1$  to  $T_2$  it is a two phase system: the melt (the saturated solution) and the solid (compound, or precipitate). The concentration of the solid ranges from  $\mathbf{c}_1$  to  $\mathbf{c}_2$  during cooling. Imposition of equilibrium conditions means that at any  $T_2 \leq T \leq T_1$  the entire solid phase of the system is uniformly at the corresponding concentration given by the solidus line, and at  $T_{c}$  the solid is at the stoichiometric concentration of the intermetallic compound. As before, average concentration of the system is constant, since it is closed, permitting no change in the amount of each component. A number of variations can be envisioned, such as solidus lines of different shape and stoichiometry on the other side of the congruent point.



Figure 39. Hypothetical intermetallic compound (solid phase S) with a nonzero phase width and  $c_m$  not at stoichiometry.



Figure 40. Gradient for a dilute concentration of an alloying element in the melt. (After Ref. 106)

So far we have discussed the behavior of the alloy system in equilibrium or in quasi-static processes. But in the Bridgman crystal grower the system, which is the whole charge in the crucible, is certainly not in equilibrium for three reasons:

- (1) There is always a temperature gradient.
- (2) The process for growing most metal crystals reduces the temperature of any portion of the solid shortly after its solidification to an extent that diffusion is too slow for the solid to approach new equilibria in practical times.
- (3) Some degree of mass flux, thermal fluctuations, and other transient phenomena are normally present during crystal growth.

What predictions can the equilibrium phase diagram make about the concentrations of samples grown by the Bridgman method? That phase diagrams have been very useful for many years of crystal growing is convincing evidence that they do contain useful information, even for this nonequilibrium system. For slow cooling rates the region in the vicinity of the interface is near equilibrium. As the interface velocity (rate of solidification) increases one would expect the transient conditions to change the composition of the solid that freezes. This is the regime of growth kinetics, which is discussed next.

<u>Growth kinetics</u>. This is the study of the time dependent, microscopic process of solidification at the interface of solid and liquid.<sup>106</sup> Not only are such considerations necessary for calculating the behavior of systems not in equilibrium but they also give additional information on what happens during solidification under quasi-static conditions. Growth kinetics depend on such things as diffusion, concentration and thermal gradients at the interface, the amount of stirring of the melt, the free energies of the components of the system, and the mass of the system. For example, the equilibrium phase diagram shows simply that AuGa<sub>2</sub> will precipitate; but the solid can be dispersed as crystallites or concentrated in single crystals of macroscopic size, depending upon conditions such as the presence of a temperature gradient (reversible process assumes uniform temperature throughout the system), the rate of cooling, and the shape of the crucible.

Regarding deviation (3) in the subsection above, even an unstirred melt has at least three fluxes:<sup>152</sup> diffusion flux, arising from the concentration gradient; a convection flux arising from the temperature gradient; and a third flux due to the precipitation of atoms from the melt at the interface. All of this is referred to as solute redistribution. Calculations are complicated and depend on such details of the system as various thermodynamic quantities (specific heats, heats of fusion, distribution coefficients), kinetic properties (mass, velocity) and atomic and ionic characteristics.

Figure 40 shows a concentration gradient typical of those calculated or measured <sup>106,107</sup> for the melt of a dilute, binary alloy undergoing solidification in a closed system, such as a crucible sealed in a pyrex tube, as is done in the Bridgman method. The gradient for the solid is not shown because it varies with the equilibrium concentration (represented by the solidus line of the solid phase) and with the ability of the solid to come to equilibrium under the given conditions. For most intermetallic compounds it would be nearly a horizontal line on the scale of Figure 40. Naturally the concentration gradient in the melt tends to disappear under the effect of stirring. Our Bridgman system may be considered partially stirred: no mechanical

stirring, but the radiofrequency furnace we used induces convection currents.

Most of the analysis in the literature is for small concentrations of an alloying element (which can also be considered an impurity), but the concepts may be appropriate for our system: stoichiometric AuAg<sub>2</sub> is considered the host phase, and the excess Au or Ga is considered the impurity. It is unlikely that the equations can be used directly, because here the "impurity" has the same diffusion coefficient and free energy considerations as one of the components of the host phase.

<u>Hybrid approach</u>. Experience shows that theoretical considerations of the freezing of metals into crystals must include elements of both the phase equilibria and growth kinetics. The composition of grown crystals approaches what the equilibrium phase diagram shows, and the conditions of slow growth are an attempt to obtain a quasi-static process. But as discussed above, nonequilibrium conditions exist, and may have a significant effect on the grown product. In fact, a true quasi-static growing process would nullify hypothesis (1) of Chapter I on the variation of concentration along the growth axis of the crystal, and an explanation for the range in RRR could not invoke such a variation.

The main question in the hybrid approach is to what extent each side should be included. The inability of the solid phase to equilibrate in the time over which the charge is solidified seems, from common experience, to be one of the deviations from conditions of equilibrium that will have as big an effect as any other deviation. Consider Figure 38(b). If the precipitate is exactly AuGa<sub>2</sub> as indicated by the vertical line, then that phase is already in thermal equilibrium for

all lower temperatures. But postulate for  $AuGa_2$  a solid phase of variable concentration, near stoichiometry, and of finite width (Figure 39). As the temperature is lowered from  $T_1$  to  $T_2$  the point representing the solid phase of the system changes from  $c_1$  to  $c_2$ . The solid formed at  $T_1$  can be in equilibrium at  $T_2$  only by changing its concentration. The required mass transport is a slow process in a solid and is strongly temperature dependent. Attainment of thermal equilibrium in a binary alloy is possible in the times normally used to grow crystals, but only for temperatures in the upper third of the range from room temperature to melting point. Consequently, one suspects the whole solid will have a concentration which varies between  $c_1$  and  $c_2$  over the length of the solid.

Assuming a phase width such as Figure 39 for  $AuGa_2$  and assuming that the preceding argument applies to its growth, how is the concentration range  $c_1$  to  $c_2$  of the solid  $AuGa_2$  distributed over the physical length of the crystal? Define  $c_s$  to be the concentration of the solid at the fractional distance z from the end of the solid that froze first. Knowledge of  $c_s(z)$  is of obvious importance for the cutting of samples from the crystal in order to measure physical properties dependent on  $c_s$ . First a qualitative answer.

For slow cooling rates the region in the vicinity of the interface is assumed to be near equilibrium because for it  $T^{\approx}T_{m}$  and the equilibrium redistribution in that part of the solid can occur before the temperature at the region changes much, and before distant changes in the whole system can propagate to this "interface system." But this interface system is not closed to mass transport, so that as solidification proceeds in the presence of a temperature gradient, the concentration

at the interface changes more slowly than it would were the system closed. This effect is illustrated in Figure 41. The details depend upon the temperature profile, how it changes in time, and diffusion coefficients. But the general effect is that most of the freezing occurs over a concentration range in the melt much smaller than would be expected from the equilibrium phase diagram. For example, in Figure 38(b) most of the charge solidifies while the concentration of the melt goes from  $c_4$  to  $c_5$ ; only a small fraction of melt remains beyond  $c_5$ , and only a very thin layer remains by the time the isothermal line,  $I_2$ , is reached. This follows from the lever rule.

It should be repeated that this subsection has considered two different phenomena causing a variation of concentration in the solid. The first arises from a solid phase boundary that is slanted rather than vertical, in conjunction with the inability of the solid's concentration to rapidly respond to temperature changes. The second effect, discussed immediately above, arises from the melt concentration at the interface changing during crystal growth in a manner different from that predicted by the phase diagram. We continue to consider the second effect. Some simplifying assumptions about the system are made preparatory to making a calculation for AuGa<sub>2</sub>.

Calculations giving one of  $c_g$ , z, and T as functions of the other two are made by assuming or deriving functional forms for the liquidus and solidus phase boundaries, and are common in the literature.<sup>107,108</sup> But they either assume phase boundaries or conditions inappropriate to our case, or require the knowledge of thermodynamic or kinetic variables unavailable for our system. Furthermore, the accuracy of such calculations is low, so one would not have confidence in even qualitative results for the extremely narrow AuGa<sub>2</sub> phase.



- Figure 41. Gallium concentration of the melt at the interface of solid and liquid is lower than for an equilibrium system.
  - (a) Temperature step  $T_1$  to  $T_2$  shown on the AuGa<sub>2</sub> phase diagram.
  - (b) Reduction of T in the equilibrium system and consequent precipitation along the whole charge leaves excess Ga atoms in the remaining melt. (The dots represent Ga atoms in excess of stoichiometry.)
  - (c) Upon lowering the temperature profile in the crystal grower, ∇T allows only the melt near the interface to solidify.
  - (d) The excess Ga atoms left in the melt rapidly diffuse into the rest of the melt, lowering the concentration.

We therefore make a different calculation specifically for AuGa2, abandoning hope of making even a rough calculation of  $c_{s}(z)$  and looking instead to  $c_{\varrho}(z)$ , the concentration of the melt at the interface between solid and liquid when the interface is located at a fraction z of the length of the charge. This approach takes advantage of the fact that the AuGa<sub>2</sub> phase boundary (unlike those generally assumed in the calculations in the literature) is either a vertical line or close to being one. Thus knowledge of  $c_0(z)$ , while not giving the details of  $c_a(z)$ , will at least give a general idea of its behavior. For example, if  $c_{\varrho}(z)$ changes slowly about some value of z, then  $c_s(z)$  will, too. For use in the calculation a numerical function relating  $c_{\ell}$  and T for  $2/3 < c_{\ell} < 1$ is obtained from the phase diagram of Figure 38(a), and the solid phase is taken as a constant c = 2/3. The resulting imprecision is unimportant beside the inaccuracies introduced by the assumptions given below, assumptions necessary because of the lack of information about the interface system and because of the complexities of calculation upon introducing such details even if they were known. The assumptions are

- No concentration gradient in the melt (i.e., a perfectly stirred melt);
- (2) No diffusion in the solid (i.e., the solid makes no move toward equilibrium);
- (3) The concentrations  $c_s$  and  $c_l$  follow the solidus and liquidus of the phase diagram;

(4) The crucible and charge have a uniform cross section. Assumptions (1) through (3) define normal freezing.<sup>108</sup> The first two assumptions are obviously not entirely true, so the calculation will give only an idea of what to expect. These assumptions permit easy calculation of  $c_{l}(z)$  from the phase diagram of Figure 38(a). By assumption (4) z is proportional to the molar fraction of the charge solidified, so for AuGa<sub>2</sub>,

$$z = \frac{c_{\ell} - c_{o}}{c_{\ell} - 2/3},$$
 [117]

where  $c_0$  is the prepared concentration of the melt. The results are given in Figure 42 for two values of c<sub>o</sub>. These results, when applied to Figure 39, suggest that  $c_s(z)$  also increases slowly from  $c_1$ , then rapidly to  $c_2$  as the last of the charge solidifies. Define "measurable range" as the range in concentration exhibited by single-crystal samples which can be physically cut from the slug and are big enough to give measurable signals. If the simple model above predicts the behavior of the real alloy with only fair accuracy, measurement of the AuGa, phase width will be made even more difficult because of reduction of the measurable range of concentration. This follows from the confinement of most of the phase width to a thin portion at the top of the sample (near z=1), near the cap of the slug. The necessity of cutting away the cap (a region of questionable crystalline perfection) may reduce the Ga-rich end of the measurable range. The finite width of the dHvA samples also reduces it by averaging in values lower than the maximum concentration of the phase width.

The best one could hope to do by including ignored effects is to increase the measurable range to equal the phase width itself, which is already suspected to be small (less than one percent). There is a bright side to this distortion: a crystal grown from a melt on the Au-rich side of the congruent point should have its eutectic region confined to the top. See Figure 38(a).

We thus conclude this section on theory with the feeling that, assuming a non-zero phase width for  $AuGa_2$  the crystals grown by the Bridgman technique should show a variation of concentration that





Figure 42. Concentration of melt at solid-liquid interface versus fractional distance along crystal.

reflects the shape of the solidus line (on one side of the phase or the other) in a way that is characteristic of the method of growth, the Bridgman method in this thesis. This is the growth pattern referred to in the discussion of objectives in Chapter I.

Of course the question arises about the reproducibility of results tied to growth kinetics. The effect of the open interface system of this model should be reproducible. Growing conditions were reproduced for each of the three crystals grown, to the extent possible with the equipment. The purpose, besides providing reversible cooling conducive to the growth of single crystals, was to prevent factors of growth kinetics other than concentration differences from causing some variation among the final samples. One change of condition that did occur is that one sample is twice the length of the other two. (The diameters are the same.) The effect of this is unknown, but is probably small, at least for the lower bulk of the crystals, because the "interface system," open to mass transport, at first sees effectively infinite resources.

#### 8.2 Methods

<u>Growing</u>. All of the samples were cut from three single crystals of nominal AuGa<sub>2</sub>. Each crystal was grown by Boyd Shumaker using the vertical Bridgman method, from a melt prepared slightly off stoichiometry by a different amount (Table 9). The procedure each time was the same. Pellets of 5 or 6 nines gold from Cominco were cleaned with aqua regia, rinsed in distilled water, and weighed to the nearest .01 mg in a Mettler balance. Gallium of 6 nines purity from Alcoa was cleaned with dilute nitric acid, rinsed in distilled water, and added to make a charge of desired concentration, referred to as the prepared melt

	Gri	owing Process			inished Cry	stal (Slug)	
	Gallium 6allium Prep	Concentration of the ared Melt			Diameter		
Label	Absolute <sup>a</sup> (wt%)	Relative to Sty. (2/3) <sup>b</sup> (at.%)	Lift Speed of RF Coil (cm/hr)	Total Mass <sup>C</sup> (grams)	(Except Bottom Tip) (cm)	Length (cm)	Angle <sup>d</sup> (degrees)
A	41.6726	+0.204 at.%	2.1	24.9936	0.85	4.60	30
В	41.1367	-0.288 at.%	1.3	10.3453	0.86	2.11	25
U	42.0526	+0.549 at.%	1.3	10.0290	0.86	2.24	26

Data on the Three Au $\mathrm{Ga}_2$  Crystals Grown by the Bridgman Method TABLE 9.

V4 WL6.  bError = ±0.005 at.% absolute, estimated ±0.0004 at.% relative (i.e., differences).

<sup>c</sup>Error < ±0.0001 gm.

dAngle between slug axis and <lll>.

concentration. The charge was mixed by melting several times in one induction (radiofrequency- RF) furnace (Lepel  $2\frac{1}{2}$  kW) and grown in another (Stanelco, 30 kW, 380 kHz). To start, the charge was put into a vitreous (pyrolytic) graphite crucible about 3" long, which acts as susceptor in the induction furnace. The crucible with its charge was then put into a combination vacuum chamber and RF coil and held in a vertical position by a short vycor tube. The chamber was then evacuated and filled with one-third of an atmosphere of a mixture of argon plus hydrogen (10%). The furnace was turned on and the charge heated to approximately 1100 to 1200°C, as measured by a pyrometer, and then held about 30° above the melting temperature for about one-half hour. After the water-cooled RF coils brought the chamber to room temperature (about one-half hour after the furnace was shut off) the chamber was opened, and the charge removed. It was then weighed as a check that no evaporation of metal out of the crucible occurred to change the concentration. After being washed with methanol, the charge was placed upside-down on the vertical crucible: the end of the charge formerly up being now downward, to increase the amount of mixing beyond the normal stirring generated by the induction furnace. The chamber was once again evacuated, and the whole procedure repeated, at least four times for each crystal, following which the charge was once again weighed, washed, and reversed in its crucible in preparation for the final sealing and the growing. This was done by inserting the crucible and charge into a vycor tube  $2\frac{1}{2}$  feet long by 19 mm o.d. and closed at one end. The tube was flushed with argon, and then sealed closed by flame while maintaining one-third of an atmosphere of the argon-hydrogen mixture in it. The closed tube was placed vertically within the RF coil of the Stanelco induction furnace.

