

THE CONSTRUCTION OF A VIBRATING
SAMPLE MAGNETOMETER AND A
STUDY OF MAGNETIC INTERACTIONS
IN DILUTE ALLOYS WITH ATOMIC
ORDER-DISORDER TRANSITIONS

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This is to certify that the
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ABSTRACT

THE CONSTRUCTION OF A VIBRATING SAMPLE MAGNETOMETER AND A STUDY OF MAGNETIC INTERACTIONS IN DILUTE ALLOYS WITH ATOMIC ORDER- DISORDER TRANSITIONS

By

Terry Wayne McDaniel

An experimental investigation of the influence of binary host atomic order-disorder transitions on interactions among dilute magnetic impurities has been conducted. This study has been carried out with magnetic susceptibility measurements on three host alloy systems with the emphasis on $(\text{Cu}_{0.83}\text{Pd}_{0.17})_{1-x}\text{X}$, where $\text{X} = \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}, \text{and Gd}$.

Susceptibility measurements were performed with a vibrating sample magnetometer that was constructed and developed as the initial segment of this study. The details of the design, calibration, and operation of this instrument are presented.

A discussion of important experimental considerations in a systematic investigation of alloys with varying impurity concentration is given. The possibility of the coexistence of several magnetic interaction mechanisms in metallic systems and the desire to experimentally distinguish among them served as motivation for the exploitation of the atomic order-disorder transition as a potential internal control on these interactions. A consideration of the relationship between the

paramagnetic Curie point Θ and magnetic interactions precedes the presentation of the experimental data.

Striking effects of the order-disorder transition have been observed in $(\text{Cu}_{0.83}\text{Pd}_{0.17})\text{Mn}$ and $(\text{Cu}_{0.83}\text{Pd}_{0.17})\text{Ni}$. Possible explanations of the observed behavior with respect to the Kondo effect, the RKKY interaction, and local environment-direct interaction effects are offered. A local environment-direct interaction picture appears to be most consistent with the data obtained.

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I. INTRODUCTION

A. Brief History of the Problem

The earliest systematic studies of magnetism in metals were undertaken in the first third of this century. At least two major developments in physics during this period account for this fact. Experimental techniques at low temperatures were being rapidly developed by the mid-1920's following their first appearance at the beginning of the century. This made possible direct measurement of bulk magnetic properties such as magnetization and susceptibility as a function of temperature which is essential in any attempt to understand magnetism. Low temperature results for other properties of metals which were potentially related to magnetism were being published with increasing frequency. The second development was the establishment of quantum mechanics which was to provide the theoretical basis for the understanding of magnetism in matter, even up to the present day. In retrospect, it seems clear that progress in providing satisfactory explanations of magnetic phenomena would have been impossible without the establishment of quantum mechanics. There is little doubt, however, that the improved experiments demonstrated the necessity of the development of a new theory and thus hastened it.

The experimental thrust proceeded quite predictably. The first task was to study the magnetic behavior of the pure metallic elements and these investigations exposed the broad classes of magnetism

characteristic of metals. The most striking magnetic systems had long been known to be those which exhibited spontaneous magnetic ordering, namely certain of the 3d transition metals and the lanthanides. From the outset, therefore, it was clear that a central task was to understand simple ferromagnetism and antiferromagnetism, and it is remarkable that some fifty years later this objective remains to be accomplished. This is not to say that little progress has been made, but is simply an observation that magnetic phenomena have proven to be plentiful, diverse, and often exceedingly complicated. Our intent here is to present a brief historical review of one particular path which was taken in the hope of attaining a better understanding of cooperative magnetic phenomena. As commonly occurs in physics, those who followed this path found new effects which appeared to be more fundamental than the magnetic ordering that was ultimately to be explained. As we sketch the historical development of the approach we have adopted, it should be remembered that this discussion is obviously not intended to supplant recent, more complete reviews in the literature.⁽¹⁻⁴⁾ Rather, it serves as an introduction to the topic of this thesis.

At this point we should make clear to what we refer when we speak of magnetism in metals. We are restricting our use of this phrase to those situations where a permanent (on some relative time scale) local magnetic moment exists in a metal in the absence of an applied magnetic field. Normally, a reliable experimental indicator of this situation is a strongly temperature dependent magnetization or susceptibility. In this definition we are excluding weak, nearly temperature independent effects such as atomic core and conduction electron contributions to the paramagnetic or diamagnetic susceptibility. Although

the source of most of these contributions to the magnetic character of pure metals was understood shortly after the advent of the quantum theory of solids,⁽⁵⁾ it must be emphasized that accurate quantitative calculations of the susceptibility are exceedingly difficult many-body problems.^(6,7) Moreover, there still exist serious discrepancies between experimental and calculated susceptibility values for non-dilute alloys and intermetallic compounds quite apart from the usual discrepancies attributable to approximations for computational convenience. Perhaps this emphasizes the need for reliable methods of calculating the properties of alloys. This is certainly a more palatable notion than the thought that all of the mechanisms of magnetic susceptibility are not yet known after nearly fifty years of quantum mechanics. In any case, it is generally true that the major operational difficulty in dealing with the (weak) induced magnetization in metals is a correct separation of the total susceptibility into its constituent parts.

After the properties of the pure metallic elements had been surveyed, the experimental attack turned toward alloy systems. The idea was that one might better approach an understanding of magnetic phenomena if their presence and magnitude could be externally controlled in systematic ways. As an example, consider the gradual dilution of a pure ferromagnet by alloying with a non-magnetic metal (one whose constituent atoms carry no permanent magnetic moment in the metal). It is clear that at some composition of this binary system the spontaneously ordered magnetic state will cease to exist at any temperature, and one would expect the critical temperature for ordering to vary over some intermediate range of composition. On the other hand, many experimentalists felt that a more fruitful

utilization of alloying was to start with the comparatively uninteresting non-magnetic system and gradually add small amounts of magnetic impurities. If one could gain an understanding of the magnetic behavior of the alloy system in a piecewise approach as the concentration of the impurity was incrementally increased, it was hoped that ultimately the cooperative magnetic state would come to be understood in terms of interactions among its fundamental constituents, the atoms about whose sites the permanent moment is localized.

In practice, this logical plan of attack did not always yield information that could be easily interpreted. For instance, it did not at first sight seem surprising that dilute transition metal or rare earth impurities in a non-magnetic host displayed a permanent moment (as evidenced by a Curie-Weiss impurity susceptibility). It was widely presumed that the free atom or free ion more or less maintained its electronic configuration as it went into solid solution without really asking how exactly this happens in a metallic environment where conduction electrons might be expected to mix with the atomic states responsible for an impurity atom's magnetic moment. In fact, there was strong experimental evidence that some impurities did not carry moments in some hosts (for example, Mn in Al). Clearly, before one could proceed to an investigation of interactions among atoms carrying permanent moments, one had to understand what determined the formation of moments in the dilute alloy. The answers were slow in coming. It was not until the mid-1950's that Friedel⁽⁸⁾ and coworkers addressed the question of moment formation in metals when he introduced the concept of a virtual bound state, a d state strongly admixed with a band of conduction electron states. This guiding work and an increasing

store of experimental data on dilute alloys kindled theoretical progress on this problem; the classic papers of Anderson⁽⁹⁾ and Wolff⁽¹⁰⁾ appeared shortly thereafter. Anderson solved a simple parameterized model which included s-d mixing, while Wolff treated the conduction electron-impurity system as a resonant scattering problem. These papers first considered explicitly the necessary conditions for the existence of a localized impurity moment.

There exists another large set of experimental results that were accumulated between the 1920's and mid 1960's which have come to be of central importance to the study of local moments in metals. This set of experiments have been referred to by van den Berg⁽¹⁾ as anomalies in dilute metallic solutions containing transition element impurities. These experiments consist primarily of measurements of transport and equilibrium properties at low temperature in these dilute impurity systems. The "anomalies" refer to originally mysterious minima in thermal and electrical resistivity versus temperature curves, very large thermoelectric powers at low temperatures, Schottky type peaks in the specific heat, and others. Although long suspected, it was not until recently that the occurrence of a minimum in electrical resistivity versus temperature was shown to be in one-to-one correspondence with the existence of a magnetic impurity.⁽¹¹⁾ Kondo⁽³⁾ was able to explain the electrical resistivity behavior with an isotropic s-d exchange Hamiltonian by carrying the calculation to the second Born approximation. His result predicted a logarithmic increase in impurity resistivity as temperature is decreased and this agrees with experiment in many systems over a wide temperature range. The perturbation calculation leads to a logarithmic divergence for many physical

properties as the temperature is lowered toward absolute zero indicating a breakdown of perturbation theory below some temperature.

In the years since Kondo's remarkable result appeared, there has been much experimental and theoretical activity in the area of dilute moment systems. Kondo's original ideas have been pursued with the hope of removing the low temperature divergences in perturbation theory. It seems that the "Kondo system" bears some resemblance to the phenomenon of superconductivity in that one is dealing with a genuine many-body effect when a localized moment interacts with the sea of conduction electrons. Many-body techniques are being applied to the problem in the hope that a unified description of these systems for all temperatures can be developed, but much remains to be done. Several of the non-perturbative calculations⁽³⁾ and also several experiments^(2,4) have suggested the existence of a many-body singlet ground state characterized by strong impurity-conduction electron spin correlation as the temperature approaches absolute zero. On the other hand, impurity systems in which moments do not develop are satisfactorily described by Hartree-Fock one-electron calculations. The question of how one can describe a spectrum of behaviors extending between the two extremes with a single fundamental parameter has been of continuing interest. One such parameter that appears to be appropriate is the mean spin fluctuation lifetime which is but one of several characteristic times that are useful in a dynamical picture of dilute impurity systems. Theories dealing with so-called "localized spin fluctuations" (LSF)⁽¹²⁾ have received increased attention lately. Coles⁽¹³⁾ has recently synthesized these various concepts in a convenient classification scheme.

Thus, we see from this brief sketch of developments in the dilute magnetic impurity problem how this particular approach toward understanding cooperative magnetic phenomena has, for quite a long time, been apparently diverted from proceeding toward the original goal. But the diversion is only apparent, for in the meantime we have come to better appreciate the full complexity of problems in magnetism while much new physics has been learned. The necessary tools and concepts are being developed for continued assaults on the puzzle of magnetism in metals.

B. Preface of Thesis Content

The experiments described in this thesis can now be placed into the perspective of the continuing efforts to extend beyond the dilute magnetic system to one in which impurity-impurity interactions compete with and ultimately dominate the already complex isolated impurity-conduction electron interaction that has been the focal point of most studies through the 1960's. The purpose of this study has been to carry out a systematic investigation of the influence of a particularly convenient, externally controllable parameter on magnetic impurity interactions. The parameter of interest, namely the degree of atomic order present in the host matrix, is characteristic of a very small class of non-dilute binary alloys. (The atomic order-disorder transition under consideration is distinct from the formation (common to many binary alloys) of an ordered atomic phase which occurs only at, or very near, simple stoichiometric compositions and which is usually referred to as an intermetallic compound. Genuine atomic order-

disorder binary alloys are characterized by equilibrium phase diagrams with regions of atomic order spanning composition ranges of the order of 10 atomic percent. Sharp transition temperatures separate the ordered and disordered states. A prototypical atomic order-disorder alloy is the Cu-Au system.) As conceived, these experiments were seen as one possible way of controllably switching on or off particular types of magnetic interactions without depending upon distinctly different alloy systems to distinguish among interaction mechanisms. The specific program, then, has been as follows: Given a single non-magnetic binary host alloy which could be ordered or disordered with a proper preparation procedure, one would study interactions among some species of magnetic impurity atoms with susceptibility measurements as a function of impurity concentration and host atomic order. The study would be open-ended in that several impurities and hosts could be investigated if interesting effects were discovered. In no way was it presumed that this particular approach would render experimental interpretation to the realm of the trivial, but at least sufficient controls seemed to be built into the experiment to effectively reduce the complications of competing effects to a manageable level.

We have restricted the admissible types of atomic order-disorder transitions for this study to a smaller subset of the already limited possibilities. Because one of the possible effects anticipated was the influence of the local crystalline environment on magnetic impurity behavior and interaction, it was thought essential to hold one important feature of the host crystalline structure constant in any order-disorder transition, namely, the lattice structure of atomic sites. For example, if at some fixed composition of the binary alloy the lattice of atomic

sites in the disordered phase is face-centered cubic (fcc) (i.e., a random arrangement of the two species on an fcc lattice), then we insist that upon ordering the system by the appropriate means that an identical fcc lattice of atomic sites be retained and the atoms simply rearrange on that lattice to create an atomically ordered array. While crystallographers would maintain that what is described in the preceding sentence is a change in crystal structure (i.e., a new unit cell with a new basis), the essential feature for our concern is just that the lattice of atomic sites remains unchanged in the ordering. This does not always occur. It can happen that the lattice of sites distorts upon ordering, and we have considered this to be an added complication to be avoided. Therefore, we have been doubly selective in choosing host matrices for studying interactions. (See Section A of Chapter IV for specific details of the particular alloy systems we have investigated. In Chapter III, Section A, a further discussion of atomic order-disorder in regard to magnetic interactions is presented.)

Before proceeding to a discussion of the details and results of the experiments, we describe in Chapter II the considerations that went into the selection of a particular device for performing susceptibility measurements, as well as the details of its construction and operation. Also treated are the modifications we have incorporated into our instrument that perhaps make it unique among instruments of its type.

II. INSTRUMENTATION

A. General Experimental Considerations in a Study of Magnetic Properties

When one decides to embark on extensive survey studies of the magnetic character of a wide variety of physical systems with the constraint of limited resources to allocate for instrumentation, several choices as to approach are presented. Magnetism is a phenomenon which is present in nature in a multitude of forms and which manifests itself directly or indirectly in many experimentally accessible physical properties. There are several reasons why one would prefer to measure a direct magnetic property. Indirect methods involve measuring a property which can yield information on the magnetic properties of a given system under the following conditions: (1) Enough prior knowledge of the system is at hand to allow a meaningful interpretation of the indirectly related data; (2) The indirect properties are present and experimentally accessible in all materials that might be chosen for study. The properties directly related to the magnetic state of a material fall into two general categories: (1) Bulk properties which reflect macroscopic spatial averages of localized effects; (2) Microscopic or local properties which might be separably related to any one of the components of a bulk sample (e.g., nuclei or electrons, impurity atom or host atom). Both bulk and local properties are useful, but in different ways and under different circumstances. Bulk properties are

most useful when one is beginning a study in some previously unmeasured system because they allow one to determine the general type of magnetism present and some useful parameters (e.g., ordering temperature, paramagnetic Curie point, effective moments, etc.). It is perhaps simpler to determine systematic trends in magnetic behavior as some external parameter is varied with bulk measurements. Knowledge of local magnetic behavior is most valuable after the categorization and systematization acquired from bulk measurements is completed. Only a local magnetic probe can adequately resolve the details of magnetic behavior once the guidelines have been sketched with bulk measurements.

To carry out the type of survey of magnetic interactions envisioned in Chapter I, and keeping possible diverse future studies of magnetism in mind, we decided to undertake direct bulk measurements of magnetic properties. The history of past work of this kind indicates that the property bearing most directly on bulk magnetic character is the magnetic susceptibility, or alternately, the bulk magnetization. (See Appendix A for definitions of these terms and a discussion of the various units in use.) From Appendix A we have

$$\vec{M}(\vec{r}, t, T) = \chi(T) \vec{H}(\vec{r}, t) \quad (2.1)$$

where $\vec{M}$ is the magnetization, χ is the magnetic susceptibility, $\vec{H}$ is the total magnetic field intensity, $\vec{r}$ denotes spatial position in the material, t is the time, and T is the temperature at $\vec{r}$. For a uniform field $\vec{H}$ the resulting magnetization $\vec{M}$ is uniform. One can measure static or dynamic susceptibility. Static measurements are entirely satisfactory for the determination of the properties of interest in this

thesis. Only when knowledge of fluctuations and relaxation effects are required is it essential to measure the dynamic susceptibility.

Two physical effects associated with magnetic materials are commonly exploited to directly measure the static bulk magnetic susceptibility (hereafter referred to as simply susceptibility). The force methods and the induction methods are the two broad classes of measurements derived from these effects. A recent and rather complete discussion of the various methods within these broad classes is available.⁽¹⁴⁾ We shall briefly review the principles involved in each method before proceeding to a detailed discussion of the vibrating sample magnetometer (VSM).

The existence of a force on a continuously magnetized material placed in an external field gradient arises in the following simple way.⁽¹⁵⁾ The magnetostatic potential energy of an inductively magnetized, linear, isotropic, homogeneous specimen in a field H is

$$U = - \frac{1}{2} \int_{\text{specimen volume}} d\vec{r} [\vec{M}(\vec{r}) \cdot \vec{H}(\vec{r})] = - \frac{1}{2} \chi \int d\vec{r} [\vec{H}(\vec{r}) \cdot \vec{H}(\vec{r})] . \quad (2.2)$$

Write $\vec{r} = \vec{r}_0 + \vec{r}'$. For fixed $\vec{r}_0$, $d\vec{r} = d\vec{r}'$. Thus

$$U(\vec{r}_0) = - \frac{1}{2} \chi \int_{\text{specimen volume}} d\vec{r}' [\vec{H}(\vec{r}_0 + \vec{r}') \cdot \vec{H}(\vec{r}_0 + \vec{r}')] . \quad (2.3)$$

The force on the specimen is

$$\vec{F}(\vec{r}_0) = - \vec{\nabla} U(\vec{r}_0) , \quad \text{where} \quad \vec{\nabla} \equiv \hat{i} \frac{\partial}{\partial x_0} + \hat{j} \frac{\partial}{\partial y_0} + \hat{k} \frac{\partial}{\partial z_0} .$$

$$\vec{F}(\vec{r}_0) = \chi \int d\vec{r}' \left[\hat{i} \left(\frac{\partial \vec{H}(\vec{r}_0 + \vec{r}')}{\partial x_0} \cdot \vec{H}(\vec{r}_0 + \vec{r}') \right) + \dots \right] \quad (2.4)$$

For the isotropic specimen, we see that $\vec{F}$ is proportional to the susceptibility χ . In practice, one shapes the field such that the force

is non-negligible only along a single Cartesian coordinate. Furthermore, the specimen volume is made small enough such that $\frac{\partial \vec{H}(\vec{r})}{\partial x_{oi}} \cdot \vec{H}(\vec{r})$ is essentially constant over the volume. Then, for example,

$$F_{z_0} \approx \chi(\text{volume}) \left(\frac{\partial \vec{H}(\vec{r}_0)}{\partial z_0} \cdot \vec{H}(\vec{r}_0) \right). \quad (2.5)$$

This result applies to the Faraday method. A related force method which relies on the same physical principle is the Gouy method. In this method, the sample is of a long cylindrical geometry, with one end in a highly uniform magnetic field and the other in negligible field. From Equation (2.3), the total force on the sample is

$$\vec{F}(\vec{r}_0) = \frac{1}{2} \chi \int_{\text{specimen volume}} d\vec{r}' \left[\hat{i} \frac{\partial}{\partial x_0} H^2(\vec{r}) + \hat{j} \frac{\partial}{\partial y_0} H^2(\vec{r}) + \hat{k} \frac{\partial}{\partial z_0} H^2(\vec{r}) \right] \quad (2.6)$$

If the cylinder axis is along z_0 , then $\frac{\partial}{\partial x_0} H^2(\vec{r})$ and $\frac{\partial}{\partial y_0} H^2(\vec{r})$ are negligible compared to $\frac{\partial}{\partial z_0} H^2(\vec{r})$ over the length of the specimen. Furthermore, the integrand $\frac{\partial}{\partial z_0} H^2(\vec{r}_0 + \vec{r}')$ has $\vec{r}'$ held constant. Thus $d\vec{r} = d\vec{r}_0$ and

$$\vec{F}(\vec{r}') \approx \frac{1}{2} \chi A \int_{\text{specimen length}} dz_0 \left[\hat{k} \frac{\partial}{\partial z_0} H^2(\vec{r}' + \vec{r}_0) \right] = \frac{1}{2} A H^2(\vec{r}') \hat{k} \quad (2.7)$$

where A is the cross-sectional area of the cylindrical specimen.

The induction methods of measuring static susceptibility all are based on Faraday's law of induced electromotive force. A magnetized specimen produces a magnetic field in space. If the field lines are linked with a detection coil, this constitutes a magnetic flux in the coil. When some relative motion of the coil and specimen are effected, a voltage will be induced in the coil which is equal to $\left| \frac{d\Phi}{dt} \right|$, where $\Phi = \sum_n \int \vec{B} \cdot d\vec{A}_n$ is the flux. Thus Φ is derived from $\vec{B}$, the magnetic field produced by the magnetized specimen, and the field in turn depends upon the specimen magnetization or susceptibility. So all of the induction methods involve the measurement of a time varying voltage

induced in some geometrical array of detection coils, and the voltage is proportional to the specimen magnetization. The proportionality factor includes the frequency of vibration and a complicated geometrical factor which must be calibrated out.

B. Advantages of a Vibrating Sample Magnetometer

A successful VSM was first described in detail by Foner⁽¹⁶⁾ in 1959. A schematic diagram of the essential features of such a device is shown in Figure II-1. The basic principles of operation are as follows. A specimen whose magnetization is to be measured is positioned in a sample holder between the poles of a laboratory magnet. The sample holder is rigidly supported on a shaft which is attached to an electrical-to-mechanical transducer which sustains a sinusoidal vibration of the sample. Some geometrical array of detection coils is secured to the poles of the magnet and they sense the time varying field produced by the motion of the uniformly magnetized specimen. This results in the induction of a sinusoidal voltage in the coils which is directly proportional to the magnetization of the specimen. Note that measurement of the magnetization does not require the application of an external magnetic field to the sample if a magnetization exists without the external field. This contrasts directly with the force methods which require a field gradient and a field to create a force. When a field must be applied to induce a magnetization for detection with the VSM, the appropriate field is one that is constant in time and uniform in space in the vicinity of the sample. This insures that a uniform magnetization is detected with the VSM and that

Figure II-1. Schematic diagram of VSM with cryostat.
(A) Support flanges (B) Support platform (C) Sample vibrator housing (D) Thermocouple vacuum gauge (E) Exchange gas valve (F) Vacuum pumping ports and hoses (G) Quick couple-capillary tube feed-through for electrical leads to sample holder (H) Connector flange (I) Vacuum tube quick couple (J) Dewar support platform (K) Dewar support flange (L) Outer vacuum jacket of Dewar (M) Inner vacuum jacket of Dewar (N) Stainless steel vacuum tube (O) Brass guide tube (P) Laboratory magnet pole pieces (Q) Detection coils in plexiglass form (R) Sample holder

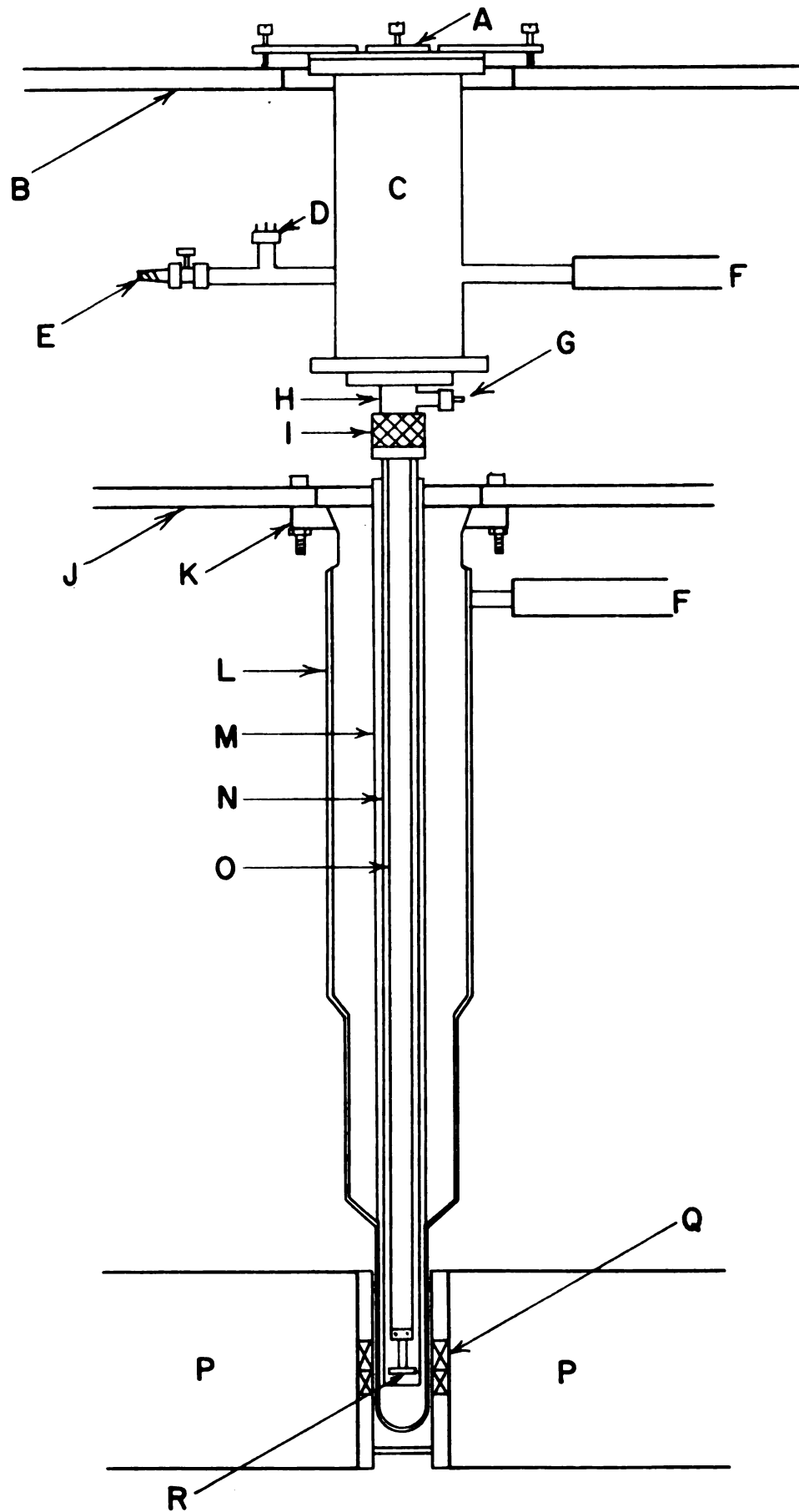


Figure II-1

magnetization as a function of uniform applied field can be conveniently measured. This contrasts again with the force methods in which case field dependence measurements are difficult since $\left| \frac{\partial \vec{H}}{\partial x} \right|$ may vary when $|\vec{H}|$ does.

The basic principle of operation of the VSM is seen to be quite simple and much opportunity for flexibility exists. One can measure sample magnetization as a function of specimen orientation or temperature (Section H, Chapter II). The sensitivity of the instrument depends upon the production of as large a voltage in the detection coils as possible consistent with practicability and with maintenance of desired flexibility (Sections C, E, and F, Chapter II). Because one makes an analog measurement with voltage corresponding to magnetization, it is a simple matter to electrically measure magnetizations which range over all magnitudes found in atomic matter.

Faraday measurements at low temperatures are known to involve complications.^(17,18) Gerritsen and Damon⁽¹⁷⁾ have discussed the effects of buoyancy and thermomolecular flow due to exchange gas and the errors that can arise. The VSM may be susceptible to induced eddy currents in metallic samples at low temperatures when sample resistivity is very low. These currents would produce unwanted signals, but experiments have shown that such signals are reduced by highly homogeneous magnetic fields.⁽¹⁹⁾ Furthermore, such signals are rejected in the normal lock-in detection since they occur at twice the vibration frequency. We conclude that the VSM is not plagued with low temperature problems as serious as those encountered with the Faraday balance.

The geometry of a specimen is not as critical with the VSM as it is with the force methods. The Faraday method requires a specimen

whose volume is small if the simple approximation $F_z \approx \chi(\text{volume})\left(\frac{\partial H}{\partial z} \cdot \vec{H}\right)$ is to hold. Furthermore, the linear dimensions should be comparable in all directions, e.g., spherical samples might be desirable. On the other hand, the Gouy method requires very long samples, and this can result in large expenses for sample materials. We found it convenient to fabricate cylindrical samples which are neither very long nor of nearly equal linear dimensions. These were appropriate for anticipated electrical resistivity and thermoelectric power measurements on the same specimens used for susceptibility determinations. The VSM can be calibrated for any geometry as long as the entire specimen lies within the uniform applied field.

To summarize the considerations involved in selecting an instrument for performing bulk susceptibility measurements, it was first determined that the Foner VSM is clearly the best of the induction instruments for the many reasons discussed in Foner's paper.⁽¹⁶⁾ Only the better analytical balances can match or surpass its sensitivity. However, these force methods were judged less desirable than the VSM with regard to required applied magnetic field conditions during measurement, low temperature reliability, and specimen geometry requirements. Furthermore, the force methods are mechanically more complicated, requiring specialized magnets and delicate balances, while the Foner VSM can be assembled with materials normally available in a reasonably well-equipped laboratory. Thus, one could hope to build a Foner type instrument at a considerable savings, and yet have a competitive piece of apparatus which is adaptable and flexible to a degree that most analytical balance magnetometers are not. In the following sections of Chapter II, we cover in more depth the designs

we have adopted in the construction of a VSM. Each section deals with a particular component of the VSM, or with testing and calibration.

C. The Sample Vibrator

The transducer assembly which provides the sinusoidal vibration of the specimen under measurement is shown in Figure II-2. The essential element is the permanent magnet and moving coil structure of a low frequency loudspeaker. The cone material and the original speaker frame have been removed. An appropriate loudspeaker for this purpose is one that can deliver enough acoustic power (without significant distortion) at frequencies below approximately 100 Hertz (Hz) to sustain peak to peak vibrations of amplitudes up to 1 millimeter (mm) while driving a long rigid shaft supporting a specimen and holder. This requirement is apparently not so difficult to meet. We have produced sufficient vibrations while driving with less than 3 watts at 33 Hz an inexpensive, lightweight, 20.3 centimeter (cm) diameter loudspeaker that utilizes a small ceramic permanent magnet. The permanent magnet assembly that has been used in actual operation is a much larger, metal one of cylindrical geometry. Its length is about 7.5 cm and the diameter is approximately 9 cm, so it is quite massive. The magnet assembly is rigidly mounted to the top plate of the brass vacuum housing such that the excursions of the speaker coil are in a vertical direction parallel to the axis of the cylindrical vacuum housing.

A lightweight rigid rod affixed to the moving coil form transmits the mechanical vibration through a small hole in the center of the

Figure II-2. Sample vibrator assembly

(A) Three support screws 120° apart (B) Support flanges
 (C) Electrical feed-throughs to speaker and nulling coils
 (D) Top plate (E) O-ring in channel (F) Support
 platform (G) Magnet support posts (H) Speaker
 magnet assembly (I) Vacuum housing (J) Magnet gap
 and speaker drive coil (K) Drive rod guide (L) Flat
 disk between sponge rubber rings (M) Vacuum pumping
 and monitoring ports (N) Vibration transmittance rod
 (O) Nulling signal coils (P) Permanent magnet
 (Q) Capillary tube for electrical leads (R) Quick
 couple with O-ring seal (S) Guide tube support flange
 (T) Al coupling (U) Connector flange (V) Quick
 couple collar (W) O-ring in channel (X) Vacuum tube
 restraining collar (Y) Drive rod guide tube
 (Z) Stainless steel vacuum tube (AA) Glass drive rod

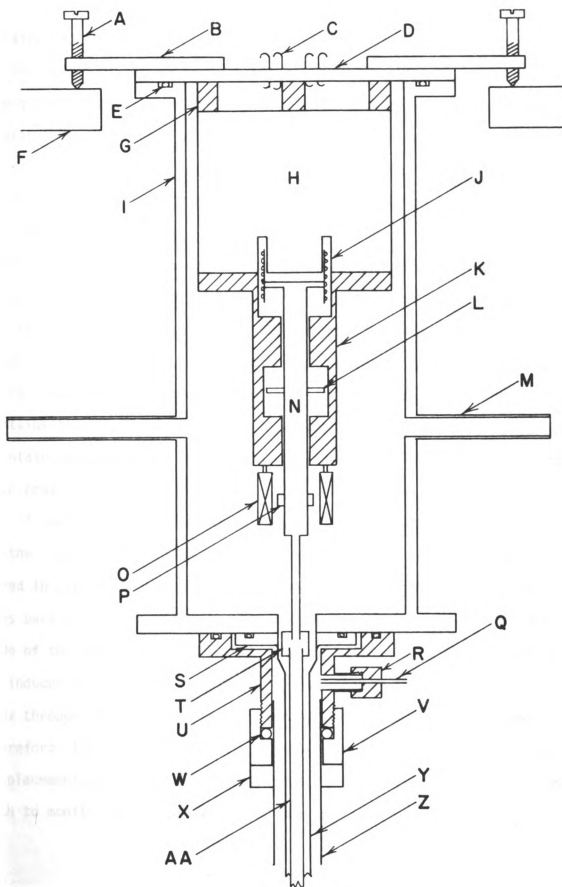


Figure II-2

bottom plate of the vacuum housing. The motion of this rod is constrained to a vertical line by a cylindrical guide over about 10 cm of the length of the rod. The contact of the rod with the walls of the guide is made nearly frictionless with three vertical lines of ball bearings mounted in the walls of the guide, and the guide itself is fixed with screws to the magnet assembly. The guide for the rod also serves the purpose that the speaker frame originally served by keeping the cylindrical, single layer moving coil centered in the narrow circular gap of the speaker magnet. It is crucial that the rod be constrained to linear motion only so that the coil and its form do not rub the magnet in the gap. At a position near the center of the rod guide, a flat disk of 3.2 cm diameter is centered on the rod and fixed to it. The rod guide has a cavity above and below the disk which contains two readily deformable sponge rubber rings. These serve to maintain the moving coil and rod in a vertical equilibrium position, and also provide restoring forces during the vibration.

A small cylindrical permanent magnet is mounted through a hole in the transmittance rod below the rod guide. A pair of pickup coils wired in series is mounted on the bottom of the rod guide with their axes parallel to the rod. They are positioned symmetrically on either side of the small permanent magnet. As the speaker is driven, a voltage is induced in these coils equal to $\left| \frac{d\Phi}{dt} \right|$ where Φ is the total magnetic flux through the coils due to the field of the small permanent magnet. Therefore, the wave form of this voltage is an indicator of the physical displacement with time of the driven rod. The signal is ultimately used both to monitor the sample vibration and as a nulling signal which is

mixed with the signal produced by the specimen under measurement. This will be discussed further in Section E of this chapter.

All components of the sample vibrator discussed thus far belong to a unit which is attached to the top plate of the vacuum housing. Electrical leads from the nulling signal pickup coils and the speaker drive coil are soldered to vacuum tight feed-throughs on the top plate. Three support flanges are bolted to the top of the top plate. A heavy cylindrical brass vacuum housing for the vibrator assembly fits around the assembly and is held to the top plate with screws. A 10 cm diameter rubber O-ring and silicon grease insure a vacuum seal at the top. A 1.6 cm diameter pumping port with an O-ring valve is soldered into a side wall of the housing. A thermocouple vacuum gauge and a needle valve are ported into the housing opposite the pumping port to allow monitoring and control of exchange gas pressure in the specimen environment.

The vibration transmittance rod discussed above protrudes 1.3 cm through a hole in the bottom plate of the vacuum housing. An 84 cm length of glass tubing transmits the speaker vibration to the sample holder (Section D, Chapter II). This tubing, with inside diameter 0.39 cm and outside diameter 0.59 cm, is chosen for its straightness, low mass, and low thermal conductivity. An aluminum coupling was machined to slide 3.8 cm into the glass tubing at the top and is held by a black wax which is easily loosened with the application of low heat. The other end of the coupling fits around the protruding transmittance rod and is held with three small Allen set screws. A hole is drilled through the coupling to insure that the interior of the glass tubing can be evacuated. A length of brass tubing is soldered to a flange

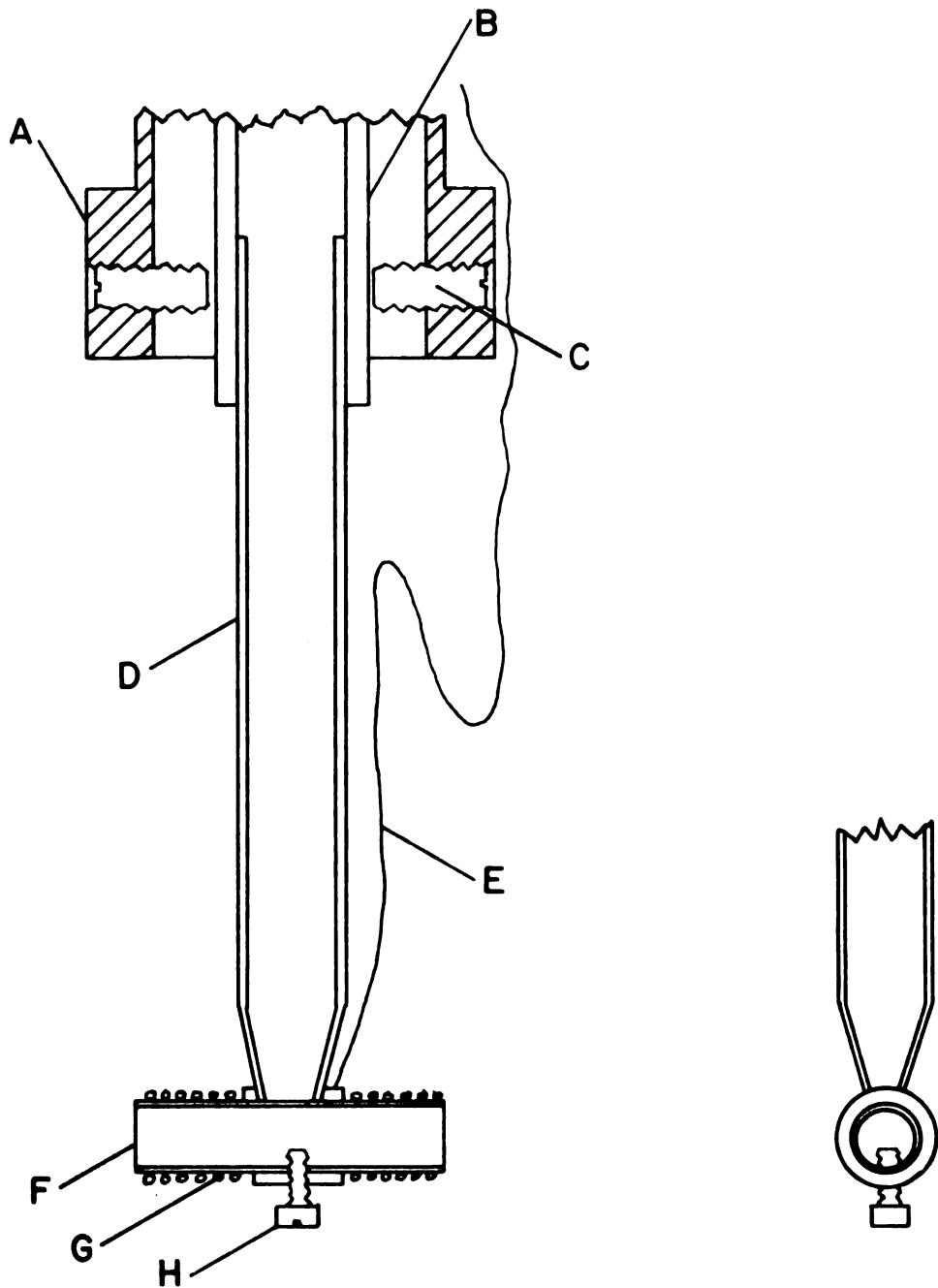
which is held with screws to the bottom surface of the vacuum housing with an O-ring cushion. The brass tubing serves as a housing and guide for the glass drive tubing. Its inside diameter is 1.1 cm, the outside diameter is 1.27 cm, and the length is such that when it is secured at the top to the vacuum housing, 2.4 mm of glass rod clear the lower end of the tubing. Three teflon set screws are spaced 120° apart near the bottom of the brass tube, and they center and guide the glass drive rod within the tube. The O-ring cushion between the brass tube support flange and the vacuum housing allows one to adjust the position of the brass guide tube vertically so that the glass drive tubing and the guide tubing are coaxial, and binding of the glass tube is avoided. Several holes are drilled through the brass tube support flange inside the cushion O-ring to transmit the vacuum from the vibrator housing to the specimen environment. A larger flange with two O-ring quick couples is positioned and centered around the brass guide tube support flange. It also is held by screws to the bottom plate of the vibrator housing around a rubber O-ring. (For more details on the purpose of this flange, see Section H, Chapter II.)

D. The Sample Holder

The purpose of the sample holder on the VSM is to secure the sample in a fixed orientation relative to the detection coils while directly transmitting sinusoidal mechanical vibration to the sample. There are three overriding considerations in the design of the holder: convenience, magnetic properties, and thermal properties. It should be a quick and simple operation to change a specimen. This not only saves

time, but reduces the possibility of physically disturbing the position or delicate wiring of the holder. This important point will be discussed in more detail in Section G, Chapter II. Since the holder and its support are undergoing an identical vibration as the specimen, and since the holder is as near the signal detection coils as the sample, any magnetization in the holder assembly will contribute a signal coherent with the specimen signal. Obviously, one wants every part of the sample assembly to have weak, temperature independent magnetic properties to prevent the masking of weak magnetic effects in the sample. In this regard, it is clearly advantageous to minimize the amount of material used for the holder assembly. Finally, the holder ought to have high thermal conductivity to insure a uniform specimen temperature, but a low heat capacity to reduce thermal inertia during heating or cooling.

To conform as closely as possible with the above considerations, we have used brass for the holder shown in Figure II-3. The specimen cavity is formed by a cylindrical tube with inside diameter 2.80 mm and length 1.27 cm. A short brass support tube, tapered at the lower end, joins the specimen cavity perpendicular to its axis. The joint consists of an 0-80 filister brass screw, the head of which is soldered into the tapered support tube, and mating 0-80 threads tapped into the wall of the specimen cavity. The support tube inserts about 2.5 cm into the glass drive rod and is bonded with a 1:1 mixture of GE 7031 varnish and toluene-alcohol (1:1) (hereafter called GE varnish). A small 0-80 set screw is threaded into the underside of the specimen cavity. Hence, a specimen can be easily removed or mounted just by turning a set screw before or after sliding the specimen through the



A BRASS GUIDE TUBE B GLASS DRIVE ROD
C TEFLON GUIDE SCREWS D BRASS EXTENSION
TUBE E ELECTRICAL LEADS F HOLDER
G DUMMY COIL AND THERMOMETER H SET SCREW

Figure II-3. Sample holder.

cylinder. It should be noted that special care has been taken in all phases of construction and in handling of the holder so as not to contaminate it unnecessarily with potentially magnetic impurities.

The outer surface of the specimen cavity was tightly wound with 55 turns of #36 Belden Nyclad insulated copper wire and this coil was cemented in place with GE varnish. This serves as a specimen nulling coil or as a dummy specimen when a direct current is passed in the coil. A platinum resistance thermometer is formed by a 16 turn bifilar winding of 2 mil Pt wire (Sigmund Cohn Corp.). The thermometer has a resistance of 12 ohms at $T = 295$ Kelvin (K). (See Section H, Chapter II for more details.) The thermometer, dummy coil, and holder are electrically insulated from each other, but are in intimate thermal contact. Current and potential leads (#36 Belden Nyclad) are soldered to the ends of the Pt wire and cemented into a multilayered coating of GE varnish over the specimen cavity tube. The six electrical leads from the holder are twisted pairwise and secured by taping along the outside of the brass guide tube up to the quick couple flange just below the vibrator housing. Care is taken to position the leads with sufficient slack between the holder and the brass guide tube so that any restraint on the vibration is avoided, even at low temperatures.

E. Signal Detection and Processing

In Figure II-4 a block diagram of the electronic system associated with the VSM is shown. A 33 Hz oscillator supplies a 4 watt audio frequency power amplifier which drives the sample vibrator speaker coil. As the drive rod and sample vibrate in phase, the magnetized sample

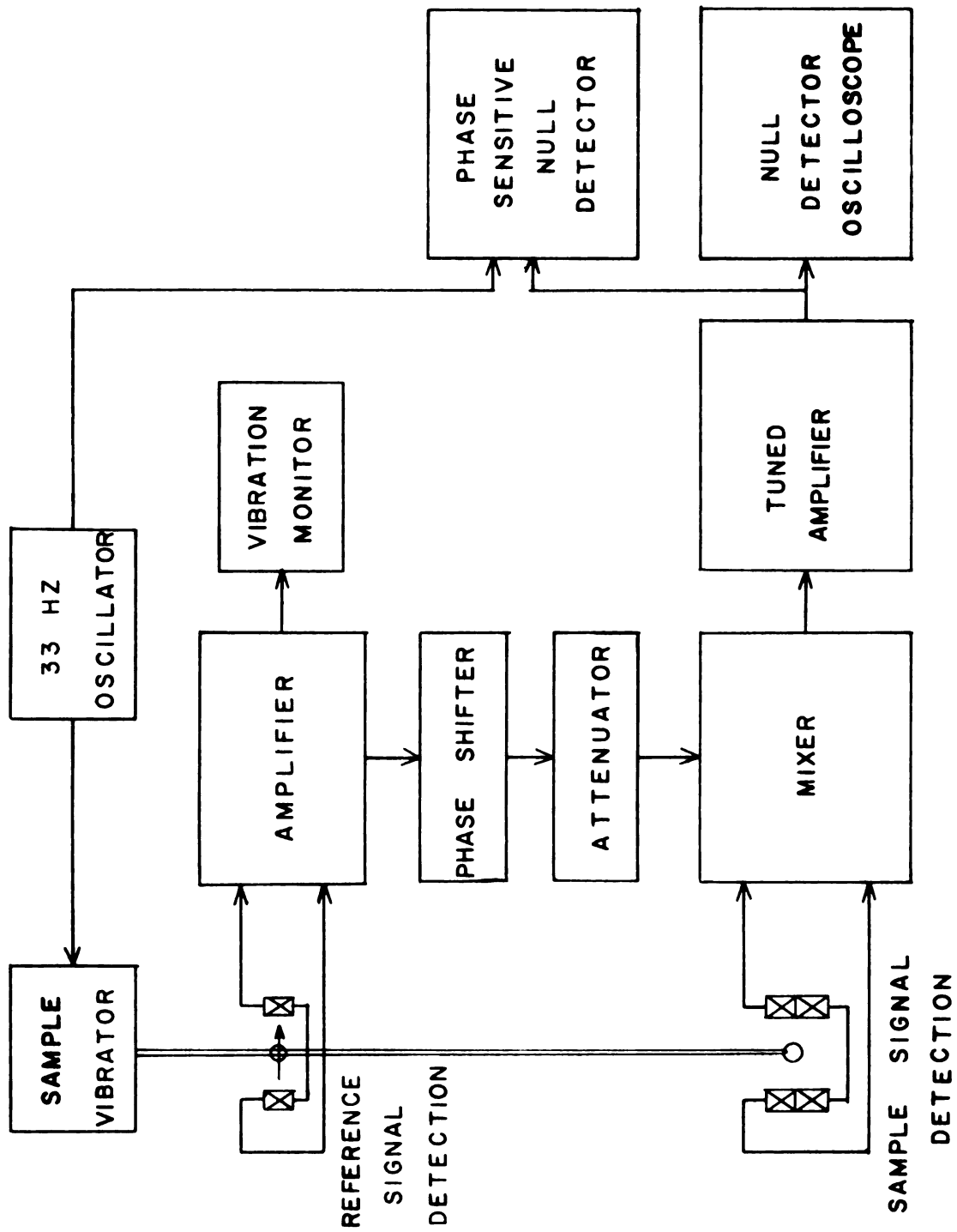


Figure II-4. Block diagram of electronics.

and the permanent magnet in the vibrator housing produce a pair of coherent electrical signals in their respective detection coil arrays. The latter signal is the nulling signal, and it first is amplified and then controllably phase shifted. Next it enters a variable attenuator after which it is added in the mixer directly to the signal produced by the specimen. The sum of the two signals is fed to a high gain ($A \approx 10^6$), sharply tuned preamplifier, the output of which enters a phase-lock amplifier and a null detector oscilloscope. The phase shifter in the nulling circuit is adjusted so that the two signals are 180° out of phase, and the variable attenuator is set to produce a null reading at the phase-lock amplifier. Therefore, at null, the attenuator setting is proportional to the magnetic moment of the sample, and is independent of vibration amplitude, frequency, or the characteristics of the electronics beyond the mixer.

The nulling signal as produced at typical vibration amplitudes is of the order of tenths of millivolts with a signal-to-noise ratio of greater than 10^2 . The amplifier which it enters is in two stages. Stage one has a gain of about 10^2 and drives the phase shift and attenuator networks. The signal from stage one is amplified by about 10^2 in stage two and the resultant voltage allows one to monitor the vibration amplitude with a 3 volt full scale a.c. voltmeter. The weakest detectable signals from the sample detection coils is put at approximately $2(10^{-9})$ volts by several independent estimates. Therefore, extraneous signals at this level at the output of the nulling signal attenuator and in the mixer must be avoided if possible. Given the geometry of the sample detection coils used, we judge the limit of electrical sensitivity to be governed by input noise in

the tuned preamplifier.

F. Signal Detection Coils

Several papers have discussed optimum signal detection coil geometries since Foner's original treatment.⁽¹⁶⁾ A closed analytical calculation of $\frac{d\phi}{dt}$ for general specimen geometry and detection coil configuration is not possible, but helpful special cases have been treated and these serve as guideposts. At any rate, one must stay within certain practical constraints in the design of detection coil systems. Of course one wants to produce as much signal with as high a signal-to-noise ratio as possible, but the space for detection coils is limited by the dual requirements of a small magnet gap (high, uniform magnetic field) and sufficient space for a cryostat.

Our earliest instrument tests were conducted with a pair of 4500 turn matched coils. They were wound with Belden #40 T-2 copper wire and had a d.c. resistance of 1020 ohms each. Following Foner, the pair was wired in series (Figure II-5(c)) and positioned as shown in Figure II-5(a) with the coil axes parallel to the direction of specimen vibration and perpendicular to the applied magnetic field. Although this configuration turns out not to be the most sensitive to the changing field of the moving sample,⁽²⁰⁾ it has the distinct advantage of being largely insensitive to applied field fluctuations if the coils are nearly matched. The coils are mounted tightly into a form which is essentially a pair of circular plexiglass plates with threaded expanders around the perimeter. When in place, the circular plates press outward against the 17.8 cm diameter flat pole pieces of the

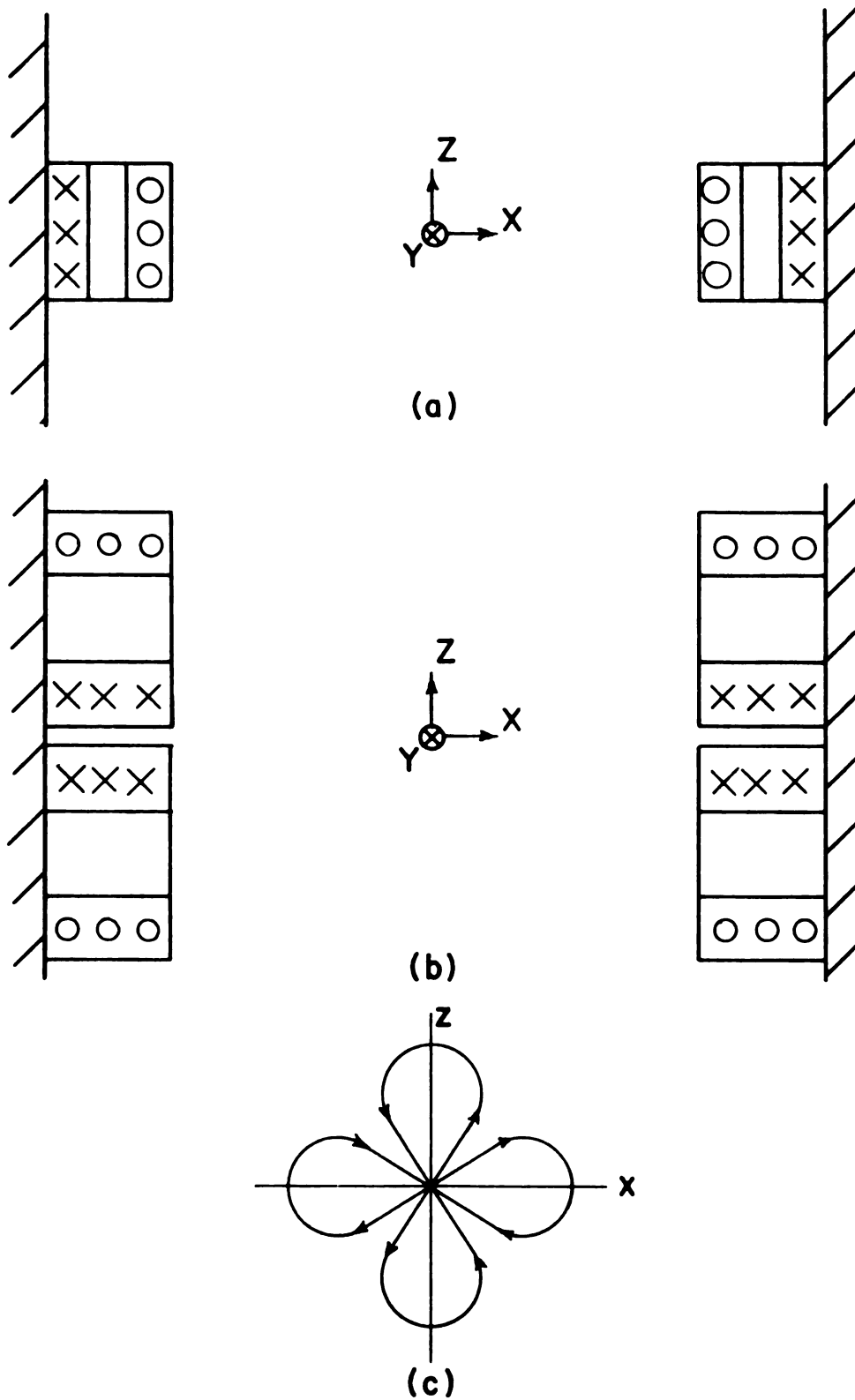


Figure II-5. Detection coil geometry. a) Foner coils. b) Mallinson coil array (with coordinate system and holder position). c) Time varying B field (after Foner).

laboratory magnet, and the coils remain fixed with respect to the magnet. A moment's reflection makes it clear that this condition is essential, because 9000 turn coils do not have to move very much in a few kilogauss (kG) of magnetic field to generate greater than 10^{-8} volts of unwanted signal.

These coils proved to be adequate for our preliminary tests of the instrument's capabilities. The maximum resolution under normal conditions was about 10^{-4} emu of magnetic moment. (This is approximately the moment induced in $3(10^{-2}) \text{ cm}^3$ of copper in a 4 kilogauss applied field.) In an attempt to gain sensitivity we wanted to try the coil array described as "optimum" by Mallinson⁽²⁰⁾ (Figure II-5(b)). Matched coils are much more crucial with this geometry since the coil axes are parallel to the applied field, and thus each coil encloses the maximum possible flux. Four coils are wired in series in the sense shown in Figure II-5(b). Note that each coil adds signal due to the vibrating field of the specimen (Figure II-5(c)), but that each pair on the pole faces of the magnet is insensitive (in theory) to applied field fluctuations. As a first approximation to Mallinson's infinitely extended coils, we used four Miller #986 air core chokes. The hope was that these machine-wound coils would be well matched. Each coil has 1347 turns and a d.c. resistance of about 95 ohms. They are 2.16 cm in diameter and 0.95 cm thick.

In spite of having fewer turns than the Foner coils, the four coil array increased sensitivity by greater than a factor of five. Their low source impedance reduced input noise, and, surprisingly, they seemed to be as insensitive to the applied field as the original pair of coils. When we discovered this, a second four coil array using

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Miller #991 coils was built. Each coil has 2160 turns and a d.c. resistance of 256 ohms. This set proved to be perhaps twice as sensitive as the first Miller coil array, but input noise also increased so that it was not clear that one had increased the signal-to-noise ratio. For this reason, and because coil thickness was a bit too great for our forms, we put aside the second Miller coil array and concentrated our efforts toward calibration of the first.

G. Calibration and Operation

Calibration of the VSM has been discussed extensively elsewhere.^(16,21,22) In addition to covering the basic points, we shall present some considerations not dealt with adequately in the literature. We feel that our particular approach in calibration is the correct one for our instrument.

1. Sample Holder-Detection Coil Positioning

In Figure II-5(b) we show the sample holder-detection coil geometry used in our measurements. It is obvious that recalibration must be performed for every change in the detection coils and/or sample location and geometry because the time variations of the flux coupling in the coils (hence, the voltage induced) will be a sensitive function of these factors. Our approach has been as follows.

The hardened cardboard forms on which the four Miller #986 coils were wound were turned down on a lathe to very nearly the width of the winding itself. Only then could the four coils be mounted into the 1.27 cm wide plexiglass forms which were to house them. The diameter over the winding of the coils is 2.16 cm and the cavity in which they

reside is 2.54 cm in diameter, so it was necessary to center and fix the coils coaxially in each cavity with three small styrofoam pads per coil. In addition, similar pads were placed over the coils before the thin plexiglass caps were tightened over the coil cavities. This padding insures against vibration of the coils with respect to the form and hence the magnet.

The form was then positioned in the gap of the laboratory magnet and aligned such that the plane formed by the coil axes vertically bisects the round pole faces. Several constant magnetic fields were applied to the coil system to determine if it was suitably insensitive to field variations caused by the magnet power supply. After having been satisfied by this test, the coil positions were tightly secured with respect to the magnet by expanding the form as far as possible. Next, the magnet was moved on its track until the sample holder was suspended near the point of inversion symmetry of the four coils. This position of the laboratory magnet was carefully marked such that it could always be accurately reproduced. A plumb line was hung from the VSM support stand (fixed to the wall of the laboratory) and a point on the magnet yoke directly below the plumb was marked. Because the magnet is constrained to translation on its track plus rotation about a vertical axis, this method allows a unique and highly reproducible positioning of the magnet.

Next, the sample holder was carefully positioned so as to be centered on the inversion symmetry point of the detection coils with its cylindrical axis parallel to the coil axes. The long brass guide tube was made parallel to the plumb line. These fine adjustments are made with three support screws threaded through support flanges bolted

to the top of the vibrator housing vacuum can. One is able to rotate, translate, or cant the entire VSM by small amounts as needed to restore the holder to a centered position in the magnet gap, and this is checked before every operation of the instrument.

2. Sample Positioning and Geometry

Once the holder and coils are correctly positioned relative to one another, the only flexibility remaining is sample positioning and geometry. Both are important and one would like to know how the output voltage of the coils varies with certain parameters describing sample position and geometry. Let us discuss the former first. Studies of variation in coil output with sample position are normally presented as "saddle point curves". One produces a permanent magnetic moment in the holder with either a magnetized sample of standard geometry (i.e., for our sample holder, a standard geometry would be a circular cylinder of 1.3 cm length and 2.7 mm in diameter) or a d.c. current in the dummy coil (Section D). The vibrating holder is then displaced along the x, y, and z axes respectively by small amounts and the output voltage measured. Plots of output voltage V_{out} as a function of displacement yield curves symmetric about the origin for symmetric detection coil geometries. At the saddle point $dV_{out}/dx_i = 0$. For a given sample geometry, the nature of the saddle point curves depends wholly on the coil size, shape, and orientation. From the standpoint of reproducibility of measurements, coils with wide saddle points are preferable to those with narrow ones since precise sample positioning is less critical for the former. The width of a saddle point is defined by the displacement allowable to maintain the output voltage within some percentage

of its value at the saddle point. In Figure II-6 we show saddle point curves for our four coil Mallinson array. A study of displacements along the z axis was not performed since sample height is highly reproducible for our VSM, and controlled displacements along z are difficult to effect. It can be seen that ± 2 mm displacements along both the x and y directions introduce deviations of about one percent in V_{out} . This compares favorably with saddle point analyses for other coil systems given elsewhere.^(16,23) It is relatively easy to maintain the holder within ± 1 mm of the center of inversion without painstaking centering measurements before each operation of the instrument.

As alluded to earlier, sample geometry is an important consideration in calibration. However, sample geometry is not important when the sample dimensions are small compared to the separation between sample and detection coils, because then a magnetized sample acts as a dipole.⁽²⁴⁾ In practice, one rarely has this simple situation with the VSM since one wants to use as large a specimen as possible positioned as closely to the detection coils as possible to achieve maximum sensitivity. Therefore, one must calibrate for sample size effects. We have combined the sample geometry calibration tests with the calibration of the voltage divider in the nulling signal network to arrive at self-consistent results. We review in the following subsection a typical calibration test.

3. Calibration Tests-Measurement Procedure

The primary susceptibility standard we use is high purity Al. A specimen of nearly the volume of the sample holder was produced by cold rolling a length of the Al into a rod of octagonal cross-section

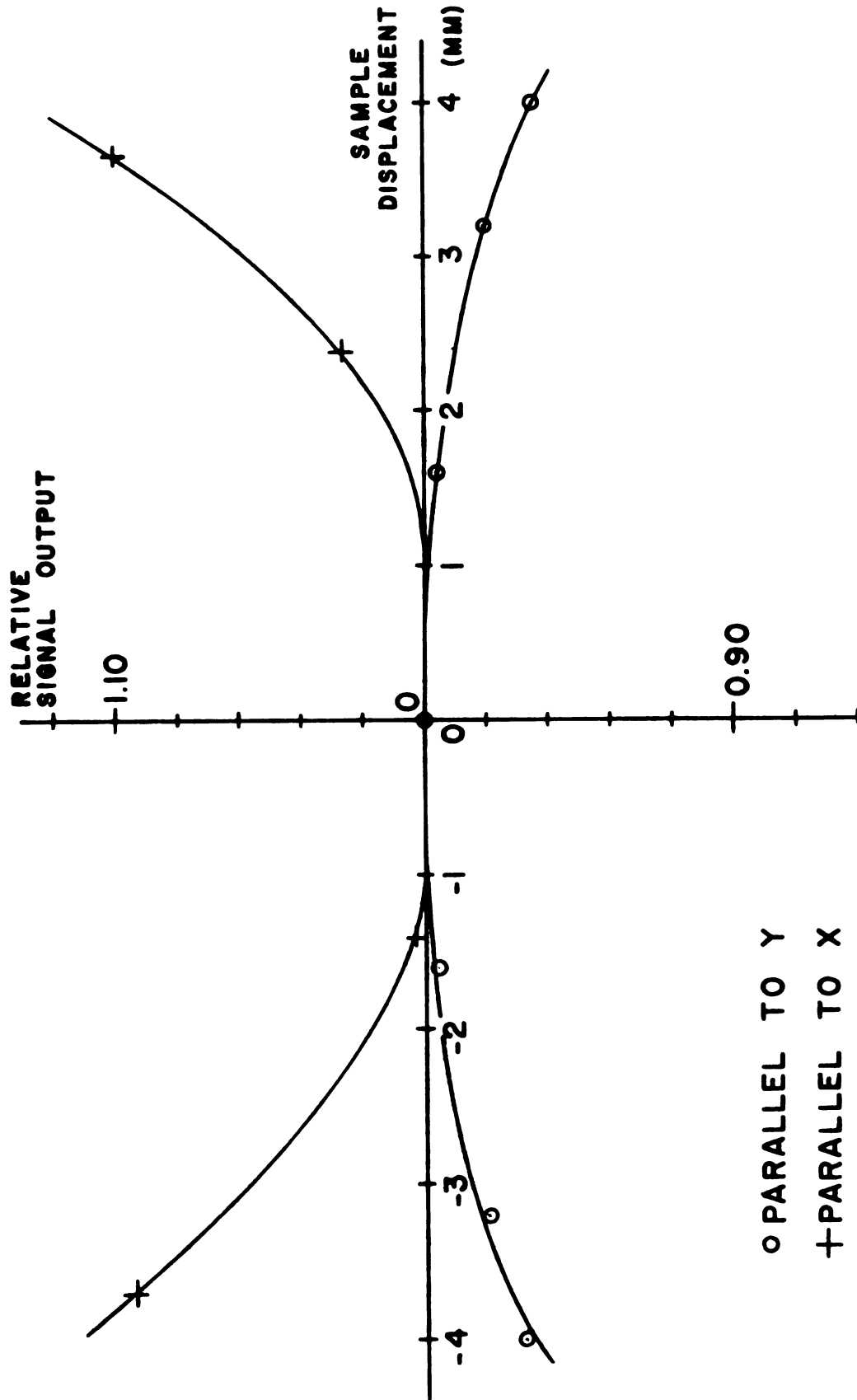


Figure II-6. Saddle point plots.

with a maximum width of the cross-section being 2.66 mm. The rod was then spark cut to a length of 1.33 cm, both end faces being planes nearly perpendicular to the axis of the rod. This specimen was lightly etched to remove possible surface contamination from the rolling and cutting.

We now recount a typical calibration run. The Al specimen is centered and secured in the holder. We vibrate all samples at the same amplitude, one that is as large as feasible with our sample vibrator system. The phase shifter in the nulling signal circuit is tuned while supplying a d.c. current to the dummy coil on the sample holder so as to put the nulling signal 180° out of phase with the sample signal in the mixer. The phase setting of the phase-lock amplifier is adjusted for maximum sensitivity to the signal from the mixer. Then, with the current in the dummy coil off, we null out the signal produced by the Al standard as the applied magnetic field is held at several values from 0 to 4.7 kilogauss. The null is recorded as a setting on a precision ten-turn potentiometer in the nulling signal attenuator. An identical procedure is performed for the empty sample holder. The difference of the null readings at given field values is then proportional to the magnetization of Al at that field. A plot of the null difference versus applied field should be linear for paramagnetic or diamagnetic materials, and the slope is proportional to the susceptibility of a sample. Therefore, using the known susceptibility for Al, we have a correspondence between sample magnetization and the settings on the nulling potentiometer for the particular geometry of the Al sample. We know

$$V_{\text{out}} = \frac{d\Phi}{dt} = |\vec{m}| \omega G \quad (2.8)$$

where $|\vec{m}|$ is the magnitude of the sample dipole moment, ω is the frequency of vibration, and G is a complicated composite geometrical factor for the change in flux in the detection coils as the sample is displaced in one direction. We expect G to be factorable into a detection coil part G_c and a sample geometry part G_s . Therefore

$$V_{\text{out}} = |\vec{m}| \omega G_s G_c = |\vec{M}| V \omega G_s G_c ,$$

$$\text{or} \quad V_{\text{out}} = \chi |\vec{H}| V \omega G_s G_c , \quad (2.9)$$

where we have used $\vec{m} = \vec{M}V$, with V the sample volume and $\vec{M} = \chi \vec{H}$, the definition of volume susceptibility (see Appendix A). Furthermore, $V_{\text{out}} = A (\Delta N)$, where A is a constant and ΔN is the difference in the setting on the nulling potentiometer with and without the sample in the holder. Now A , $|\vec{H}|$, ω , and G_c are fixed constants for any inter-comparison of nulls at a given applied field. Therefore, letting the superscript x represent any specimen whose susceptibility is to be measured, we have

$$\frac{V_{\text{out}}^x}{V_{\text{out}}^{A1}} = \frac{A (\Delta N^x)}{A (\Delta N^{A1})} = \frac{\chi^x |\vec{H}| V^x \omega G_s^x G_c}{\chi^{A1} |\vec{H}| V^{A1} \omega G_s^{A1} G_c} , \quad (2.10)$$

$$\text{or} \quad \chi^x = \chi^{A1} \left[\frac{\Delta N^x}{\Delta N^{A1}} \frac{V^{A1}}{V^x} \frac{G_s^{A1}}{G_s^x} \right] . \quad (2.11)$$

One can obtain the mass or molar susceptibility from this relation by using the definitions of those quantities from Appendix A. To relate

mass or molar susceptibilities, simply replace V^{Al}/V^x by $\frac{\text{mass}^{Al}}{\text{mass}^x}$ or $\frac{\text{mole fraction}^{Al}}{\text{mole fraction}^x}$ respectively. It is clear from the above expression that unless the geometries of the unknown sample and the standard are identical, one needs to have values for G_S^{Al}/G_S^x . It is only in the limit of small specimens (both Al and x) that the dipole approximation holds, and $G_S^{Al}/G_S^x = 1$ regardless of the shapes of the Al and x. For our particular holder, sample dimensions are quite small in two directions (transverse to the holder cylindrical axis), but not in the direction of the sample length. We then expect

$$\frac{G_S^{Al}}{G_S^x} \equiv G_0\left(\frac{\ell^x}{\ell^{Al}}\right), \quad (2.12)$$

where $G_0(\ell^x/\ell^{Al})$ is some smooth function of the sample length ratio which must be determined empirically.