The axial length of the coil was only three or four times that of the charge, and the temperature gradient was changed by slowly raising the coils (see Table 9). Rough estimates for temperature gradients are 100 to 200°C over the length of the crucible. The roughly equal vapor pressures<sup>109</sup> of Au (1 mm at 1867°C) and Ga (1 mm at 1349°C) ensured that any mass loss during the heating cycles would be small, and any difference in mass loss would be even smaller.

<u>Cutting</u>. The crystals were cut by spark erosion. A .002" molybdenum wire cutter at about 300 volts was used to cut off sections of the right thickness and face angle, preparatory to cutting cylindrical samples .4 cm to .5 cm by .1 cm in diameter with a Servomet spark cutter. This used a small tube of the proper diameter as the cutting electrode.

After a (111) axis of the slug was identified sections about .5 cm in thickness (and about the diameter of the slug) were cut by the wire. These were glued face down to a brass mounting block on a goniometer and oriented so that an x-ray beam paralleled a (111) direction. The crystal, still on the goniometer, was transferred to the spark cutter, which was aligned so that its axis was automatically in the (111) direction of the crystal. The spark cutter then lowered onto the crystal to cut out the sample. The plane had been previously cut so that it was close to being perpendicular to (111); thus the samples were nearly right cylinders. The accuracy of orientation of the crystal in the probe and cryostat needed to be only within several degrees, because final orientation was obtained from crystalline symmetry as observed in the dHvA signal. Figure 43 sketches the locations of the dHvA samples. This figure also shows from where were cut the samples used in the analysis of composition by a microprobe (Chapter IX). The dimension of the dHvA samples are



Figure 43. De Haas-van Alphen and RRR samples (circled numbers) and samples for microprobe analysis (not circled). Cut from the crystals of AuGa<sub>2</sub> grown by the Bridgman method. Sample 19 is for RRR only.

Sample No.	Type of Measurement	Length L (cm)	Diameter <sup>a</sup> D (cm)	Ratio L/D
5	dHvA and RRR	.60 approx.	.13 square	(Ъ)
6	dHvA only	.38 approx.	.218	(c)
10	dHvA and RRR	.518	.218	2.38
12	11 11	.483	.221	2.19
13	17 17	.163	.216	0.75
14	11 11	.259	.211	1.23
15	11 11	.231	.218	1.06
16	17 17	.203	.211	0.96
19	RRR only	.902	.150 x .145 rect.	6.12
20	dHvA and RRR	.602	.216	2.79
26	dHvA only	.445	.218	2.05
27	11	.287	.224	1.28
30	**	.290	.224	1.29

# TABLE 10. Dimensions of dHvA and RRR Samples

<sup>a</sup>Diameters are maxima. Some of the "cylinders" were oblate at one end, due to spark erosion in the tube cutter, with a minor axis as much as 15% smaller than the diameter of the bigger end (the one entered). Some samples have different shapes, as noted.

<sup>b</sup>Variable cross-section. L/D roughly 3.3.

<sup>C</sup>Variable cross-section. L/D roughly 1.6.

given in Table 10. All of the dHvA and RRR samples were numbered in one series (circled in the figures) and all other pieces cut from a slug were numbered in a separate series for each slug. Some samples cut for dHvA runs were not used because they appeared not to be single crystals. Some of them are shown in the figures by unlabeled, dotted lines. Sample 19 was cut specifically for a RRR measurement. The (111) axis is at an angle to the long axes of the slugs. Note that Sample 6 is not (111); it was used for a measurement of  $T_D$  only. Figure 43 also shows the microprobe samples, discussed in Chapter IX.

X-Raying. Both orientation and checking for single crystals were done on a Phillips x-ray machine, with a copper target, without filters, by the Laue method (back-scattered x-rays). The cubic crystalline structure made orientation relatively easy using the standard techniques: Grenninger chart, measurement of angles between x-ray spots that were the intersections of zones, and identification of symmetry. With the crystalline surface 3.0 cm from the film plane it was possible to have two of the <100>, <110>, and <111> axes on the emulsion and the third not far off, so that the arcs formed by spots from zone planes could easily be extended to intersection. (The objective was always to put the <111> axis at film center.) In general, though, only one axis might be in the picture. A good picture was usually required in order to have enough spots to identify the correct zone arcs. Even with a good picture, an arc passing through the (burned out) center of the picture was difficult to identify.

The exposure with the copper target and Polaroid type 57 B&W film was 3/4 to 1 hour at 30 kV and 22 to 24 mA.

The side surface of the slug as taken from the crucible gave good x-ray pictures without further preparation. Surfaces freshly (that day) spark-eroded by the wire cutter generally gave good pictures; sometimes a very light cleaning with acetone and a toothbrush was needed to remove the carbon breakdown products of the kerosene. A soft toothbrush left no surface damage. Two exceptions were encountered. Worn guide tips for the wire permitted slight motion with resulting surface striations when the cutting head was fixed to move vertically. Visible striations frequently gave bad pictures, almost certainly from the striations and not a crystalline defect because each time it happened spark planing (using a spinning disk as the electrode or the spark cutter) to just barely remove the striations resulted in good pictures. It was discovered that this nuisance could be obviated by setting the cutter to draw the cutting head horizontally.

The other exception was a mysterious "aged cut" effect: a surface resulting from a fresh cut by the wire would give very good pictures. From it a cylindrical sample would be cut and the remaining crystal left on the mounting block shut in a drawer. Sometimes nothing would be done to a piece between the initial cut and x-ray and the storing of it. A week or more later the piece would be removed and x-rayed again, perhaps to check the orientation, and the picture would be very bad, or unusable. Acetone did not improve it; only a light spark planing did.

Before cutting the smaller pieces and the samples, the pieces of parent crystal were checked to see that they were single crystals. Each sample was also checked for the same purpose, and those samples which gave unusual de Haas-van Alphen signals received repeated scrutiny. All of the final samples were determined by numerous checks to be single crystals within the limits prescribed by the resolution of

angular measurement with a Grenninger chart ( $\pm 0.5$  degrees), and by the resolution in comparing spot patterns using tracings ( $\pm 0.25$  degrees). However, despite the thoroughness of the x-ray check, there is always the possibility of inclusions of other crystallites in the parent crystal, which remain undetected in the sample.

Two types of single crystal checks were used. The first was a series of x-rays over one face or side of a crystal, with transport between pictures provided by a track and screw mounted on the x-ray machine to keep the crystal's orientation in the beam as constant as possible. No attempt was made to identify spots; the pictures were simply compared to see that the spot patterns for each picture were a single crystal pattern and that the patterns were the same on each picture. This method was also used on the sides of the samples. But the beam diameter was only a little smaller (between .05 and .10 cm) than that of the samples, so that a good picture from a basal surface was taken to indicate a single crystal, at least on that end.

The second method of checking for single crystals was used only for the samples, and had a higher confidence level, because it involved ascertaining that both ends had the same orientation. The probability of another crystallite being included between the ends was low (but not zero) because samples were smaller size than the parent pieces. A 180° rotation about the vertical axis, with the x-ray beam horizontal and the film plane vertical, transforms a spot into its mirror image across the horizontal axis of the film plane.

# 8.3 Melt Concentrations

Slug A (see Table 9) was grown from a melt prepared 0.20 at.% Ga-rich, since Longo found that such a starting point gave crystals

with (RRR) residual resistance ratios (a measure of crystalline perfection) among the highest of the crystals that he grew. Samples cut from the bottom, middle, and top of this slug were judged from x-ray pictures to be single crystals and were measured for dHvA frequency F, Dingle temperature  $T_{D}$ , and RRR. Only RRR showed a variation definitely above uncertainty in measurement, and that increased monotonically from the bottom to the top of the slug. It was apparent that unless the measurable range of variation of AuGa<sub>2</sub> was bigger than the range over this slug, our dHvA measurements would not be able to distinguish the samples. Furthermore, the monotonic increase in RRR suggested that all portions of slug A lay to one side of stoichiometry. The growing of another crystal, from a melt of different concentration, seemed in order. Interested in seeing what would happen if the melt were slightly Au-rich, we grew a second sample (B) from a melt prepared .29 at.% on the Au-rich side of stoichiometry. (This is expressed in the tables and figures as a deviation from stoichiometry of -.29 at.% in Ga concentration.) This time lower RRR were obtained, as well as a definite variation in dHvA F and  $T_{D}$ . However, there were no extrema, as one would expect in going through stoichiometry. Upon reconsidering the behavior of RRR in slug A we realized that moving more toward the Garich side would approach and perhaps pass through the concentrations of high RRR (and presumably stoichiometry). The distortion of concentration versus distance discussed in the first section made it purely a guess as to what the concentration of the top samples of slug A may have been, but taking a clue from Longo's data (Figure 1), we grew a final slug (C) from a melt +.55 at.% Ga-rich. The values for  ${\rm T}_{\rm D}$  passed through a definite minimum, signaling the passage of our

#### CHAPTER IX

#### CHARACTERIZATION OF SAMPLES

A variation of the de Haas-van Alphen frequency of the  $C_3^i$  orbit with the position of the sample in the Bridgman crystal could arise from a number of mechanisms, some of which relate an increase of dHvA frequency to an increasing proportion of Ga while others, to a decreasing proportion. Therefore, an independent measure of composition would be useful. This chapter reports the results for the following methods of analysis performed on samples from the single crystals grown by the Bridgman method. For brevity, the entire single crystal taken from the crucible is termed a slug.

> Slug A.....Chemical, Microprobe, RRR Slug B.....Microprobe, RRR Slug C.....None

All of the samples were cut from regions that were either adjacent or close to the corresponding dHvA samples.

#### 9.1 Anticipated Difficulties

It was suspected that a method of high precision relative to that of the x-ray, thermal, electrical, and microscopic methods commonly employed to determine phase relationships would be needed to characterize
the samples. Phase equilbria studies of the Au-Ga system report AuGa<sub>2</sub> to be of apparently fixed composition.<sup>105</sup> Furthermore, AuGa<sub>2</sub> has been grown and studied for years by many metals physicists, who have not reported any properties which indicated to them the existence of a phase width.

One way to achieve high resolution in the determination of composition (of the order of .01 wt.%) is by accurate prior weighing of the components, followed by melting and annealing for a sufficient time at the desired temperature. The structure of the resulting equilibrium system is then analyzed, usually by x-ray methods. Obviously the composition of our samples cannot be predetermined, since one of our hypotheses is that the composition of a crystal grown by the Bridgman technique from a melt of prepared composition varies along the direction of solidification in a manner determined by the equilibrium phases and the growth kinetics. Annealing would render the composition uniform; samples from different positions along the slug would no longer show the variation of composition resulting from the growth process. Of course, one could study the phase equilibria about stoichiometry by annealing crystals grown from melts with compositions in a small range about stoichiometry, but the method chosen, i.e., measurements on samples taken from the unannealed crystal as grown by the Bridgman technique, permits both the investigation of the growth pattern and the possibility of obtaining information on the existence of a solid, equilibrium phase about stoichiometry for AuGa2.

## 9.2 Direct Analysis

For the purpose of characterizing the samples, a direct measurement of the composition is the most satisfactory. This was attempted by means of wet chemical analysis and x-ray analysis by electron microprobe. No conclusion could be drawn from the chemical analysis because the variation was less than the quoted error of the method. The method is discussed briefly, for the data gives an upper limit on the range of concentration. The differences in concentration were not much greater than the uncertainties of measurement by the microprobe, either. However, the data taken on four samples from Slug A were rather consistent, with eight of nine partially or completely independent results showing the top of the slug to have a lower concentration of Ga than the bottom (see Table 15). Therefore, despite the relatively high uncertainty in the data, some conclusions were drawn about the existence and direction of a variation of concentration  $c_{c}(z)$  of the solid with position in Slug A. Four of six microprobe measurements on Slug B gave the same result: Ga concentration decreases in the distance from the bottom of the slug. The other two results would be quantitatively close to the first four if one changed their signs; there may have been a mistake in recording relative positions.

<u>Chemical analysis</u>. Wet chemical analysis was performed on samples taken from the top and bottom of Slug A. Figure 44 shows both the samples for chemical analysis (numbered) and the de Haas-van Alphen samples (numbered in a separate series and circled). The samples were sent for analysis to laboratories in groups of two: one sample from the top and one from the bottom of Slug A, except that one "group"



Figure 44. Location of samples cut from Slug A. Numbers are order of cutting, in two series: dHvA samples (circled) and samples for chemical analysis (not circled). Not drawn to scale.

had only one sample in it. Each group was sent to a different laboratory or in a different week. The samples are identified by group number.

Gold content was measured two ways: by titration with hydroquinone of a solution containing the dissolved sample and by gravimetry. Gallium was measured by gravimetric precipitation of gallium-oximate from an ammonical solution. This method could have a bias of 1 to 2% of Ga concentration due to a failure to recover all of the precipitate. Much effort was made to obtain the most precise commercially available methods, and consultations with other analytical chemists suggested these errors are as small as could be expected short of undertaking a special project.

The atomic (or molar) fractional Ga concentration is

$$a = \frac{n_{Ga}}{n_{Ga} + n_{Au}},$$
 [118a]

where n is the atomic density (atoms  $cm^{-3}$ ). The atomic percent of Ga is

$$c = 100 a.$$
 [118b]

The absolute change  $\triangle c$  in concentration in going from the bottom of the slug to the top is the ultimate quantity sought. It is

$$\Delta c = c_{top} - c_{bottom}.$$
 [119a]

A related variable is the percentage change

$$%\Delta c = 100 (\Delta c/c_{bottom}).$$
 [119b]

Frequently Ga concentration is reported with respect to stoichiometry:

$$\Delta c_{\rm S} = c - \frac{2}{3} 100.$$
 [120]

The "unit" for c,  $\Delta c$ , and  $\Delta c_S$  is atomic percent Ga (at.% Ga). It will not always be written out. This percentage is distinct from other percentages in which the data is occasionally expressed, such as percentage changes.

Table 11 shows that the chemical analysis does not appear to distinguish between the concentrations at the top and bottom of Slug A. The absolute errors in the analysis for gold at the two laboratories were 0.5wt% (Schwarzkopf) and 0.25 wt% (National). By taking the differential of the formula for converting weight fraction w to atomic fraction a,

$$\frac{1}{a_1} = 1 + \frac{M_1}{M_2} (\frac{1}{w_1} - 1), \qquad [121]$$

where M<sub>i</sub> are the atomic masses, these errors become 0.46 at.% Ga and 0.23 at.% Ga, respectively. It is interesting to note that all five values of wt% Au for the five samples in Groups I, II, and III lie within 0.11 wt% Au of their average; and if all four groups are averaged, the reported values lie within 0.39 wt% of their average. Thus, either Group IV was a blunder and the resolution of the chemical test for Au is better than estimated, or Groups I, II, and III just happen to cluster together, and a bigger sample would exhibit a more normal distribution. It should be mentioned that Schwartzkopf said the basic error in the test for Au is only 0.1 wt% Au, but that other considerations increase it to 0.5 wt%.

The total assay for Group IV was 2% deficient, whereas the other complete analysis for Au and Ga are less than 0.2 % deficient. But even when Group IV is dropped from the average, the standard error in  $\Delta c$  is as big as  $\Delta c$  itself. The distribution of the values of c for

			Wt% Ga <sup>d</sup>		∆c <sub>s</sub> of	Average <sup>h</sup>	∆c of	
	Sample	Reported	Taken as	Reported <sup>e</sup>	Samples <sup>f</sup>	$\Delta c_{S}$	Ends <sup>h</sup> ,1	% Ac
Group <sup>b</sup>	Number	Wt% Au <sup>c</sup>	100-% Au	Wt% Ga	at.% Ga <sup>g</sup>	at.% Ga <sup>g</sup>	at.% Ga <sup>g</sup>	(œ <u>C</u> ) cb
н	53	58.60	41.40	I	05	TOP .		
H	55	58.75	41.25	ı	18	15±.05 <sup>J</sup>	•	•
III	56	58.79	41.21	41.37	22		09±.07 <sup>J</sup>	14±.12 <sup>J</sup>
IV	48	58.05	41.95	39.90	+.46			
II	58	58.59	41.41	I	04	BOTTOM .		
III	59	58.64	41.36	41.46	08	06±.05 <sup>J</sup>		
IV	51	57.86	42.14	39.97	+.63			
<sup>a</sup> Grown f	from a melt	prepared gal	lium rich b	y .204 at.%.				
b <sub>G</sub> roups Schwarz	I & II ana. zkopf Micro	lyzed by Nati analytic Labo	onal Spectr ratory, Woo	ographic Labc dside, N.Y.	oratories, Cle	eveland, Ohio.	Groups III	& IV by
<sup>c</sup> Laborat	tory estima:	ted absolute	error ±.25	wt% Au for Gr	coups I & II,	and ±.5 wt% A	u for Groups	III & IV.
d Convers for Grc	sion of err oups I & II	ors in note c , and ±.46 at	: gives, thro 7 Ga for	ugh equation Groups III &	(9-4), estimá IV.	ated absolute	errors of ±.2	4 at.% Ga
errom se	sparate che	mical tests;	precision <sup>1</sup>	3 wt% Ga, bu	it possible bi	las -1 to -2 w	t%.	
•	•			ē				

 ${}^{f}\Delta c_{S}$  is deviation from stoichiometry, in at.% Ga.

<sup>8</sup>Using wt% Ga from the fourth column.

 $^{
m h}$ Drop Group IV because it has about 2 wt% deficit in report of total composition.

 $^{1}\Delta c$  is c(top) - c(bottom), in at.% Ga.

J Uncertainties are obtained from range and number of data rather than from laboratory estimated error, and are adjusted to give the 80% confidence interval. Groups I, II, and III suggests some separation, but the sample of five is so small that no conclusion can be drawn.

<u>Microprobe</u>. Samples from Slugs A and B were analyzed on two electronprobe microanalyzers. Slug A was analyzed on an Applied Research Lab (ARL) model EMX-SM microprobe at MSU by the technician, V. Shull, with the assistance of the author, and samples from both slugs were analyzed at the University of Michigan under the direction of Prof. W. C. Bigelow, of the Dept. of Materials and Metallurgical Engineering. The most reliable measurements correspond to a difference of Ga concentration of  $-.35 \pm .10$  (std.dev.) at.% Ga between the top and bottom of Slug A. The range in Slug B may be  $-.24 \pm .10$  at.% Ga. Again, the differences were not much greater than the resolution of the measuring technique.

The microprobe samples were cut from the top, middle, and bottom of the slugs A and B, from regions adjacent to the dHvA samples, and mounted in plastic (Figure 43). Samples from each slug were mounted and tested separately. Mount A contains two pairs of samples from slug A: one pair from each end. Within each pair one sample exhibits a face approximately parallel to a {111} plane and the other sample, perpendicular to {111}, a precaution against the dependence of the mircoprobe response on orientation. However, no such dependence was subsequently found. Mount B contains samples from the top, middle, and bottom of Slug B, and has a test for reproducibility of the microprobe data: samples 8 and 16 exhibit faces that were originally congruent. The data from them was more nearly the same than was data from the other samples.

The exposed faces were polished ultimately with six micron alumina after mounting. Early mounted samples were lightly etched with dilute aqua regia and examined under a metallurgical microscope. Occasionally

regions of slightly different, homogeneous appearance were seen. They appeared to be neither surface residues nor crystallites of different orientation; they may have been different phases. But for the most part the observed surfaces were without structure. The later samples, for which data is presented, were not etched because the slight gold color upon etching indicated the probability of removing a higher percentage of gallium atoms from the surface, thus potentially biasing the data. Possible inclusions were avoided by examining the samples when they were in the microprobe, using both an optical microscope and the image current of the microprobe (described below). A description of the operation of the microprobe at MSU follows. The essential features were the same for both machines (UM and MSU).

The sample mount was inserted into a vacuum chamber in the microprobe and the chamber was evacuated. An electron beam, usually about one nanoAmpere and with a diameter 1 or 2 microns, was directed onto the target area on the polished face of the sample, and conducted out of the sample by conducting paint previously applied. X-rays resulting from the collision of the electron beam with the sample were analyzed by three LiF x-ray photometers set to detect the Au M, the Ga L, and the Ga k lines. The electron beam was swept over a small surface area, usually 80 x 64 microns. Sometimes the beam was swept along a line on the face of the sample while the intensities were recorded against position by a chart recorder. Repeated sweeps over the same line averaged out the noise. The latter mode was used to check for regions of different composition. All quantitative comparisons of samples were made with data taken by the first mode.

In addition to the quantitative information obtained from the intensities of the x-ray lines, the microprobe can give an image of the

surface, showing its general quality: regions of different appearance, pits, fissures. The electrons of the beam which penetrate the sample's surface and are conducted out of the sample constitute the image current. Electrons ejected from atoms in the x-ray process contribute to a lesser extent. Surface conditions modulate the image current, which in turn controls the intensity on a c.r.t. screen. This image helped in selecting a homogeneous region for measurement of the composition.

The Ga K and Ga L photometers used electronic filters to prevent interference from neighboring x-ray lines, but the Au line was sufficiently isolated that no electronic filter was required. During the first runs sporaddc deflections of the beam indicated charge build-up occurring in the sample and holder region for some unknown reason. Coating the faces of the plastic holder and sample with about one micron of carbon greatly reduced this tendency. The beam had to be swept over a small area (80 x 64 microns) to obtain Ga x-ray intensities that did not decrease with time. Presumably the higher energy flux preferentially boiled off the Ga.

What is the relation of the x-ray count N to the desired information, namely  $\Delta c$  or  $\%\Delta c$ ? To answer this question requires both a consideration of the physical principles of the microprobe and statistical analysis. The discussion below summarizes the relevant information on the operation of the microprobe from References 110 through 112. Basic principles of the statistical analysis are given in Young,<sup>113</sup> with a more complete discussion in Mandel.<sup>114</sup> Reference 110 also contains a discussion of statistical analysis tailored specifically for the microprobe.

Regarding the physical principles of operation, the LiF detectors count only a small fraction (about .01), called here the x-ray count N, of the total x-ray intensity generated by the electron beam. The total

intensity is composed of both bremsstrahlung and characteristic radiation. The detectors are set to detect a specific x-ray line of a specific element, whose x-ray intensity I is roughly proportional to both the mass concentration of that element and the beam current  $I_b$ . For our thick samples I is independent of the absolute mass density of the element,<sup>110</sup> and depends nonlinearly on the voltage. Both I and N depend on a multitude of other factors, most of which have either overwhelming or significant effect on the precise results. Most of these factors are common to all x-ray spectrographic techniques, but some are unique to the microprobe. The most important ones are mentioned here. Statistical errors are discussed below. Machine parameters must be held constant or changed in a controlled manner. Those to which the count N is most sensitive are take-off angle (the angle between the sample surface and the small element of solid angle subtended by the detector), focus of the detector, and beam current  $I_b$  and voltage V. Sample preparation is also important. Its most important factor is that the surface is smooth and that each surface be presented at the same angle to the beam (usually perpendicular). For example, a groove half a micron deep or a 2 degree tilt can both give a possible 10% error for N when the beam is focused to a spot.<sup>112</sup> A swept beam is not so sensitive, resulting in a .2% to 1% error.<sup>115</sup> The samples should not be etched, and must be thoroughly cleansed of the polishing slurry if it contains elements with interfering lines. Obviously inhomogeneities in the sample could give unexpected results. Finally, there are various inherent errors (in addition to statistical variation) common to x-ray analysis, of which the largest are absorption and enhancement (related to fluorescence).

Thus the first answer to the question above is that the x-ray count N of a specific x-ray line is roughly proportional to the weight

concentration of the corresponding element, but that many complicated corrections are necessary for accuracy of the order of 1 to 5 absolute wt.% determinations in the absence of standards.<sup>111,112</sup> However, the precision of measurements is an order of magnitude better. The ultimate in reliability and reproducibility comes with the use of a standard. One has two samples, one the standard, both being uniform and nearly identical in composition, with smooth surfaces prepared in the same manner. In this case the measurement of the relative weight fraction is very precise and straightforward:<sup>110,111</sup>

$$\frac{\mathbf{w}_{u}}{\mathbf{w}_{s}} = \frac{\mathbf{N}_{u}}{\mathbf{N}_{s}},$$
 [122]

where u is the unknown, s is the standard (nearly identical in both physical and chemical aspects with the unknown), and N is the x-ray count when the instrument is set to detect the same characteristic radiation from both samples. The weight fraction w is,

$$w_1 = \frac{m_1}{m_1 + m_2}$$
[123]

where m<sub>i</sub> is the mass, or mass density, of element i of a binary sample.

Our samples meet the rigid requirements above because they are essentially the same composition (in fact, the question is will the microprobe be able to detect any difference in composition), are homogeneous, and are held in the same mount, where they are polished simultaneously. The bottom samples are considered the standards when comparisons between the top and bottom (or middle and bottom) of a slug are made. Sometimes the distribution of counts from each sample is considered separately.

Regarding the statistical analysis, if one makes a number of trails (or, replications) of the x-ray count on a sample under fixed conditions, one obtains a sample of counts  $N_t$ , t = 1, 2, 3, ..., whose population is governed by two distributions. One of these arises from the small fluctuations in the parameters mentioned above, unavoidable even though the conditions may be controlled well enough to prevent bias or major error. This distribution is usually taken to be Gaussian, although for any specific method of measurement this is always open to question.<sup>110</sup> The other distribution is that of Poisson, and applies to any phenomena for which the population is huge and the probability of an event from any one member is infinitesimal, <sup>110,113</sup> as first considered by Einstein in 1917.<sup>110</sup> The shape of the Poisson distribution is markedly different from the normal curve only if a count of zero has a non-negligible probability. As the average of the distribution increases so that a zero result means only that the machine broke, the distribution becomes a special Gaussian whose standard deviation is the square root of the mean. 110, 113

The fact that x-ray emission has Poisson's distribution provides a check on the reliability of data from x-ray spectrography. This comes from considering means and standard deviations as follows. The definition of the sample variance SV is independent of the distribution function of the population. In symbols appropriate to the x-ray count it is

$$SV = \frac{1}{(T-1)} \sum_{\substack{t \text{ trial } t}}^{\text{one run}} (N_t - \overline{N})^2, \qquad [124a]$$

where T is the total number of trials in the run and  $\overline{N}$  is the mean of N<sub>t</sub> over the run. The sample standard deviation SSD is

$$SSD = (SV)^{\frac{1}{2}}$$
. [124b]

Suppose that the variation in  $N_t$  is entirely due to the x-ray mechanism, with no error contributed by the measuring technique. Then the parent distribution is that of Poission, and for a large sample, for which the statistics approach the population statistics, the relation mentioned above holds:

$$SSD = \overline{N}^{\frac{1}{2}}, \qquad [125a]$$

$$SV = \overline{N}$$
. [125b]

For all of the data of this chapter  $\overline{N}$  is greater than 5000, large enough that the x-ray distribution has the shape of the normal (i.e., the Gaussian) curve. If the distribution of the errors introduced by the machine and sample are also normal, then the total distribution is also normal and the great body of statistical theory for such a distribution may be used. Equation (125) is a theoretical minimum for SV and SSD in (124), and a substantial increase in either signals a deterioration of precision by random errors in the process of measurement. This analysis contains no safeguard against bias or blunder. Also, because the sample is finite (125) does not hold exactly, and when machine error is very small, it may happen that SSD is slightly (1% to 2%) smaller than  $\overline{N}^{\frac{1}{2}}$ . This occurs occasionally in the data presented in the tables and in examples in References 110 and 112.

An 80% confidence interval,<sup>113</sup> computed from  $\bar{N}$ , SSD, and Student's values, implies that there is an 80% chance that if the experiment were repeated under the same conditions and for the same number of trials, the new average  $\bar{N}'$  would lie within one confidence interval of  $\bar{N}$ . The

relative 80% confidence interval RCI for a run is the confidence interval CI divided by  $\overline{N}$ :

$$RCI = \frac{1}{\bar{N}} \frac{t \text{ SSD}}{T^{\frac{1}{2}}},$$
 [126a]

where T is the number of trials in the run and t is the corresponding Student's t for an 80% interval. An interval could have been computed for any percentage of confidence, but the value 80% was chosen as perhaps being sufficient to distinguish real effects without demanding resolution not available from the method of Measurement.