In order to check all of these assertions, we produced a series of high purity tungsten samples of various lengths, cross-sectional areas, and irregular end face geometries which would fit into our sample holder. These were made from a long cylindrical W rod by spark cutting and chemically etching to various desired sizes. Each specimen was centered in the holder, and nulls were achieved for several applied fields for each. From the plots of null setting versus applied field (linear in every case), a null value at some chosen field was taken. We calculated the molar susceptibility of each sample using

$$\chi_M^W = \frac{\Delta N^W}{MF^W} \left[\frac{\chi_M^{Al} \cdot MF^{Al}}{\Delta N^{Al}} \right], \quad (2.13)$$

where $MF = \text{mole fraction} = \frac{\text{sample mass}}{\text{sample molar mass}}$, and the bracketed quantity is a constant determined from the Al calibration. Note that

we have effectively taken $G_S^{Al}/G_S^W = 1$ for every sample, which cannot be correct. In Figure II-7 we show $\chi_M^W/\chi_{M,0}^W$ plotted against ℓ^W/ℓ^{Al} , where $\chi_{M,0}^W$ is the accepted value for the molar susceptibility of W. For W samples with irregular end faces, an average length has been used.

We find that the plot is linear with a small positive slope, and that the fit passes through $\chi_M^W/\chi_{M,0}^W = 1$ at $\ell^W/\ell^{Al} = 1$. This single plot is a strong indication of the self-consistency of the above analysis. Although samples of various cross-section and irregular end face geometry were used, the dominant geometrical parameter is the length, for only in that dimension is there appreciable departure from the dipole approximation. From this plot, the functional form of $G_0(\ell^X/\ell^{Al})$ is deduced to be $G_0 = [0.29 \frac{\ell^X}{\ell^{Al}} + 0.71]^{-1}$ for $0.5 \leq \frac{\ell^X}{\ell^{Al}} \leq 1.5$. Furthermore, the reliability of the Al standard is increased by this test since a correct susceptibility result for tungsten emerges. The Al standard has been further successfully cross-checked against Pd, CuPd, Cu₃Au, AuGa₂ and other pure samples.

H. The Cryostat and Temperature Control

As mentioned earlier, one of the attractive features of the VSM is its adaptability for temperature dependence studies of susceptibility. Such studies are essential for understanding bulk magnetic behavior as discussed in Chapter I.

At the conclusion of Section C, Chapter II, a flange with two vacuum quick couples soldered to it was briefly described. Its primary purpose is to accommodate a thin-wall (20 mil) stainless steel vacuum tube of length 85.6 cm and outside diameter 2.54 cm. This tube is

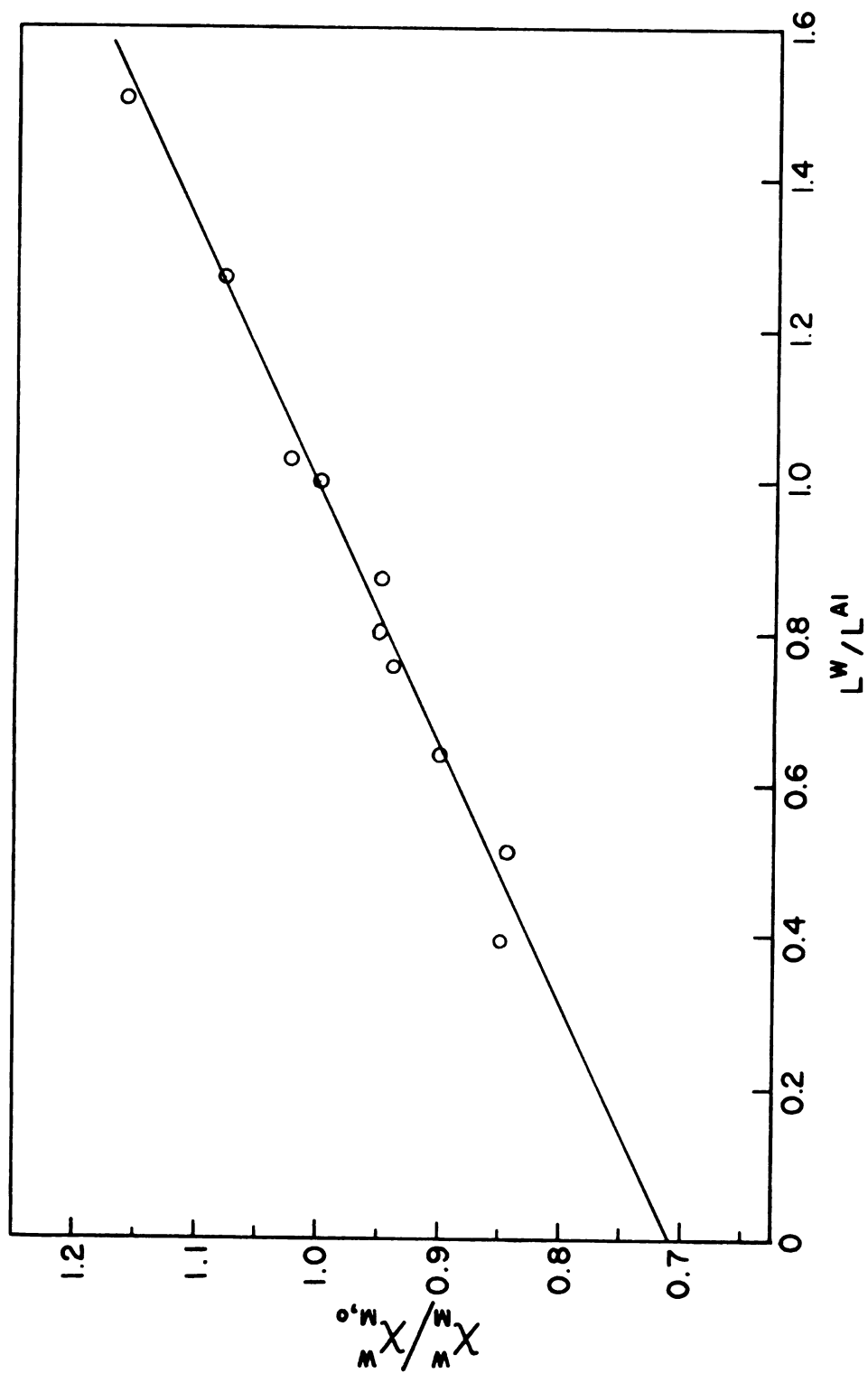


Figure II-7. $X_M^W / X_{M,0}^W$ vs. L^W / L^A .

sealed off with a brass plug at the lower end, and has a heavy brass restraining collar soldered around it 2.5 cm from the top of the tube. This tube slides up around the sample holder and brass guide tube, and mates with a 2.54 cm inside diameter vacuum quick couple on the aforementioned flange at the base of the vibrator vacuum housing. The restraining collar on the tube limits its penetration into the quick couple when a partial vacuum exists inside the tube. The tube serves a dual purpose as retainer for the partial vacuum in the space around the specimen and as a barrier against the cryogenic liquid into which it is immersed. This particular tubing was chosen for this purpose because of its strength, low thermal conductivity, and low magnetic permeability. This latter characteristic insures that the externally applied magnetic field or the field produced by the sample is not shielded by tubing.⁽²⁴⁾

The vacuum tube is aligned coaxially with the brass guide tube by pumping out the system with a mechanical forepump so that the vacuum tube restraining collar is held tightly to the quick couple. The laboratory magnet is then rolled into position and the vacuum tube is centered between the detection coils by shimming the contact between the restraining collar and the quick couple. We find that once the shims are positioned, subsequent readjustment is unnecessary. This centering is essential so that the vibrating sample holder and the vacuum tube surrounding it do not make physical contact, for any vibration transmitted to the vacuum tube results in coherent background signal in the detection coils reflecting the magnetic properties of the stainless steel tube. Even when care is taken to eliminate direct physical contact, we found that the recoil vibration of the vibrator

housing, small as it is for the massive housing, couples directly to the vacuum tube. This produced unwanted background signal which we were able to reduce only by loading lead bricks onto the top of the vibrator housing to increase the mass of the recoiling unit. We believe that the appreciable recoil we find results from the heavier than necessary drive transmittance rod with ball bearings that is used in the vibrator assembly. We are in the process of correcting this deficiency in a subsequent design.

The electrical leads from the dummy coil and thermometer on the holder leave the vacuum system via a small vacuum quick couple with a 1.6 mm diameter hole which is soldered into the same flange which supports the vacuum tube quick couple (see Figure II-1). The leads are fed through a stainless steel capillary tube and sealed in the tube with molten black wax. The tube seals in the quick couple with a rubber O-ring.

The vacuum system can be pumped out to a pressure of several microns of Hg with the mechanical forepump and this is sufficient for our purposes. The heat exchange gas can be controllably admitted to the sample region with a needle valve mounted on a port in the vibrator housing. A thermocouple pressure gauge monitors the pressure in the vacuum chamber.

We employ a custom Kontes-Martin Dewar (Figure II-1) for low temperature experiments. The Dewar fits around the vacuum tube and is supported by a padded flange which bolts to a plywood platform supported by the same structure which holds the VSM. The Dewar is lifted into position and secured with the laboratory magnet rolled away. When the magnet is returned to its proper position under the VSM, the tail

of the Dewar is centered between the detection coils. A clamping device mounted on the magnet yoke is used to hold the Dewar securely with respect to the magnet. This insures that the Dewar does not touch the detection coil form as the cryogenic liquid boils in the Dewar. There is approximately 1.5 mm clearance between the coils and either side of the Dewar tail. The Dewar tail cross-section is shown in Figure II-8. The unfilled space along the longer diameter of the tail serves as a reservoir for cryogenic liquid.

A typical temperature dependence measurement over the temperature range 78 K to 300 K is conducted as follows. The sample region is pumped out to the capability of the forepump. Liquid nitrogen is transferred into the open top of the Dewar to a height of 30 to 36 cm (about one liter). When the boiling ceases after about 2 minutes, the temperature of the sample has fallen approximately 10 K below room temperature. With a vacuum of several microns of Hg, the cooling rate decreases continually as the sample temperature falls. One adjusts for a null condition as the temperature slowly drops. The applied magnetic field and the sample vibration amplitude are held constant throughout. The rate of cooling is controlled by adding He exchange gas. Of course, a convenient cooling rate depends upon the magnitude of the temperature dependence of the specimen susceptibility. A cool down from 300 K to 78 K usually can be comfortably completed in about 60 minutes. The heat flow into the liquid nitrogen bath is reduced by the low thermal conductivity of the vacuum tube. The glass drive tube helps to thermally isolate the sample holder from the warmer environment above the holder.

The sample temperature is monitored by measuring the potential drop across a Pt wire for a constant known current in the wire. As

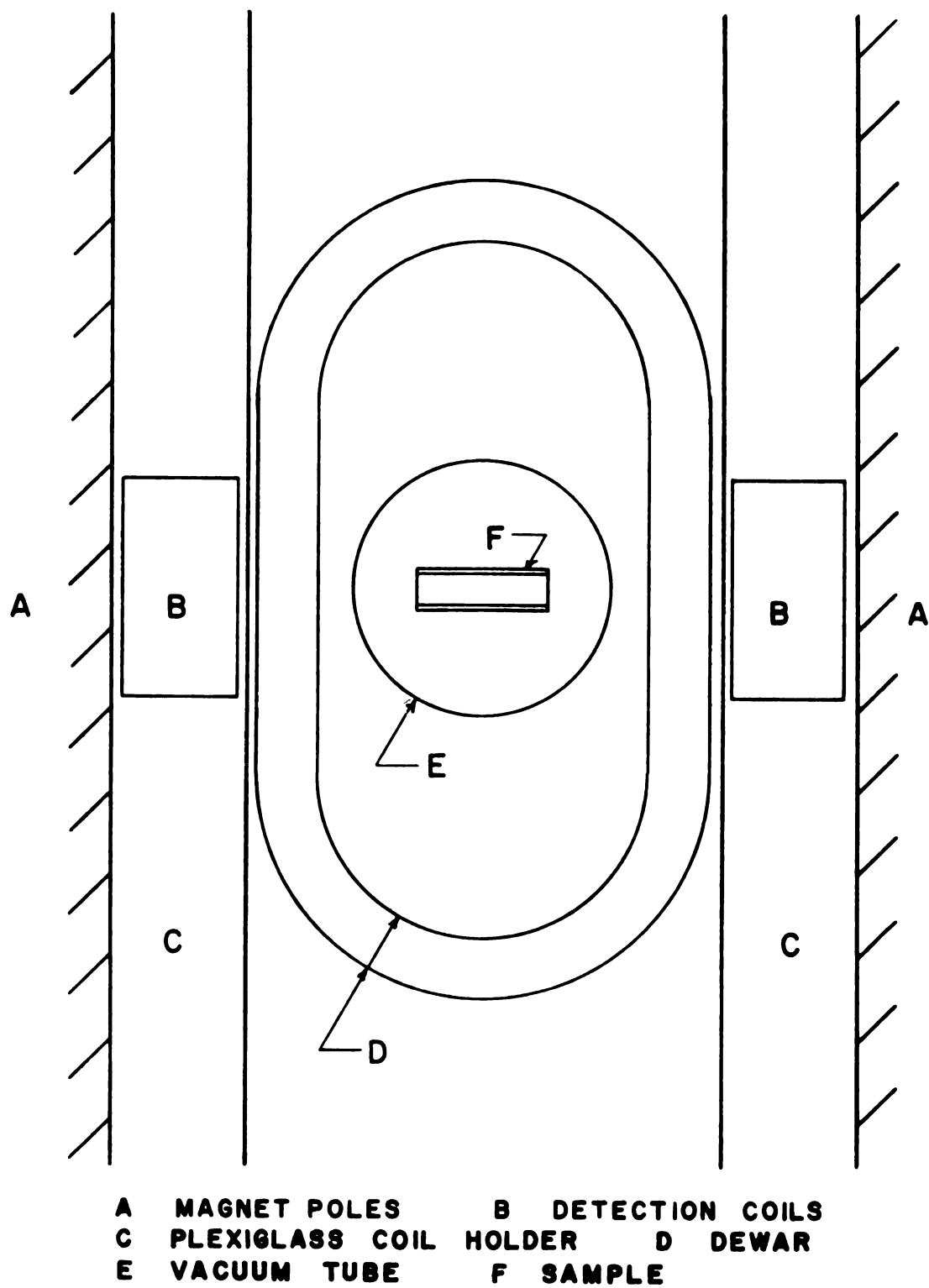


Figure II-8. Top cross-sectional view of magnet gap with cryostat.

discussed in Section D of this chapter, the Pt wire is in close thermal contact with the holder which surrounds the sample. This feature is unique to this magnetometer since the temperature of a specimen is conventionally monitored at some location whose thermal communication with the specimen is via exchange gas. (17,25,26)

The platinum thermometer was calibrated against the measured temperature dependence of a very pure Pt wire carried out previously in this laboratory. The calculated temperature dependence for our thermometer was made to fit experimentally established resistances at liquid nitrogen temperature, the ice point, and at room temperature. As a cross-check on our temperature scale, we have successfully reproduced the temperature dependence of the susceptibility of pure Pd and Al between 78 K and 300 K. Of course, the measured weak temperature dependence of the sample holder must be subtracted out in all measurements.

III. SELECTED TOPICS ON MAGNETIC INTERACTIONS IN ALLOYS

A. Thoughts on the Relationship of Local Moment Theory and Experiment

In Chapter I we alluded to the theoretical difficulties inherent in even the simplest magnetic impurity problem imaginable, the single isolated impurity in an otherwise pure simple metallic host. As involved as the isolated impurity problem clearly is, it is just the beginning of one approach toward an understanding of cooperative magnetic phenomena as previously discussed. In any real alloy one will surely have impurity-impurity interactions present to some extent. Of all the experimental work done in the area of dilute alloys, only a small fraction has been performed on systems approaching the dilute impurity limit. (The experimental dilute limit corresponds to impurity concentrations of the order of 10 to a few hundred parts per million.) Only in these dilute limit cases could one argue that isolated impurity effects dominate impurity-impurity interactions. These difficult experiments have certainly been essential to the development of our present understanding of moment formation in metals, but the point we make here is that impurity-impurity effects must also be understood if we are to proceed in the approach of gradually building up the cooperative magnetic state out of known interactions. But as soon as one admits the possibility of interactions among impurities, the problem for the theorist has been made

more complex than before.⁽²⁷⁾ The experimentalist, in moving away from the dilute limit, has unburdened himself of two very significant problems, but has acquired new ones which appear potentially more troublesome. This being a treatise on experimental work, let us confine our attention to the concerns of the latter worker.

When working in the dilute limit of impurity concentration and attempting to measure effects due to the presence of those impurities, it is apparent that one requires the ultimate sensitivity in those measurements that current technology can provide. This is what one would expect when only 10^{-5} to 10^{-4} of the constituent atoms of the sample are responsible for the effect under measurement. Of course, it is not impossible that effects might be large in this case, but in general it is not expected. The second significant problem connected with work in the dilute limit is the metallurgical-technological one of requiring extremely pure materials. Interestingly, both of these problems are strongly coupled with financial factors, cost scaling with increasing sensitivity and/or purity of materials.

As one proceeds from the dilute limit, one expects the above problems to diminish. The new troubles might be classified as metallurgical and interpretational. The metallurgical problems are largely those of solubility. There are countless examples of binary alloy systems in which a solute will not dissolve and remain in true solid solution beyond some small solubility limit. With the degeneration of a solid solution comes the formation of solute clusters and the breakdown of the fundamental structure one hopes to study. Metallurgical problems present insurmountable barriers for systematic concentration dependence studies in many systems of potential interest. Another

metallurgical consideration that has bothered some workers follows from the simple observation that no two alloys of the same composition are exactly alike. The probability of producing two identical systems of 10^{23} particles each in a few attempts is vanishingly small. This unsettling thought can usually be put to rest by claiming that values of bulk properties which result from an average over 10^{23} atoms have an overwhelmingly high probability of lying within a factor of $N^{-1/2} = 10^{-23/2}$ of some most probable value. This means that if one strives to produce homogeneous random alloys, then there is negligible probability of making an alloy with a bulk property value noticeably removed from a mean value. The point is that one should be quite certain he is producing homogeneous random alloys if a systematic concentration dependence study is contemplated.

The interpretational problem is obvious. If impurity-impurity interactions are superimposed on impurity-host effects, the separation of the two may not be clear cut. The situation is generally more complicated than a simple superposition of effects. As the impurity concentration becomes appreciable, the host itself is altered, so the impurity-host interaction is perturbed. Ideally, one wants to seek out experimental methods which suggest that some degree of separability of effects might be possible.

As pointed out in Chapter I, the specific motivation for the work described in this thesis followed directly from a desire to investigate the influence of the local crystalline environment on magnetic interactions and to incorporate into the investigation a possible method of distinguishing between competing interaction effects in a local moment system. With regard to the former, Jaccarino and Walker⁽²⁸⁾ in 1965

offered an interesting explanation for the variation with c (atomic fraction expressed as a decimal in formulae or as a percent in the text) of the local moment in Fe impurity sites (1 atomic percent) in the non-magnetic binary alloy hosts $\text{Nb}_{(1-c)}\text{Mo}_c$ and $\text{Rh}_{(1-c)}\text{Pd}_c$. They suggested that within the framework of the Anderson model, one could explain the development of Fe moments as c increases on the basis of the local environment of an impurity rather than some average character of the host. In fact, they proposed that moment formation might be sudden as some local condition is satisfied, and not a gradual buildup as the average properties of the host change. From bulk susceptibility measurements it is impossible to distinguish between a probabilistic occurrence of Fe sites fulfilling the magnet moment existence conditions as the host composition is changed and the gradual development of a moment on all sites at a rate determined by the average properties of the whole host crystal. These workers cited direct evidence for their model in that the NMR resonance on Co^{59} in $\text{Rh}_{(1-c)}\text{Pd}_c$ indicates that some Co sites remain unmagnetized up to at least $c = 12.5$ atomic percent, while bulk measurements indicate that the average moment per Co atom is near 50% of its final value at that concentration. Further experimental support for this model has been given recently by Brog and Jones.⁽²⁹⁾

A search for local environment effects indicates the necessity of using binary hosts. Studying all possible interactions suggests working away from the dilute impurity concentration limit. In order to suppress as much as possible the potential problem of the uniqueness of each alloy produced (as outlined above), we sought host systems with an internal degree of freedom not present in an ordinary binary alloy, namely the possibility

of turning on or off a long range atomic order on some fixed lattice of atomic sites. This single feature seemed very attractive in that it ought to bear on each of the considerations discussed above. Consider magnetic impurity atoms which dissolve in the order-disorder host matrix by substituting randomly for the two host constituents. It would seem that some average over local environments at impurity sites would be different for the ordered and disordered hosts and this might be reflected in the magnitude of the average moment developed. (This is one measure of the impurity-host interactions.) Furthermore, it would seem plausible that impurity-impurity interactions might differ with the changing character of the host medium. For example, a disordered host would increase the scattering of conduction electrons carrying spin polarization information between local moment sites and effectively reduce mediated impurity-impurity interactions. Finally, the production of an order-disorder transition in a single alloy avoids the uncertainties involved in drawing comparisons between distinctly different alloys.

B. The Paramagnetic Curie Point Θ and Magnetic Interactions

It has been known for a long time that many pure metals and alloys with atoms which sustain permanent magnetic moments display a Curie-Weiss type of paramagnetic susceptibility $\chi = \frac{C}{T - \Theta}$ over some temperature range. In fact such behavior is the usual experimental criterion for the existence of well-defined local moments. This generalization of the familiar Curie law $\chi = \frac{C}{T}$ was introduced by P. Weiss⁽³⁰⁾ in 1907. The additional parameter came about originally as the result of relating

several of the properties of ferromagnets to the presumed existence of a strong internal molecular field (originally called the Weiss field, now referred to as the exchange field⁽¹⁵⁾ in reference to the quantum mechanical electrostatic forces believed to be responsible for strong spin correlations in matter). This exchange field was postulated to be proportional to the magnetization, $\vec{H}_{ex} = \lambda \vec{M}$. With this isotropic internal molecular field, it is easy to derive the Curie-Weiss law and find the conditions under which it is expected to hold. For a system of N magnetically free atoms or ions per unit volume with angular momentum quantum number J in an externally applied magnetic field, the magnetization is given⁽⁵⁾ by

$$M = Ng J \mu_B B_J(x) , \quad x \equiv \frac{gJ\mu_B H}{k_B T} , \quad (3.1)$$

where g is the Landé g -factor, μ_B is the Bohr magneton, k_B is the Boltzmann constant, and $B_J(x)$ is the Brillouin function defined as

$$B_J(x) = \frac{2J+1}{2J} \operatorname{ctnh} \left(\frac{(2J+1)x}{2J} \right) - \frac{1}{2J} \operatorname{ctnh} \left(\frac{x}{2J} \right) . \quad (3.2)$$

Suppose we let $H \rightarrow H + H_{ex} = H + \lambda M$. If $x = gJ\mu_B(H+\lambda M)/k_B T \ll 1$, we can approximate $B_J(x)$ by using the series expansion

$$\operatorname{ctnh} u = \frac{1}{u} + \frac{u}{3} - \frac{u^3}{45} + \dots$$

Then,

$$\begin{aligned} \lim_{x \rightarrow 0} B_J(x) &= \frac{2J+1}{2J} \left[\frac{2J}{(2J+1)x} + \frac{(2J+1)x}{3(2J)} \right] - \frac{1}{2J} \left[\frac{2J}{x} + \frac{x}{3(2J)} \right] \\ \lim_{x \rightarrow 0} B_J(x) &= \frac{(2J+1)^2 x}{3(2J)^2} - \frac{x}{3(2J)^2} = \frac{x}{3(2J)^2} [(2J)^2 + 2(2J) + 1 - 1] \end{aligned}$$

$$\lim_{x \rightarrow 0} B_J(x) = \frac{x}{3(2J)} (2J + 2) = \frac{x}{3J} (J + 1) . \quad (3.3)$$

Substituting back into Equation (3.1),

$$\begin{aligned} M &= Ng\mu_B \frac{J+1}{3J} \left[\frac{gJ\mu_B(H+\lambda M)}{k_B T} \right] \\ M &= \frac{Ng^2 J(J+1)\mu_B^2}{3k_B T} (H+\lambda M) \equiv \frac{C}{T} (H+\lambda M) . \end{aligned} \quad (3.4)$$

Solving for M,

$$\begin{aligned} M(1 - \frac{C}{T} \lambda) &= \frac{C}{T} H \\ M &= \frac{C}{T(1 - \frac{C}{T} \lambda)} H , \end{aligned}$$

and $M \equiv \chi H$ implies that the volume susceptibility

$$\chi = \frac{C}{T - C\lambda} \equiv \frac{C}{T - \Theta} , \quad (3.5)$$

where the Curie constant

$$C = \frac{Ng^2 J(J+1)\mu_B^2}{3k_B} \equiv \frac{N(p\mu_B)^2}{3k_B} . \quad (3.6)$$

Here $p \equiv g[J(J+1)]^{1/2}$ is the effective Bohr magneton number. $\Theta \equiv C\lambda$ is the paramagnetic Curie point.

We see from this derivation that the Curie-Weiss law applies to magnetically free magnetic moments in a uniform magnetic field $H + \lambda M$ when $\frac{gJ\mu_B(H+\lambda M)}{k_B T} \ll 1$. The presence of the molecular field λM is associated with a spatially uniform effective field at some moment site which arises from the magnetization due to all other magnetic entities of the specimen, and therefore corresponds to an effective interaction

among them. Thus, $\Theta = C\lambda$ is traditionally related to any interaction which can be phenomenologically associated with the production of an effective molecular field at a magnetic moment site. In this sense, then, one might associate a non-zero Θ in a metallic system with interactions between a localized moment and other such moments, or between localized moments and the conduction electrons. The extreme example of the former case is $\Theta \approx T_{\text{Curie}}$ or $\Theta \approx T_{\text{Néel}}$ for systems displaying spontaneous magnetic order, and the (large) interaction is assigned to exchange interactions between closely packed localized moments. The latter case is demonstrated by the non-zero Θ values found experimentally for extremely dilute local moment systems such as AuFe, CuFe, and CuMn,^(18,31,32) where the probability of appreciable direct or even indirect impurity-impurity interactions is extremely low. Whether or not the appropriate interactions in this latter case can be cast into a classical effective field will be discussed below.

Before proceeding too far with such an obviously oversimplified theory as an effective field model, let us make clear the context in which this presentation is made. It should be emphasized that the Curie-Weiss law is an experimental fact for many dilute and concentrated magnetic systems over wide temperature ranges. In cases where it is not realized experimentally, it should not be invoked in analysis under any circumstances. But when it holds experimentally, the connection of real interactions with effective fields is justifiable as a first analysis of systematic trends provided one is aware of the shortcomings of such a model.^(33,34)

Dellby⁽³⁵⁾ has recently extended the effective field model by explicitly including several magnetic interactions between electronic

states in a metallic alloy. His particular concern was the behavior of alloy systems with exchange enhanced hosts, but some of his results are presumably applicable when enhancement is absent. Without giving the details of Dellby's derivation, let us define the relevant quantities which appear in his main result. Then we shall present his result and consider the explicit interactions introduced into the Curie-Weiss law.

Dellby considers the following electronic states in his treatment: conduction electrons (s), non-conduction electrons in unfilled bands associated with a base (host) matrix (b), and impurity resonant bound electron (i). The label "dia" refers to diamagnetism of all states. Five molecular field coupling constants (c.c.) corresponding to the role played by λ in $H_{ex} = \lambda M$ are given as follows:

- c.c. between s and b or s and i states (α),
- c.c. between b and i states (β),
- c.c. between s states among themselves (γ)
- c.c. between i states of different impurity atoms (δ), and
- c.c. between b states associated with different base atoms (ϵ).

The susceptibilities corrected for interactions within the same state are labeled χ_s , χ_b , or χ_i , and uncorrected susceptibilities have the superscript (o), for example, χ_i^o . The relation between corrected and uncorrected susceptibilities is (for the s state) $\chi_s = \chi_s^o [1 - \gamma \chi_s^o]^{-1}$.

Dellby calculates an expression for the total alloy susceptibility (χ_{meas}) and for the pure host ($\chi_{base} \equiv [\chi_{meas}]_{\chi_i=0}$). He takes the difference of these two quantities (the usual approach for isolating impurity effects) and assumes a Curie law for non-interacting impurities, $\chi_i^o = \frac{C}{T}$, where C is the Curie constant as defined in Equation (3.6). His

result is

$$\Delta\chi \equiv \chi_{\text{meas}} - \chi_{\text{base}} = \frac{C[1 + \alpha\chi_s + (\frac{\alpha^2\chi_s + \beta}{1 + \alpha\chi_s})(\chi_{\text{base}} - \chi_s - \chi_{\text{dia}})]^2}{T - C[\delta + \alpha^2\chi_s + (\frac{\alpha^2\chi_s + \beta}{1 + \alpha\chi_s})^2(\chi_{\text{base}} - \chi_s - \chi_{\text{dia}})]} \quad (3.7)$$

This has the form of the Curie-Weiss law where the bracketed quantity in the numerator is an enhancement factor for p , the effective Bohr magneton number, and the bracketed quantity in the denominator is an explicit expression for λ in Dellby's particular alloy system.

Let us consider two simple cases to check the reasonableness of the expression for $\Delta\chi$ and look at Dellby's interpretation of some of the terms. First, suppose that the host material is an insulator (α and χ_s are zero). This implies that no enhancement exists ($\chi_{\text{base}} = \chi_s + \chi_{\text{dia}}$). The trivial result is

$$\Delta\chi = \frac{C}{T - C\delta}, \quad (3.8)$$

a very simple Curie-Weiss law with an unenhanced p and only a direct interaction between impurity moments. For an unenhanced metallic host, the impurity susceptibility from Equation (3.7) is

$$\Delta\chi = \frac{C(1 + \alpha\chi_s)^2}{T - C(\delta + \alpha^2\chi_s)} \quad (3.9)$$

Dellby interprets the p enhancement factor $(1 + \alpha\chi_s)$ as due to polarization of the conduction electrons near an impurity site which in effect dresses the impurity moment. Exchange scattering⁽³⁾ is the mechanism presumed responsible for the additional net polarization⁽³⁾ of the conduction electron-impurity moment system. The new interaction between impurity moments represented by the $\alpha^2\chi_s$ term in the denominator

of Equation (3.9) can be associated with an indirect coupling via double scattering of conduction electrons.

Dekker⁽³⁶⁾ obtained a result corresponding to Equation (3.8) from a simple statistical mechanical model for the behavior of the random alloy $\text{CuMn}(c)$ in the low c range. He assumes both ferromagnetic (FM) and antiferromagnetic (AFM) interactions for certain impurity configurations. He finds that a Curie-Weiss law for the susceptibility is valid for $T \gg 0$, and he derives a form

$$\Theta = f(c) [g(c)\Theta_f - h(c)\Theta_a] . \quad (3.10)$$

Here $\Theta_f \equiv \gamma_f/k_B$ and $\Theta_a \equiv \gamma_a/k_B$, where γ_f and γ_a are positive exchange integrals, and thus are measures of the FM and AFM coupling strengths. $f(c)$, $g(c)$, and $h(c)$ are power law functions of c reflecting the probability of occurrence in a random alloy of the FM and AFM configurations he assumes. Dekker's result for Θ is a quite general form of Dellby's term $\Theta = C\delta$ in Equation (3.8). While Dellby considers his δ to represent a direct coupling between impurities which may assume either sign, Dekker has explicitly shown how the sign of Θ reflects the dominant interaction when there is competition. Furthermore, he has included concentration dependence in a rather rigorous way. The only explicit concentration dependence in Dellby's model is the linear dependence normally included in the Curie constant C . Dekker's Θ varies linearly with concentration as c approaches zero as all other less detailed effective field theories do.

Owen et al.⁽³⁷⁾ used a molecular field model to obtain a result analogous to Dellby's result Equation (3.9). Their direct interaction term showed explicit competition between FM and AFM coupling like

Dekker's, but without the concentration dependence other than that in the Curie constant. The indirect interaction term appeared exactly as in Dellby's result. It is important to note that term $C\alpha^2\chi_s$ in Equation (3.9) yields a positive contribution to Θ regardless of the sign of α . The physical mechanism associated with α is exchange scattering between conduction electrons and impurity atoms which gives rise to a relative spin correlation. But this is precisely the source of the well-known Rudermann-Kittel-Kasuya-Yosida (RKKY)⁽³⁸⁻⁴⁰⁾ interaction (see Section C.2., Chapter V). Since the RKKY interaction can couple impurity moments ferromagnetically or antiferromagnetically depending on spatial separation of those moments, the contribution to Θ arising from this interaction can be of either sign. A realistic calculation of Θ arising from the RKKY interaction requires the performance of a complicated lattice summation procedure,^(41,42) and the sign of Θ can be either positive or negative^(43,44) depending upon the details of the host's crystalline and electronic structure. An effective field model like that of Dellby or Owen et al. cannot account for this behavior because it is not sensitive to the non-uniformity in space of the magnetization of a particular species. The spatially oscillatory conduction electron spin density characteristic of the RKKY interaction represents magnetization of precisely this type. These effective fields take just a mean value of this oscillatory magnetization. With this situation it is easy to see that impurity moments always couple ferromagnetically whether α is positive or negative.

A similar weakness may be present in Dellby's interaction term

$$C \left(\frac{\alpha^2\chi_s + \beta}{1 + \alpha\chi_s} \right)^2 (\chi_{\text{base}} - \chi_s - \chi_{\text{dia}}) \quad (3.11)$$

from Equation (3.7). Equation (3.11) represents the additional coupling between impurity moments arising from the exchange enhanced nature of the host metal and is always positive if $\chi_{\text{base}} - \chi_s - \chi_{\text{dia}} > 0$. Nevertheless, Dellby's model is useful in that it suggests which types of interactions contribute to p and θ in the Curie-Weiss law. To rigorously consider all interaction processes in a system like PdMn(1.0) (the alloy system Dellby considers) is probably far too difficult for present theoretical capabilities, so one must tolerate some of the weaknesses of the molecular or effective field model in order to proceed with a complicated magnetic interaction problem.

Finally, Dellby hints that a classical effective field model would be unable to account in any way for the Kondo effect, a many-body phenomenon. This appears to be the case. Heeger⁽⁴⁾ has shown (Section C.1., Chapter V) that the susceptibility of a Kondo system can approximate Curie-Weiss behavior over a certain temperature range. In that case, θ is proportional to

$$T_k \equiv \frac{D}{k_B} \exp(-1/|J|\rho) \quad (3.12)$$

where J is an effective s-d exchange integral, and ρ is the conduction electron density of states per atom. In Dellby's model, the term $C\alpha^2\chi_s$ in Equation (3.9) would be most closely related to a Kondo mechanism of s-d scattering. However, if α and J are proportional, and if χ_s is taken as proportional to ρ as in the free electron model, it is clear that the functional dependencies of T_k and θ_{Dellby} on J and ρ are entirely different. Furthermore, since Dellby's $C\alpha^2\chi_s$ is always positive and T_k must be positive, there is a sign discrepancy (see Equation 5.6). The Kondo effect, an isolated impurity moment

phenomenon, is not accounted for in considering the interaction between an impurity moment and conduction electrons in the effective field models of Dellby and Owen et al.

IV. PREPARATION OF $(\text{Cu}_{0.83}\text{Pd}_{0.17})_{1-x}\text{C}_x$ AND PRELIMINARY TESTS

A. Properties of $\text{Cu}_{0.83}\text{Pd}_{0.17}$ and Alloy Preparation

The desire to use a non-magnetic binary alloy with an atomic order-disorder transformation as a host matrix for magnetic impurities drastically limits the possible choices. The classic atomic order-disorder system Cu-Au immediately comes to mind as a candidate. This system has been studied rather extensively, however, and at least two papers on impurity susceptibility in Cu_3Au have appeared recently.^(45,46) The binary alloys of Cu with Pd and Pt also have atomic order-disorder transformations.⁽⁴⁷⁾ Although some magnetic susceptibility studies have been done on the Cu-Pd system,⁽⁴⁸⁻⁵²⁾ only one paper⁽⁴⁸⁾ relates the susceptibility to the order-disorder aspects of the alloy. Apparently very little work has been done on the magnetic properties of Cu-Pt.⁽⁵³⁾ Pd and Pt would seem to be interesting candidates as one of the components to complement the noble metal Cu in a binary host, particularly with regard to local environment effects. This speculation is suggested by the exchange enhancement effects known to occur in Pd- or Pt-rich alloys. One might expect a magnetic impurity atom to behave very differently with Pd or Pt neighbors as opposed to Cu neighbors due to polarization effects that occur in Pd and Pt hosts.^(54,55) Although we have carried out some preliminary measurements in systems with Cu_3Pt and Cu_3Au as host matrices, we focus in this thesis on

more extensive results obtained to date in $\text{Cu}_{0.83}\text{Pd}_{0.17}$ (hereafter notated CuPd(17)) based alloys.

A careful study of the transformations in the Cu-Pd alloys by Jones and Sykes⁽⁵⁶⁾ substantiated that the maximum degree of atomic order as demonstrated by superlattice x-ray lines⁽⁵⁷⁾ and electrical resistivity⁽⁵⁸⁾ occurs at 17 atomic percent Pd (Figure IV-1). Furthermore, the lattice structure of the disordered Cu_3Pd type alloys is face-centered cubic (fcc) in the disordered state in analogy with Cu_3Au , and below 20 atomic percent Pd, the L1_2 Cu_3Au fcc structure is retained upon ordering. This is not the case for Cu_3Pd type alloys of greater than 20 atomic percent Pd which develop a tetragonal distortion upon slow cooling below the ordering temperature.⁽⁵⁶⁾ Similarly, the CuPd type alloys exhibit a phase change upon ordering, becoming body-centered cubic (bcc) from fcc. As pointed out in Chapter I, a change in the lattice of atomic sites would be undesirable in our intended search for local environment effects induced by ordering. Therefore, to realize the greatest degree of atomic order while maintaining a fixed lattice of atomic sites, it was natural to choose the composition CuPd(17) as a host matrix.

A master CuPd(17) alloy was prepared from 6 9's grade Cu and 5 parts per million (ppm) impurity Pd sponge from Johnson, Matthey, and Company. Approximately 10 grams of Cu was chemically etched with dilute nitric acid to remove surface impurities. The Cu was carefully weighed on a Mettler balance to a precision of $\pm 1 \times 10^{-5}$ grams and placed in a high purity alumina crucible. The appropriate complementary mass of Pd sponge was weighed into the crucible. This procedure allows one to control the nominal composition before melting to within 0.1 atomic

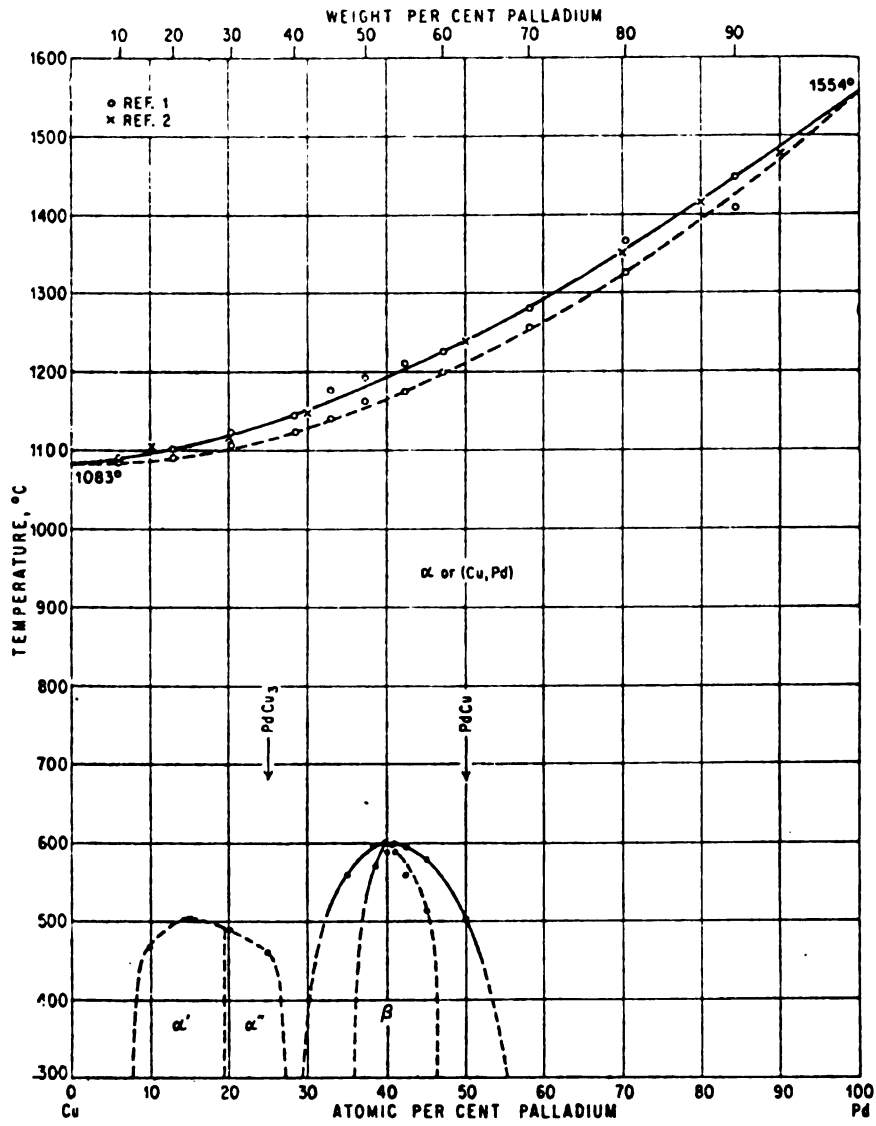


Figure IV-1. Phase diagram of Cu-Pd (Reference 47).

percent of the desired value with little difficulty. A graphite crucible which served as a susceptor for induction heating in a Lepel furnace was outgassed at approximately 1000°C under a vacuum of 10^{-4} mm Hg for several minutes and allowed to cool in a vacuum of less than 10^{-5} mm Hg. Then the alumina crucible with its charge was placed in the graphite crucible and slowly heated under vacuum until the constituents became molten. The crucible could be physically agitated to insure a thorough mixture of the melt. To minimize any evaporation from the melt, the furnace temperature was held as close to the melting point as possible, and the molten alloy was poured into a clean Cu chill cast mold as soon as all visible dissolution had occurred in the crucible. The Cu mold has a mass of about a kilogram, and thus the quench from the melt is very fast. As we shall discuss later, there has been no evidence of appreciable unwanted atomic ordering in this initial sample preparation quench.

The mass loss in a typical melting and pouring is less than 0.5 percent. Most of this is attributable to material sticking to the alumina crucible after pouring and to the evaporation of Cu from the melt. The latter is known to be non-negligible since a Cu film is deposited on the top of the furnace vacuum housing after a melt. One reason for its occurrence is that the melting point of Pd is 470°C higher than that of Cu, and in order to dissolve the Pd quickly, one must exceed the melting temperature of Cu more than one would like. Cu evaporation could be reduced by the admission of a noble gas into the furnace, but this could contaminate the melt depending upon the purity of the gas or its solubility in the alloy. In any case, the loss of Cu due to evaporation is not deemed serious in that the exact

composition of the Cu Pd(17) surely cannot deviate by as much as ± 0.5 atomic percent from the nominal composition. This is the maximum uncertainty based on the total mass loss in the pouring assuming that the loss is 100% Cu.

The chill cast alloy was of cylindrical geometry with a length of about 5 cm and a diameter of 0.64 cm. This master alloy was later cut into segments of approximately 2 grams each for the production of alloys doped with dilute impurities. This and all other cutting of samples was done on a spark erosion machine employing 2 mil Mo wire. After spark cutting and prior to remelting, the CuPd(17) was chemically etched with a 2:1:1 mixture of nitric acid-acetic acid-water. All of the CuPd(17) X(c) (henceforth concentration c expressed in atomic percent) alloys have been produced according to the above procedure except that the total mass of each alloy with impurity was typically 2 or 3 grams. X represents Mn, Fe, Co, Ni, and Gd. c ranges from zero to as high as 10.2. Each of X were of from 4 9's to 6 9's purity.

After being chill cast, a 0.64 cm diameter alloy slug is cold-rolled to a proper susceptibility specimen cross-section which corresponds to a maximum diameter of 2.75 mm. The percentage reduction in cross-sectional area upon cold-rolling is approximately 88 percent. The surface of the roller is carefully cleaned with acetone before each roll to remove undesirable oil and metal residues. After rolling, an alloy slug will have been elongated to about 8 cm. Two segments of length 1.33 cm are spark cut from the rod. These cuts are planar and perpendicular to the axis of the rod. The 1.33 cm long samples match closely the geometry of the pure Al susceptibility standard discussed in Section G, Chapter II. After cutting, the two susceptibility

samples are etched with the same etchant used for the CuPd(17) to insure clean surfaces. After drying, they are carefully weighed. The unused portion of an alloy rod is retained for possible later measurement.

B. Magnetization as a Function of Applied Magnetic Field

Every susceptibility specimen, particularly those with magnetic impurities, is tested immediately after preparation by measuring the induced magnetization as a function of applied magnetic field up to about 4.7 kilogauss. We require that an acceptable sample display linear magnetization versus field behavior within experimental error. The slope of the line corresponds to the susceptibility, which is expected to be independent of applied field for a dilute magnetic system in which very strong moment-moment correlations are absent.

To clarify this point, consider the conditions under which non-linear $M(H)$ behavior is to be expected. In the purely paramagnetic regime, one expects⁽⁵⁾ independent (or only weakly coupled) moments to obey

$$M = N g J \mu_B B_J \left(\frac{g J \mu_B H}{k_B T} \right) . \quad (4.1)$$

This is identical to Equation (3.1) and all quantities are defined there. As long as the argument of B_J is small compared to 1, M is linear in H . As the argument increases, B_J approaches unity. This behavior is entirely reversible. At $H = 4\text{KG}$ and $T = 300\text{ K}$, $\frac{g J \mu_B H}{k_B T} \approx 10^{-3}$, so this sort of non-linear behavior is not what we expect to observe in our tests. More reasonably, we know that a non-linear $M(H)$ is

characteristic of ferromagnets. If for metallurgical reasons, we have enough clusters of magnetic impurity atoms for the occurrence of spontaneous ordering of spins within a cluster, it is easy to imagine the magnetic saturation of such a cluster in low H fields. Depending upon the details of the environments of such clusters and possible interactions among them, one might anticipate hysteresis effects, although not necessarily. (36,37,59,60)

We have encountered clear cases of non-linearity of $M(H)$ both with and without hysteresis (remanent magnetization for zero applied field). A reasonable explanation for each such instance to date has been possible. It is most concise to categorize these non-linearities into three groups.

(1) Surface effects. Several samples which were not chemically etched after cold-rolling and cutting initially failed the test. Upon etching these samples, a linear $M(H)$ was obtained. Therefore, a surface effect is indicated and two possibilities exist. (a) Surface impurities were accumulated during cold-rolling or cutting. This is considered unlikely since the roller is carefully cleaned before each operation. The spark erosion operation is designed specifically to minimize contamination of the material being cut. (b) The metallurgical kinetics involved in quenching a ternary alloy from the melt causes surface inhomogeneities (i.e., clusters of magnetic species). A notable example of a surface effect was the alloy CuPd(17) Gd(0.4). Plots of M versus H before and after etching are shown in Figure IV-2. We suspect that (b) was responsible for this behavior. This suspicion was supported by subsequent susceptibility measurements (Section B, Chapter V) which clearly indicated that the actual concentration of Gd

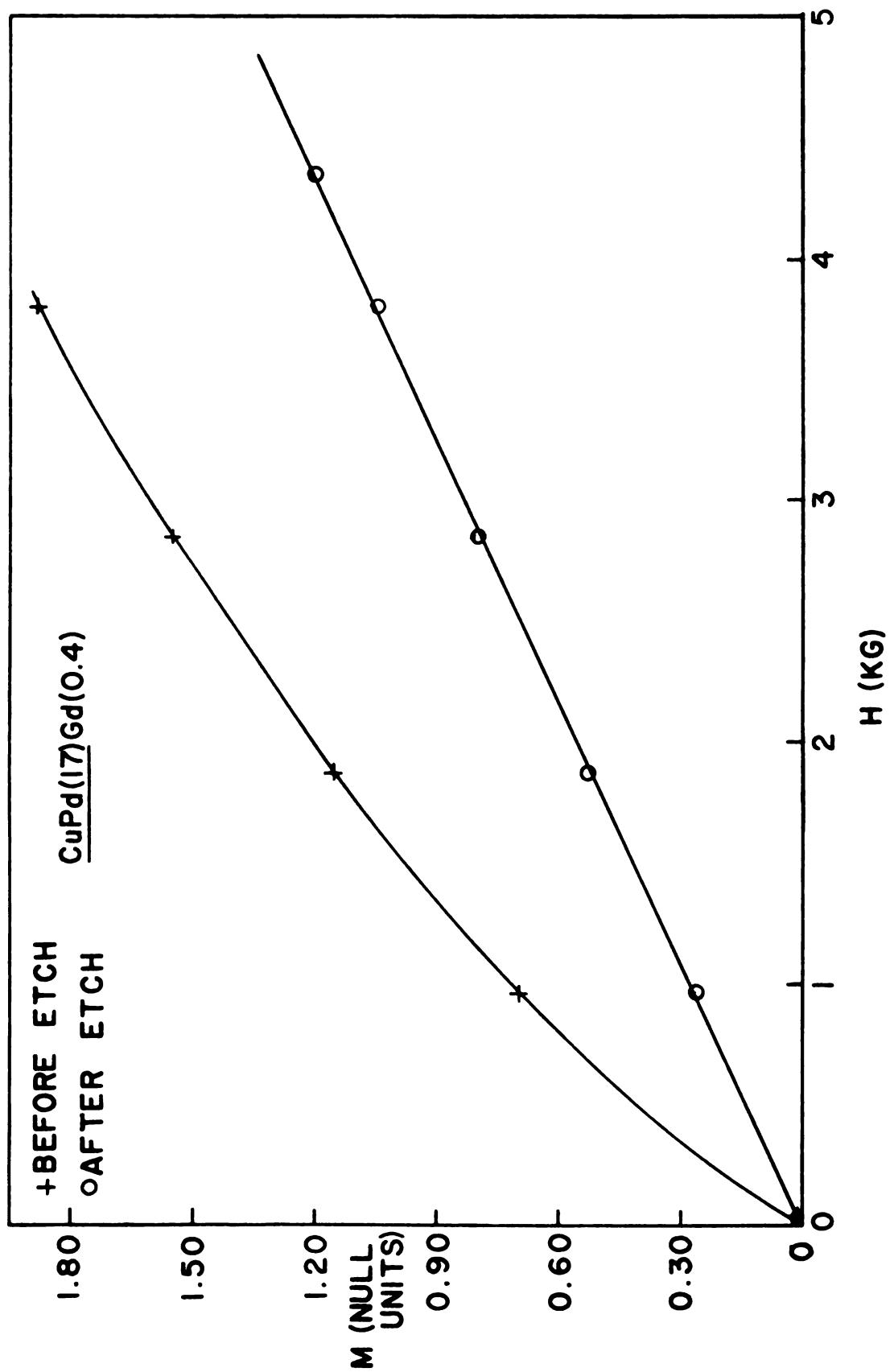


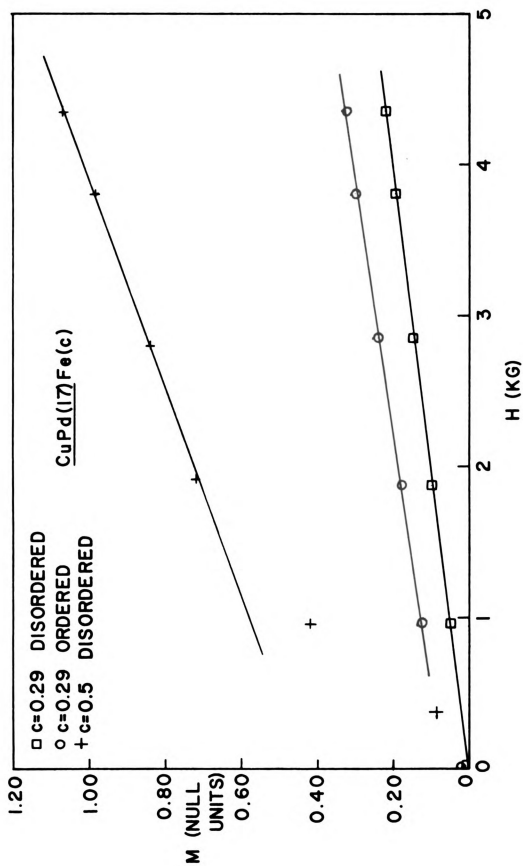
Figure IV-2. M vs. H for CuPd(17)Gd(0.4).

in solution was only approximately 60 percent of the nominal concentration at preparation. Metallographic studies of the Cu-Gd system⁽⁶¹⁾ indicate eutectic solidification from the melt. The freezing out of some Gd (melting point $\approx 1300^\circ\text{C}$) at the surface during quenching is not implausible.

(2) Fe as an impurity in Cu-rich alloys. It is well established⁽⁴⁷⁾ that Fe is only slightly soluble in pure Cu. In only limited experience with these alloys, we have not produced samples with beyond a few tenths of a percent of Fe that did not give rise to curvature in $M(H)$ (Figure IV-3). When a successful solution of 0.29 atomic percent Fe in CuPd(17) was achieved in the quenched melt (as evidenced by the linear $M(H)$ in Figure IV-3), we found clear evidence of the Fe coming out of solution as the sample was annealed and slow cooled to produce atomic ordering. This behavior is not surprising on the basis of the known solubility limit of Fe in pure Cu.

(3) Co as an impurity in Cu-rich alloys. The solubility limit is quite low,^(1,47) similar to that of Fe in Cu. $M(H)$ is non-linear for 0.67 and 1.06 atomic percent Co in disordered CuPd(17) (Figure IV-4).

No obvious solubility problems have been encountered in CuPd(17)Mn(c) for $c \leq 3.2$ (Figure IV-5) or CuPd(17)Ni(c) for $c \leq 10.2$ (Figure IV-6). This has enabled us to carry out systematic susceptibility and resistivity studies on these two systems as a function of impurity concentration. Chapters V and VI are devoted to the details of the studies in these respective systems.

Figure IV-3. M vs. H for $\text{CuPd}(17)\text{Fe}(c)$.

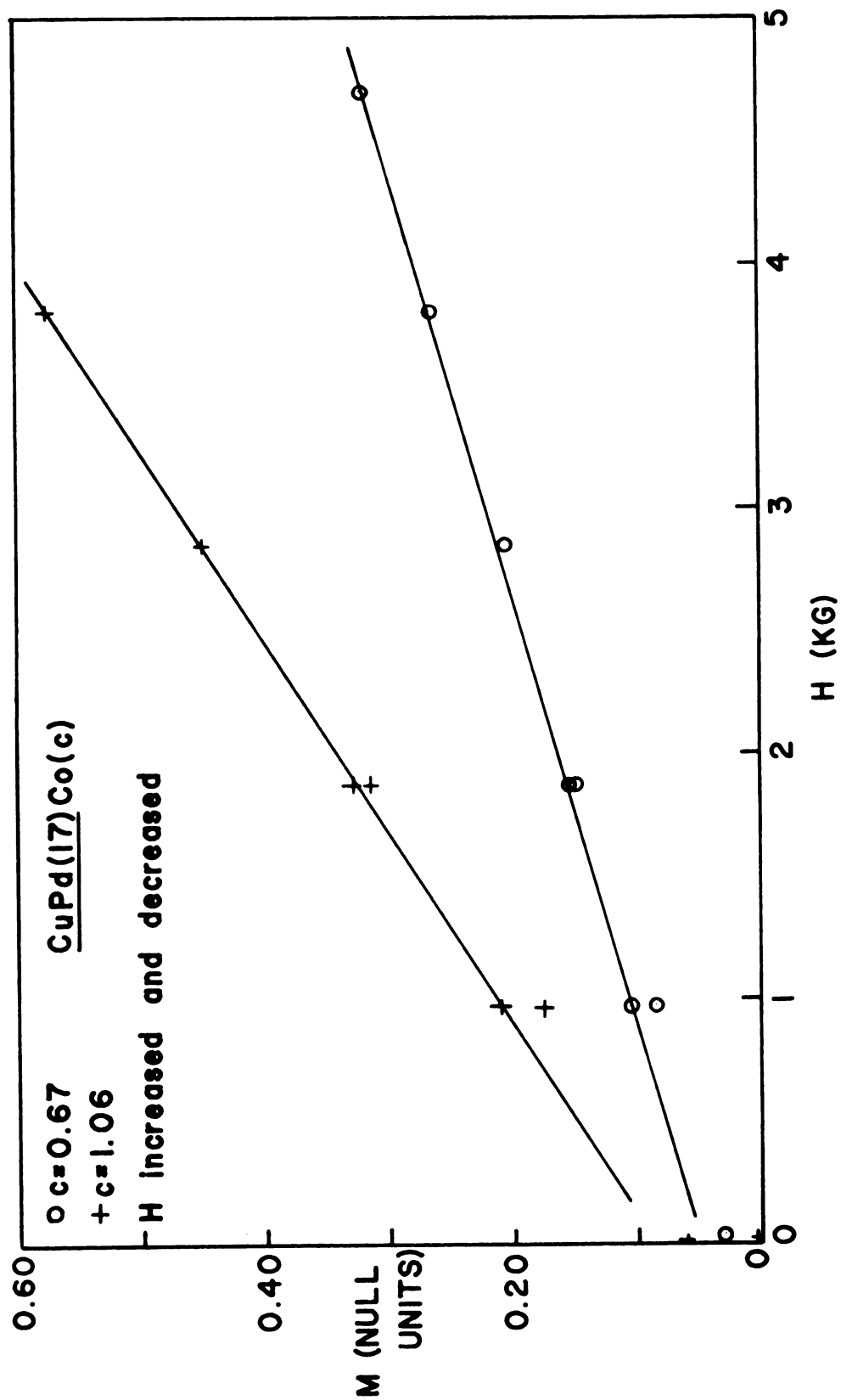


Figure IV-4. M vs. H for CuPd(17)Co(c).

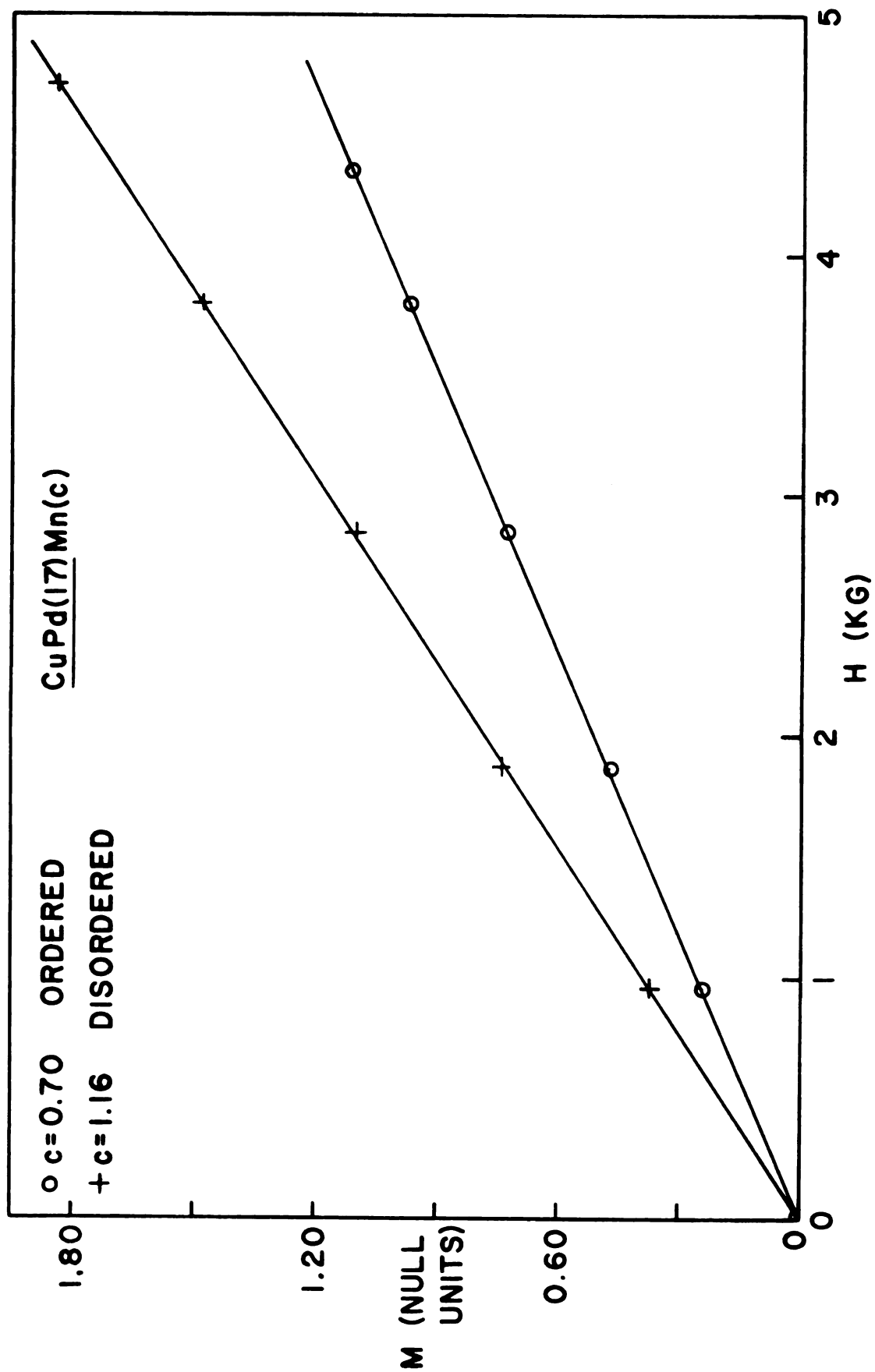


Figure IV-5. M vs. H for CuPd(17)Mn(c) .

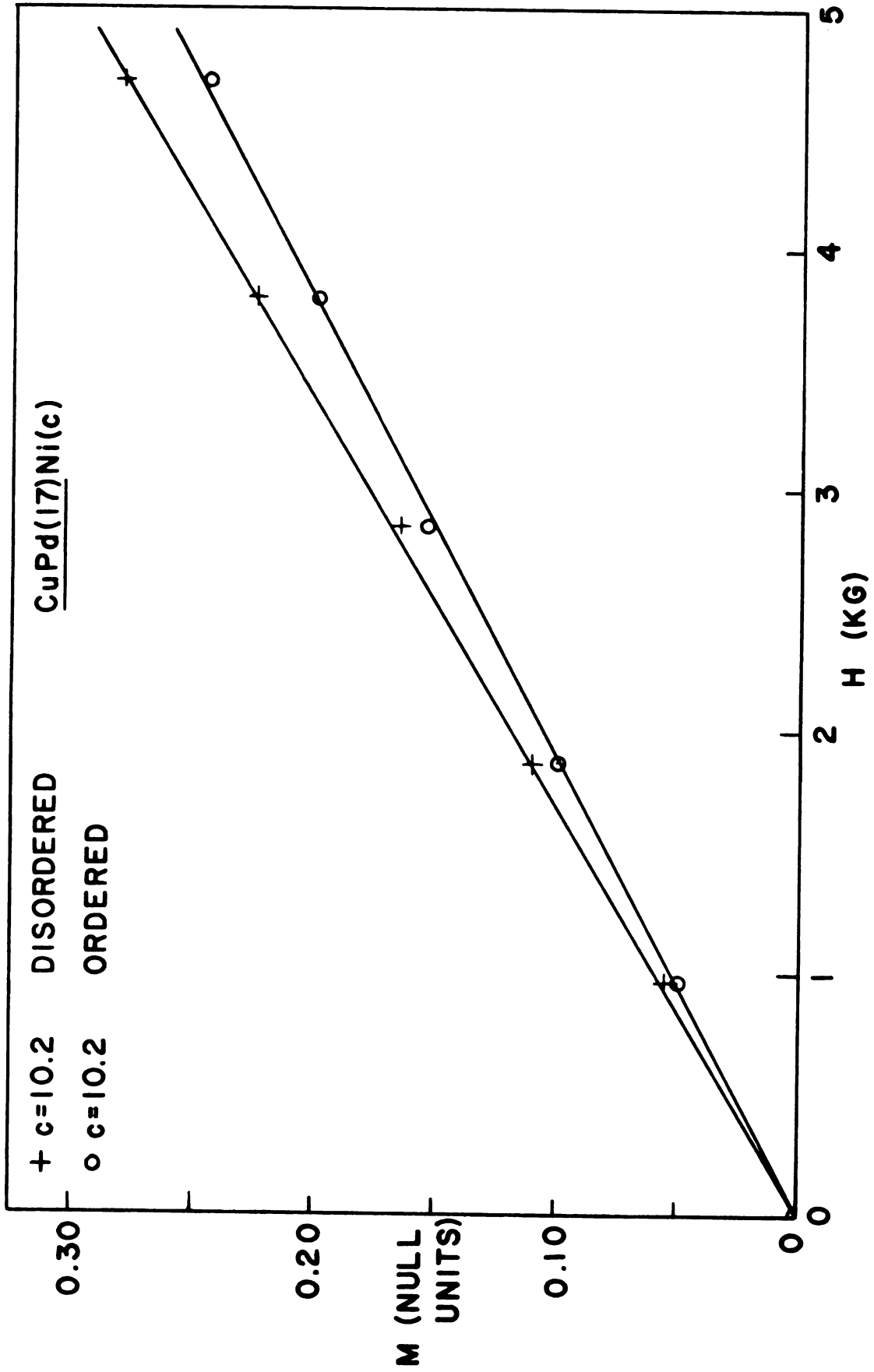


Figure IV-6. M vs. H for CuPd(17)Ni(c) .

C. Heat Treatment

Jones and Sykes⁽⁵⁶⁾ indicated that significant ordering was produced in CuPd(15) by soaking the alloy at 470°C (just below the critical temperature) for 12 hours and cooling at 30°C per hour. As a first attempt to obtain atomic ordering in our CuPd(17) alloy, we rather arbitrarily decided to anneal at 470°C (critical temperature approximately 500°C) for 24 hours and cool to room temperature at about 20°C per hour. One specimen of CuPd(17) and one of CuPd(17) Fe(0.1) were individually sealed in one-third atmosphere of approximately 99 percent pure Ar gas inside clean Vycor tubes which had been previously evacuated to 10^{-4} mm Hg. The anneal was conducted in a Lindberg Hevi-duty furnace which has a manually controllable temperature range of about 300°C to 1350°C. The furnace is adjustable in steps of 0.05°C and appears to be stable over long time periods to $\pm 0.1^\circ\text{C}$. The furnace temperature was monitored near the samples with a chromel-alumel thermocouple.

Susceptibility measurement on the annealed CuPd(17) indicated significant ordering in the heat treatment (Section D, Chapter IV). The diamagnetic susceptibility of the sample quenched from the melt increased in magnitude by about 100% upon annealing. This is in qualitative agreement with the only other such data⁽⁴⁸⁾ known to us. Furthermore, the room temperature electrical resistivity (Section A.2., Chapter V) of the annealed CuPd(17) was found to have decreased by a factor of about one-third from the value for the material quenched from the melt.

A later heat treatment of alloys with 0.70 and 1.16 atomic percent Mn in CuPd(17) caused some surface tarnishing of the samples in the 99 percent pure Ar atmosphere. Although this surface effect did not seem to affect the magnetic properties of the alloys (susceptibility measurements before and after etching agreed), subsequent anneals were conducted using a very high purity grade of Ar (impurity concentration in ppm). There has been no further evidence of thermally induced surface effects.

We have carried out a heat treatment on one specimen from the pair of samples cut for nearly every alloy which displayed a linear $M(H)$ in the disordered state. However, as pointed out above, only the systems CuPd(17) Mn(c) and CuPd(17) Ni(c) provided complete series of alloys of varying c with both ordered and disordered hosts available for detailed magnetic studies (Chapters V and VI).