Table 12 summarizes the microprobe data and Table 13 shows typical run data used to compute Table 12. It turns out that although the uncertainty can be reduced to the statistical minimum (125) for a count taken with most of the microprobe controls left unchanged, the error in the reproducibility is several times greater. Thus the data is grouped and compared by run. A run (column 1) is all the data on samples in one count and one setting of the machine, with only the precision controls being varied. Each trial (column 6) holds all variables fixed while counting for a precise time, usually 10 seconds, to get the number N, proportional to the characteristic intensities detected (referred to below as an x-ray line). Using  $\overline{N}$ , the mean from all of the trials in a run, improves the reliability of the results. Columns 7 through 9 of Table 12 give a slight modification of the relative 80% confidence interval: it is expressed as a percentage,

in order to more easily compare it with the results, which are very small fractions. This percentage should not be confused with the

	c		TABLE 1 ,	2. Microp -	robe Analy	sis of S]	lugs A <sup>a</sup> a	nd B <sup>b</sup>			- -
2 3 4 5	3 4 5	4 5	Ω		9	7	<b>∞</b>	6	10	11 ĭ	I
					No of	%CI	<sup>c</sup> for 80%	ړ CI	% Inci	ease <sup>c</sup> ir	ız.
Machine Slug Position Sampl	Slug Position Sampl	Position Sampl	Sample	പ	Trials	Ga-K	Ga-L	Au-M <sup>g</sup>	Ga-K	Ga-L	Au
MSU A TOP 49 TOP 47 BOTTOM 25	A TOP 49 TOP 47 BOTTOM 25	TOP 49 TOP 47 BOTTOM 25	49 47 25		14 16	.59 .78 .55	.31 1.08 .50	1.14 1.14 .79	-7.61	-3.63	0+
MSU A TOP 47 BOTTOM 25	A TOP 47 BOTTOM 25	TOP 47 BOTTOM 25	47 25		23 23	.509	.708 .472	.294 .397	-1.23	-1.01 <sup>f</sup>	• •
UM A TOP 49 TOP 47 BOTTOM 52	A TOP 49 TOP 47 BOTTOM 52	TOP 49 TOP 47 BOTTOM 52	49 47 52		125 "	.093 .084 .083	.062 .052 .064	.148 .144 .151	-0.51	-1.05	9 7
UM A TOP 47 BOTTOM 25	A TOP 47 BOTTOM 25	TOP 47 BOTTOM 25	47 25		= =	.055	.030 .053	.102 .099	-0.74	-1.06	-1.
UM B TOP 11 MIDDLE 16 MIDDLE 8 BOTTOM 18	B TOP 11 MIDDLE 16 MIDDLE 8 BOTTOM 18	TOP 11 MIDDLE 16 MIDDLE 8 BOTTOM 18	11 16 8 18			.099 .118 .099 .097	.062 .079 .069 .068	.152 .152 .147 .161	-0.60 -0.38	+0.64 +0.29	+0.2

Ga from stoichiometry. <sup>a</sup>Grown from a melt prepared .204 at.% Ga-rich. <sup>b</sup>Grown from a melt prepared Au-rich, equivalent to -.288 at.%

Cpercentage increase in the average x-ray count in going from the bottom to the top of the slug is given by  $(\%\Delta\bar{N}) \pm (\%CI)\sqrt{2}$  at 80% confidence level. Fluctuation in I<sub>b</sub>, V, and filters probably contributes the most to the statistical standard error within a run, related to %CI given in columns 7, 8, and 9. These variables were better controlled in Run 2 (see note e) and in Runs 3 through 5. Operating voltage 14.9 kV, current I<sub>b</sub> = 15.2 ± .1 nanoAmperes (±0.6%, which has added about 0.2% to %CI

fof columns 7, 8, and 9. Trials 8, 9, and 11 rejected.

<sup>g</sup>X-ray lines K, L, and M, all alpha.

				X-Ray Line (all alpha)			
			Ga-K	Ga-L	Au-M		
Run Machine	1 MSU	Ñ	20588	58640	7553		
Sample	47	SSD.	293	1259	241		
No. of Trials	14	$\overline{N}^{\frac{1}{2}}$	143	242	87		
Run	2	Ñ	10224	19600 <sup>a</sup>	5375		
Machine	MSU			а			
Sample	47	SSD	171	198 <sup>a</sup>	58		
No. of Trials	23	<u>N</u> -2	101	140	73		
Run	3	N	8180	20947	2748		
Machine	UM						
Sample	47	SSD	91	144	53		
No. of Trials	125	$\overline{N}^{1}$ 2	90	144	53		

TABLE 13. Typical Statistics Used to Compute Table 12

<sup>a</sup>Trials 8, 9, and 11 rejected because of big fluctuation clearly caused by a drift in the electronic filter on line L. See Figure 46.

percentage in the concentrations. Columns 10 through 12 compare the concentrations of samples from the different regions of the slugs, using percentage changes rather than the ratios of (122). Define

$$\Delta \bar{N} = \bar{N}_{t} - \bar{N}_{b}, \qquad [127]$$

where  $\bar{N}_b$  and  $\bar{N}_t$  are the average of  $\bar{N}$  over samples in each group bottom and top. (In Slug B the middle is also compared with the bottom.) The percentage increase in the count is then

$$\%\Delta \overline{N} = 100 \frac{\Delta \overline{N}}{\overline{N}_{b}}.$$
 [128]

Percentage difference is easier to use than relative difference because the change is so small. Equations (122), (127), and (128) prove

$$\%\Delta w = 100 \frac{\Delta w}{w_{b}} = \%\Delta \bar{N}.$$
 [129]

The procedure is to obtain  $\[mathcal{AN}\]$  by measurement, assume  $w_b$  is the stoichiometric value to obtain  $w_t$  or  $w_m$  (top or middle) from (129), then  $a_b$  and  $a_t$  or  $a_m$  through (121), and finally  $\Delta c$  and  $\[mathcal{AC}\]$  through (118) and (119). Combination of these equations yields

$$\left(\frac{\Delta c}{c}\right)_{Ga} = \frac{1.5}{1+m\left(\frac{1}{1+\Delta\bar{N}/\bar{N}} \frac{1}{w} - 1\right)} - 1, \qquad [130]$$

where m is the ratio of the atomic mass of Ga to that of Au, and the variables c,  $\overline{N}$ , w are the standard's values for Ga, assumed stoichiometric. It is important to distinguish between the absolute change  $\Delta c$  in the percentage concentration c and the percentage change  $\%\Delta c$  in the percentage concentration c. Because the final results,  $\Delta c$  in at.% Ga concentration, are about as small as the uncertainties, consideration of the propagation of error is important. First, the error in % $\Delta N$  is  $\sqrt{2}$  that of  $\overline{N}$ . Differentiation of (130) shows that the propagation of error in each x-ray count gives the following uncertainties to the final result

CI for 
$$c_{Ga}$$
 by Ga lines =  $.38d(\%\Delta\bar{N}) = .54(\%CI)$  [131a]

CI for 
$$c_{Ga}$$
 by Au line =  $.54d(\%\Delta\bar{N}) = .76(\%CI)$ , [131b]

where  $\overline{N}$  refers to the respective x-ray line. Note that the confidence interval on the left is absolute, in units of at.% Ga, and that on the right is relative, the value given in Table 12. For example, suppose one has an exact formula for the conversion of  $\overline{N}$  to  $c_{Ga} = c$ , and this formula is used to compute c from  $\overline{N}$  of the Ga-k line measured for Sample 47 in Run 1. From (131a) and the second line of column 7 of Table 12, the 80% confidence interval for c is then given by (.54) (.78) = .42 at.% Ga, i.e., c (at.% Ga) is uncertain by .42 at %.

Before examining these tables in detail, consider the chronology for this microprobe analysis project. Run 1 has been made, and the results are as shown in Table 12 and the first section of Table 13. Four points stand out. On the good side: 1) the x-ray count between top and bottom differs by .4% to 7.6%, 2) these differences are three to ten times  $2^{\frac{1}{2}}$ %CI. On the bad side: 3) the two Ga line intensities change at a different rate, and 4) the sample variance is up to five times the theoretical value. Points 3 and 4 raise the question of whether the differences % $\Delta \bar{N}$  are truly differences in sample concentration, despite the small RCI, or are only from the variability inherent in the method of measurement. Because the homogeneity range of  $AuGa_2$ , or at least that part of it covered by the samples, could have been wide (about 1%) or practically non-existent (less than .001%) it was unknown before the run how much machine precision would be required. The x-ray intensity depends upon many physical and machine parameters. Although the microprobe is designed for precision work in the sense of placing a very tiny beam at a known point, other machine parameters that could affect our results are not designed for precision. For example, the current  $I_b$  is set using a meter with approximately 5% reading precision, and the current's exact stability is unknown (but better than 1%). Therefore, some tests were made to see if the above parameters are indeed sufficiently constant and if the precision controls (beam focus, position and counting time) can be reset, both to give the required reproducibility and resolution.

The tests were on standards of pure gold and pure gallium, which were mounted in plastic and polished as were the AuGa<sub>2</sub> samples. The results are presented in Table 14.

First is the question of bremsstrahlung radiation contributing to the count from each characteristic x-ray line. This background intensity for all three lines was measured using pure Au and Ga samples; it was found to lie between 2 and 3% of the intensity of the same line from AuGa<sub>2</sub> for the same operating conditions. The background was not subtracted from the data of Table 12 because (1) only relative intensities were needed, while background remains constant, and (2) it is not clear that the bremsstrahlung spectrum will be the same in AuGa<sub>2</sub> as in pure Au or Ga. From the inherent variance test of Table 14, the SSD is closer to  $\overline{N}^{\frac{1}{2}}$  for these tests than for Run 1. The focus is critical, having a SSD of 1.5%. This later improved. Putting the focus very

Reproducibility and Resolution Tests of the MSU Microprobe TABLE 14.

	r s Results	Au Amounts of 2% to 3% of N for Ga all 3 x-ray lines. Ignored in analysis of data because 1) want relative differences 2) exact correction for AuGa,	is unknown. SSD = 108, close to the theo- retical value of 125 for this	N. ASSU = 0.00%. (See note d) Maximum deviation N is 0.83% of N. %SSD = 1.5% of N. Shows correct focus is critical	on Deviation = $\pm 4.0\%$ of $\overline{N}$ .	$%$ SSD = 2.0% of $\overline{N}$ . (See note d) $\overline{N}$ = 15426 .02% difference $\overline{N}$ = 15423 .02% difference
MO ON	Trials	9 for 4 9 for (	16	с С	2 (one each sig	11 11 2
neter <sup>b</sup>	Fixed	F, P, S	F,P,S	P and S	P and S	S none
Paran	Varied	none	none	Γц	Έų	F,Р F,Р,S
	Sample <sup>a</sup>	Pure Au and pure Ga separ- ately	Au ∦1	Au #1	Au #1	Au #1 Au #1 Au #2
	Test Name	Background	Inherent Variance	Focus I. Each trial put in heet forme	Focus II. Very slightly out	Surface Effect Sample Effect
4 0 E	No.	:	2.	3.	4.	5. 6.

 $^{a}$ Au #1 and #2 are two pieces of 6 nines Au mounted and polished as were the samples. The Ga was 6 nines,

 $b_{\rm F}$  mounted in the same holder, but not polished (too soft). F = Focus, P = Position, S = Sample. Area of electron beam = 64 x 80 microns. I<sub>b</sub> nominally constant at  $c_{\rm P}^{\rm I}$ 14.5 nanoAmperes; voltage nominally constant at 25 kV. A quick test showed N  $\propto$  I<sub>b</sub>.

See equation (122) and text. %SSD = (SSD/ $\overline{N}$ )100. <sup>c</sup>N for each trial was of the order of 15 000 for Au. <sup>d</sup>SSD = sample standard deviation. See equation (122) and text. <sup>f</sup>All three points are within SSD. <sup>f</sup>Obviously fortuitous, in view of the results of tests 2 and 3.

slightly out made a 4% change in N. The null effect in test 6 is fortuitous because the focus was reset between most of the trials.

These tests show that rather careful analysis will be required to extract any information about differences of concentration in the samples and even then it will probably be qualitative. Furthermore, all must be operating well: no current or voltage drifts, grounding problems, or the like. Finally, precise comparisons can be made only among microprobe data taken during one run, during which those machine parameters which cannot be set precisely are assumed to remain sufficiently constant not to affect the data. This last claim is further substantiated by changes in  $\overline{N}$  of one x-ray line from run to run (Table 13) being much greater than the variation in  $\overline{N}$  across x-ray lines within one run.

The above seems to make the microprobe an unpromising tool for detecting uncertainties of the order of 1% or less. However, the statistical samples for the tests and for Run 1 were small, there was some drift in  $I_b$ , and we were not yet fully acquainted with the subtleties of operation. More care in focusing and in selecting the target area gave better statistics in Run 2. Also, a far more sophisticated statistical analysis of x-ray fluorescence, focus, position, and sample effects were made on the UM machine by their operators. Their focus was more reproducible, and their SSD were closer to the theoretical values. See Tables 12 and 13.

After the preceding look at the results of the first run and at the analysis of the resolution available for the microprobe, we return to Table 12, columns 10-12, to consider the results from all the runs. The test results (Table 14) suggest the focusing may not have been as careful in Run 1, so its numerical results have less meaning than the other runs, although the indicated direction of change may be reliable.

Table 15 presents the values for the absolute change  $\Delta c$  in at.% Ga, with respect to the bottom of each slug, as computed from the values of  $\%\Delta N$  + %CI of Table 12, using (130) and (131). The following are noted:

- (1) Eleven of twelve values for  $\[1mm]\Delta\bar{N}$  are evidence that the concentration of Ga is lower at the top of the slug than at the bottom, giving a value  $\Delta c = -.35 + .10(SSD)$  at.  $\[1mm]Ga$ .
- (2) The twelfth value for  $\&\Delta \overline{N}$ , namely that for Au-M in Run 4, is far different from that of the other three runs. In view of &CI for  $\overline{N}$  being about 0.1,  $\&\Delta \overline{N} = -1.79\%$  is difficult to explain by other than some mistake during recording the data, or an unidentified, occasional bias.
- (3) For the data for Slug B, either a mistake was made, such as in identifying one of the samples during the recording/transfer of the data, or N for each run truly has an uncertainty of the order of 1%. If the latter is true, then the finding of a confidence interval of the order of .1% is inconsistent, requiring that some basic assumptions, beginning with equation (122), do not hold. The raw data of Run 5 were not available for checking that the samples were correctly identified.

The above observations imply further analysis of the data is desirable for deciding if it reflects real differences among the samples. Were the contradictory results, especially for Slug B, blunders or true statistical uncertainty? Do the bigger values of  $\%\Delta\bar{N}$  from Run 1 arise from inexperience in precision operation of the microprobe or from true statistical uncertainty? And if the answer to these two questions is that  $\%\Delta N$  has a statistical uncertainty of the order of 7%, then why are SDD so small?

Three ways of examining the matter are presented: (1) a more careful consideration of the accuracy of (122), including the inclusion of background in the x-ray count N from each detector-counter, (2) a complete display of the data of Run 2, (3) a comparison of some of the variances of the data from the UM runs, and (4) a sketch of the distributions (both theoretical and actual) of the data.

## TABLE 15. Tentative Conclusions<sup>a</sup> for the Relative Change in the Gallium Concentration with Respect to the Bottom of Slug

 $(\frac{\Delta c}{c_b} \pm 80\% \text{ CI}^b)$ 

		C 1 -		X-Ray Line	
Slug	Run <sup>C</sup>	Position	Ga-K	Ga-L	Au-M
A	2	TOP	47 ± .28	39 ± .32	24 ± .27
	3	TOP	19 ± .05	40 ± .03	$41 \pm .11$
	4	TOP	28 ± .03	41 ± .02	+1.50 ± .08
	Mean		349 ± .099	(note d)	
В	5	TOP	23 ± .05	+.25 ± .03	24 ± .12
	5	MID	15 ± .06	+.11 ± .04	24 ± .11

<sup>a</sup>See text for reservations.

<sup>b</sup>80% confidence interval determined from counts from each x-ray line within each run.

<sup>C</sup>Experimental conditions made Run 1 unreliable.

<sup>d</sup>Au-M of Run 4 was dropped as a possible blunder. Standard deviation rather than confidence interval is given for the mean.

(1) In examining the accuracy of (122) consider first the background. Although it is not necessary to subtract background (bremsstrahlung) radiation when using a suitable standard, <sup>110</sup>, <sup>111</sup> it is desirable to examine the possible effects of background more closely, in view of  $\Delta c$  being only about three times SSD. (The statistical sample here is the eleven more or less independently measured values of  $\Delta c$  that are not suspected of having a strong bias.) The following discussion drops the average bar from the count, and assumes that statistical precision obtains. Define

$$N = N_c + N_b, \qquad [132]$$

where the counts are total, characteristic, and background. Assume  $w = kN_c$  is exact and substitute (132) into (122) to obtain

$$%\Delta w = %\Delta N + \frac{N'}{N} (r' - r) (1/k - 1)100 + 0(r^2), \qquad [133]$$

where  $r = N_b/N_c$ ,  $r' = N'_b/N'_c$ , and the second term on the right is very close to 100(r - r'). Consider this as an error in the measured value of % AN which propagates to the final result Ac in Table 15. In order that Ac be changed by less than .01 at.% Ga (which is 10% of SSD and certainly could be neglected), Equation (131b) shows that (r - r')/rmust be less than 0.9%. This is a change of one count in the Au background and 5 counts in the Ga background for any one trial, and so would be hidden in the fluctuation of the background count. Besides, the continuous x-ray spectrum depends only on the energy of the electrons incident on the sample, and not on the composition of the sample.<sup>116</sup> Even if this is not strictly true for general compositions, any variation in the background among our very similar samples is almost certainly less than .9%. Hence background can be safely ignored.

It is also customary to assume that the x-ray intensity  $I_c = kw.$ <sup>110,111</sup> In view of the many factors influencing excitation and photon emission, absorption, and fluorescence, deviations from strict proportionality are almost certain, producing error in (122), although to what extent and whether the effect on the final result  $\Delta c$  is significant are unknown. However, what is important is measured x-ray count N, not the theoretical intensity I, and measurements of N versus w for both dilute and major components of numerous alloys show visible departures from linearity, depending on take-off angle, voltage, and other factors. Graphs corresponding to a 90° angle appear to be straight lines, and as the angle decreases to 10° curvature becomes obvious. The take-off angle of both the microprobes is 52.5°. The effect depends upon composition, so that to truly evaluate its influence upon our results would require a measure of N versus w for the Au-Ga system. Fortunately the similarity of composition of all our samples makes the effect of even a pronounced deviation from proportionality small. This is shown below. The procedure is to draw an estimate of the relation between N and w on a normalized graph (i.e., w = N = 0 and w = N = 1), then to compute from the graph the true proportionality constants which are  $tan\theta$  and  $tan\theta'$  in Figure 45(a), as a function of  $\Delta w = w' - w$ . Assume that w is at AuGa<sub>2</sub> stoichiometry (a few percent deviation produces negligible error in the final result). Assume that over the range  $\Delta w$  the graph can be replaced by its tangent. The construction is shown in Figure 45(b). Then compute  $r = \Delta w/w$  for two cases: (1) using the calculated (and different) portionality constants at each point w and w' in N = kw; (2) using (122) as written, which assumes N versus w is the corner-to-corner



## Figure 45. Error introduced into measurements of concentration differences by deviations from linearity in x-ray count.

- (a) Typical nonlinear graphs of x-ray count N versus concentration w in a binary sample. For normalized scales the proportionality at w is tan  $\theta$  and at w' is tan  $\theta$ '.
- (b) Construction for Equation (134).
- (c) Hypothetical relations for the Au-Ga system. Curves ±2 are highly unlikely.

diagonal line of Figure 45. Finally compute the relative error (dr/r) in using (122). This gives

$$\frac{\mathrm{d}\mathbf{r}}{\mathrm{r}} = \mathrm{Rel. \ Error \ in \ } \&\Delta w = \frac{\mathrm{tan} \ \theta}{\mathrm{tan} \ \theta} - 1, \qquad |134|$$

TABLE 16.	Error in Concentration Differences
	$\Delta c$ Due to Hypothetical Deviations
	from Linearity in the X-ray Count
	versus Concentration

From Figure 45 Curve	$\frac{\mathrm{d}\mathbf{r}}{\mathbf{r}}$	Error in ∆c (at.% Ga)
0	0	0
1	30	+.11
-1	+.20	08
2	48	+.18
-2	+.67	26

where tan  $\theta$  is the proportionality N/w and tan  $\phi$  is the slope of the graph at w. (See Figure 45.) These angles are measured from the graphs and dr/r is converted into the error in  $\Delta c$  by (131a) (here retaining a sign change not shown in the equation). See Table 16.

Deviations of the Au-Ga system beyond curves 3 and 4 for 53<sup>0</sup> takeoff angle would be abnormal. Even that much curvature gives an error less than SSD.

(2) Figures 46 through 48 display in greater detail the data of Run 2 of Table 13. The question is, does one observe characteristics of the data that may be sample effects rather than from such effects as machine drift, x-ray fluctuation, and focusing? Such a display can help illuminate sample effects because one should see a pattern of differences in the data. The procedure was as follows: trials of 10.000 seconds of counting x-ray fluorescences were made alternately on each of two



Figure 46. Display of the data: 10 second x-ray count N for the Ga K line versus trial number in Run 2. Arrows show tuning of electronic filter.



Figure 47. Display of the data: 10 second x-ray count N for the Ga L line versus trial number in Run 2. Arrows show tuning of electronic filter.



Figure 48. Display of the data: 10 second x-ray count N for the Au M line versus trial number in Run 2.

samples, one from the top of Slug A and one from the bottom, in the same mount. Alternating between the 2 samples will help identify in the data effects due to drifts in the machine and any tendency for systematic operator error in setting the focus. Each trial measured simultaneously three x-ray lines, and the time between trials was uniformly 10 to 20 seconds, except three or four times to make machine adjustments. To eliminate surface effects the electron beam was returned each time to the same position, using the micrometer transport, which could easily reposition the beam (of cross-section 64 x 80 microns) over 95% of its previous area. A small change (to new base positions beginning with trial 4) had no effect on the data. Drift is noticeable in these figures. The arrows show where the electronic filters on the x-ray counters were seen to have drifted off and were readjusted. There was no filter on the Au line, so the common dip and rise at the end of the run indicates either machine drift or perhaps operator effect (systematic error in focus). The possibility of a surface effect arising from changing surface character due to electron bombardment is unlikely because (1) the beam was swept (rather than stationary), (2) the beam remained at one point only about ten seconds, and (3) such an effect would be expected to show a monotonic change in the data. But it should be mentioned that electron bombardment effects can be important. A stationary beam of 30 kV and 1 nA will apparently boil off Ga. And a beam (even when swept over areas the size we used) can cause oil (from the vacuum pump) to carbonize on the surface under the beam, producing a visible effect after ten to twenty minutes. No such effects were observed corresponding to any of the data discussed in this chapter.

The conclusion from Figures 46 thru 48 is that when the data is displayed two types of patterns are seen, one arising from differences

between the samples and the other, from random and systematic error. It is also evident that the slight sample difference visible in the displayed data will be obscured by statistical averaging.

(3) The third way of examining the question of whether the sample's differences are real is the comparison of variances. The variance due to each effect adds arithmetically to the total variance. Table 17 lists the subtotals for the variances due to the cumulative effects of x-ray fluctuations, focus error, going to a new position on the same sample (whose surface is possibly not uniform), and going to another sample (which ideally should constitute all the change in N). The fact that the first three subtotals in variance increase only slightly shows that the machine is adding (within a run) less than the same uncertainty inherent in the x-ray process. The big jump in variance when the sample effect is included shows that either (1) the sample effect is real, coming from the samples, not the machine, or (2) somehow, in going from one sample to the other something is changed in the machine, in a not very systematic way, to produce a change in  $\overline{N}$ . V. Shull, the operator of the MSU microprobe, and W. C. Bigelow, Prof. of Materials and Metallurgical Engineering, and in charge of the UM microprobe, both thought it highly unlikely that any type of machine effect could differentially affect samples in the same mount to such an extent. Table 17 supports the conclusion that the differences in  $\%\Delta\bar{N}$  are due to sample effects, with the contradictions arising from mistakes in recording the data.

(4) In Figure 49 Gaussian curves illustrate the distribution of the counts N for each x-ray line of each run. But the use of a smooth Gaussian for the small number of samples in Run 2 is misleading. Figure 50 is a histogram of the data used to construct that set of Gaussian curves. The picture here is not so pleasant. However, there

	Slu Rui	ıg A Slu n 3 Rui		g A 1 4	Slu Rui	g B n 5
X-Ray Line Variances	Ga-L	Au-M	Ga-K	Au-M	Ga-K	Au-M
Inherent <sup>b</sup>	1	1	1	1	1	1
Focus	1.08	0.99	1.22	0.79	1.39	1.36
Position	1.28	1.53	1.29	2.62	2.53	1.52
Sample	36.63	41.00	34.66	55.45	14.37	11.16

TABLE 17. Comparing Variances in Microprobe Data

<sup>a</sup>Variances are for the cumulative effects of (and in this order) miscellaneous and inherent variability in both the x-ray fluctuations and in unidentified machine variables; focus; position of the electron beam on the surface of a given sample; and moving the beam among samples.

<sup>b</sup>All the other variances are normalized to the inherent variance for each x-ray line.



Figure 49. Theoretical frequency distributions of x-ray count N. Constructed from each run's mean count  $\overline{N}$  and standard error SE =  $T^2$ , where T = number of trials. Slugs A and B: bottom (solid line), middle (dots) and top (dash) samples. All are same area, same scales. Tails are 2.5SE on each side. Au line reversed in N.



Figure 50. Histograms of x-ray count N for three x-ray lines of AuGa<sub>2</sub>, Run 2 on Slug A.

appears to be some separation. The UM runs, with 125 trials for each sample, were recorded on automated equipment and unavailable for display in histograms. This ends the additional analysis of the data.

With regard to Slug A, the final conclusion is that the Ga concentration at the top is lower than that at the bottom by  $-.35 \pm .10$ at.% Ga. This average was obtained after dropping results from the Auline of Run 4, clearly a deviant point. Even though the standard deviation here is as big as that for the results of the wet chemical analysis, this number is more reliable because of the bigger sample, and because Figures 46 thru 48 give evidence of a real difference in the sample.

With regard to Slug B, no definite conclusion is warranted because the reversal in signs seems to contradict the statistical precision. It is tempting to believe that the contradiction of four of the data by the two from the Ga-L line is due to a mislabeling of the L line record.

For both slugs the presence of some contradictions in the data and the big standard deviation force the retention of the possibility that the differences in the means are dominated by effects other than sample concentration.

A lower Ga concentration at the top than at the bottom of Slugs A and B could also account for the variation of residual resistance ratios presented in the next section.

Other methods considered. This section ends with brief comments on other methods of analysis. A very common one for precision analysis is x-ray fluorescences (or spectrography), and it was considered at the time that the microprobe studies began. We did not use it for three reasons. Conversations with Prof. S. R. Crouch of the MSU Chemistry
Dept. and with Mr. R. Mirti of National Spectrographic Lab, which offers commercial spectrographic analysis, left the impression that the best resolution to be reasonably expected was of the order 1%. At the time the resolution of which the microprobe was capable was not known, so it was decided to put all the effort into a thorough analysis on the microprobe. X-ray fluorescence has many of the problems of sample preparation and collection of x-rays that the microprobe has, and some of its own. In a measurement pushing the limits of the method it is better to have hands-on operation, and be able to vary the measurement as seems profitable.

Secondly, x-ray fluorescence exposes big surface areas to the x-ray beam, with the result that inhomogeneities will influence the analysis. The microprobe, with its combination of small beam and image current, allowed the careful selection of the target area. During exploratory measurements it was found that an occasional region of the surface gave anomalous counts, and it was possible to avoid these.

Thirdly, x-ray fluorescence requires, for precise analysis, inconveniently large surfaces, at least  $1 \text{ cm}^2$ . Most of our samples had surfaces about .1 cm<sup>2</sup>, and cutting samples with surfaces ten times bigger would have soon used up the regions of the slug where we needed to cut several analysis samples.

During the course of the thesis, Prof. J. Wilband of the MSU Geology Dept. corroborated the earlier estimates of precision obtainable from x-ray fluorescence. It was his opinion that for our purposes the precision offered by the microprobe was equal to or better than that offered by x-ray fluorescence.

Neutron activation analysis was attempted, but it gave no usable results. The technique is to irradiate the sample with a known flux of

thermal neutrons from a nuclear reactor, creating radioactive isotopes of Au and Ga, and the intensity of one decay mode of one isotope is isolated, measured, and related to the concentration of Ga. Problems arose with both a strongly interferring radiation from an isotope of Au, and limitations of the equipment available. Other methods, such as flame analysis (photometry) were considered, but rejected because of information that their resolutions were even less than chemical analysis.

#### 9.3 Residual Resistance Ratio

This section describes the methods of measuring the residual resistance ratio (RRR). The first subsection discusses the relevance of RRR to these experiments. The experimental results were presented in Chapter VII.

Relation to concentration and Dingle temperature. It is well known that RRR, defined in equation (1), is a measure of the scattering of conduction electrons by crystalline imperfections in the static crystal. The assumption of an isotropic relaxation time  $\tau_{\rho}$  in the Boltzmann equation gives the electrical conductivity proportional to  $\tau_{\rho}$  times an integral of velocity over the Fermi surface. In this simple model

$$\operatorname{RRR} \propto 1/\rho \propto \sigma_{o} \propto \tau_{\rho}$$
 [135]

where  $\tau_{\rho}$  is the relaxation time of the conduction electrons at low temperature and in an applied electrical field. In general scattering is anisotropic over the Fermi surface, so that it must be contained in integral over the Fermi surface. If an electron is in the state <u>k</u> its probability of being scattered out of that state and into state <u>k'</u> depends upon the scattering rate  $1/\tau_{kk}$ . The inverse of the relaxation time  $\tau_{\rho}$  is the average of the scattering rate over the Fermi surface. For a free electron model the weighting function is (1-cos $\theta$ ) and the relation  $\sigma_{\rho} \propto \tau_{\rho}$  is regained (Ziman, pp. 186-187).

Assume that at liquid He temperatures any increase of electrical resistivity  $\rho_{4.2}$  of nonstoichiometric AuGa<sub>2</sub> over the resistivity at stoichiometry is due to the sublattices not containing solely Au or Ga atoms, and that scattering due to other imperfections of the crystal is constant. Simple theory gives resistivity due to point imperfections proportional to their density. These two assumptions give

$$\Delta \rho_{4,2} = \mathbf{k}_{i} |\Delta \mathbf{c}_{S}|, \qquad [136a]$$

where  $k_i$  depends on the type of impurity. This can be related to a change in RRR. Let the quantities pertaining to the crystal at exact stoichiometry be indicated by superscript zero. From (1) and from the fact that resistance at room temperature is independent of  $\Delta c_s$ ,

$$\Delta \rho_{4.2} \propto \Delta R_{4.2} = R_{4.2} - R_{4.2}^{(o)} = \frac{R_{RT}}{RRR} - \frac{R_{RT}}{RRR}(o)$$
 [136b]

$$= -\frac{R_{4.2}}{RRR} \Delta RRR, \qquad [136c]$$

where

$$\Delta RRR = RRR - RRR^{(o)}.$$
 [136d]

Combining (136a) and (136b) gives

$$|\Delta c_{S}| = k'_{i} \frac{\Delta RRR}{RRR(o)}$$
 [136e]

to first order, the relative increase in RRR is proportional to deviation from stoichiometry.