D. Survey of Magnetic Properties

We have measured the susceptibility of three different samples of CuPd(17) quenched from the melt. The susceptibility is independent of temperature over the range 78 K to 300 K to within our experimental accuracy. This is in agreement with measurements by Ekström et al.⁽⁵²⁾ on CuPd(23). We measure the molar susceptibility as $-6.6 \pm 0.7 \text{ cm}^3 \text{ mole}^{-1}$ at $T = 300 \text{ K}$. The magnitude of the uncertainty in this result is slightly greater than the present precision of our magnetometer, and reflects an apparent spread of values for χ_M among the three samples which were produced from different master alloys. Whether the spectrum of values is reflective of some variation in nominal composition, and/or

of some variation in the degree of atomic ordering unavoidably introduced in a quench from the melt is not known at this time. Ekström et al.⁽⁵²⁾ report a similar lack of reproducibility for CuPd(20). However, on the basis of marked changes in χ_M and the electrical resistivity ρ (Section A.2., Chapter V) induced by the heat treatment of CuPd(17), we have tentatively concluded that the degree of unwanted atomic ordering occurring during a fast quench from the melt is slight. That is, any apparent spread in values of χ_M or ρ (comparable to the precision of any single determination) for the quenched alloy is very much less than the difference between the annealed alloy values and the mean quenched alloy values. For the ordered CuPd(17), we find $\chi_M = -13.1 \pm 0.5 \text{ cm}^3\text{-mole}^{-1}$ and this value is independent of temperature from 78 K to 300 K to within experimental accuracy. In light of the clear cut effects of our heat treatment procedure, we shall hereafter refer to the quenched samples as disordered and the annealed samples as ordered.

We shall now survey the magnetic character of the system CuPd(17)X(c) where X represents the 3d transition elements from Mn to Ni. Most of the details for X = Mn and X = Ni are reserved for Chapters V and VI respectively.

For CuPd(17)Mn(c) we have observed a Curie-Weiss impurity susceptibility superimposed on the temperature independent contribution of the host for values of c in the range 0 to 3.2 with the host both ordered and disordered. For the disordered host, the paramagnetic Curie point θ is essentially independent of the concentration over c from 0.22 to 3.2. p , the effective Bohr magneton number, shows a slight tendency to increase with c. The ordered system shows markedly

different behavior with θ decreasing linearly with c . $\frac{d\theta(c)}{dc}$ is large ($\approx -10 \frac{\text{K}}{\text{at.\% Mn}}$) and of opposite sign compared to $\text{CuMn}(c)$ and many other dilute magnetic impurity in simple host systems. Again, p appears to increase slightly with c similarly to the disordered case, but the magnitude is approximately 3 to 5 percent greater for the ordered host.

We have pointed out above (see Figure IV-3) the solubility problems which plague $\text{CuPd}(17)\text{Fe}(c)$. Three alloys have been prepared which displayed a linear $M(H)$ at $T = 300 \text{ K}$. Only at $c = 0.1$ were we able to anneal the alloy without inducing significant Fe precipitation. A good disordered alloy at $c = 0.29$ was obtained upon quenching. Each of these samples exhibited a Curie-Weiss susceptibility, but unfortunately the Fe concentrations, and hence our experimental precision, are too low to conclusively state whether or not significant order-disorder effects are present. It seems clear that the p and θ values for $X = \text{Fe}$ are significantly different from those for $X = \text{Mn}$ at equivalent c values. Figure AC-1 in Appendix C shows the temperature dependence of χ_M^I for $\text{CuPd}(17)\text{Fe}(0.29)$.

As shown in Figure IV-4, we were not able to obtain a linear $M(H)$ relationship for $\text{CuPd}(17)\text{Co}(c)$, $c = 0.67$ and 1.06 , and the magnitude of the magnetization is reduced from that of comparable concentrations of Fe. The susceptibility shows considerable temperature dependence, increasing with decreased temperature, but more slowly than a Curie-Weiss susceptibility. Hence, we have concluded that Co as an impurity in $\text{CuPd}(17)$ probably sustains a localized magnetic moment, but that there is a strong tendency toward clustering of Co atoms as is well-known in CuCo and AuCo .⁽¹⁾

The contribution of the Ni in CuPd(17)Ni(c) to the total alloy susceptibility per atomic percent Ni is the smallest of the four 3d impurities we have considered. In fact, we find that the impurity susceptibility per atomic percent impurity falls monotonically as we proceed through the 3d transition metals from Mn to Ni just as one would expect on the basis of a filling d shell. The susceptibility of CuPd(17)Ni(c) is temperature independent over 78 K to 300 K for $c = 1.23$ and 10.2 , ordered and disordered, and on this basis we believe that Ni atoms in CuPd(17) do not carry local moments. This does not, however, preclude the possibility that this is an interesting system magnetically. We present evidence in Chapter VI that suggests that magnetic interactions may be important at Ni concentrations beyond approximately 1 atomic percent, particularly in the ordered alloy.

In summary, we submit that compelling evidence has been found for markedly modified magnetic interactions in the system CuPd(17)X(c), $X = \text{Mn, Fe, Co, and Ni}$, as the state of atomic order of the host matrix is changed. Experimentally, it has been much easier to systematically study these effects for $X = \text{Mn and Ni}$, since metallurgical difficulties intrude for $X = \text{Fe and Co}$. In Chapters V and VI we shall present the details of our experimental findings for $X = \text{Mn and Ni}$ respectively, and offer suggestions directed toward understanding the physics involved. We emphasize at this juncture that order-disorder effects are clear in the magnetic behavior of both systems, but that the nature of the magnetism in each is very different. One might infer that Fe and Co would supply the smooth transition from local moment to "no moment" magnetic character in CuPd(17)X(c) if metallurgical difficulties could be avoided.

V. STUDIES OF CuPd(17)Mn(c)

A. Detailed Sample Reliability Tests

Prior to presenting the data on magnetic interactions in CuPd(17)-Mn(c) and a discussion of the findings, we describe in the following two subsections work that was undertaken in part with the intention of further establishing, as conclusively as possible without detailed crystallographic or chemical analyses, the homogeneity and continuity of the alloys of the impurity concentration series CuPd(17)Mn(c). Chronologically, most of the analysis reported was carried out after the interesting effects mentioned in Section D of Chapter IV had been discovered simply to cross-check some readily accessible properties of this alloy system that has at no time given any indication of metallurgical difficulties. A further intention was to empirically check a simple additivity relation for the susceptibility of dilute alloys. We maintain that the results presented, coupled with the earlier linear magnetization versus applied field data, are, beyond all reasonable doubt, supportive of the reliability of the alloys CuPd(17)Mn(c) and justify the application of the type of analysis offered in the latter portion of this chapter.

1. Susceptibility Versus Mn Concentration at Constant Temperature

When a non-magnetic host material is alloyed with magnetic impurities, the simplest concentration dependence for the total alloy susceptibility one could expect is

$$\chi^A(c) = (1-c)\chi^H + c\chi^I, \quad (5.1)$$

where $\chi^A \equiv \chi^{\text{alloy}}$, $\chi^H \equiv \chi^{\text{host}}$, $\chi^I \equiv \chi^{\text{impurity}}$, and c is the impurity atomic fraction. When χ^H and χ^I are taken independent of c , the validity of Equation (5.1) is restricted to the limit of $c \rightarrow 0$ if one believes that a simple superposition of susceptibilities will break down when an appreciable host-impurity interaction exists. One might extend the validity of Equation (5.1) to larger c and account for the breakdown of superposition by letting $\chi^H \rightarrow \chi^H(c)$ and $\chi^I \rightarrow \chi^I(c)$, but then one is faced with the need for explicit expressions for $\chi^H(c)$ and $\chi^I(c)$. We have checked Equation (5.1) empirically at fixed temperatures for CuPd(17)Mn(c), $0 \leq c \leq 3.2$, with the host ordered and disordered. Our hope was that in the concentration range studied we could represent χ^H by the constant $\lim_{c \rightarrow 0} \chi^A(c)$ and $\chi^I(c)$ by $\frac{C(c)}{1-\theta(c)}$, where $C(c)$ is the normal Curie constant (i.e., independent of temperature) as a function of c with its usual explicit linear c dependence placed in the coefficient of $\chi^I \rightarrow \chi^I(c)$ in Equation (5.1). We then have

$$C(c) \equiv \frac{[p(c)\mu_B]^2}{3k_B} \quad (5.2)$$

Note that if we can adequately describe $\chi^A(c)$ for CuPd(17)Mn(c) in this way, we will have justified in an independent manner the customary cavalier separation of χ^I from χ^A by simply subtracting out a constant

host susceptibility. It is not obvious a priori that such a procedure is valid as c becomes appreciable and additivity questionable. Furthermore, a successful description of $\chi^A(c)$ by the adopted generalization of Equation (5.1) serves as a self-consistency check on the values of $p(c)$ and $\Theta(c)$ determined from temperature dependence measurements of $\chi^A(c)$.

Figures V-1 and V-2 show $\chi_M^A(c)$ as a function of c at $T = 300$ K and $T = 80$ K for CuPd(17)Mn(c), ordered and disordered. The Mn concentrations as plotted are the nominal ones. The absolute accuracy of the values of χ_M is put at $\pm 1 \times 10^{-6} \text{ cm}^3\text{-mole}^{-1}$. There are at least two important points to be made with regard to these plots.

(1) If χ^H and χ^I were independent of c , then the plot of $\chi^A(c)$ versus c would be linear. This is very nearly the case for the disordered host at both temperatures. Any slight systematic departure from linearity could be due to uncertainty in the actual Mn concentrations or to real c dependence in χ^I or χ^H . In light of the c dependence of p and Θ inferred from the data of the next section, one can conclude that χ^I for the disordered host is only very weakly concentration dependent, if at all. At $c = 0$, $\chi^A(c)$ extrapolates to χ^H . Equation (5.1) works very well for the disordered alloy. For the ordered host, $\chi^A(c)$ departs from linearity weakly for $T = 300$ K and drastically for $T = 80$ K. This can be accounted for in a self-consistent way when one considers the concentration dependence of p and Θ found for these alloys from the temperature dependence studies. Also, $c\chi^I(c) \gg (1-c)\chi^H$ for $c \geq 0.22$ and $T = 300$ K in CuPd(17)Mn(c), and the temperature dependence of $\chi^I(c)$ insures that for $T = 80$ K, $\chi^I(c)$ completely dominates $\chi^A(c)$. Therefore, these plots of $\chi^A(c)$ versus c are rather sensitive probes of

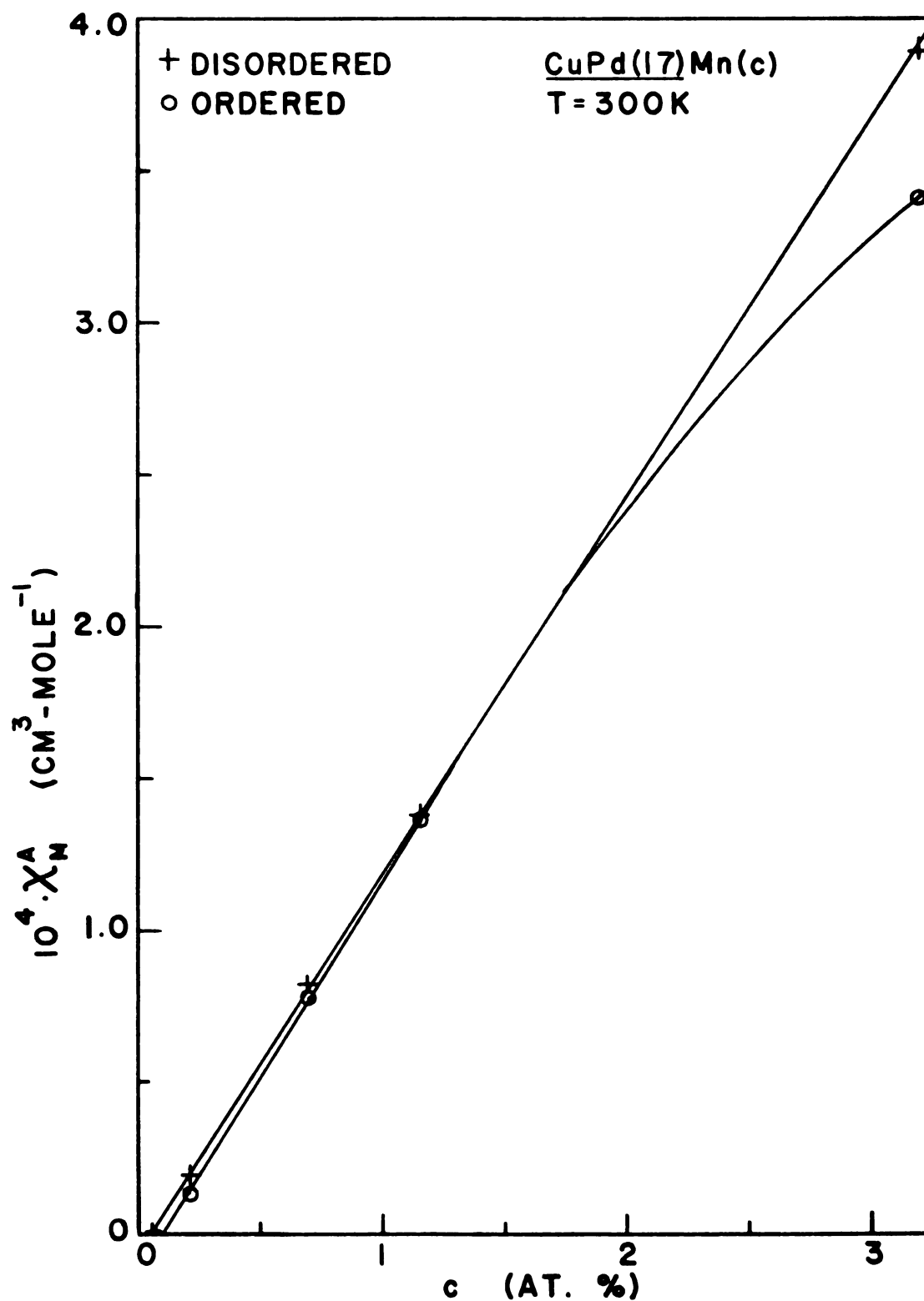


Figure V-1. $\chi^A(c)$ vs. c at $T = 300$ K for ordered (ORD) and disordered (DO) CuPd(17)Mn(c).

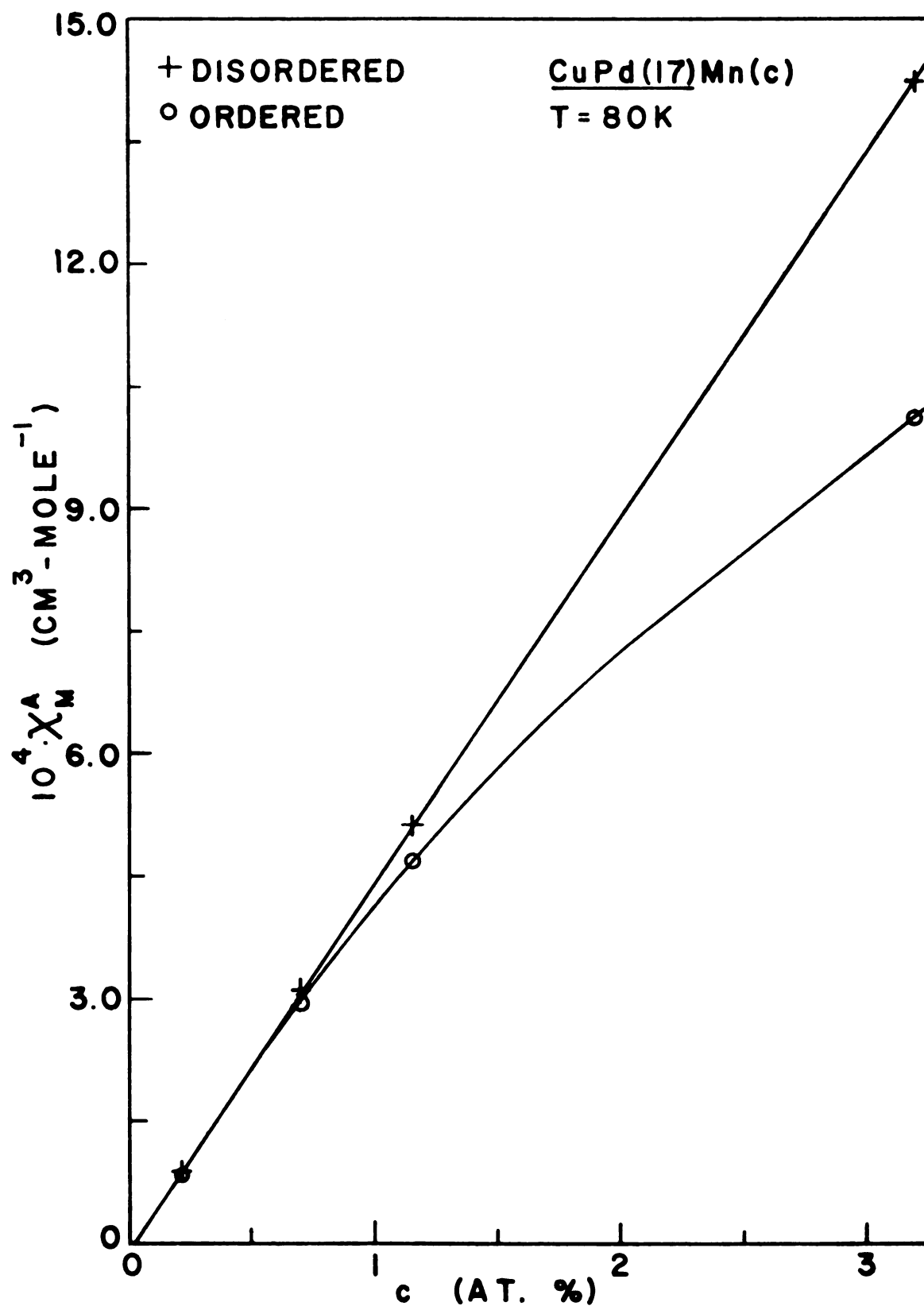


Figure V-2. $\chi^A(c)$ vs. c at $T = 80$ K for ORD-DO CuPd(17)Mn(c).

the c dependence of p and Θ , especially for $T = 80$ K. Again, for the ordered host, a linear extrapolation to $c = 0$ implies that $\lim_{c \rightarrow 0} \chi^A(c) = \chi^H$ and Equation (5.1) as generalized is adequate.

(2) Two of the nominal concentrations for the Mn series were adjusted to more reasonable values on the basis of the $\chi^A(c)$ plots for the disordered host. From the Θ values deduced from the temperature dependence studies, there was reason to expect that $\chi^A(c)$ should be linear in c for disordered CuPd(17)Mn(c). But the values of $\chi^A(c)$ for $T = 300$ K at $c = 0.14$ and $c = 3.42$ fell well below the linear trend established by the values at $c = 0, 0.22, 0.70$, and 1.16 . When the assumed nominal c values for the anomalous samples yielded seemingly unreasonable p values from the temperature dependence studies of these two alloys, it became clear that the nominal c values were in error. By forcing the $\chi^A(c)$ values for $c = 0.14$ and 3.42 onto the linear plot, we could deduce revised c values, and from the revised values of c and the temperature dependence measurements, recalculate p for each. The modified p values fell smoothly and self-consistently onto the established trend for $p(c)$ and we were able to conclude that $c = 0.14$ should go to $c \approx 0.07$ and $c = 3.42$ should be $c = 3.15$. This procedure is admittedly more trustworthy for the alloy of lower c , because an extrapolation of $p(c)$ or $\chi^A(c)$ from $c = 1.16$ to $c = 3.15$ is speculative at best. However, we have cross-checked our procedure with electrical resistivity measurements (see below) and they too are consistent with these adjustments.

2. Electrical Resistivity-Measurement and Results

Electrical resistivity measurements of estimated ± 8 percent accuracy have been carried out on each alloy of the series CuPd(17)Mn(c).

Measurements were made at $T = 300\text{ K}$ and 78 K for ordered and disordered hosts. The purpose of these determinations was (1) to check the degree and consistency of atomic ordering achieved with identical anneals for increasing impurity concentration, (2) to look for correlations between electrical resistivity and magnetic susceptibility behavior as a function of impurity concentration and host atomic order, and (3) to provide a further check on the nominal impurity concentration values. The relatively low accuracy of these measurements, although clearly sufficient to satisfy (1) and (2), and probably (3), is attributable to the method of measurement necessitated by a desire to perform the measurements on the same samples for which the susceptibility was determined. We did not want to introduce surface magnetic contamination as could readily occur if current and potential leads were soldered or arc welded directly to the sample. Instead, we felt that current and potential contacts with the sample could be best achieved by forcing appropriately shaped, non-magnetic conductors against the sample surface. Electrical leads would be soldered directly to the conducting contacts and specimen contamination thereby minimized.

Four probe resistivity measurements at room and liquid nitrogen temperatures were effected by fabricating a small sample holder which mounted on the end of a dipstick. The body of the holder consists of a cylindrical electrical insulator (teflon) through which two ports were cut to admit coolant. The ends of the teflon encasement are formed by plane-faced brass plugs, one of which is removable via threads. The brass plugs provide the current source and sink which press against the ends of a cylindrical sample. To promote uniform conductive contact over the entire end cross-section of the samples,

we have placed several folded layers of Pb foil between the brass plugs and the specimen end faces. We find that the malleable Pb provides a relatively high conductivity path in places that would be free of direct brass-sample contact in its absence, since all samples do not have smooth planar end faces precisely perpendicular to their axes. Uniform conductive contact helps to insure uniform current densities throughout the specimen, a necessity for meaningful resistivity determinations. The potential drop along the length of the specimen is probed by a pair of 0-80 brass screws whose ends have been filled to straight knife edges. These screws are threaded into the wall of the teflon such that the knife edges contact anticipated equipotentials on the surface of the specimen. The maximum possible separation of the potential probes along the direction of current flow is arranged to insure maximum sensitivity in the potential difference measurements. An Allen set screw through the wall of the teflon opposite the pair of potential contacts presses the specimen firmly against the knife edge.

We could conveniently pass a maximum current of 0.1 amperes through the samples. This resulted in potential drops over a length of 0.97 ± 0.02 cm of specimen of the order of $40 \mu\text{V} \pm 1\%$. The primary sources of error in our resistivity results are the determination of octagonal cross-sectional areas of the susceptibility samples and lack of certainty as to the degree of uniformity of current densities given the relatively large cross-sectional areas. The estimated accuracy we quote is based on a composite of these factors and the reproducibility of any given determination.

We plot in Figure V-3 the electrical resistivity of CuPd(17)Mn(c) as a function of c at $T = 300$ K and 78 K with the host ordered and disordered. Allowing for the assumed accuracy of the measurements, the fits of each of the four sets of data is linear in c . $\frac{d\rho^{300K}}{dc}$ equals $1.9 \frac{\mu\Omega\text{-cm}}{\text{at.\%Mn}}$ for the disordered host and $1.2 \frac{\mu\Omega\text{-cm}}{\text{at.\%Mn}}$ for the ordered host. The quantity $\Delta\rho \equiv \rho^{300K} - \rho^{78K}$, reflective of some portion of the lattice thermal component of ρ , is $1.3 \pm 0.4 \mu\Omega\text{-cm}$ for the disordered host and $1.8 \pm 0.4 \mu\Omega\text{-cm}$ for the ordered material.

These data suggest internal self-consistency among the samples and provide rather irrefutable evidence of atomic ordering achieved in the heat treatments. We note that $\rho(c)$ for the ordered host is linear, while $\chi^A(c)$ was not. This differs from the linear $\chi^A(c)$ -linear $\rho(c)$ correlation for disordered CuPd(17)Mn(c). Although the linear fits we find for $\rho(c)$ are entirely consistent with the modified nominal concentrations discussed in Section A.1., the limited accuracy of our resistivity results precludes a definitive statement as to the correctness of the reassignment.

B. Temperature Dependence of Susceptibility

We have measured $\chi^A(c,T)$ for CuPd(17)Mn(c) over the temperature range 78 K to 300 K for both ordered and disordered hosts. To isolate the temperature dependence of $\chi^I(c,T)$, we have made the separation

$$\chi^I(c,T) = c^{-1}[\chi^A(c,T) - (1-c)\chi^H(c)] \quad (5.3)$$

in accord with Equation (5.1) which appears to be valid. We have no evidence that χ^H depends on c for $c < 3.2$. In Figures V-4 through V-7

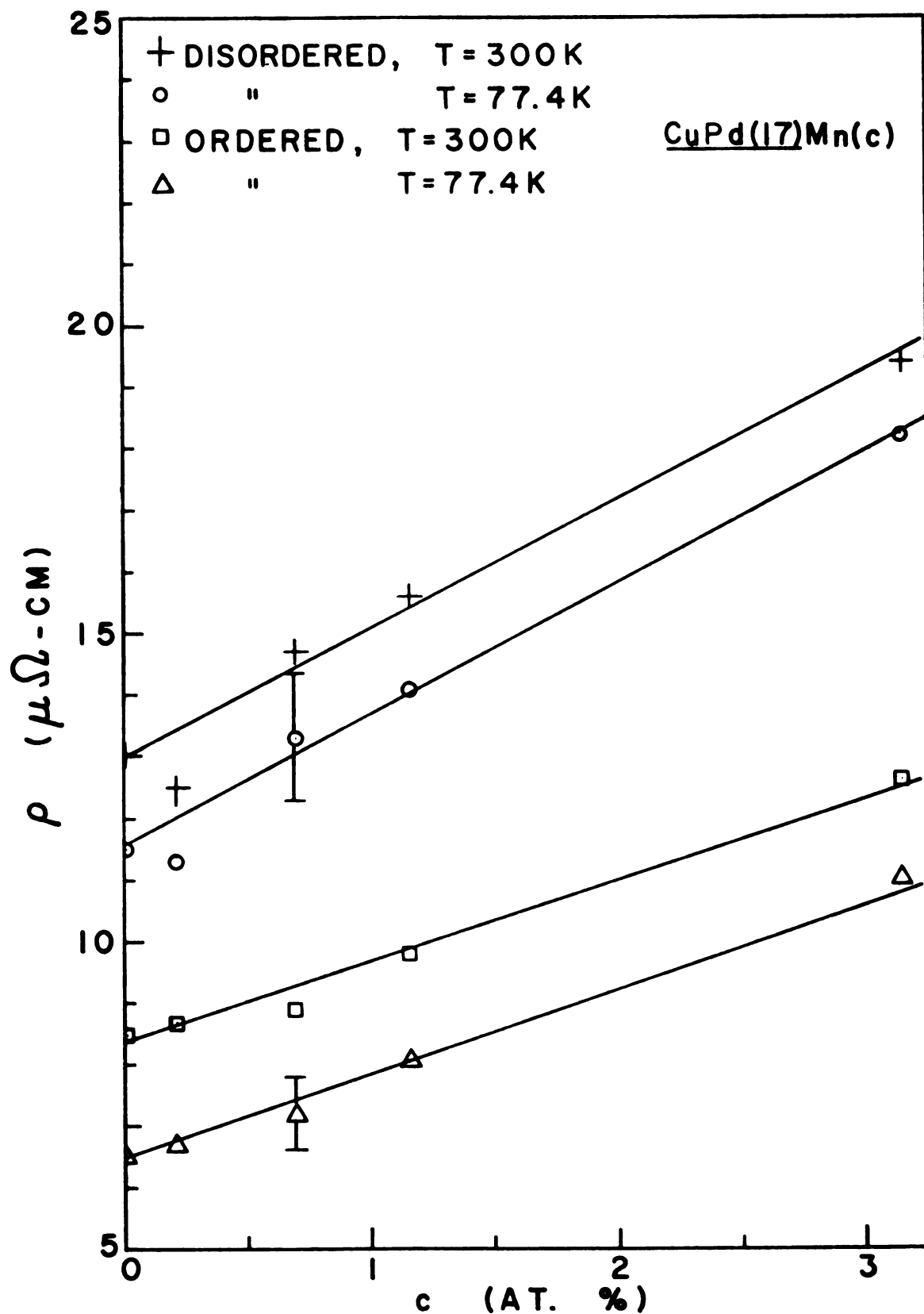


Figure V-3. $\rho(c)$ vs. c at $T = 300\text{ K}$, 78 K for ORD-DO CuPd(17)Mn(c).

we show $[\chi_M^I(T)]^{-1}$ as a function of temperature for $c = 0.22, 0.70, 1.16$, and 3.15 . Each figure includes data for each state of host order. In every case, a linear least-squares fit adequately characterizes the data. (See Appendix B for a tabular listing of all $[\chi_M^I(T)]^{-1}$ versus T data in this thesis.) The absolute accuracy of each value of χ^I is $\pm 1 \times 10^{-6} \text{ cm}^3\text{-mole}^{-1}$. From the fit we extract the Curie-Weiss parameters Θ and p which appear in

$$\chi^I(c, T) = \frac{C(c)}{T - \Theta(c)} = \frac{[p(c)\mu_B]^2}{3k_B[T - \Theta(c)]} \quad (5.4)$$

Table V-I lists the values of Θ and p for each of these measurements. In Figure V-8 we plot $\Theta(c)$ for CuPd(17)Mn(c) and CuMn(c) for comparison. The CuMn(c) data is from Hurd,⁽¹⁸⁾ Owen et al.,⁽³⁷⁾ and Morris et al.⁽⁶²⁾

From Figure V-8 we see that $\Theta(c)$ for disordered CuPd(17)Mn(c) is nearly independent of c . In sharp contrast is the strong, linear in c behavior of $\Theta(c)$ for ordered CuPd(17)Mn(c). As quoted earlier, $\frac{d\Theta(c)}{dc} \approx -10 \frac{\text{K}}{\text{at.\%Mn}}$ for the ordered alloy. For CuMn, Morris and Williams⁽⁶²⁾ indicate $\frac{d\Theta(c)}{dc} \approx +7 \frac{\text{K}}{\text{at.\%Mn}}$. There seems to be much inconsistency with regard to the exact magnitude of the latter figure, but there is little doubt that for CuMn(c), $d\Theta(c)/dc$ is positive and of the order of $10 \frac{\text{K}}{\text{at.\%Mn}}$. Two striking features of our data that require explanation are the very different behavior of $\Theta(c)$ for ordered and disordered CuPd(17)Mn(c) and the opposite signs of $\frac{d\Theta(c)}{dc}$ for CuMn(c) and ordered CuPd(17)Mn(c).

As a control test on our susceptibility versus temperature results for CuPd(17)Mn(c), we measured the temperature dependence of the susceptibility of CuPd(17)Gd(0.4) for both states of host order. The Gd impurity, being a $4f^7$ rare earth ion with tightly bound magnetic

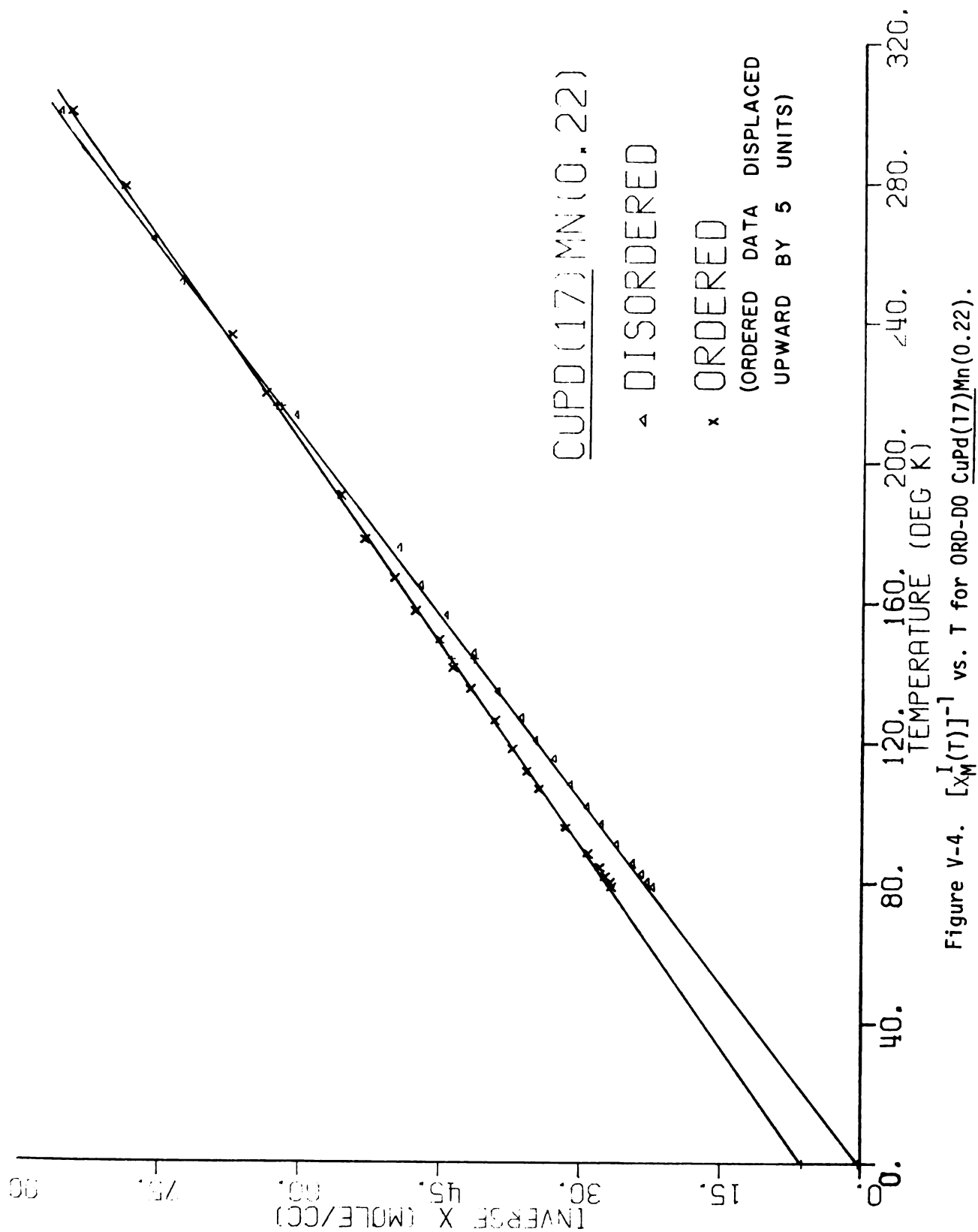
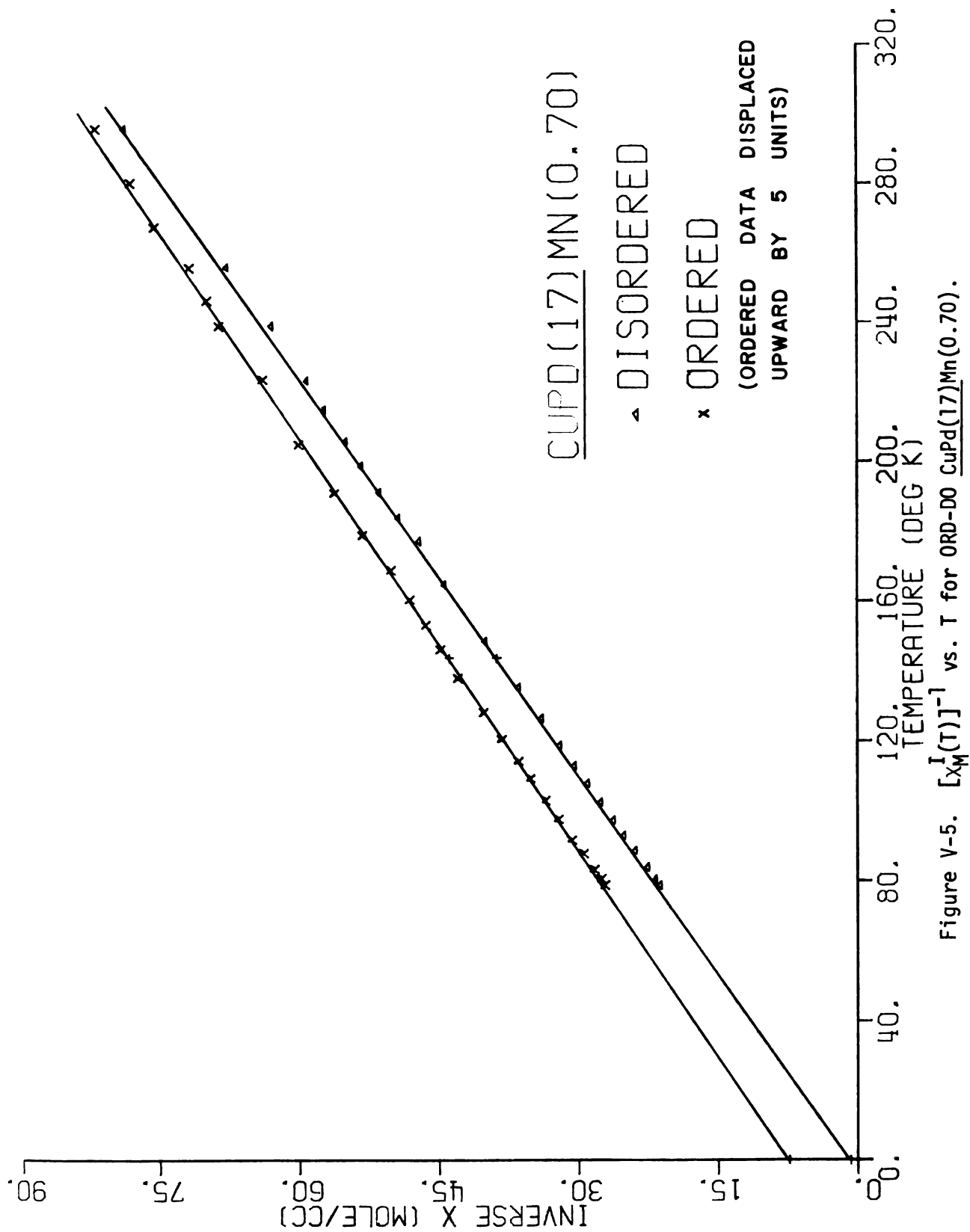


Figure V-4. $[X_M(T)]^{-1}$ vs. T for ORD-DO CuPd(17)Mn(0.22).