It is interesting to note that if  $\Delta c_S^{<0}$  arises from Ga-site vacancies and  $\Delta c_S^{>0}$  from Au-site vacancies, Linde's rule (resistance  $\propto Z^2$ , where Z is the valence difference between impurity and host) predicts an asymmetrical variation of RRR about stoichiometry because Z = -3 in the first case and Z = -1 in the second. Asymmetry would also result if one side of stoichiometry corresponds to substitutions (Au for Ga or vice versa) and the other side to vacancies. If only substitutions occurred, the relation between RRR and  $\Delta c_S$  would be symmetrical (Z = -2 for either type of substitution).

However, considerations not taken into account above may be important, so that symmetrical or asymmetrical RRR would perhaps not definitely exclude any of the mechanisms for deviations from stoichiometry. For example, the core potential is also important for scattering, and its dependence on valence difference is much less obvious.

The relation of RRR to  $\Delta c_S$  and the calculation of  $\tau_p$  are difficult undertakings. The scattering rate  $1/\tau_{\underline{k}\underline{k}}$  is not known for most real Fermi surfaces, nor is the weighting function. Our main motivation for measuring RRR is a check on the measured dHvA frequency and Dingle temperature variation. Do the samples also exhibit a variation in the independently measured RRR, and does the same sample have both the highest RRR and the lowest  $T_D$ ? If the samples have different concentrations about stoichiometry one would expect the answers to be "yes." In summary, we shall take RRR as a qualitative measure of the approach of concentration toward stoichiometry.

The lifetime  $\tau$  of an electron on an extremal orbit is related to the Dingle temperature through (67), and  $1/\tau$  is an average over the orbit of  $1/\tau_{\underline{k}}$ , the rate at which electrons near state  $\underline{k}$  on the orbit would scatter out of that state, assuming all other states were available for occupation. Hence  $\tau_{\rho}$  and  $\tau$  are different; their ratio  $\tau_{\rho}/\tau$  may vary from 1 to 1000. The extent of disparity depends mostly upon the scattering mechanisms, and to a lesser amount upon the orbit to which  $\tau_k$  belongs and the amount of anisotropy of scattering over the Fermi surface.

Published values of  ${\rm T}_{\rm D}$  range from a low of .01 K in very pure samples to around 5K for samples prepared with defects. The low is near the limits imposed by the sensitivity of the measuring technique and theoretical level broadening caused by the crystal lattice. In recent years many dHvA studies have been done on samples prepared with known concentrations of a scatterer, especially in the noble metals. Measurements (see Table 18) of both RRR and T<sub>D</sub> in Cu have shown that the ratio  $\tau_0/\tau$ varies widely with the type of scatterer, with obtained from RRR by the free electron model. The interpretation  $^{80}$  of Table 18 is that it demonstrates the very small weighting given small angle scattering in the average conduction relaxation time  $\tau_0$ . Large and small angle scattering are two somewhat different regimes. Large angle scatter occurs close to the scatteres in the table; small angle scatter is effectively a dispersion of the electron wave function caused by the lattice strain fields surrounding the defects. The strain fields for impurities and vacancies fall off as  $1/r^3$ ; those for loop dislocations fall off as  $1/r^2$ ; and those for edge dislocations fall off as 1/r. The long range strain field of edge dislocations means that when they are the predominant scatterer, the proportion of small angle scattering events is very high, with consequent increase in  $\tau_{_{\rm O}},$  but not in  $\tau.$ For orbit C3 of AuGa2, with a room temperature resistivity of  $13\mu\Omega\text{-cm}$ (from Ref. 10, which was roughly confirmed by a measurement of 9.3  $\mu\Omega$ -cm

TABLE 18.	Scattering dHvA and 1 and 4	g Rate RRR in Au (Re	s C	fr u 1	om 66)
Scatterer			τρ	)/τ	-
Impurity				1	
Vacancy (in	n Au)		1	-	2
Dislocation	n loop		3	-	7
Edge dislo	cation	10	) <sup>3</sup>	-	10 <sup>4</sup>

on one of our samples),  $T_D = 1$ , RRR = 1500, m = m<sub>o</sub>, and the free electron relation between  $\rho$  and  $\tau$  give

$$\tau_{\rho}/\tau = 2.70 \text{ (AuGa}_2, \text{ orbit C}_3^{\prime}).$$
 [137]

This results shows that the values of  $T_D$  for our samples are probably not dominated by edge dislocations, and that  $RRR^{-1}$  may be roughly proportional to  $T_D$  as concentration varies. The next sections show the method of measuring RRR.

<u>AC method</u>. Because the small size of the samples makes the measurement of reproducible, precise RRR values by the standard direct current method very difficult, we used an AC method.<sup>117,118</sup> By means of a solenoid a magnetic field  $H_0$  is applied parallel to the axis of a sample of uniform cross-section. The sudden removal of the field induces eddy currents in the sample, whose decay time is related to the size, shape, and resistivity of the sample. The eddy current induces a voltage in a secondary coil. Gating the current in the primary solenoid allows repeated display and measurement of the induced voltage on a c.r.t. (see Figure 51(a).





# (b)

Figure 51. Apparatus for residual resistance ratio measurements.

- (a) AC method. The sample sits inside pick-up coil.
- (b) DC method sample holder. The standard electrical circuit was used.

A condensation of the theory follows Ref. 117. The voltage induced in the secondary coil is found by integrating Faraday's equation. The flux density is integrable analytically when the sample is a simple geometrical shape. For an infinitely long cylinder the induced voltage is  $^{117}$ 

$$v(t) = 10N\rho H_{o} \sum_{n=1}^{\infty} exp(-10^{9} \lambda_{n}^{2} \rho t / \pi \mu D^{2}),$$
 [138]

where v is in volts, N is the number of turns in the secondary coil,  $\rho$  is the sample's resistivity in  $\Omega$ -cm, H<sub>o</sub> is the uniform, steady (before cut-off), applied magnetic field in Gauss,  $\lambda_n$  is the n-th root of the zero order Bessel function of the first kind,  $\mu$  is the esu magnetic susceptibility, and D is the diameter of the sample in cm. The method is to wait until the longest lived ( $\lambda_1$ ) term dominates the voltage before recording it, so that

$$v \propto N\rho H_{o} \exp(-t/T_{\omega}),$$
 [139]

where the time constant for a cylinder of infinite length is

$$T_{\infty} = 5.43 \times 10^{-10} D^2/\rho,$$
 [140]

if  $\mu$  is taken to be 1 and  $\lambda_n = \lambda_1$ . A plot of ln v versus t is then a straight line whose slope is proportional to  $\rho$ . The resistivity can be calculated directly, or the RRR may be found by taking the ratio of slopes measured on the same sample at room temperature and in LHe. If  $\rho$  is desired for a cylindrical sample, the measured time constant T must be multiplied by a finite sample factor, <sup>118</sup>

$$T = T_{\infty} (1 - \exp(-1.2)(L/D)^{0.68})),$$
 [141]

where L is the length of the sample.

The electrical circuit for the AC RRR measurements (Figure 51(a)) was designed after those in References 117 and 118. The solenoids were wound on plastic formers. The secondary coils slip into the primary former. The primary solenoid was 1.05" long, .27" ID and .46"OD. It had two layers of 50 turns each af AWG 36 magnet wire, each turn separated from its neighbors, and with the layers separated by Teflon tape to reduce distributed capacitance (so as to approach optimum values as calculated from the equations of Ref. 118). The current was around 3/4 Amperes, giving a calculated 29.0 Gauss at the center. The maximum sensitivity was needed to measure the samples with high RRR values. Then the current was 1.2A, the maximum obtainable from the circuit, giving a field of 46G. The potential across the primary with 3/4 Amperes was about 3 Volts. The current was gated by the oscillator and transistor switch. The secondary was composed of two coils, a pick-up surrounding the sample and a balance coil in series, each consisting of 187 turns of AWG 40 manganin resistance wire (about  $12\Omega/ft$ ). Each coil was about 0.2" long, so that the samples protruded from the ends of the pick-up coil. The purpose of the balance coil was to reduce the initial voltage pulse induced by the current in the primary. The induced voltage in the secondary was displayed on a Hewlett Packard Scope with a maximum sensitivity of 0.1 mV/cm, permitting a minimum reading of 0.2 mV using a scale. This sensitivity was required when measuring the time constants of the most conductive samples at LHe temperatures, because by the time the interfering exponential terms decayed sufficiently the remaining voltage was very small. This oscilloscope also recovered quickly (3µs) from the large (1 volt) pulse induced by cut-off of the primary's current.

A detailed circuit analysis<sup>118</sup> shows that the primary, secondary, and sample form a coupled circuit whose time constants (corresponding to the resonant frequencies) become equal to the theoretical time constant of the eddy current for the proper choice of the damping resistances. (However, both damping resistances are large, so their absence does not lead to serious error.) The circuit must also be designed to reduce ringing resulting from the cut-off of the current. The inductance of the coils is reduced by making their diameters as small as possible and using as few turns as is consistent with the sensitivity required. In addition, the secondary is wound with resistance wire to reduce its Q value and decrease ringing.

A long piece of Ag, .15 x .15 cm in cross section, was used to test the method. A piece of Ag 0.5 cm long was cut from one end, leaving the remainder long enough (about 3 cm) to be reliably measured in the standard way, using direct current. (See the next subsection for details of the DC method.) Assuming homogeneity of composition of the original piece, and taking the DC value as the standard, comparison of RRR obtained by the two methods should be a check of accuracy of the AC method. The RRR of the short Ag and AuGa<sub>2</sub> (#9) samples were also measured by the DC method and the RRR compared with the AC values. The results are shown in Table 19. Sample 9 was not used for dHvA.

The ratio of the first and second terms of (138) at time t<sub>o</sub> is a measure of how straight the plot of ln v versus  $t>t_0$  will be. The ratio is

$$r = \exp(-\frac{10^{9} \rho t}{\pi D^{2}} (\lambda_{2}^{2} - \frac{1}{1} \lambda^{2})), \qquad [142]$$

\_\_\_\_\_

.

	DC Me	thod	AC Method		
Serre 1 c	No. of	DDD	No. of	מממ	
Sampie	Irlais	KKK	iriais	KKK	
Long Ag	2	635 <u>+</u> 30	-	-	
Short Ag	4	608 <del>+</del> 20	3	603+120	
AuGa, (#9)	6	209+57	3	360 <del>+</del> 50 <sup>a</sup>	

TABLE 19. Results of Comparing RRR from DC and AC Methods

<sup>a</sup>This measurement required the maximum sensibility of the meter. AC values. The results are shown in Table 19. Sample 9 was not used for dHvA.

The ratio of the first and second terms of (9-21) at time t is a measure of how straight the plot of ln v versus t > t will be. The ratio is

r = exp(
$$-\frac{10^9 \rho t}{D^2} (\lambda 2^2 - 1\lambda^2)$$
), |142|

showing that  $t_0$ , the waiting time before the plot forms a straight line, increases as  $\rho$  decreases. But the induced voltage is steadily decreasing, so that highly conductive samples may not be measurable with the available instrument gain. A rough calculation of the highest RRR values measureable with our circuit follows. The first two roots of the Bessel function are  $\lambda_1 = 2.405$  and  $\lambda_2 = 5.520$ . Assume  $\mu = 1$ . Combining (138) and (142) gives

$$\operatorname{RRR}_{\max} = A \frac{(r_{\max})^{2343}}{v_{\text{start}}}, \qquad |143|$$

where A is 1.118 for  $AuGa_2$  and .1376 for Ag,  $r_{max}$  is the maximum ratio that can be tolerated, and  $v_{start}$  is the minimum voltage at which recording of the voltage can start and still leave enough voltage sensitivity to record points for a plot as voltage decreases further. The exponent is a constant. The factor A assumes room temperature resistivities of 9.3  $\mu\Omega$ -cm for  $AuGa_2$ (as measured for sample #9) by direct current and voltage; Ref. 10 gives 13  $\mu\Omega$ -cm for its samples of  $AuGa_2$ ) and 1.6 for Ag.

One must wait until ringing stops (3µs) and r is small. For AuGa,

at room temperature the first limit applies (i.e., r was less than .01 by the time 3  $\mu$ sec had passed), but at LHe temperature, the ringing had long since died before the plot began to straighten itself. About the minimum measurable voltage range was from 0.1 mV to 0.02 mV. The maximum r that can be tolerated is not clear without making a plot and computing the corresponding r. Assuming  $r_{max} = .05$  and  $v_{start} = 10^{-4} V$ gives RRR 682 for Ag and 3900 for AuGa<sub>2</sub>. This appears to be about right for Ag, because the short Ag (RRR = 603) was at the limit of the sensitivity of the equipment. But the graphs of 1n v versus time for AuGa, samples having RRR greater than 500 did not become straight lines before the voltage became to low to detect. However, because the readings were made in the last sixth of the reticle on the most sensitive range of the oscilloscope, it is possible that the curvature in the graph was due to either persistent background transients or to distortions introduced by the electronic amplifiers. Subtracting background was attempted by measuring the induced voltage with no sample in the coil. The resulting graphs appeared to be even more distorted. From the point of view of coupled circuits one could not assume that the background would be the same with a sample in place. Therefore the reported results are as read directly from the oscilloscope. For  $AuGa_2$  samples with RRR greater than 400 the AC RRR results are taken as lower limits. Graphs for AuGa<sub>2</sub> with RRR 200 or less were clearly straight lines.

DC Method. The holder shown in Figure 51(b) is designed to submerge the small (0.5 cm x 0.2 cm dia.) samples directly into the storage dewar. One copper end plate was heated and tinned, and the sample pushed against the plate. The plate held enough heat to prevent a cold joint. The other end plate was then heated, tinned, and pushed against

the sample while the first plate was heat sunk. Two AWG 50 Cu magnet wires, tinned with superconducting solder, were wrapped around the sample, about 1/5 of the distance from each end, twisted, and the ends of each soldered to the corresponding voltage terminals. These wires were the potential contacts to the sample. They were secured by soldering. With the end plates clamped into position the sample was reheated to just below the melting temperature of the solder. A very small amount of flux was applied to each potential wire and a small iron tip, lightly tinned with a lower melting solder, was touched to the wires. Usually the blob of solder spread out by less than the diameter of the wire. Mechanical strength was checked by a little tension. The current entered the sample through the end plates. The leads were connected and the end of the probe holding the sample put into its temperature bath. For room temperature this was a kerosene bath; for LHe, the storage dewar. Ten Amperes from a Hewlett-Packard power supply went through the sample, and the potential across the sample was measured by a Keithley 180 digital voltmeter. Checks against heating of the sample by the current were made by watching and by linearity of the graphs. The voltage plotted was the average after a current reversal, to eliminate thermal potentials.