Figure V-5. $\frac{1}{X_M(T)}$ vs. T for ORD-DO CuPd(17)Mn(0.70).

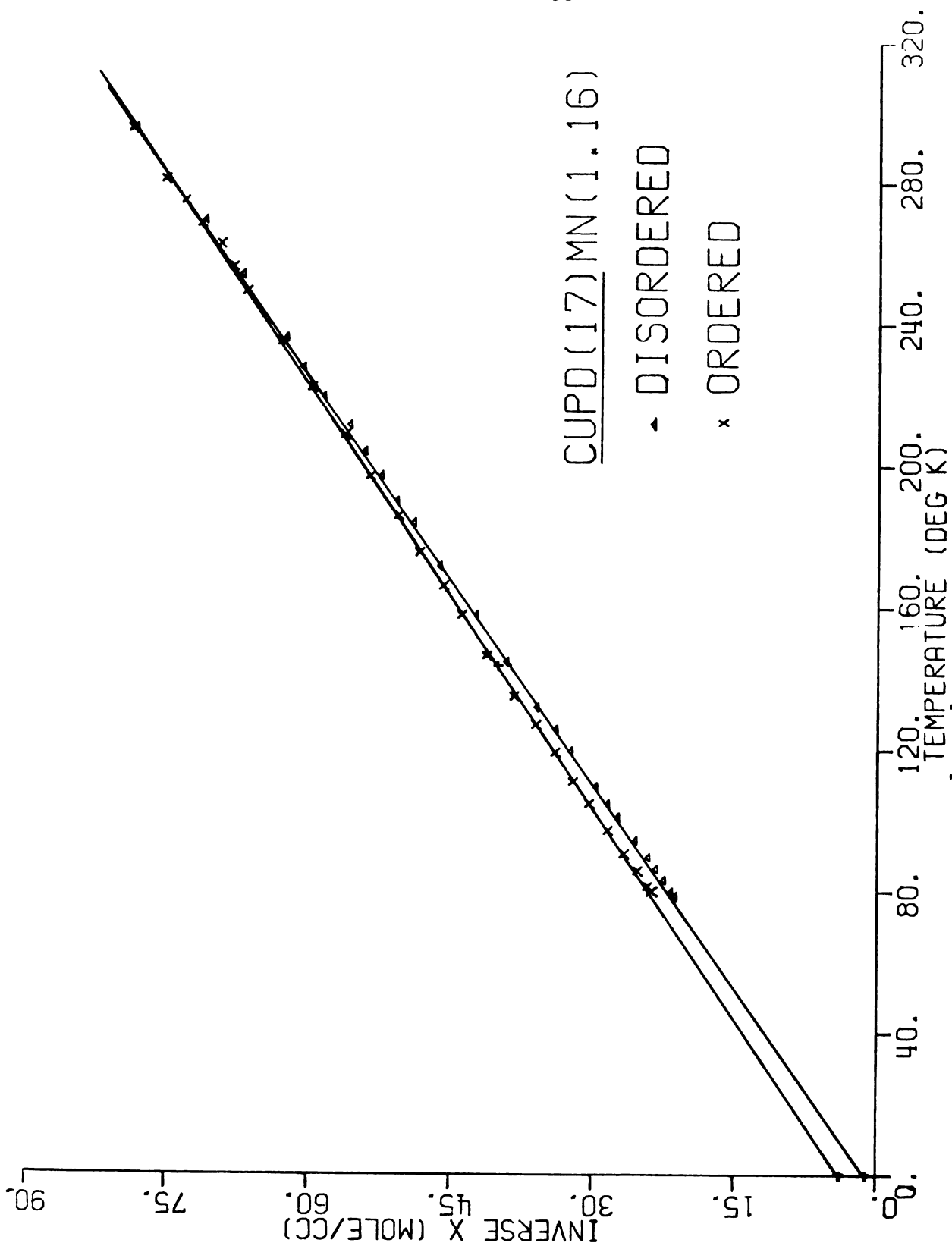


Figure V-6. $[x_M^I(T)]^{-1}$ vs. T for ORD-00 CuPd(17)Mn(1.16).

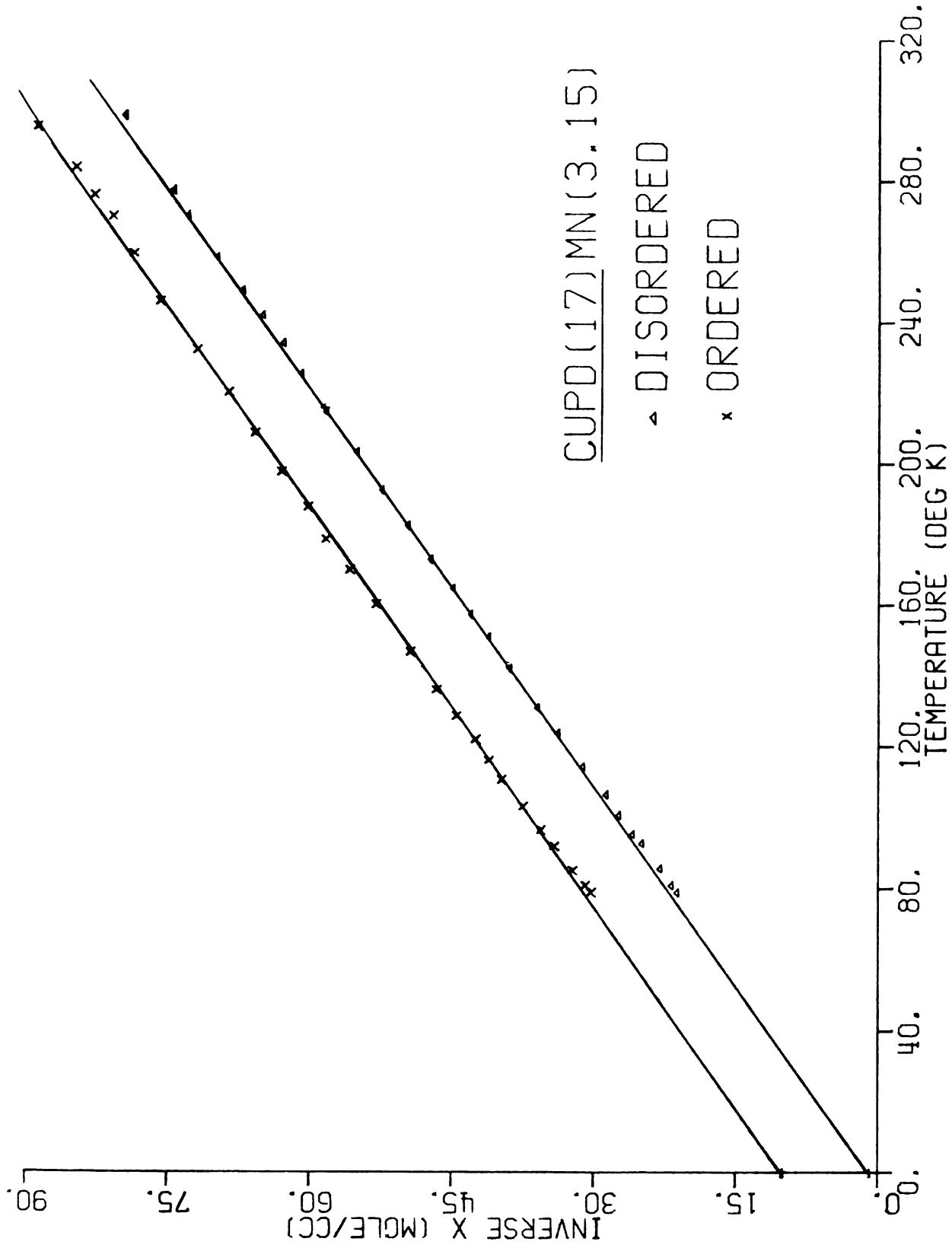


Figure V-7. $[X_M^I(T)]^{-1}$ vs. T for ORD-DO CuPd(17)Mn(3.15).

TABLE V-1

p, ^(H) VALUES FOR Mn, Gd IN CuPd(17)				
SAMPLE	p		^(H)	
	DO	ORD	DO	ORD
<u>CuPd(17)Mn(0.22)</u>	5.3 ±0.2	5.5	0 ±2	-3.6
<u>CuPd(17)Mn(0.70)</u>	5.5	5.6	-2.5	-9.0
<u>CuPd(17)Mn(1.16)</u>	5.5	5.6	-2.5	-14.1
<u>CuPd(17)Mn(3.2)</u>	5.5	5.5	-3.2	-35.5
<u>CuPd(17)Gd(0.4)</u>	6.2*	6.2*	-3.0	-2.7

*SEE PAGE 68.

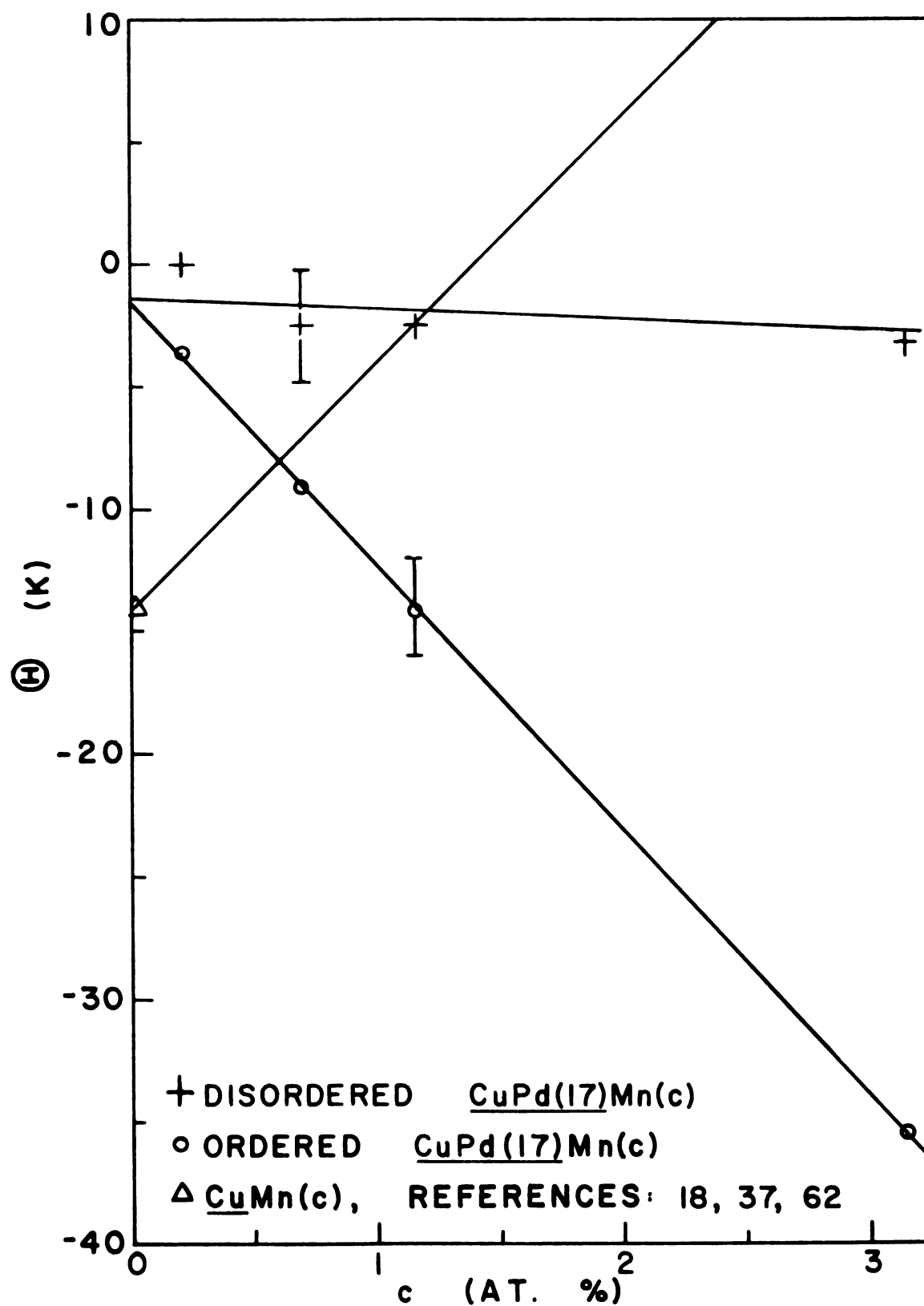


Figure V-8. $\Theta(c)$ vs. c for ORD-DO CuPd(17)Mn(c) and CuMn(c).

electrons, was expected to carry a moment in CuPd(17) of a different type than the Mn. This expectation is based upon the experimental fact that the effective moment of Gd atoms in dilute solid solution is essentially the free ion moment. This is partially because the Gd^{+++} ion is in an S state, and thus Gd^{+++} does not interact with crystalline electric fields, and partially due to the fact that the occupied f states lie somewhat below the Fermi level so that the degree of s-f mixing⁽⁶³⁾ is considerably less than the corresponding s-d mixing associated with 3d virtual bound states. In short, the Gd should carry a "clean" magnetic moment as compared to Mn, and differences in the magnetic behavior as the host matrix atomic order changes could offer clues in the interpretation of the observed effects in CuPd(17)Mn(c). In Figure V-9 we plot $[\chi_M^I(T)]^{-1}$ against temperature for CuPd(17)Gd(0.4). Least-squares fits for the host ordered and disordered indicate that p and Θ are the same for each (see Table V-1). Electrical resistivity measurements indicate that ordering comparable to that for all of the CuPd(17) alloys was achieved. We find resistivities of 13.7 and 12.0 $\mu\Omega\text{-cm}$ at $T = 300$ K and 78 K respectively for disordered CuPd(17)Gd(0.4). For the ordered alloy, $\rho = 8.8$ and 7.0 $\mu\Omega\text{-cm}$ at $T = 300$ K and 78 K. Each resistivity determination carries the ± 8 percent accuracy limit. Thus, it is clear that Gd and Mn in CuPd(17) do behave differently magnetically. Any interpretation of the effects observed in CuPd(17)Mn(c) must be consistent with their apparent absence in CuPd(17)Gd(0.4).

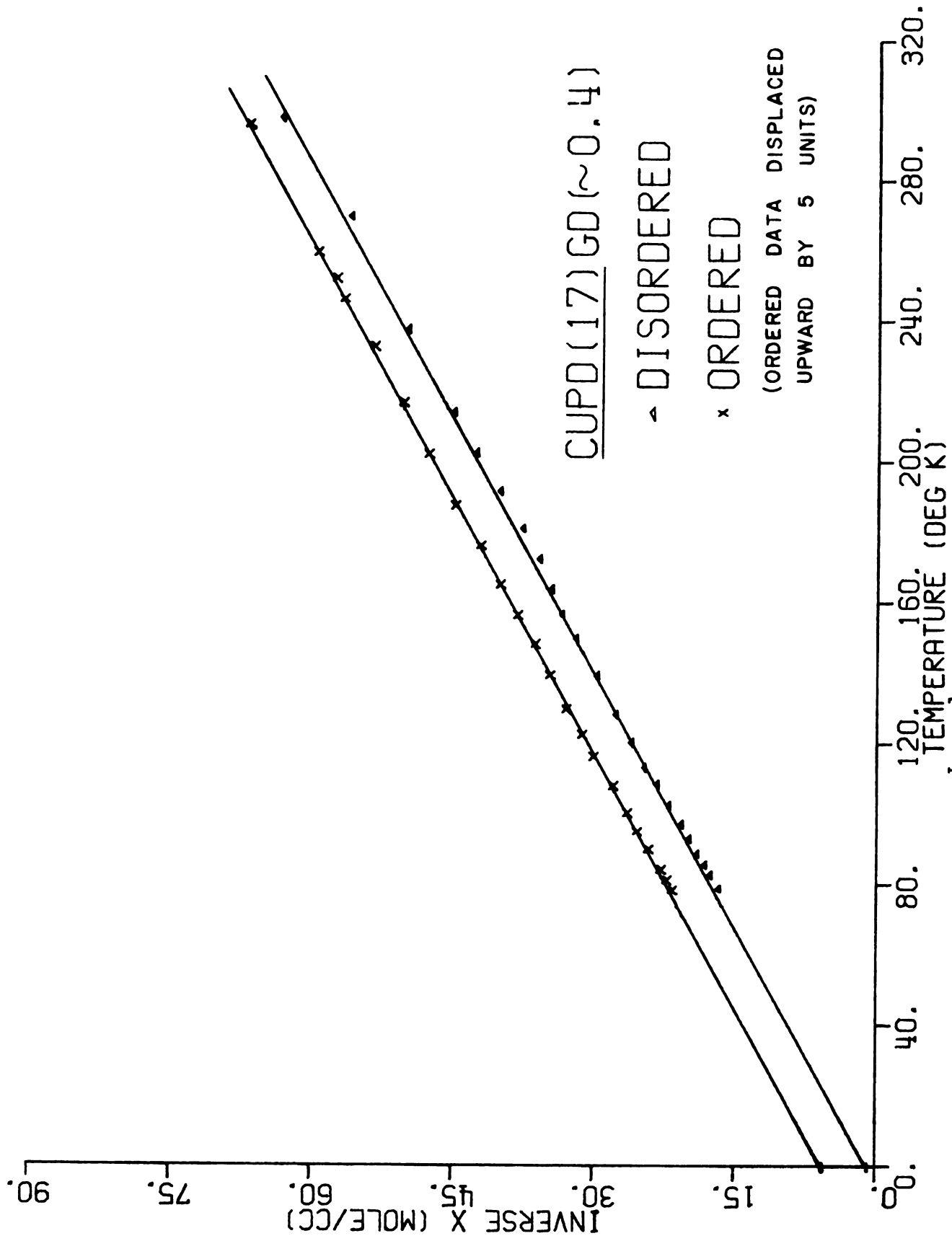


Figure V-9. $[X_M^I(T)]^{-1}$ vs. T for ORD-00 CuPd(17)Gd(0.4).

C. Discussion of Results

To attempt to understand the behavior of the paramagnetic Curie temperature as a function of concentration for ordered and disordered CuPd(17)Mn(c), we have considered three classes of interactions. We discuss the possible applicability of each with reference to the experimental evidence we have obtained.

1. The Kondo Effect

Recent reviews by Kondo⁽³⁾ and Heeger⁽⁴⁾ discuss contributions to the impurity susceptibility in dilute magnetic alloys arising from the s-d exchange interaction. A perturbation calculation carried to fourth order by Yosida and Okiji⁽⁶⁴⁾ indicates that

$$\chi_{s-d} \approx \frac{(g_d \mu_B)^2 S(S+1)}{3k_B T} \left[1 + g_s J \rho + \frac{(g_d J \rho)^2 \ln\left(\frac{k_B T}{D}\right)}{1 - g_d J \rho \ln\left(\frac{k_B T}{D}\right)} \right] \quad (5.5)$$

g_d and g_s are the g-factors for d and s electrons respectively (usually equal to 2); the constant J is an average of various exchange integrals, ρ is density of states per atom per spin of the host metal, and D is a conduction electron bandwidth of the order the Fermi energy. Both the impurity moment and the conduction electrons contribute to this susceptibility as these states mix. Equation (5.5) diverges as T approaches T_K (see Equation (3.12)) if $J < 0$, as is well-known. According to Equation (5.5), departures from a Curie law are expected and such departures are observed.⁽⁶⁵⁾ Heeger⁽⁴⁾ has shown that over restricted temperature ranges, Equation (5.5) can be represented by a Curie-Weiss law to high accuracy. Specifically, for $7 < T/T_K < 100$, he finds that

an expression similar to Equation (5.5) can be fit to within 1/2 percent accuracy by

$$\chi = \frac{(g\mu_B)^2 S(S+1)}{(1.22)3k_B(T+4.5T_K)} \quad (5.6)$$

The point to be made is that for very dilute magnetic alloys, when impurity-impurity interactions can be ignored, the s-d interaction (Kondo effect) can produce an apparent Curie-Weiss susceptibility over restricted temperature ranges. The non-zero Θ value deduced should be independent of impurity concentration if one is observing just a localized s-d effect.

We have concluded that the behavior of $\Theta(c)$ for ordered CuPd(17)Mn(c) which we observe is not due to the Kondo effect simply because the non-zero Θ values are strongly concentration dependent. The connection between a Curie-Weiss susceptibility and the Kondo effect discussed above is relevant only for very dilute systems when Θ is independent of concentration.^(18,31,32) This is not to say that s-d interactions may not be important in the ordered CuPd(17)Mn(c) system for the range of c we have considered, but that localized s-d effects (Kondo) are clearly being dominated by other interactions as c increases. In addition to masking a Kondo effect, strong impurity-impurity interactions are often said to reduce T_K , or equivalently, to stabilize local moments.⁽¹³⁾

We have not ruled out the possibility that the Kondo effect is responsible for the apparent finite negative values of Θ that we would predict by extrapolating our linear $\Theta(c)$ curves to $c = 0$ for both the ordered and disordered hosts. In fact, one might suppose that atomic order in the host is irrelevant to the Kondo effect except for

possible changes in the host electronic structure (for example, ρ and D). If one then chooses to relate the linear $\Theta(c)$ for ordered CuPd(17)Mn(c) to impurity-impurity interaction effects, and the concentration independent Θ for disordered CuPd(17)Mn(c) to the inhibition of those same impurity-impurity effects by host atomic disorder (see below), one could speculate that the Mn impurities are still essentially independent at $c = 3.2$ in the disordered material, and that the finite Θ due to the Kondo effect persists to a rather concentrated impurity system.⁽⁴⁹⁾ While this is an interesting idea, it is obvious that low temperature measurements of susceptibility or resistivity would be required to provide a definitive answer.

2. The RKKY Interaction

An additional consequence of the s-d interaction responsible for the Kondo effect is the Rudermann-Kittel-Kasuya-Yosida (RKKY)^(3,38-40) interaction which is germane to magnetic interactions in metals. A magnetic impurity atom produces a spatially oscillatory spin density distribution in the conduction electron gas around the impurity. A second impurity interacts with conduction electrons spin polarized by the first impurity, and an effective impurity-impurity interaction mediated by the conduction electrons results. The sign and the magnitude of the interaction are critically dependent upon the spatial separation of the impurities.

For a concentration c of randomly distributed magnetic impurities in a periodic host lattice, the paramagnetic Curie temperature Θ arising from the RKKY interactions is^(42,44)

$$0 = \frac{cJ(J+1)(g-1)^2}{3k_B} \cdot \frac{9\pi Z^2 J_{ex}^2}{E_f} \sum_{j \neq i} F(2k_f R_{ij}) , \quad (5.7)$$

where J is the total angular momentum quantum number of the impurity atom with g -factor g and valency Z . J_{ex} is an effective s - d exchange integral, E_f and k_f are the Fermi energy and wavenumber, $R_{ij} \equiv |\vec{R}_i - \vec{R}_j|$ is the separation of the j^{th} lattice site from the origin at site i , and

$$F(x) = \frac{x \cos x - \sin x}{x^4} . \quad (5.8)$$

This result is valid for the free electron model. Coulomb and exchange effects in the electron gas have been ignored. The source of the polarization is a point.⁽⁶⁶⁾ The lattice sum has been evaluated by Mattis⁽⁴³⁾ for various cubic structures and by DeGennes⁽⁴¹⁾ for the hexagonal close-packed structure. Apart from the seemingly oversimplified assumptions inserted in the derivation of the model, quantitative calculations are plagued with added uncertainty because the lattice sum does not converge rapidly, and can be positive or negative depending upon the value of k_f . A mean free path for the conduction electrons in a dilute alloy host can be introduced^(41,43,67) and has the effect of damping and phase shifting $F(x)$. This improves convergence while not changing the value of the sum significantly for finite mean free paths (according to Reference 43). An additional complicating factor entering into the lattice summation in any anticipated analysis of experimental data with this model is the anisotropy in the range of the interaction introduced by a non-spherical Fermi surface for the conduction electrons.⁽⁶⁸⁾ Finally, Watson and Freeman⁽⁶⁹⁾ have shown that the use of a constant J_{ex} can introduce serious errors.

The linear dependence that we observe for $\Theta(c)$ for CuPd(17)Mn(c) is very suggestive of an RKKY interaction (Equation (5.7)). One might envision that the RKKY interaction is effective over long ranges in the ordered host giving rise to an appreciable negative Θ . On the other hand, in the disordered host (a non-dilute alloy) there are sufficient conduction electron scatterers to drastically reduce the range and magnitude of the RKKY oscillations, which in effect decreases the coupling (interaction) of any impurity spin with another resulting in a reduced value of Θ . This picture is admittedly intuitive, but it would appear that any realistic calculation of Θ for this interaction attempting to account for the character of the Fermi surface and conduction electron mean free paths for CuPd(17) in both states of atomic order would be incredibly complex. We have consulted Mattis⁽⁴²⁾ table of lattice sums for an fcc lattice and a k_F value appropriate to a free electron model for ordered CuPd(17) where Cu contributes 1 electron per atom and Pd from zero to one electron per atom, and we find that the lattice sum implies that Θ is positive just as for CuMn(c).⁽⁴⁴⁾ So a simple-minded application of the free electron RKKY model does not account for the sign of Θ for ordered CuPd(17)Mn(c).

In spite of the attractiveness of the RKKY model for CuPd(17)Mn(c) with regard to the linear concentration dependence of $\Theta(c)$ and the plausibility of the attenuation of the interaction by a disordered host, there is considerable evidence in opposition to this model. While we do not view the failure of the free electron RKKY theory to correctly predict the sign of Θ as sufficient reason to abandon the RKKY mechanism (after all, how similar are pure Cu and ordered CuPd(17)?), we have supplementary experimental evidence which suggests that RKKY is

probably not the dominant magnetic interaction in CuPd(17)Mn(c). We have prepared the alloys Cu₃AuMn(c) and Cu₃PtMn(c), $c \approx 1.0$. As pointed out in Chapter IV, these host alloys have atomic order-disorder transformations⁽⁴⁷⁾ analogous to CuPd(17), i.e., atomic rearrangement without changes in the lattice of atomic sites. The alloys were annealed and electrical resistivity measurements indicated significant ordering. No evidence of Mn solubility problems appeared. However, susceptibility measurements indicate that neither system has a shift in Θ exceeding experimental uncertainty between the ordered and disordered state (see Appendices B and C for data and plots of $[\chi_M^I(T)]^{-1}$ versus T for these systems). If RKKY were the dominant interaction giving rise to Θ shifts in CuPd(17)Mn(c), it would seem plausible that the same effects would appear in Cu₃Au- and Cu₃Pt-based alloys.

To analyze the validity of the experimental comparison we have made, one should consider the extent of the similarity of the three hosts CuPd(17), Cu₃Pt, and Cu₃Au. Pd and Pt are chemically analogous and Au is adjacent to Pt in the periodic table. All three alloys are at least 3:1 Cu-rich, and CuPd(17) is usually considered by metallurgists to be of the Cu₃Pd type (without tetragonal distortion). Cu₃Pt and Cu₃Au order into identical structures, but the spatial periodicity of ordered CuPd(17) must necessarily be longer than the other two due to the approximate stoichiometry Cu₅Pd. Presumably, the ordered alloys are characterized by Brillouin superzones, and these may perturb the electronic structure to an extent that renders the free electron RKKY model highly inappropriate. Perhaps it is precisely the different atomic periodicity of ordered CuPd(17) that gives rise to clear RKKY effects in this system only (see below). However, existing data for

transport properties,⁽⁷⁰⁾ magnetic susceptibility,⁽⁷¹⁾ and optical properties⁽⁷²⁾ of Cu_3Au , Cu_3Pt , and $\text{CuPd}(c)$, $c \approx 15$ and $c = 17$, clearly indicates the very close similarity of these three order-disorder systems. The optical data (not available for Cu_3Pt) for Cu_3Au and $\text{CuPd}(15)$ is particularly interesting in that, while it suggests the creation of new Brillouin zone boundaries upon atomic ordering, the associated changes in the optical density of states are not substantial and are remarkably similar for each. Thus, an intercomparison of these three order-disorder hosts makes it difficult to understand contrasting Mn-Mn interaction behavior for these systems on the basis of the RKKY theory.

Neither does the $\text{CuPd}(17)\text{Gd}(0.4)$ data support the picture of a dominant RKKY interaction in $\text{CuPd}(17)\text{Mn}(c)$. Although it is well-known that the RKKY interaction is the predominant coupling among rare earth moments in metallic environments, recall that we observed no shift in Θ between ordered and disordered $\text{CuPd}(17)\text{Gd}(0.4)$. It is true that the magnitude of J_{ex} in Equation (5.7) can reasonably be taken to be somewhat smaller for the s-f interaction than the s-d, but our null result would tend to place a calculable upper bound on $J_{\text{ex}}^{\text{sf}}/J_{\text{ex}}^{\text{sd}}$ if Equation (5.7) is valid and the parameters J , g , and Z are known for Mn and Gd impurities in $\text{CuPd}(17)$.

Kok and Anderson⁽⁴⁴⁾ have recently calculated Θ for amorphous and crystalline systems on the basis of the RKKY theory for dilute alloys. Their central result is that for an amorphous material the well-defined RKKY lattice sum does not exist because there is no long range order in the lattice of atomic sites, and hence, Θ is shown to be suppressed toward zero for amorphous systems. Apart from the actual application of

the RKKY theory to CuMn, the central result of Kok and Anderson, while very interesting, seems at first glance not to be very relevant to our work. However, a surprising feature of their calculation is that no mention is made of spatial attenuation of spin density polarization about an impurity site due to increased conduction electron scattering in an amorphous medium. It would seem that such an effect could be at least as important as the smearing out of an atomic site pair correlation function in moving from the crystalline to the amorphous material. Were we to apply the Kok and Anderson analysis to the system CuPd(17) Mn(c), the implication is that the RKKY sum would be identical for the ordered and disordered states if Mn substitutes randomly on Cu and Pd sites. Only changes in the host conduction electron band structure could cause Θ to change. The range of the interaction would be unaffected by host order. On the other hand, if one were to assume that Mn substitutes preferentially for Cu or Pd (there is no direct experimental justification for such an assumption), then the Mn impurities would be located on a new sublattice in the ordered alloy and different lattice sums for each state of order are plausible. Of course, one might make the same arguments for Cu₃AuMn, Cu₃PtMn, and CuPd(17)Gd(0.4). Again, the experimental absence of shifts in Θ upon ordering in these systems is puzzling in the RKKY picture.

We believe that the disorder of atomic species in a crystalline, non-dilute, binary alloy host and the disorder of atomic sites in a pure amorphous host will have similar important effects on the range of the RKKY interaction. Both types of disorder ought to drastically attenuate the range of the interaction. The Kok and Anderson approach should be understood in terms of an altered lattice summation procedure

and a reduced range for the interaction combining to suppress Θ toward zero in amorphous systems. In summary, we realistically expect a long range RKKY interaction to be of potential importance for our crystalline binary host systems only in the ordered state. But, in light of the close similarity of the three hosts investigated, the most plausible explanation with the RKKY model of the contrasting interaction behavior would appear to require an unwarranted assumption (at the present time) of preferential occupancy of certain lattice sites by Mn. Such a preferential occupancy could amplify the most striking difference among ordered Cu_3Au , Cu_3Pt , and $\text{CuPd}(17)$, namely the deficiency of Pd atoms in $\text{CuPd}(17)$. The appropriate lattice sum for $\text{CuPd}(17)$ would then differ from that for Cu_3Au and Cu_3Pt , and a different Θ would result. On this basis, the absence of a Θ shift upon ordering for Cu_3Au and Cu_3Pt must be regarded as fortuitous until reliable methods of calculating Θ for non-simple hosts become available.

3. Direct Interaction-Local Environment Effects

A third class of interactions which conceivably could account for the effects observed in $\text{CuPd}(17)\text{Mn}(c)$ are the short range direct exchange between impurities and indirect exchange via intermediate host atoms. Obviously, the microscopic details of the metallic environment around a magnetic impurity are of the utmost importance in this problem. The physical picture that one has for $\text{CuPd}(17)\text{Mn}(c)$, $c \approx 1$, are Mn ions with split resonant d states that represent a permanent magnetic moment on the impurity site. Because of the mixing of the host band states (s and d character) with the Mn d levels, the virtual state is not so localized at the Mn site as Mn atomic d levels would

be, and thus some overlap of the virtual state with the d states of neighboring Cu or Pd atoms is to be expected. This overlap results in an exchange interaction which gives rise to coupling between electronic spins on neighboring atoms. For impurity-host atom near neighbors, one often speaks of a magnetic impurity magnetically polarizing the host atoms in its vicinity. These polarization effects are widely known experimentally, the most dramatic examples being the dilute Pd based alloys PdMn, PdFe, PdCo, and PdGd.^(54,73) When magnetic impurity atoms are near neighbors, a direct exchange interaction may couple them ferromagnetically or antiferromagnetically. A rule of thumb for which of these direct couplings to expect has been given a theoretical basis by Moriya.⁽⁷⁴⁾ 3d transition metal atoms with nearly half-filled d levels couple antiferromagnetically and those with nearly full or nearly empty d levels couple ferromagnetically. Impurity atoms may couple via intermediate host atoms in a mechanism analogous to super-exchange⁽³⁷⁾ in insulators. All of these short range direct and indirect interactions have been considered by theorists and the theoretical basis for their existence is well established.^(27,74-76)

The model that emerges from this physical picture is one in which the local environment around each Mn impurity in CuPd(17) determines the nature of the magnetic state in its vicinity.⁽²⁸⁾ The RKKY conduction electron spin polarization certainly coexists with the short range interactions. In Section C.2. we emphasized the long range nature of the RKKY interaction, and for our rather dilute impurity alloys neglected the short range part of that interaction. However, the short range part of the RKKY potential can be comparable to, and actually dominate, direct interaction effects.^(27,69,77) The composite

of the various interactions at short range is exceedingly complicated. This is precisely the reason why it is so difficult to state why pure Fe is ferromagnetic and to what extent the magnetic electrons are localized or itinerant. A careful treatment of the short range effects of the RKKY interaction would appear to require consideration of the spatially extended nature of the moment which is the source of the conduction electron polarization. This ought to be particularly true for a 3d virtual state in a dilute magnetic alloy, but not so important for the more localized moment on a rare earth impurity. So although we are restricting the discussion below to the short range d-d interaction, it should be kept in mind that the short range part of the s-d interaction is operative and may well be of comparable importance. As a specific example, the coexistence of these interactions appears to be well established in CuMn.^(37,60) Various authors^(37,44,60) have disagreed as to whether direct exchange, superexchange, or RKKY exchange is dominant and accounts for the monotonic increase of $\Theta(c)$ to approximately 20 percent Mn.

With these introductory remarks relating to the countless varieties of possible local environments in a random alloy and their associated magnetic interactions, and in light of the established validity of the local environment model of Jaccarino and Walker,^(28,29) it is clear that one could engage in endless speculation as to how the bulk effect we have observed in CuPd(17)Mn(c) relates to an ensemble average of microscopic magnetic systems. This is to say that one probably needs some concrete knowledge of how the microscopic arrangement of Mn atoms with respect to other Mn atoms and the host atoms changes as atomic ordering occurs before genuine progress on this problem can be made. Perhaps

then some probabilistic averaging of realizable environments could be formulated into a tractable calculation. Before abandoning this monstrous statistical problem, we would offer a few suggestions as to how interactions could plausibly differ between the ordered and disordered alloy.

Ekström et al.⁽⁵²⁾ have found that Pd in CuPd is polarized by the presence of Fe impurity moments. They conclude this on the basis of values of p that exceed those for Fe in pure Cu. The same statement could apply to Mn in CuPd in light of measurements by Andersson et al.⁽⁴⁹⁾ and by us. If Pd is more polarizable than Cu, and if coupling of Mn atoms through Pd by superexchange is possible, then an additional, potentially strong impurity-impurity interaction mechanism has been created in changing the host from Cu to CuPd(17). Assume that Mn substitutes randomly for both Cu and Pd upon alloying. In the disordered binary host system, a Mn atom will experience a random distribution of local environments, each with its own characteristic interactions, and it is not implausible that the paramagnetic Curie temperature, which reflects an algebraic sum of all interactions in the system, would be very nearly zero and independent of Mn concentration c for low c (i.e., few Mn-Mn pairs). When the host is atomically ordered, on the other hand, the relative probability of one or a few particular Mn local environments increases very significantly, and the associated magnetic interactions become dominant. A dominant probability of a local environment characterized by an antiferromagnetic coupling between Mn moments and a linear concentration dependence of the resulting negative Θ is not difficult to imagine. Until further experimental and theoretical work can clarify the situation in alloys of the CuPd(17)Mn(c)

type, we would conclude that the direct interaction-local environment picture could well account for the effect we have observed.

With regard to the local environment picture, what about the absence of a Θ shift upon ordering for CuPd(17)Gd(0.4), Cu₃PtMn(c), and Cu₃AuMn(c)? Since the Gd impurity does not form a virtual state in the conduction band in the sense of a 3d impurity, but the moment is much more localized at the Gd site, one would insist that f-f interactions for neighboring Gd atoms must be negligible as for the pure rare earth elements. Similarly f-d exchange between Gd and Pd or Cu neighbors ought to be very small. Recall that RKKY coupling dominates magnetic interactions in the lanthanides. In the case of Cu₃AuMn(c), we would maintain that any distinction between local environments should be slight since Au and Cu are chemically analogous and there is little evidence of exchange polarization of either Cu⁽⁵²⁾ or Au.⁽¹⁸⁾ The absence of an effect like that observed for CuPd(17)Mn(c) is most difficult to explain for Cu₃PtMn(c). In fact, it is not yet certain that a weaker form of the same effect is not present in Cu₃PtMn(0.81), the highest concentration of Mn impurity examined to date. Although Pd and Pt are chemically analogous, their relative magnetic polarizability is perhaps best reflected in comparing the compositions at which Pd-Ni and Pt-Ni become ferromagnetic at low temperatures, approximately 2.3 and 40 atomic percent Ni respectively.⁽⁷⁸⁾ Therefore, one might reasonably expect any local moment effect due to the polarizability of the host to be smaller for Cu₃PtMn(c) than for CuPd(17)Mn(c).

At least two future experiments are strongly suggested by our data. Higher concentrations of Mn in Cu₃Pt should be investigated. This would tend to amplify a weak local environment effect if Pt is

considerably less polarizable than Pd. Perhaps more importantly, the alloy Cu₃PdMn(c), with its tetragonal distortion upon ordering, should be investigated. If the large O shift were to persist at 25 atomic percent Pd, then the lattice distortion could probably be discounted as being of negligible importance to magnetic interactions and the contrast among Cu₃Pd, Cu₃Pt, and Cu₃Au as hosts for Mn would become even more dramatic. If there were no O shift for Cu₃PdMn(c), then the implication is that the departure from 3:1 stoichiometry of CuPd(17) may be critical. In the latter case, one would have to carefully study the extent to which tetragonal distortion of the lattice is a factor in magnetic interactions.

VI. STUDIES OF CuPd(17)Ni(c)

A. Susceptibility and Resistivity Versus Ni Concentration At Constant Temperature

We previously discussed magnetization measurements as a function of applied magnetic field which indicated that CuPd(17)Ni(c) is a good solid solution for $c \leq 10.2$ atomic percent. Measurements of the susceptibility with $c = 1.2$ and 10.2 for disordered and annealed samples over the temperature range 78 K to 300 K indicated that χ^A is independent of temperature within experimental accuracy, and thus we conclude that CuPd(17)Ni(c) is not a local moment system. We have investigated the concentration dependence of the susceptibility and electrical resistivity of CuPd(17)Ni(c) in an approach parallel to that taken with CuPd(17)Mn(c) to look for a correlation between these two properties as the state of host atomic order is changed. In extending the range of impurity concentration substantially beyond one atomic percent in this system, we were particularly watchful for any perturbation of the host by the impurity.

Figure VI-1 displays $\chi^A(c)$ at $T = 300$ K for ordered and disordered CuPd(17)Ni(c), and for CuNi(c) for comparison. The CuNi(c) data is from Pugh and Ryan.⁽⁷⁹⁾ Note the similarity between the behavior of disordered CuPd(17)Ni(c) and CuNi(c). Both display a linear $\chi^A(c)$ through 5 atomic percent with a positive deviation thereafter. Thus it would appear that Equation (5.1), where χ^H and χ^I are independent of c

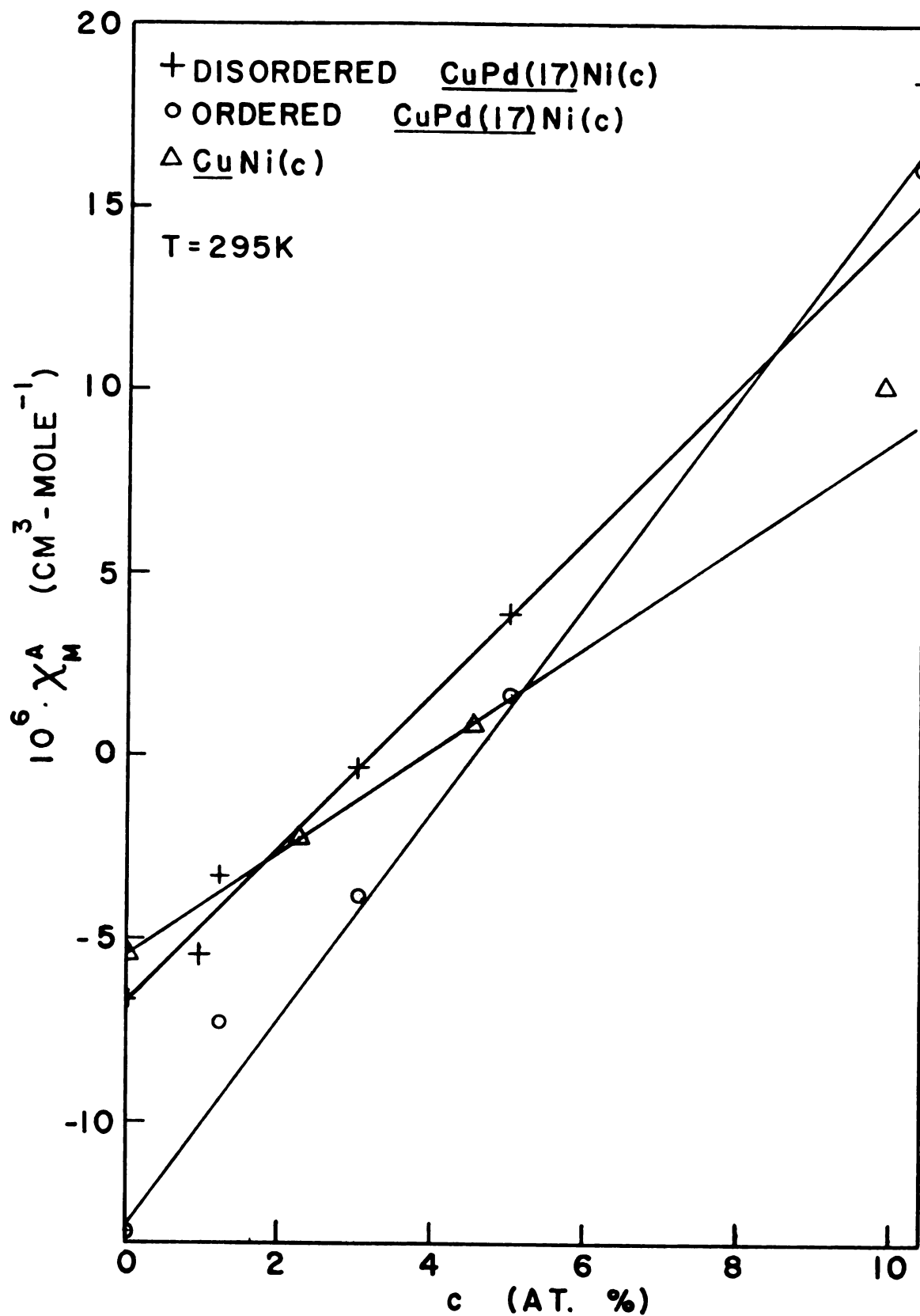


Figure VI-1a. $\chi^A(c)$ at $T = 295 \text{ K}$ for ORD-DO CuPd(17)Ni(c) and CuNi(c).

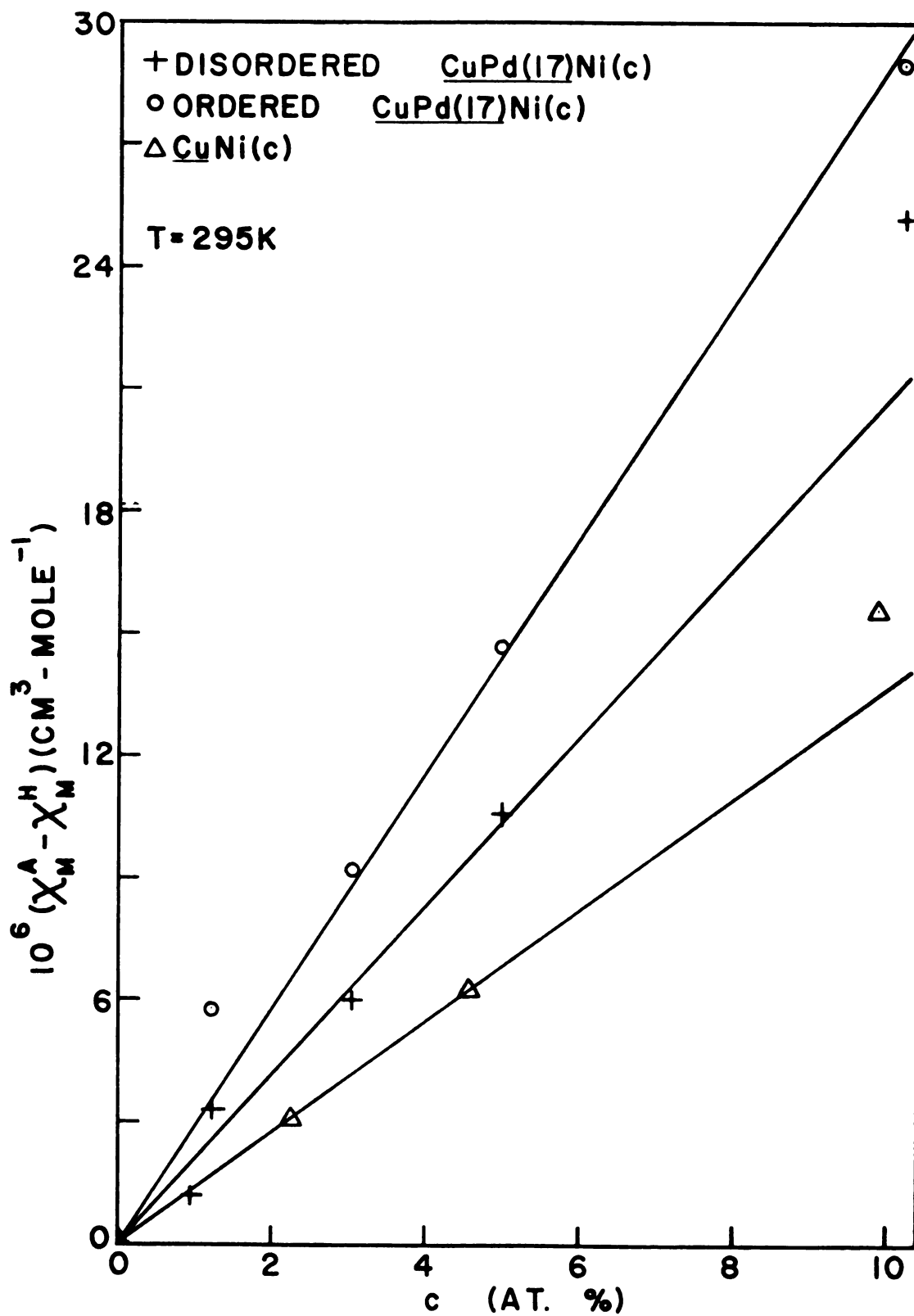


Figure VI-1b. $\chi^A(c)$ at T = 295 K for ORD-DO CuPd(17)Ni(c) and CuNi(c).

for $c \leq 5.0$, is valid for disordered $\text{CuPd}(17)\text{Ni}(c)$ and $\text{CuNi}(c)$. For ordered $\text{CuPd}(17)\text{Ni}(c)$, $\chi^A(c)$ appears to be linear through $c = 10.2$. This is somewhat surprising. Equation (5.1) would seem to be valid for $c \leq 10.2$ with an increased value of χ^I . We see that $\frac{d\chi^A(c)}{dc}$ evaluated near $c = 0$ increases as we proceed from a pure Cu host through ordered $\text{CuPd}(17)$, perhaps indicating that χ^I increases.

The electrical resistivity of the ordered and disordered alloys of the system $\text{CuPd}(17)\text{Ni}(c)$ at $T = 300$ K is shown in Figure VI-2. While $\rho(c)$ is linear for the disordered host with an impurity resistivity of about $1.0 \frac{\mu\Omega\text{-cm}}{\text{at.\% Ni}}$, the data for the ordered host is highly non-linear. The measurements cannot be well fit with any simple power law in c . It appears that the values of ρ at the three highest concentrations have defined a linear behavior with nearly the same slope as the disordered alloy plus an added constant.

B. Discussion of Results

The electrical resistivity results for ordered $\text{CuPd}(17)\text{Ni}(c)$ cast some uncertainty on the interpretation of the results for this impurity series. The data indicates that the resistivity of the alloys with the highest Ni concentration has actually increased after a heat treatment intended to atomically order the host matrix. Although this is a surprising result, there is an obvious possible cause. Metallurgists have proven that the binary alloy $\text{CuPd}(17)$ orders atomically, but to our knowledge, no systematic experiments have checked the extent to which the ternary system $\text{CuPd}(17)\text{X}(c)$ orders. Our previous resistivity results for $X = \text{Mn}$ and $c \leq 3.2$ indicate ordering is not diminished in

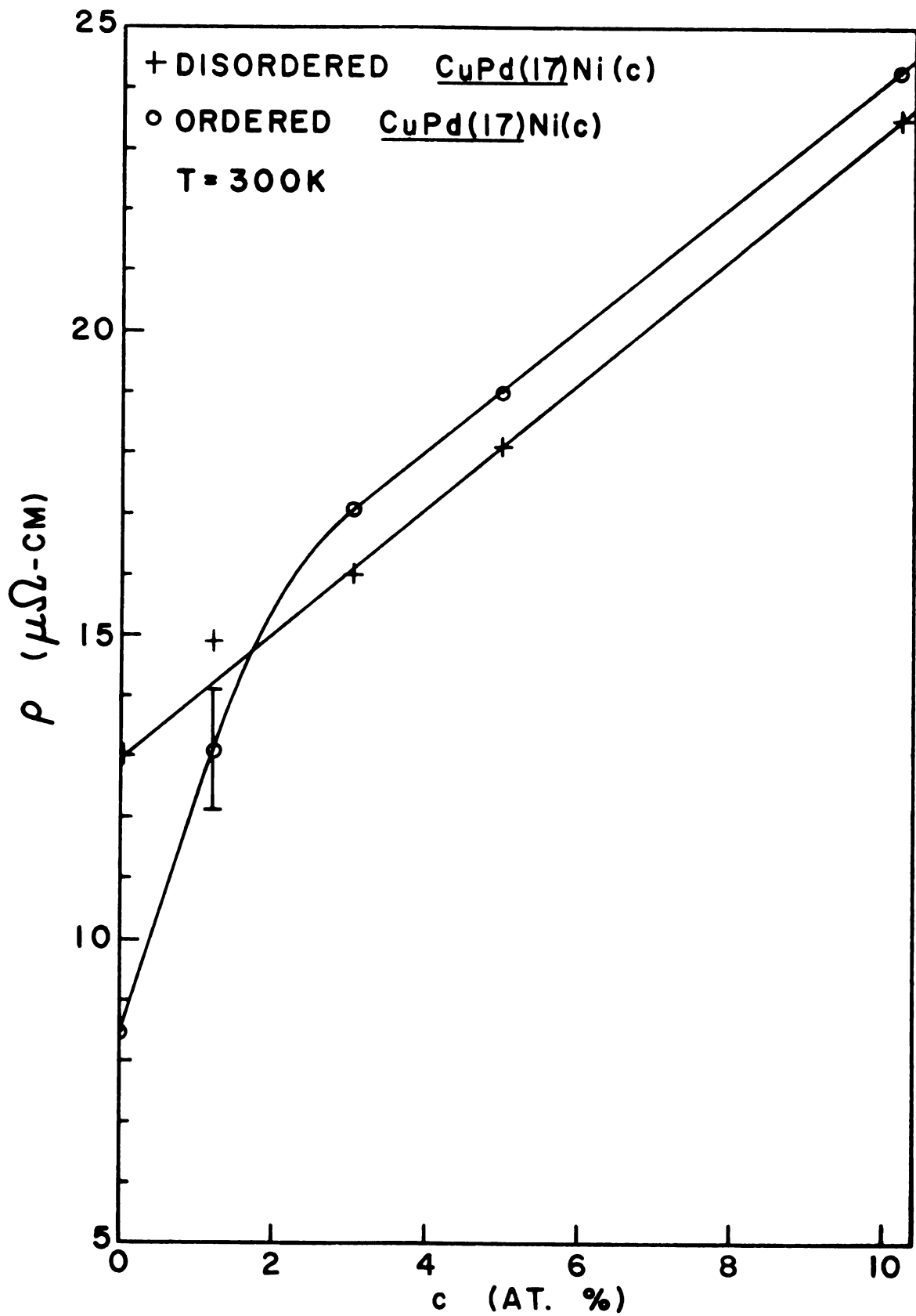


Figure VI-2. $\rho(c)$ vs. c at $T = 300$ K for ORD-DO CuPd(17)Ni(c).

that ternary alloy. However, it could well be that for $X = \text{Ni}$ and $c \geq 1.0$ ordering is impeded by the impurity. At $c \approx 10$ for nearly any impurity one would expect some perturbation of the host's normal behavior, including atomic ordering tendencies. Yet, our susceptibility results for annealed CuPd(17)Ni(c) appear to obey a simple, unique functional dependence on c (linear) for $0 \leq c \leq 10.2$. If the resistivity data is interpreted as reflecting the reduction of induced atomic order as the Ni concentration is increased, it seems surprising that $\chi^A(c)$ behaves so simply. Of course, a linear $\chi^A(c)$ could be reflective of a fortuitous combination of $\chi^H(c)$ and $\chi^I(c)$ (see Equation (5.1)), the concentration dependence of χ^H being due to the gradual reduction of the presence of order with increasing c . Detailed resistivity measurements over the temperature range 4 K to 300 K are now planned for this alloy series to attempt to answer the question of the possible diminution of atomic order with the addition of Ni.

The similarity of the behavior of $\chi^A(c)$ for CuNi(c) and CuPd(17)Ni(c) is noteworthy. As pointed out above, there is an indication that the impurity susceptibility χ^I is larger in CuPd(17). Equation (5.1) yields $\chi_M^I = 130 (10^{-6}) \text{ cm}^3\text{-mole}^{-1}$ for Ni in Cu, and $\chi_M^I = 205 (10^{-6}) \text{ cm}^3\text{-mole}^{-1}$ for Ni in disordered CuPd(17). This is possibly reflective of exchange enhancement due to the presence of Pd.

Until the question of the extent of atomic order achieved in CuPd(17)Ni(c) is settled, any analysis of the susceptibility on the basis of atomic order must be tentative. However, since the susceptibility $\chi^A(c)$ for the heat treated alloys is linear within experimental accuracy, evaluating $d\chi^A(c)/dc$ near $c = 0$ and applying Equation (5.1) indicates that χ^I is greater for the heat treated alloy than for the

disordered system. It then becomes very tempting to speculate that a local environment effect is becoming increasingly manifest as atomic ordering occurs. (Experimentally, there is no doubt that ordering occurs at low c .) Presumably there is no competing RKKY interaction to produce a long range Ni-Ni interaction in this system since there is no permanent Ni moment. Again, we emphasize that the apparent increase of $d\chi^A(c)/dc|_{c=0}$ upon ordering may be an artifact resulting from the behavior of $\chi^H(c)$ if ordering diminished with increased c .

VII. SUMMARY

A brief review of the history of studies of dilute magnetic alloys was presented. The emphasis was on the experimental approach of attempting to understand cooperative magnetic phenomena in metals by utilizing alloys to systematically construct the magnetic state in terms of the fundamental interactions among the constituent magnetic atoms. This approach forced physicists to first answer basic questions about local moment formation in metals, and then to explain the striking changes in the properties of metallic systems induced by the presence of dilute magnetic impurities. Only presently are we beginning to take the next logical step of considering the basic magnetic interactions present in a moderately dilute magnetic system. The work described in this thesis was undertaken in the hope of contributing some small part to the resolution of the difficult problem of magnetic interactions in metals.

A vibrating sample magnetometer has been constructed and calibrated. This instrument has been used to perform reliable magnetic susceptibility measurements on a wide variety of metals, alloys, and insulators, including the alloys discussed in this thesis. At present, the signal detection coils have $\approx 5.4 (10^3)$ turns and the resolution of the magnetometer is $\approx 2 (10^{-5})$ emu of magnetic moment. For a Cu specimen of 0.5 gm in an applied magnetic field of 4700 gauss, we would measure the susceptibility with a precision of the order of ± 10 percent or

better. The sensitivity could rather easily be improved by an order of magnitude or greater by increasing the number of turns in the detection coils, the applied field, and/or the specimen size. However, the present sensitivity was entirely adequate for the work described in this thesis. An appropriate cryostat allows continuous susceptibility determinations below room temperature. Routine measurements to $T = 77$ K are reported, and measurements to 4.2 K are possible with the current design.

A discussion of the relevant aspects of a systematic experimental study of the magnetic properties of dilute alloys was given. The particular approach we have adopted of using binary alloys with atomic order-disorder transitions as host matrices for magnetic impurities was given justification. The most important points presented include (1) the possibility of inducing local environment effects, (2) the capability of altering long range interactions, and (3) the avoidance of the uncertainties of depending entirely upon the reliability and continuity of distinctly different alloys.

Because most of our susceptibility measurements indicated the applicability of the Curie-Weiss law, we discussed the relation of the paramagnetic Curie point Θ to magnetic interactions. The effective field models of Dellby,⁽³⁵⁾ Dekker,⁽³⁶⁾ and Owen et al.⁽³⁷⁾ were seen to be helpful in incorporating several types of interactions into Θ . One must not take these models too seriously, however, since these simple effective field models cannot, for example, account for the RKKY interaction or the Kondo effect.

The selection of the alloy system CuPd(17)X(c) was considered, and the preparation and initial reliability testing of the alloys was

explained. We found that a simple heat treatment process to induce atomic ordering was effective as confirmed by susceptibility and electrical resistivity measurements. Of the four transition metal impurities $X = \text{Mn, Fe, Co, and Ni}$, only Mn and Ni were sufficiently soluble in CuPd(17) to withstand heat treatment and remain in solution up to moderate concentrations. Thus, more detailed descriptions of experimental results and their significance could be given for the impurity concentration series CuPd(17)Mn(c) and CuPd(17)Ni(c) .

Rather strikingly different magnetic susceptibility behavior was reported for the ordered and disordered states of CuPd(17)Mn(c) . These results were offered after a careful justification of the reliability of the various alloys that were measured. Possible explanations of the impurity concentration dependence of Θ were distilled from a consideration of three types of interactions.

The Kondo effect was ruled out as a source of the effect because it is a concentration independent phenomena characteristic of very dilute alloys. It was suggested that the Kondo effect might account for the apparent non-zero Θ values obtained by extrapolating to zero impurity concentration or for the non-zero Θ values of the disordered alloy where atomic disorder effectively isolates impurities at low concentrations.

At first sight, the RKKY interaction seems a plausible mechanism to explain our results. One is tempted to believe that the change in atomic order simply turns on or off this long range coupling of impurity moments. The failure of the free electron RKKY model to account for the observed sign of Θ is worrisome, but not implausible given a binary alloy host containing Pd. The observed absence of any

significant shift in θ for the order-disorder systems $\text{Cu}_3\text{AuMn}(1.0)$, $\text{Cu}_3\text{PtMn}(0.8)$, and $\text{CuPd}(17)\text{Gd}(0.4)$ is extremely difficult to reconcile if RKKY is indeed the dominant interaction in $\text{CuPd}(17)\text{Mn}(c)$. Although the RKKY interaction cannot be totally ruled out on the basis of our results, it does not appear to be the most likely possibility.

Local environment-direct interaction effects are still sufficiently mysterious that one can attribute much of his ignorance to them. We have offered some intuitive plausibility arguments as to why direct interactions (direct exchange, superexchange, short range RKKY) might be more important in $\text{CuPd}(17)\text{Mn}(c)$ than in $\text{Cu}_3\text{AuMn}(c)$ or $\text{Cu}_3\text{PtMn}(c)$. Until detailed microscopic measurements are made on these atomic order-disorder systems, we believe that considerable speculation is involved in attempting to differentiate among them.

The $\text{CuPd}(17)\text{Ni}(c)$ system is still a puzzle. While susceptibility measurements show a systematic distinction between the disordered and the heat treated alloys, the accompanying resistivity measurements raise questions about the extent of atomic ordering achieved at the higher Ni concentrations. Several features of this system are clear. Ni does not sustain a localized magnetic moment at any concentration up to 10.2 atomic percent for either state of host order. The impurity susceptibility of Ni in disordered $\text{CuPd}(17)$ is enhanced over that in pure Cu by almost 60 percent and for Ni in "ordered" $\text{CuPd}(17)$, the apparent enhancement is still larger. The anomalous resistivity results for the heat treated alloys must be explained before the susceptibility effects in the "ordered" alloy become more than tentative.

APPENDICES

APPENDIX A

1. UNITS OF MAGNETIC SUSCEPTIBILITY
2. A GENERAL DEFINITION OF MAGNETIC SUSCEPTIBILITY

APPENDIX A

1. UNITS OF MAGNETIC SUSCEPTIBILITY

There appears to be considerable variance and ambiguity in the literature of magnetism concerning the units of magnetic susceptibility. Most of the uncertainty stems from the use of the so-called emu, or electromagnetic unit, in CGS unit systems. When it appears, it is usually not defined and hence can lead to incorrect dimensionality for the susceptibility. We hope to alleviate some of this confusion with the following treatment. Let us first clarify the relationship between susceptibilities in the two most commonly used systems of units, the Gaussian system and the rationalized MKS system. The Gaussian system is a CGS system which combines the older electrostatic and electromagnetic systems. Often the terms Gaussian and CGS are used interchangeably, so we shall denote Gaussian susceptibilities with the subscript CGS. Susceptibilities in the rationalized MKS system are labelled with the subscript MKS.

The relation among magnetic induction $\vec{B}$, magnetic intensity $\vec{H}$, and magnetization $\vec{M}$ is

$$\vec{B} = \mu_0 (\vec{H} + \vec{M}) \quad [\text{MKS}] \quad (\text{A.1})$$

or
$$\vec{B} = \vec{H} + 4\pi\vec{M} \quad [\text{CGS}] . \quad (\text{A.2})$$

In both systems, the volume magnetic susceptibility is defined for linear, isotropic materials and we call this susceptibility χ .

$$\vec{M} \equiv \chi_{\text{MKS}} \vec{H} \quad [\text{MKS}] \quad \text{or} \quad \vec{M} \equiv \chi_{\text{CGS}} \vec{H} \quad [\text{CGS}] \quad (\text{A.3})$$

It follows that in linear, isotropic materials M , H , and B are all proportional. Therefore, we have

$$\vec{B} = \mu_0 (1 + \chi_{\text{MKS}}) \vec{H} \equiv \mu \vec{H}, \quad [\text{MKS}] \quad (\text{A.4})$$

$$\text{and thus} \quad \mu = \mu_0 (1 + \chi_{\text{MKS}}), \text{ or } \chi_{\text{MKS}} = \frac{\mu}{\mu_0} - 1. \quad (\text{A.5})$$

$$\text{Similarly,} \quad \vec{B} = (1 + 4\pi \chi_{\text{CGS}}) \vec{H} \equiv \mu \vec{H}, \quad [\text{CGS}] \quad (\text{A.6})$$

$$\text{and thus} \quad \mu = (1 + 4\pi \chi_{\text{CGS}}), \text{ or } \chi_{\text{CGS}} = \frac{\mu - 1}{4\pi}. \quad (\text{A.7})$$

We see that χ is dimensionless in both systems of units. To see how the magnitude of χ characteristic of a given physical system transforms between the two unit systems, consider the following. The quantity $\vec{B}$ describes the same physical field regardless of the system of units. Only the magnitude (not the dimensionality) of the unit of $\vec{B}$ differs from the MKS to the Gaussian (CGS) systems. In fact, the equivalence relation is the familiar 1 tesla [MKS] = 10^4 gauss [CGS]. Therefore, let us hypothesize a universal definition of volume magnetic susceptibility χ' . Let χ' be the ratio of the portion of $\vec{B}$ due to the magnetization of matter to the remainder of $\vec{B}$. Therefore

$$\chi'_{\text{MKS}} = \frac{\mu_0 M}{\mu_0 H} = \frac{M}{H} = \chi_{\text{MKS}}, \quad (\text{A.8})$$

and
$$\chi'_{\text{CGS}} = \frac{4\pi M}{H} = 4\pi \chi_{\text{CGS}} \quad . \quad (\text{A.9})$$

By the nature of the definition of χ' , it must be true that

$$\chi'_{\text{MKS}} = \chi'_{\text{CGS}} \quad , \quad (\text{A.10})$$

or using Equations (A.8) and (A.9),

$$\chi_{\text{MKS}} = 4\pi \chi_{\text{CGS}} \quad . \quad (\text{A.11})$$

This is the transformation of volume susceptibility values between the unit systems.