#### CHAPTER X

# DISCUSSION OF THE RESULTS

Figure 37 shows that the samples of AuGa, have a variation in dHvA frequence F, Dingle temperature  $T_D$ , and residual resistance ratio RRR. The variation is correlated with the sample's original position in the parent crystal, or slug. Each of the three slugs were grown under very similar conditions to prevent wide variations in the conditions of growth. This means that except for concentration the change in the conditions of growth was greater between top and bottom of a slug than between corresponding positions in different slugs. Therefore, if growth kinetics were the dominant factor in causing whatever structural and compositional changes give rise to the variation in F,  $T_D$ , and RRR exhibited in Figure 37, then such variations should approximately repeat with each slug. This does not happen, rather the variations seem to go smoothly between the slugs. We interpret this to mean that the dominant factor in determining the composition of the AuGa<sub>2</sub> crystals grown from pure materials by the Bridgman method is the concentration of the melt in the immediate region where crystallization is taking place. Such a dependence suggests that the concentration of the resulting crystal follows the equilibrium phase diagram; and conversely, information about the concentration of the crystal and of the melt from which the crystal formed give information about the equilibrium phase diagram. In short,

the equilibrium phase boundaries, in conjunction with the prepared melt concentration, appear to determine the concentration of the initial precipitate, and both the equilibrium and kinetic properties control the range and distribution of concentration thereafter.

# 10.1 Concentration

At the start of this research it was felt that we would find some method of analyzing the concentration of the samples, but no suitable method was found, and it appears that there is no readily available and reliabile method for measuring such small differences of concentration in bulk constituents. In the absence of firm information about the concentration, the relative positions of the slugs pictured in Figure 37 were chosen to give a smooth variation in the most complete set of data,  $T_D$ . The choice shown is consistent with the assumption, based on the prepared melt concentrations, that Slugs B and C lie in concentration on either side of Slug A and fairly close to it. This arrangement is not unique; others are discussed in Section 10.4

#### 10.2 dHvA Phase Constant

As described in Section 7.4, the phase constant  $\gamma$  can be obtained from a plot of the infinite field intercept INF of dHvA phase  $\psi$  versus inverse magnetic field (see Table 8). The theoretical value for  $\gamma$  is  $\frac{1}{2}$ ; the measured value is  $\gamma = .46\pm.09$ , assuming the Dingle factor  $\cos(\pi \text{gm}^*/2\text{m})>0$ , as would be the case for g near 2. The measured value of  $\gamma$  will be in error by  $\frac{1}{2}$  if an odd number of polarities in the detection system is unwittingly reversed. The magnetic field, coil, and amplifier polarities were checked to see that the final calculated value for recorded voltage had the correct sign. Experimental values of g in metals are between l and 2 (but are much greater for the semi-metal Bi). Coleridge and Templeton<sup>49</sup> show that of possible  $\gamma$  given by their INf, only  $\gamma = .5 \pm .1$  is consistent with possible g-values (calculated by others) for Cu, Ag, and Au. They also report some error reflecting the difficulty of measurement in the presence of an interfering component and sensitivity of INF to slight curvature in the experimental plots; they say that such effects, which may be either instrumental or fundamental, may well be responsible for small discrepancies between the calculated and observed figures for INF. Later work<sup>83</sup> on several hundred ppm In in Cu measures shifts of up to .3 cycle (for 255 ppm) in the neck orbits. But the dHvA F is three times higher than that of AuGa<sub>2</sub>, and consequently  $\gamma$  may be much more sensitive.

# 10.3 dHvA Frequency

The parameter S defined in equation (85a) gives the sensitivity of some region of the Fermi surface to an increase  $\Delta n$  (or dn) in the electron density. The sensitivity is directly related to the deviation of molar concentration  $\Delta a_{c}$  from stoichiometry through

$$\frac{\Delta n}{n} = \frac{\Delta z}{\langle z \rangle} \Delta a_{\rm S}, \qquad |144|$$

where  $\Delta z$  is the valence difference at the site of the point imperfection and  $\langle z \rangle$  is the average valence,  $\langle z \rangle = 7/3$ . This assumes one type of imperfection is present, and holds exactly for substitutions: either Ga into Au-sites, or vice versa. It has negligible error when vacancies are the cause of the deviation. Combining (85a), (118b), and (144) gives

$$\Delta c_{S} = 100 \frac{\Delta F < z}{F \Delta z S}$$
 [145a]

= 6.89 x 
$$10^{-5} \frac{\Delta F}{\Delta z \ S}$$
 |145b|

As described in Chapter IV, for  $AuGa_2$  the rigid band equation (85c) yields S = 27.3 irrespective of impurity, whereas S = 3.8 was measured<sup>55</sup> for Pd impurity, indicating failure of the rigid band model, or at least the presence of another influence on dHvA F.

We use (145b) to consider two questions: (1) What is the resolution for seeing changes in Ga concentration? (2) Do the observed differences in F correspond to  $\Delta c$  measured by the microprobe? Let  $\Delta F$  be the resolution in measuring F, which appears from Figure 37 to be about 10 kG (i.e.,  $\pm 5$  kG). The corresponding resolution in  $\Delta c$  given by (145b) ranges from .0084 at.% ( $\Delta z = 3$ , S = 27.3) to .18 at.% ( $\Delta z = 1$ , S = 3.8).

To answer (2), reverse the above procedure, taking the difference in concentration  $\Delta c = .35\%$  between top and bottom of Slug A as measured by the microprobe to calculate whether our apparatus should be able to distinguish the dHvA frequencies. Taking  $\Delta T_D$  proportional to  $\Delta c$  over small ranges<sup>72, 87</sup> and using the  $T_D$  values of Samples 10, 15, and 6 gives  $\Delta c = .24\pm.09$  at.% between Samples 10 and 5. From this, and using S = 3.8, euqation (145b) gives  $\Delta F$  between 13.3±5 kG and 39.9±5 kG, depending on the types of point defects. Our measurements should definitely be able to distinguish the bigger value. Some possible reasons for not seeing any difference are that the microprobe's measurements of  $\Delta c$  are up to 4 times too high, the value of S may vary greatly with the type of point defect, or the rigid band model must be modified by more than just a change in S. Equation (145b) shows a smaller  $\Delta F$  would be consistent with S even smaller than 3.8, a possibility for vacancies in view of the discussion in Section 4.1 on opposing changes in F. Examples of deviations from the RB model are changes in the density of states and in the lattice parameter, both arising from structural changes due to point defects.

Figure 37 shows that the difference in F between Samples 10 and 15 is much smaller than the apparent uncertainty in F. To compare  $\Delta c_{S}$  between Samples 10 and 15 as computed from measured  $\Delta F$  and Equation (85) with measured  $\Delta c_{S}$  perhaps has little validity. The variation in concentration across the whole range of samples lies between a minimum of .219 at.% Ga and .426 at.% Ga, as calculated from (145b), using S = 3.8 and all four substitution and vacancy mechanisms for deviations from stoichiometry. (The corresponding free electron values are .0304 and .0592 at.%.) Thus the variation is in the order of magnitude of the variation measured along half of Slug A. One could perhaps conclude that the agreement between the dHvA experiment and the independent analysis experiment is qualitative.

Equation (145) shows  $\Delta c$  proportional to  $\Delta F$  when one type of point defect is present. A mixture of defects of different  $\Delta z$ , or perhaps the same  $\Delta z$  but different effects on the crystalline structure, may give a changing proportion. This effect may in part account for the large change of F over Slug B ( $\Delta c$  less than .24%) and the negligible difference in F between Samples 5 and 10 of Slug A (with  $\Delta c = .24\% \pm .09\%$ as computed above), certainly not a proportional change. The big uncertainty in concentration differences may account for much of this nonproportional variation.

Lack of a method for quantitative analysis of the small changes in concentration of our samples and lack of knowledge of the types of point defects present preclude a quantitative comparison of our dHvA F with the rigid band model.

#### 10.4 Possible Phase Width

The discussion in this section is entirely qualitative. The most certain results on these AuGa<sub>2</sub> crystals are:

- Grown from melts prepared with different known melt concentrations.
- (2) F,  $T_{p}$ , and RRR vary over the samples.
- (3) A relative minimum in  $T_D$  and the highest measured RRR occur in the same sample, at the top of Slug A.
- (4) Magnetic interaction is strong enough to visibly distort the dHvA signal at the lowest fields (about 40 kG) for Sample 15, is less important in neighboring samples, and doesn't appear through 50 kG in Samples 13, 14, 20 and 30. Magnetic interaction is strongest in samples of greatest long range order, and hence biggest dHvA amplitude.

The following conclusion is not as definite, but seems probable, as discussed in Sections 9.3 and 10.1:

- (5) The cause of the variations above is a changing concentration of point defects: vacancies in the Au and Ga sublattices or Au-Ga substitution.
- (6) The resulting deviations from stoichiometry correspond to a nonzero range of concentration in the fluorite phase, and all the samples lie in this phase.

In order to make some predictions about the geometry of the phase boundaries, we make the following assumption:

(7) F,  $T_D$ , and RRR are continuous functions of concentration over the phase width.

In the absence of further information many hypothetical configurations of phase boundary are possible. When beginning this work the type of diagram that seemed most likely was that shown in Figure 52. Figure 52(a) sketches the equilibrium diagram for the Au-Ga system. The vertical line labeled sty. represents  $AuGa_2$  of nominally fixed composition (i.e., exactly two Ga atoms for each Au atom). Figure 52(b) shows the circled portion of the equilibrium diagram greatly magnified, so that the line representing  $AuGa_2$  in Figure 52(a) how has considerable width. Also sketched in Figure 52(b) are the three melt concentrations used and estimated ranges of concentration existing in the melt during crystallization of the bulk of each slug (purely a guess, based on the variation of the measured variables). Figure 52(c) shows the variation of the measured variables.

Figure 52(b) shows one of many configurations of solidus boundaries applicable to real alloys. It turns out that other possibilities are consistent with the six statements above. The following test, based on the assumption that the ends of the slugs lie close to one another (perhaps overlapping) with respect to concentration, was used to identify them. All of the relative positions and orientations of the three slugs that left  $T_D$  continuous were found by rearranging Figure 37. ( $T_D$  was used because it is the most complete set of data.) Each possible phase boundary was examined in light of the prepared melt concentrations to see



Figure 52. Possible AuGa $_2$  phase boundary. Based on assuming T $_D$  varies continuously with position.

- (a) Full phase diagram.
- (b) Expanded AuGa, phase (hypothetical).
- (c) Variation of parameters.

if it would be possible to grow one of the allowed arrangements. The slug starts growing at the bottom (pointed end), and as it grows the remaining melt becomes richer in Au or Ga, depending on which side of the congruent point the prepared melt concentration lay. It was assumed that the bulk of the slug has crystallized before the concentration of the remaining melt has changed enough to cause much overlap, as indicated on Figure 52(c), and in agreement with Figure 42.

Application of this test to all configurations of phase boundaries that appear in real systems leaves those shown in Figure 53. The first two hypothetical phase diagrams (counting from the top) are consistent with the further assumption:

(8) The direction of change of concentration in Slug A is correctly given by the microprobe data.

The third diagram has been expanded in Figure 52(b), and the first diagram is expanded in like manner in Figure 54. The first guess for the position of stoichiometry is that it coincides with maximal residual resistance ratio RRR. Such a position is supported by the result (4) for magnetic interaction. The boundaries for all diagrams but the second permit this placement. For the second diagram, stoichiometry must lie on the Ga-rich side of the congruent point.

The final conclusions are that the dHvA frequency F, Dingle temperature  $T_D$ , and RRR of AuGa<sub>2</sub> vary as the melt from which the crystal is grown varies in concentration about stoichiometry. As these parameters depend upon the extent of order and the density of conduction electrons their variation constitutes strong indirect evidence for such a range of concentration of the AuGa<sub>2</sub> phase. There also is some direct



Figure 53. Hypothetical phase boundaries for AuGa<sub>2</sub> consistent with continuous Dingle temperature and the prepared melt concentrations. The solid phase (shaded) lies between the solidus lines shown. Liquidus lines are not shown. The top two diagrams are also consistent with the direction of concentration change measured in Slug A by the microprobe.



Figure 54. An expansion of the first phase boundary in Figure 53, diagrammed in the manner of Figure 52.

- (a) Full phase diagram.
- (b) Expanded AuGa, phase (hypothetical).
- (c) Variation of parameters.

evidence for such a range. The range of concentration of the samples appears to be less than 1%; the full extent of the phase is not known. Stoichiometry does not coincide with the congruent point (liquidus maximum).

Two experiments are suggested that may answer some of the questions remaining. The first and simplest is RRR measurement on the samples from Slug C. It is expected that RRR will decrease as concentration becomes more Au-rich with respect to stoichiometry. This implies, by all of the phase boundaries diagrammed in Figure 53, that RRR should decrease from the bottom to top of Slug C.

A more time consuming experiment, and one probably with its own set of unforeseen difficulties, is to anneal the entire slug over a time and at a temperature sufficient to render the composition uniform. This approach would obviate the need to find a reliable method of precise analysis of bulk concentration, because the prepared melt concentrations would apply. A series of crystals could be grown using prepared melt concentrations near stoichiometry. The measured correspondence between RRR and prepared melt concentration summarized in Figure 37 and Table 8 could be used as guides to the melt concentrations to use. Suitable crystals could possibly be grown on the Bridgman grower by greatly decreasing the lift speed. More likely the grown crystals would require annealing in a furnace providing better temperature control. Determining the length of time required to obtain sufficient homogeneity, the extended time possibly required, and preventing diffusion of impurities into the crystal during that time are probably the most likely difficulties. The accuracy of nominal concentration in such an experiment would depend upon the degree of homogeneity achieved, the precision of weighing

the components when preparing the charge, and the amount of differential evaporation during mixing, growth and anneal. Regarding the weighing, the balance we used read to .01 mg (by a vernier). For a 10 gm charge (approximately the mass of our slugs), an error of 1 mg in measuring Ga (the component contributing the smallest mass to the charge) gives an error of .005 at.% Ga, a negligible error if the measured value of .35 at.% Ga for the range of concentration in Slug A is even only approximately correct. But if, as a result of the differences in the Ga and Au vapor pressures more Ga than Au is lost during the mixing, by an amount of 1% of the mass of the charge (making a differential loss of 100 mg), the resulting change in Ga concentration is .5 at.%, enough to seriously distort the results.

In conclusion, although the results are fairly qualitatively and difficult to compare with theoretical predictions because of the inherent complications in the system, it is felt that the variation of the de Haas-van Alphen parameters will be of interest to those in the presently active area of using the dHvA effect to study both scattering and the rigid band model. The information on the AuGa<sub>2</sub> phase width and RRR could be of practical interest to those studying the physical properties of highly ordered samples of AuGa<sub>2</sub>. And finally, the measurement of the phase constant  $\gamma = .46\pm.09$  adds to the small number of phase constant values reported in the literature, and is more evidence, from a slightly different direction, of the validity of the Lifshitz-Kosevich theory.