Two commonly derived magnetic susceptibilities are (1) the mass susceptibility χ_g and (2) the atomic or molar susceptibility $\chi_A = \chi_M$. These susceptibilities are defined in the same way in the MKS and Gaussian unit systems.

$$(1) \quad \chi_g \equiv \frac{\chi}{\rho} \quad , \quad (\text{A.12})$$

where ρ is the mass density of the material. The units of χ_g are therefore (meters³-kilogram⁻¹) in MKS units and (centimeter³-gram⁻¹) in CGS units. Note that 1 m³-kg⁻¹ = 10³ cm³-g⁻¹ must be taken into account in deriving a transformation for χ_g between unit systems.

$$\chi_{g,\text{MKS}} = \frac{\chi_{\text{MKS}}}{\rho_{\text{MKS}}} = \frac{4\pi \chi_{\text{CGS}}}{10^3 \rho_{\text{CGS}}} = 4\pi(10^{-3}) \chi_{g,\text{CGS}} \quad . \quad (\text{A.13})$$

$$(2) \quad \chi_A = \chi_M \equiv \frac{\chi A}{\rho} \quad , \quad (\text{A.14})$$

where A is the atomic mass of an element (i.e., the mass of 1 mole of the element) or the formula weight of a compound. The units of χ_A or χ_M are therefore (meters³-mole⁻¹) in MKS units and (centimeter³-mole⁻¹) in

CGS units. Since $1 \text{ m}^3\text{-mole}^{-1} = 10^6 \text{ cm}^3\text{-mole}^{-1}$, we have

$$\chi_{A,\text{MKS}} = \frac{\chi_{\text{MKS}}}{\rho_{\text{MKS}}} A_{\text{MKS}} = \frac{4\pi \chi_{\text{CGS}}}{10^3 \rho_{\text{CGS}}} (10^{-3} A_{\text{CGS}}) , \quad (\text{A.13})$$

or
$$\chi_{A,\text{MKS}} = 4\pi(10^{-6}) \chi_{A,\text{CGS}} . \quad (\text{A.14})$$

Of course, the transformation for χ_M is identical since $\chi_A = \chi_M$.

Gaussian units are more commonly used for susceptibility. The remaining discussion pertains to the Gaussian, or CGS, system of units. The confusing use of the emu seems to arise in the following way. Magnetization $\vec{M}$ is defined as the magnetic dipole moment $\vec{m}$ per unit volume, or $\vec{M} = \frac{\vec{m}}{\text{volume}}$. The Gaussian unit of $\vec{m}$ is the same as the old electromagnetic unit, namely, $1 \text{ gm}^{1/2}\text{-cm}^{5/2}\text{-sec}^{-1} = \frac{1 \text{ erg}}{\text{gauss}} = 1 \text{ gauss-cm}^3 \equiv 1 \text{ emu of magnetic moment}$. Then, the magnetization $\vec{M}$ has dimensions of $\text{gauss} = 1 \text{ emu-cm}^{-3}$. One can define $\sigma \equiv M\rho^{-1}$ which is magnetic moment per unit mass and has dimensions 1 emu-gm^{-1} . Also, $M_A \equiv M\rho^{-1}$ is the magnetic moment per mole with dimensions 1 emu-mole^{-1} . These are well-defined quantities with definite dimensionality. However, many authors assign the units of these various magnetizations directly to the corresponding susceptibilities derived above. Hence, one finds units of emu-cm^{-3} , emu-gm^{-1} , and emu-mole^{-1} for the volume, mass, and atomic (molar) susceptibility respectively. This usage is incorrect. The error in the dimensionality is obvious from the relations

$$\chi = \frac{M}{H} , \quad \chi_g = \frac{\sigma}{H} , \quad \text{and} \quad \chi_A = \frac{M_A}{H} . \quad (\text{A.15})$$

Since experimental determinations of susceptibility probe the existence of magnetic dipoles, it is useful to see how the fundamental

quantity m depends on χ , χ_g , or χ_A . From the definitions of M , σ , and M_A , and Equation (A.15), we have

$$\vec{m} = \vec{M} \cdot (\text{volume}) = \chi (\text{volume}) \cdot \vec{H} , \quad (\text{A.16})$$

or
$$\vec{m} = \vec{\sigma} \cdot (\text{mass}) = \chi_g (\text{mass}) \cdot \vec{H} , \quad (\text{A.17})$$

or
$$\vec{m} = \vec{M}_A \cdot (\text{mole fraction}) = \chi_A (\text{mole fraction}) \cdot \vec{H} . \quad (\text{A.18})$$

The quantity A is well-defined for pure elements or molecular materials. There is often an ambiguity as to the definition of A for alloys (A^A) and intermetallic compounds (A^{IM}). For binary systems $X_{(1-c)}Y_c$, A^A is usually defined as

$$A^A \equiv (1-c) A^X + c A^Y , \quad (\text{A.19})$$

where c is the atomic fraction of component Y . For an intermetallic compound, the ratio $\frac{c}{1-c}$ is a ratio of small integers. That is $\frac{c}{1-c} = \frac{I^Y}{I^X}$, I^X and I^Y of order 1 to 10. For intermetallics, it is customary to designate

$$A^{\text{IM}} \equiv I^X A^X + I^Y A^Y . \quad (\text{A.20})$$

Note that the values $A^{\text{IM}}(I^X, I^Y)$ represent discontinuities in $A^A(c)$.

The Curie law and the Curie-Weiss law for the temperature dependence of an array of weakly coupled spins is so common in the literature of magnetism that a simple connection between a typical collection of spins and the magnitude of its associated susceptibility has proven helpful. Consider the expression for a Curie law volume susceptibility in CGS units

$$\chi = \frac{N (p\mu_B)^2}{3k_B T} , \quad (A.21)$$

where N is the number per unit volume of magnetic moments of magnitude $p\mu_B$, that is, we express the magnitude of the magnetic moment in terms of the fundamental atomic magnetic moment, the Bohr magneton. p is therefore a dimensionless constant. k_B is the Boltzmann constant and T is the absolute temperature of the environment of the spin array. If only the atomic fraction c of the total number of atoms of a specimen are the magnetic ones, then we can generalize Equation (A.21) by putting N equal to cN_T where N_T is the total number of atoms per unit volume. Since the atomic or molar susceptibility is most commonly used for alloy systems, we convert Equation (A.21) as generalized to an expression for the Curie law molar susceptibility by multiplying both members by A/ρ , which is a volume per mole for the material that has N_T atoms per unit volume. The result is

$$\chi \frac{A}{\rho} = \chi_A = \frac{c \left(\frac{N_T A}{\rho} \right) (p\mu_B)^2}{3k_B T} . \quad (A.22)$$

But $N_T A/\rho$ is the number of atoms per mole which is a universal constant, Avogadro's number N_0 . Therefore, the Curie law molar susceptibility is

$$\chi_A = \frac{c N_0 (p\mu_B)^2}{3k_B T} \quad (A.23)$$

Of course, we could equally well obtain an expression for the Curie law mass susceptibility by multiplying both members of Equation (A.23) by A^{-1} . However, let us instead evaluate Equation (A.23) for $c = 1$, $p = 1$, and $T = 1 \text{ K}$.

$$\chi_A \approx \frac{[6.02(10^{23})\text{mole}^{-1}][9.27(10^{-21})\text{ergs-gauss}^{-1}]^2}{3[1.38(10^{-16})\text{ergs-K}^{-1}]} (1\text{K})$$

$$\chi_A \approx \frac{1}{8} \text{cm}^3\text{-mole}^{-1} \quad (\text{A.24})$$

Now one can quickly calculate the molar susceptibility arising from the Curie ($\Theta = 0$) or Curie-Weiss law for any value of c , p , T , or Θ by the prescription

$$\chi_A \approx \frac{1}{8} (\text{cm}^3\text{-mole}^{-1}) \frac{c(p)^2}{(T-\Theta)} \quad , \quad (\text{A.25})$$

where c is the atomic fraction of magnetic species, and T and Θ are in Kelvin. To illustrate, let us calculate the molar susceptibility of 1 atomic percent Mn in Cu at $T = 300$ K if we know that the Mn moments exhibit a Curie-Weiss susceptibility with $p = 5.0$ and $\Theta = 5$ K. Then, substituting into Equation (A.25),

$$\chi_A \approx \frac{1}{8} (\text{cm}^3\text{-mole}^{-1}) \frac{(0.01)(5.0)^2}{(300 - 5)}$$

$$\chi_A \approx 1.06 (10^{-4}) \text{cm}^3\text{-mole}^{-1} \quad .$$

2. A GENERAL DEFINITION OF MAGNETIC SUSCEPTIBILITY

It is difficult to find a fully general definition of the concept of magnetic susceptibility in the literature of magnetism. We provide such a definition by writing down a representation of the familiar macroscopic vector quantity $\vec{M}(\vec{r}, t)$, the magnetization in a material at time t at spatial position $\vec{r}$ relative to some origin, as a function of (resulting causally from) the magnetic field intensity $\vec{H}$ at all points

in the material.

$$\begin{aligned}
 M_i(\vec{r}, t) = & a_i(\vec{r}) + \sum_j \frac{1}{V} \iint_V d\vec{r}' dt' b_{ij}(\vec{r}, \vec{r}', t, t') H_j(\vec{r}', t') + \\
 & + \sum_{j,k} \frac{1}{V^2} \iiint d\vec{r}' d\vec{r}'' dt' dt'' c_{ijk}(\vec{r}, \vec{r}', \vec{r}'', t, t', t'') \cdot \\
 & H_j(\vec{r}', t') H_k(\vec{r}'', t'') + \dots \quad .
 \end{aligned} \tag{A.26}$$

V is the specimen volume. This is a power series expansion of $\vec{M}$ in $\vec{H}$ and is valid for non-linear, inhomogeneous, anisotropic materials. It is traditional to define the magnetic susceptibility as the kernel in the term linear in H . That is,

$$\chi_{ij}(\vec{r}, \vec{r}', t, t') \equiv b_{ij}(\vec{r}, \vec{r}', t, t') \quad . \tag{A.27}$$

Clearly, the susceptibility as defined here is an important function, particularly for "linear" materials, those for which a_i , c_{ijk} , ... are zero. Linear materials form a large and important class of matter. Only materials which exhibit spontaneous magnetic order are excluded. However, linearity can break down at large values of H (the precise value usually depends on the temperature and possibly other factors).

Some special cases of $\chi_{ij}(\vec{r}, \vec{r}', t, t')$ are so commonly valid as to be widely and incorrectly accepted as the general case. When isotropic materials are to be described, χ_{ij} includes δ_{ij} , the Kronecker symbol. To describe spatially and temporally homogeneous systems (hence isotropic),

$$\chi_{ij}(\vec{r}, \vec{r}', t, t') = \delta_{ij} \chi(\vec{r} - \vec{r}', t - t') \quad . \tag{A.28}$$

Expressing this susceptibility in terms of its Fourier transform we

have (apart from δ_{ij})

$$\chi(\vec{r}-\vec{r}', t-t') = \frac{V}{(2\pi)^4} \iint d\vec{q} d\omega \chi_{\vec{q}, \omega} e^{i[\vec{q} \cdot (\vec{r}-\vec{r}') + \omega(t-t')]} \quad (\text{A.29})$$

If $\chi_{\vec{q}, \omega}$ is independent of ω , then

$$\chi(\vec{r}-\vec{r}', t-t') = \delta(t-t') \frac{V}{(2\pi)^3} \int d\vec{q} \chi_{\vec{q}} e^{i\vec{q} \cdot (\vec{r}-\vec{r}')} \quad (\text{A.30})$$

Kittel⁽⁶⁶⁾ treats several special cases of $\chi_{\vec{q}}$. He shows that $\chi_{\vec{q}} = \frac{m_{\vec{q}}}{h_{\vec{q}}}$ in general for the $\chi_{\vec{q}}$ of Equation (A.30). Here $m_{\vec{q}}$ and $h_{\vec{q}}$ are the Fourier transforms of $M(\vec{r})$ and $H(\vec{r})$ respectively.

One special choice for $\chi_{\vec{q}}$ leads to a common (but, we now see, non-general) representation of the susceptibility. Suppose $\chi_{\vec{q}} = \chi_0$, independent of $\vec{q}$. Then from Equation (A.30)

$$\chi(\vec{r}-\vec{r}', t-t') = \delta(t-t') V \chi_0 \delta(\vec{r}-\vec{r}') \quad . \quad (\text{A.31})$$

By Equations (A.26) and (A.28), the resulting magnetization is

$$\begin{aligned} M_i(\vec{r}, t) &= \sum_j \frac{1}{V} \delta_{ij} \iint d\vec{r}' dt' V \chi_0 \delta(t-t') \delta(\vec{r}-\vec{r}') H_j(\vec{r}', t') \\ M_i(\vec{r}, t) &= \chi_0 H_i(\vec{r}, t) \quad \text{or} \quad \vec{M}(\vec{r}, t) = \chi_0 \vec{H}(\vec{r}, t) \quad , \end{aligned} \quad (\text{A.32})$$

which is the classical result for a linear, homogeneous, isotropic magnetic material. One might represent $\vec{M}$ and χ_0 as functions of the temperature T at point $\vec{r}$ to further generalize this familiar form.

APPENDIX B

TABLES OF SUSCEPTIBILITY VERSUS TEMPERATURE DATA

Table AB-1

TEMP. (DEG. K) IMPURITY SUS. (CC/MOLE)

DISORDERED

300.0	.0115955
263.6	.0131158
251.7	.0136418
213.5	.0164053
175.8	.0200080
165.2	.0209961
156.7	.0222797
145.9	.0238413
134.8	.0253833
127.3	.0271385
120.9	.0283447
115.6	.0300120
108.2	.0316897
101.8	.0335661
96.9	.0354308
91.2	.0375150
85.9	.0401735
82.9	.0418200
80.5	.0428743
79.0	.0439831

CuPd(17)Mn(0.22)

ORDERED

300.0	.0125296
278.6	.0134934
236.3	.0159467
219.7	.0169365
190.6	.0196464
178.0	.0206369
167.0	.0221243
157.7	.0232777
149.5	.0248060
141.5	.0257151
135.3	.0269868
126.4	.0290627
118.2	.0306974
111.9	.0323131
106.8	.0336410
95.6	.0372090
88.4	.0409299
84.3	.0430841
81.8	.0442486
80.2	.0454777
79.0	.0456892

Table AB-2

TEMP. (DEG. K) IMPURITY SUS. (CC/MOLE)

DISORDERED

296.0	.0126243
256.2	.0146490
239.5	.0157644
223.7	.0167688
215.3	.0173110
206.2	.0180139
199.2	.0185741
191.6	.0192654
184.3	.0200361
177.5	.0209837
165.1	.0222783
148.9	.0246867
135.6	.0270994
126.8	.0290242
119.0	.0308094
113.2	.0323499
108.2	.0339038
102.8	.0356146
97.5	.0374167
93.3	.0391132
88.9	.0410792
84.2	.0434957
80.8	.0451394
79.0	.0462141

CuPd(17)Mn(0.70)

ORDERED

296.0	.0129874
280.5	.0136534
267.6	.0141367
256.0	.0149294
246.7	.0153600
239.2	.0156612
223.9	.0169221
205.3	.0180911
191.3	.0194336
179.3	.0206388
169.3	.0220337
160.6	.0230845
153.4	.0240217
146.5	.0249601
138.1	.0261876
128.5	.0282733
120.7	.0299147
114.5	.0316326
109.3	.0330050
103.3	.0348787
97.8	.0366386
91.8	.0386790
88.0	.0406474
83.4	.0425985
80.9	.0440067
79.0	.0447463

Table AB-3

TEMP. (DEG. K) IMPURITY SUS. (CC/MOLE)

DISORDERED

295.0	.0126961
270.0	.0140016
254.6	.0148207
236.8	.0159025
228.2	.0163562
220.0	.0169941
212.0	.0177994
204.7	.0183080
197.8	.0189448
190.7	.0195570
184.4	.0202477
172.1	.0214434
158.5	.0233761
145.1	.0252744
132.4	.0275082
126.3	.0291263
120.1	.0305133
110.0	.0332111
105.3	.0346919
101.5	.0360704
94.8	.0386285
89.9	.0406464
86.8	.0420549
83.7	.0435730
80.4	.0452002
79.0	.0459631

CuPd(17)Mn(1.16)

ORDERED

295.8	.0126991
281.4	.0132866
275.5	.0136582
268.7	.0139709
263.1	.0144036
256.7	.0146631
249.8	.0149780
235.6	.0158533
222.5	.0166934
209.2	.0177235
197.3	.0186012
186.4	.0196888
176.0	.0206026
166.6	.0217497
158.4	.0227108
146.9	.0241723
135.4	.0259724
127.4	.0276647
119.6	.0293262
111.3	.0310020
105.2	.0327706
97.7	.0350022
91.1	.0372734
86.3	.0393775
81.8	.0410320
80.5	.0417334

Table AB-4

TEMP. (DEG. K) IMPURITY SUS. (CC/MOLE)

DISORDERED

299.0	.0125213
277.9	.0133740
270.9	.0136679
258.8	.0142418
249.7	.0148069
242.4	.0152924
234.6	.0158108
225.8	.0162941
215.1	.0170381
203.6	.0180258
192.9	.0189408
182.8	.0199537
173.2	.0209626
165.0	.0220790
157.6	.0230330
151.2	.0240732
142.3	.0253833
131.2	.0274363
124.0	.0291511
114.7	.0316216
106.6	.0342325
100.9	.0359821
95.5	.0378432
92.8	.0393602
85.9	.0425952
81.0	.0448479
79.0	.0461229

CuPd(17)Mn(3.15)

ORDERED

295.7	.0112464
284.3	.0117977
276.5	.0120739
270.4	.0123634
259.7	.0127116
246.4	.0131756
232.5	.0138850
220.7	.0145569
209.0	.0151685
198.0	.0158338
188.0	.0165601
178.9	.0171095
170.3	.0178718
160.4	.0188026
147.0	.0201682
136.2	.0213616
128.8	.0224230
122.2	.0234423
116.2	.0242289
110.9	.0250702
103.3	.0265449
96.6	.0279853
92.0	.0291138
85.2	.0308556
81.0	.0322331
79.0	.0328192

Table AB-5

TEMP. (DEG. K) IMPURITY SUS. (CC/MOLE)

DISORDERED

298.0	.0156922
269.7	.0177120
237.9	.0198768
214.2	.0220038
202.8	.0232628
191.9	.0247087
181.3	.0262303
172.5	.0275217
164.1	.0285768
156.9	.0295199
150.0	.0308965
139.3	.0331279
128.5	.0355648
120.4	.0378205
113.5	.0399310
108.6	.0420920
102.6	.0443898
97.2	.0472008
93.2	.0491458
88.9	.0515536
85.6	.0535601
82.9	.0553842
78.8	.0582706

CuPd(17)Gd(0.4)

ORDERED

296.0	.0161163
259.6	.0182915
252.2	.0189704
246.1	.0192770
232.8	.0205386
216.9	.0219498
202.1	.0232931
187.7	.0249848
176.1	.0267801
165.3	.0283954
156.6	.0299650
148.4	.0317182
139.3	.0334375
129.8	.0354942
122.6	.0378205
116.5	.0395776
108.3	.0431062
100.4	.0461059
95.1	.0484799
89.9	.0514054
84.2	.0552132
81.3	.0573368
78.4	.0592354

Table AB-6

TEMP. (DEG. K) IMPURITY SUS. (CC/MOLE)

DISORDERED

294.0	.0112206
277.5	.0114286
251.9	.0131324
241.0	.0136327
231.1	.0142736
222.0	.0149330
212.7	.0155349
203.3	.0161875
194.0	.0170120
185.0	.0177346
158.6	.0211393
146.5	.0227212
129.3	.0255613
116.7	.0286287
107.9	.0307363
97.2	.0344331
91.2	.0368384
87.4	.0386874
82.5	.0415769
80.2	.0428207
78.4	.0439475

Cu₃AuMn(1.06)

ORDERED

298.2	.0111163
253.3	.0132042
238.5	.0139639
221.8	.0149907
207.3	.0161038
193.5	.0171900
180.1	.0184001
170.8	.0197170
162.2	.0206768
153.3	.0221121
147.2	.0230626
137.5	.0243868
128.9	.0260708
122.2	.0277002
115.2	.0292922
108.7	.0311733
103.3	.0330964
95.7	.0358932
89.0	.0390562
85.1	.0409385
82.6	.0424737
80.8	.0437497
79.0	.0445139

Table AB-7

TEMP. (DEG. K) IMPURITY SUS. (CC/MOLE)

DISORDERED

295.5	.0117365
279.5	.0124368
232.4	.0149055
220.7	.0155183
208.7	.0164505
197.4	.0173281
186.7	.0183528
167.5	.0203297
152.1	.0221690
139.8	.0241635
127.8	.0261056
115.2	.0286786
96.9	.0340646
88.5	.0371449
83.9	.0389038
80.0	.0409574
79.0	.0413209

Cu₃PtMn(0.81)

ORDERED

296.2	.0122460
281.4	.0127900
245.3	.0143955
224.7	.0158267
207.6	.0169997
184.8	.0188992
173.6	.0198705
164.1	.0211765
155.4	.0222562
147.7	.0234114
141.0	.0244256
131.5	.0258734
124.0	.0273923
117.4	.0286691
110.6	.0305458
104.2	.0323727
99.4	.0335777
91.4	.0362783
85.6	.0388845
82.2	.0401537
80.2	.0413817
78.4	.0424860

Table AB-8

TEMP. (DEG. K) IMPURITY SUS. (CC/MOLE)

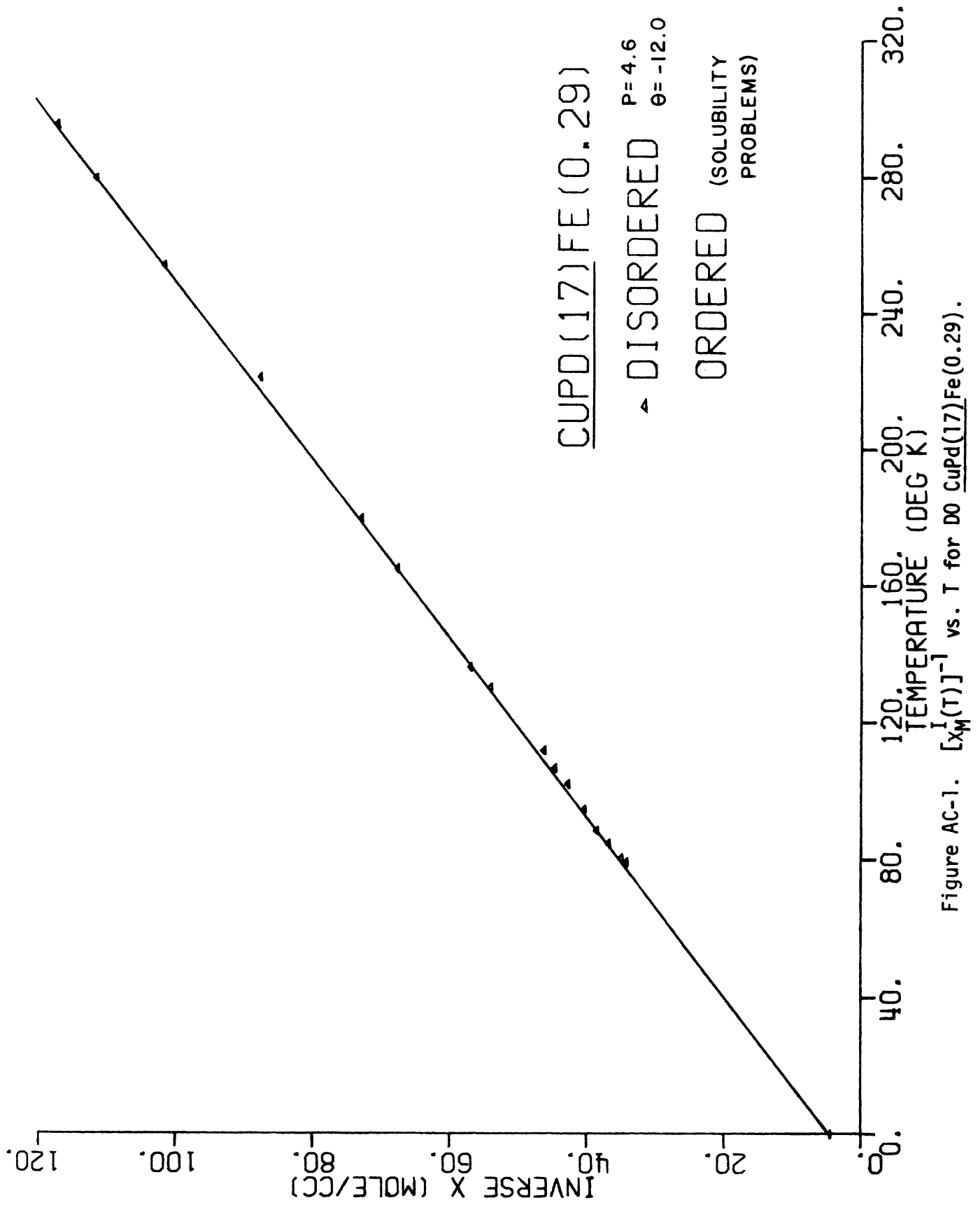
DISORDERED

295.8	.0085028
280.0	.0089234
254.6	.0097863
221.7	.0113371
180.3	.0136045
165.4	.0146621
136.7	.0173614
130.5	.0182792
112.2	.0213336
107.1	.0220712
102.4	.0230521
95.1	.0244081
88.9	.0255189
85.0	.0266670
80.8	.0281123
79.7	.0287154

CuPd(17)Fe(0.29)

APPENDIX C

INVERSE IMPURITY SUSCEPTIBILITY VERSUS TEMPERATURE PLOTS
FOR CuPd(17)Fe(0.29), Cu₃AuMn(1.06) AND Cu₃PtMn(0.81)

Figure AC-1. $[X_M(T)]^{-1}$ vs. T for D0 CuPd(17)Fe(0.29).

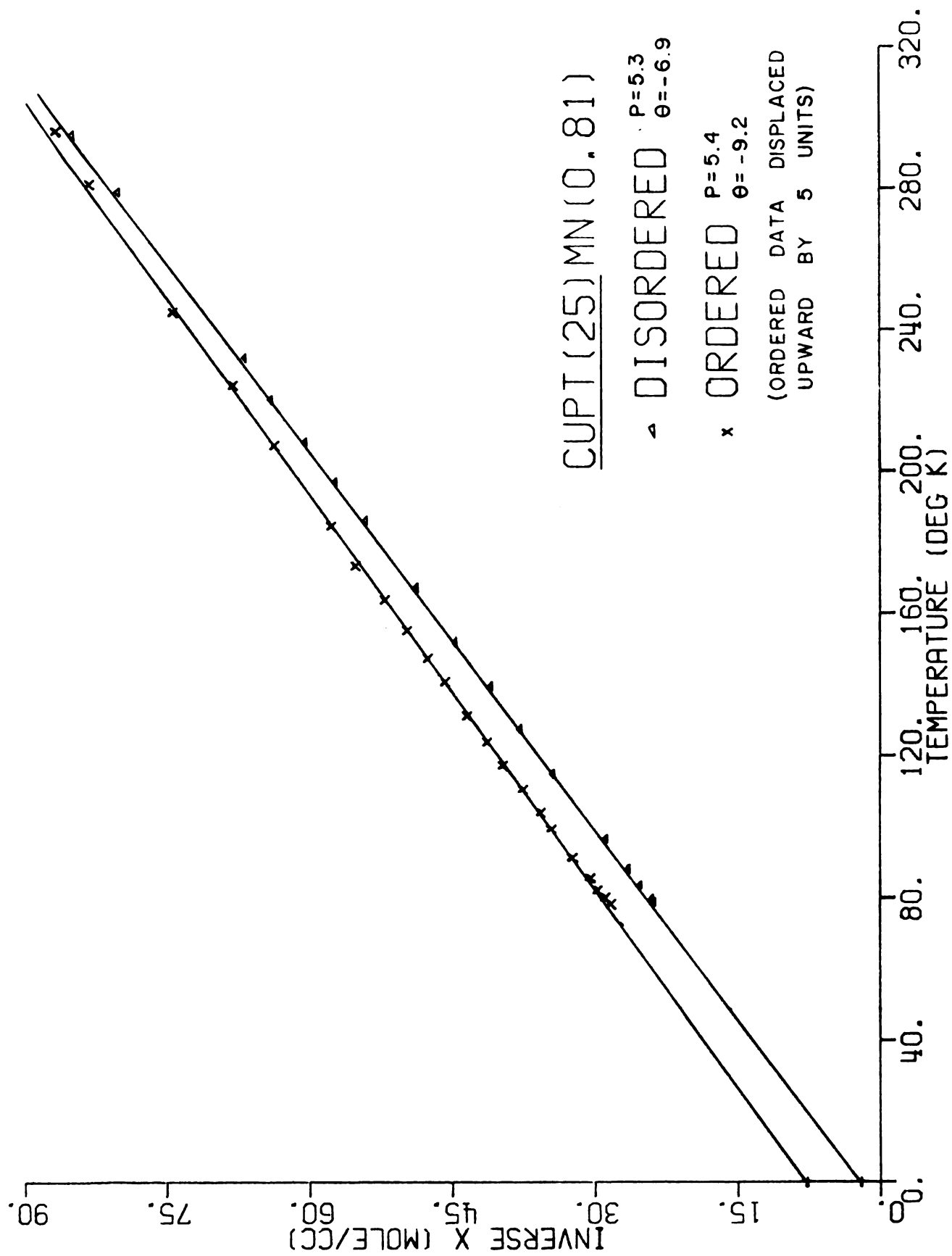


Figure AC-2. $[x_M(T)]^{-1}$ vs. T for ORD-DO Cu₃PtMn(0.81).

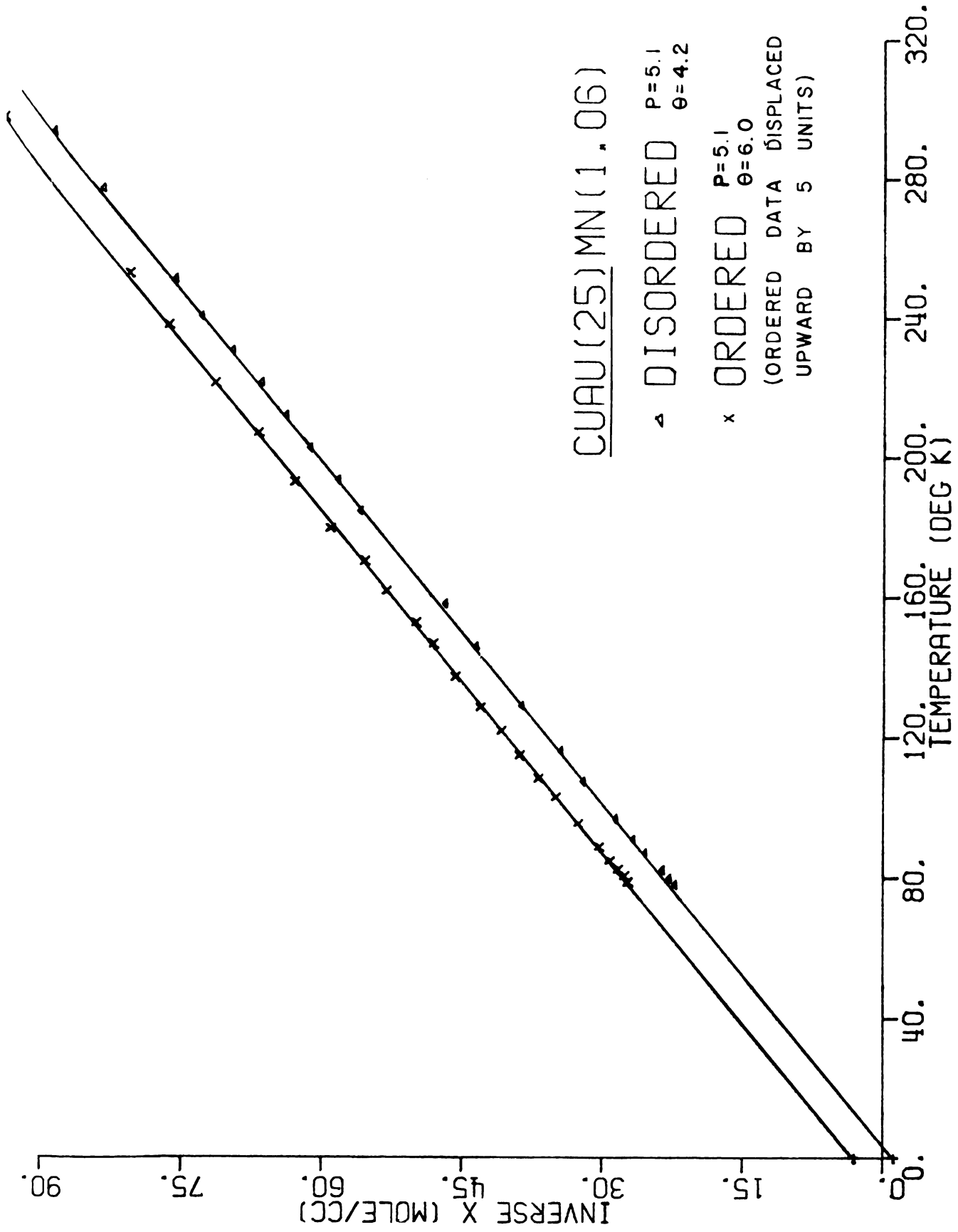


Figure AC-3. $[X_M(T)]^{-1}$ vs. T for ORD-DO Cu₃AuMn(1.06).

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