# LIST OF REFERENCES AND NOTES

# LIST OF REFERENCES AND NOTES

- 1. W. J. de Haas and P. M. van Alphen, Leiden Comm. 208d, 212A (1930) and 220d (1932).
- The concept of long range order is made quantitative in the theory of binary alloys. For a discussion of various order parameters see E. W. Elcock, <u>Order-Disorder Phenomena</u> (John Wiley, New York, 1956).
- 3. J. T. Longo, Ph.D. Thesis, Michigan State Univ. (1965), unpublished.
- 4. M. E. Straumanis and K. S. Chopra, Z. Physik. Chemie (Frankfurt) 42, 144-150 (1964).
- 5. D. J. Sellmyer, Ph.D. Thesis, Michigan State Univ. (1965), unpublished.
- 6. E. W. Elcock, <u>Order-Disorder Phenomena</u> (John Wiley, New York, 1956), pp. 20, 159.
- 7. M. E. Straumanis, private communication, cited as Reference 12 by J. T. Longo (1965), Ref. 3 herein.
- 8. W. B. Pearson, private communication.
- 9. G. A. Stringer and R. J. Higgins, J. Appl. Phys. 41, 489-497 (1970).
- J. P. Jan, W. B. Pearson, Y. Saito, M. Springford, and I. M. Templeton, Phil. Mag. <u>12</u>, 1271 (1965).
- 11. J. M. Ziman, <u>Electrons in Metals</u> (Barnes & Noble, New York, 1970), p. 1.
- 12. W. A. Harrison, Phys. Rev. 118, 1190 (1960).
- 13. J. M. Ziman, <u>Principles of the Theory of Solids</u> (Cambridge University Press, 1969), p. 75.
- 14. C. Herring, Phys. Rev. <u>57</u>, 1169 (1940).
- A. P. Cracknell and K. C. Wong, <u>The Fermi Surface</u> (Clarendon Press, Oxford, 1973), p. 91.

- 16. J. C. Slater, Phys. Rev. <u>51</u>, 846 (1937).
- 17. J. T. Longo, P. A. Schroeder, M. Springford, J. R. Stockton, Phys. Rev. <u>187</u>, 1185 (1969).
- J. E. Schirber and A. C. Switendick, Solid State Commun. <u>8</u>, 1383 (1970).
- 19. J. C. Abele, J. H. Brewer, M. H. Halloran, Solid State Commun. 9, 977 (1971).
- 20. J. E. Schirber, Phys. Rev. B6, 333 (1972).
- 21. A. C. Switendick, Bull. Am. Phys. Soc. 14, 360 (1969).
- 22. A. C. Switendick and Albert Narath, Phys. Rev. Letters <u>22</u>, 1423 (1969).
- 23. J. T. Longo, P. A. Schroeder, and D. Sellmyer, Phys. Rev. <u>182</u>, 658-670 (1969).
- 24. S. S. Vishnubhatla and J.-P. Jan, Phil. Mag. <u>16</u>, 45-50 (1967).
- 25. N. Bohr, Dissertation, Copenhagen (1911); J. H. van Leeuwen, <u>Theory of Electric and Magnetic Susceptibilities</u> (Oxford University Press, 1932).
- 26. A. B. Pippard, in <u>Solid State Physics</u>, edited by J. F. Cochran and R. R. Haering, Vol. 1: <u>Electrons in Metals</u> (Gordon and Breach, New York, 1968), pp. 1-38.
- 27. See, for example, F. W. Sears, <u>Thermodynamics, the Kinetic Theory</u> of Gases, and Statistical <u>Mechanics</u> (Addison-Wesley, Reading, Mass., 1953), pp. 162 and 174-176.
- 28. See, for example, A. H. Wilson, <u>The Theory of Metals</u> (Cambridge University Press, 1954, 2nd edition), Appendix A2.
- 29. L. Shubnikoy and W. J. de Haas, University of Leiden Research Report No. 207a, 1930 (unpublished).
- 30. L. D. Landau, Z. Physik <u>64</u>, 629 (1930); and L. D. Landau, in the Appendix to D. Shoenberg, Proc. Roy. Soc. (London) <u>A170</u>, 341 (1939).
- 31. R. Peierls, Z. Physik 81, 186 (1933).
- 32. M. Blackman, Proc. Roy. Soc. (London) <u>A166</u>, 1 (1938).
- 33. Shoenberg, Proc. Roy. Soc. A170, 341 (1939);

- 34. L. Onsager, Phil. Mag. <u>43</u>, 1006 (1952).
- 35. R. B. Dingle, Pro. Roy. Soc. (London) <u>A211</u>, 500 (1952).
- 36. R. B. Dingle, Proc. Roy. Soc. (London) <u>A211</u>, 517 (1952).
- 37. I. M. Lifshitz and A. M. Kosevich, Zh. Eksperim. Teor. Fiz. <u>29</u>, 730 (1955) [Soviet Phys.-JETP <u>2</u>, 636 (1956)].
- 38. A. V. Gold, in <u>Solid State Physics</u>, edited by J. F. Cochran and R. R. Haering, Vol. 1: Electrons in Metals (Gordon and Breach, New York, 1968), p. 39.
- 39. A. C. Thorsen, in <u>The Encyclopedia of Physics</u>, edited by R. M. Besancon (Rheinhold, New York, 1966), pp. 155-156.
- 40. P. J. Stiles, E. Burstein, and D. N. Lagenberg, Phys. Rev. Letters <u>6</u>, 557 (1961).
- 41. A. C. Thorsen and T. G. Berlincourt, Nature 192, 959-960 (1961).
- 42. See, for example, C. Kittel, <u>Introduction to Solid State Physics</u> (John Wiley, New York, 1966), pp. 286-289.
- 43. See, for example, Gold, pp. 45-47; C. Kittel, pp. 290-294.
- 44. A. D. Brailsford, Phys. Rev. 149, 456 (1966).
- 45. S. J. Williamson, S. Foner, and R. A. Smith, Phys. Rev. <u>136</u>, A1065 (1964).
- 46. A. B. Pippard, Proc. Roy. Soc. (London) A287, 165 (1965).
- 47. R. G. Chambers, Proc. Phys. Soc. (London) 89, 695 (1966).
- 48. D. W. Terwilliger and R. J. Higgins, Phys. Rev. B7, 667-673 (1973).
- 49. P. T. Coleridge and I. M. Templeton, J. Phys. F 2, 643-656 (1972).
- 50. L. M. Falicov and H. Stachowiak, Phys. Rev. 147, 505 (1966).
- 51. L. D. Landau, Zh. Eksperim, Teor. Fiz. <u>30</u>, 1058 [Sov. Phys. JETP <u>3</u>, 920 (1956)].
- 52. J. M. Luttinger and J. C. Ward, Phys. Rev. <u>118</u>, 1417 (1960).
- 53. D. Shoenberg and J. Vanderkooy, J. Low Temp. Phys. 2, 483 (1970).
- 54. D. Shoenberg, Phil. Trans. Roy. Soc. (London) A255, 85 (1962).
- 55. A. B. Pippard, Proc. Roy. Soc. (London) <u>A272</u>, 192 (1963).
- 56. J. H. Condon, Phys. Rev. 145, 526 (1966); LT-10.

- 57. M. H. Cohen and L. M. Falicov, Phys. Rev. Letters 7, 231 (1961).
- 58. E. I. Blount, Phys. Rev. 125, 1636 (1962).
- 59. A. B. Pippard, Phil. Trans. Roy. Soc. 256, 317 (1964).
- 60. The interaction of the conduction electrons with magnetic host atoms (as transition elements) and with magnetic impurities (when isolated or cooperative) in nonmagnetic hosts changes the dHvA effect. Each spin system (electron spins parallel and antiparallel to the applied field) has a different dHvA signal amplitude and broadening of the energy level (different TD, referred to as spin scattering anisotropy). Both TD and the effective g-factor may be dependent on the magnitude of the field in magnetic media. For discussion and references to the original reports, see H. Shiba in <u>Physics of Condensed</u> <u>Matter</u>, edited by G. Busch, (Springer-Verlag, Berlin, 1975), pp. 259-268.
- 61. E. I. Zornberg and F. M. Mueller, Phys. Rev. 151, 557 (1966).
- 62. J.-P. Jan and I. M. Templeton, Phys. Rev. 161, 556-558 (1967).
- 63. W. J. O'Sullivan and J. E. Schirber, Cryogenics 7, 118-119 (1967).
- 64. R. L. Thomas and G. Turner, Phys. Rev. 176, 768-772 (1968).
- 65. W. J. O'Sullivan and J. E. Schirber, Phys. Rev. 181, 1367 (1969).
- 66. M. Springford and J. R. Stockton, J. Phys. E: Sci. Instrum. <u>3</u>, 55-58 (1970).
- 67. J. R. Anderson and D. C. Hines, Phys. Rev. B2, 4752-4760 (1970).
- P. T. Coleridge, A. A. M. Croxon, G. B. Scott, and I. M. Templeton, J. Phys. E: Sci. Instrum. <u>4</u>, 414-416 (1971).
- 69. Uddin and D. Shoenberg, Proc. Roy. Soc. A156, 687-720 (1936).
- 70. V. Heine, Proc. Phys. Soc. (London) 69, 505 (1956).
- 71. P. T. Coleridge and I. M. Templeton, Can. J. Phys. <u>49</u>, 2449-2461 (1971).
- 72. I. M. Templeton and P. T. Coleridge, J. Phys. F5, 1307-1316 (1975).
- 73. J. P. G. Sheperd and W. L. Gordon, Phys. Rev. 169, 541 (1968).
- 74. P. J. Tobin, D. J. Sellmyer, and B. L. Averback, J. Phys. Chem. Solids <u>32</u>, 1721 (1971).
- 75. J. Friedel, Phil. Mag. <u>43</u>, 153 (1952).
- 76. J. Friedel, Advanc. Phys. (Phil. Mag. suppl.) 3, 446 (1954).

- 77. E. A. Stern, Phys. Rev. <u>168</u>, 730-736 (1968).
- 78. M. H. Cohen and V. Heine, Adv. Phys. 7, 395 (1958).
- 79. P. T. Coleridge, J. Phys. F 5, 1317-1326 (1975).
- 80. Y. K. Chang, A. J. Arko, G. W. Crabtree, J. B. Ketterson, R. J. Higgins, and F. W. Young, preprint, 1975.
- 81. Y. K. Chang and R. J. Higgins, Phys. Rev. B 12, 4261-4281 (1975).
- 82. P. T. Coleridge and B. Watts, Phil. Mag. 24, 1163-1178 (1971).
- 83. P. T. Coleridge, Phil. Mag. <u>26</u>, 573-584 (1972).
- 84. P. T. Coleridge, Phil. Mag. 27, 1495-1496 (1973).
- 85. P. T. Coleridge, J. Phys. F. Metal Phys. 2, 1016-1032 (1972).
- 86. W. R. Wampler and M. Springford, J. Phys. C: Sol. State Phys. 5, 2345-2356 (1972).
- 87. Lowndes, K. M. Miller, R. G. Poulsen, and M. Springford, Proc. Roy. Soc. (London) A 331, 497-523 (1973).
- 88. R. G. Poulsen, D. L. Randles, and M. SpringFord, J. Phys. F: Metal Phys. <u>4</u>, 981-998 (1974).
- B. Lengeler and W. Uelhoff, in <u>Physics of Condensed Matter</u>, edited by G. Busch (Springer-Verlag, Berlin, 1975), pp. 150-152.
- 90. Paul Soven, Phys. Rev. B 5, 260-266 (1972).
- 91. P. T. Coleridge, N. A. W. Holzwerth, and M. J. G. Lee, Phys. Rev. B <u>10</u>, 1213-1229 (1974).
- 92. B. Lax, Rev. Mod. Phys. 30, 122 (1958).
- 93. D. Shoenberg, <u>Progress in Low Temperature Physics</u>, edited by C. J. Gorter (North Holland, Amsterdam, 1957), Vol. 2, p. 226.
- 94. D. Shoenberg and P. J. Stiles, Proc. Roy. Soc. (London) <u>A281</u>, 62 (1964).
- 95. A. Goldstein and S. Foner, Bull. Am. Phys. Soc. 9, 239 (1964).
- 96. S. J. Williamson, S. Foner, and M. S. Dresselhaus, Proc. 9th Int. Conf. Low Temp. Phys., Columbus, Ohio, 1964.
- 97. A. Goldstein, S. J. Williamson, and S. Foner, Rev. Sci. Instrum. <u>36</u>, 1356 (1965).

- 98. L. R. Windmiller and M. G. Priestley, Solid State Commun. <u>3</u>, 199 (1965); Bull. Am. Phys. Soc. <u>2</u>, 632 (1964).
- 99. L. R. Windmiller, Phys. Rev. 149, 472 (1966).
- 100. J. B. Ketterson and Y. Eckstein, Rev. Sci. Instrum. 37, 44 (1966).
- 101. R. W. Stark and L. R. Windmiller, Cryogenics 8, 272 (1968).
- 102. R. A. Johnson, U.S.A.E.C. Report No. IS-T-200 (1967).
- 103. A. Rose-Innes, <u>Low Temperature Techniques</u> (Van Nostrand, Princeton, N.J., 1964), pp. 58-60.
- 104. D. A. Hill and C. Hwang, J. Sci. Instrum. 43, 581-584 (1966).
- 105. Max Hansen, <u>The Constitution of Binary Alloys</u> (McGraw-Hill, New York, 2nd ed., 1958), pp. 305-306.
- 106. See, for example, J. C. Brice, <u>The Growth of Crystals from the</u> <u>Melt</u>, and also <u>The Growth of Crystals from Liquids</u>, Vols. 5 and 12 of <u>Selected Topics in Solid State Physics</u>, edited by E. P. Wohlfarth (North-Holland, Amsterdam, 1973).
- 107. A. S. Yue and J. T. Yue, J. Cryst. Growth <u>13/14</u>, 797-813 (1972), and references therein.
- 108. C. H. Li, J. Appl. Phys. <u>42</u>, 4521-4522 (1971), and references therein.
- 109. Handbook of Chemistry and Physics (Chemical Rubber Co., Cleveland, Ohio, 46th edition, 1965), pp. D-98 and D-99.
- 110. H. A. Liebhafsky, H. G. Pfeiffer, E. H. Winslow, and P. D. Zemany, X-ray Absorption and Emission in Analytical Chemistry (John Wiley, New York, 2nd printing, 1966).
- 111. L. S. Birks, <u>Electron Probe Microanalysis</u> (Interscience, New York, 1963).
- 112. W. J. M. Salter, <u>A Manual of Quantitative Electron Probe Micro-</u> <u>analysis</u> (Structural Publications, London, 1970).
- 113. Hugh D. Young, <u>Statistical Treatment of Experimental Data</u> (McGraw-Hill, New York, 1962), pp. 57-64.
- 114. For a discussion of confidence intervals, standard deviations, and standard error see, for example, Ref. 110, or John Mandel, <u>The Statistical Analysis of Experimental Data</u>.
- 115. W. C. Bigelow, private communication.
- 116. R. M. Eisberg, <u>Fundamentals of Modern Physics</u> (John Wiley, New York, 1961), p. 482.

- 117. C. P. Bean, R. W. DeBlois, and L. B. Nesbitt, J. Appl. Phys. <u>30</u>, 1976 (1959).
- 118. J. LePage, A. Bernalte, and D. A. Lindholm, Rev. Sci. Instrum. 39, 1019 (1968).

.

;

t