ABSTRACT

PARAMAGNETIC RELAXATION OF SUBSTITUTIONAL IMPURITIES IN $AlCl_3 \cdot 6H_2O$

by Robert F. Vieth

Spin-lattice relaxation times of substitutional Fe^{+++} and Cr^{+++} in $AlCl_3 \cdot 6H_2O$ have been measured. The data was taken over a wide range of temperatures, $1.1^{\circ}K.$ to $48^{\circ}K.$ for Fe^{+++} and $1.1^{\circ}K.$ to $80^{\circ}K.$ for Cr^{+++}. Both spin-echo and saturation recovery techniques were employed providing a cross-check between the two methods. The two methods yielded data which agreed within the limits of experimental error ($\sim 10\%$). Departures from the usual Raman behaviour were observed in Fe^{+++}. In the Raman region, the spin-lattice relaxation time had a $T^5 J_4(\theta/T)$ dependence. The Cr^{+++} obeyed a $T^7 J_6(\theta/T)$ Raman dependence. The Debye θ was found to be 160° in both cases. The full dependence for Fe^{+++} was $\frac{1}{\tau_1} = 71T + 7.58 \times 10^{-4} T^5$ and for Cr^{+++} was $\frac{1}{\tau_1} = 67T + 1.2 \times 10^{-8} T^7$.

A full discussion is accorded those relaxation theories which could explain the observed effects. The

mathematical section also includes a resumé of Group and Representation Theory for use in the field of paramagnetic resonance. Applications are made to the $AlCl_3 \cdot 6H_2O$ system studied.

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By

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A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Department of Physics and Astronomy

1963

PREFACE

This thesis was written with two objectives; to provide a clear presentation of the experiment and the data, and to provide an outline of the theoretical integrants of paramagnetic resonance and relaxation. In cases where methods or results were used but not proven, an effort has been made to provide references which do not require additional reading to understand. The bibliography is arranged so that it can be a useful entity.

Acknowledgement and thanks are due to all my professors. Special recognition is certainly due to Professor Jerry A. Cowen for his suggestion of the problem and continued assistance, to Professor Robert D. Spence for his many useful suggestions, and to Professor Truman Woodruff and Dr. Peter Schroeder for their helpful comments during the preparation of the dissertation. I should not forget the machine and electronics shops whose assistance and skill were always welcomed. The support for the research by the U. S. Army Signal Corps has been deeply appreciated.

This thesis is dedicated to my parents and wife who have provided me a constant source of encouragement, assistance, and inspiration.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF APPENDICES

CHAPTER I

INTRODUCTION

History

Spin-lattice relaxation phenomena in crystal salts has been a subject of both experimental and theoretical interest for three decades. Gorter[89] in the 1930's studied the relaxation phenomena using susceptibility techniques and Waller,[106] Van Vleck,[101] and Kronig[57] established a theoretical explanation of the results. With the advent of electron paramagnetic resonance the interest in relaxation phenomena was renewed, since resonance provided the possibility of measuring relaxation times in a more direct fashion. Experimental resolution limited the results to 4.2°K. and below until the late 1950's. During this period emphasis on spin-spin interactions played the major role.[33] Work in $K_3Co(CN)_6$ and $K_3Fe(CN)_6$[104] coupled with advances in resonance technology has reopened interest in Van Vleck's theory. Orbach[22] and Klemens,[18] within the past two years, have made modifications in the theory. Castle[19] has reported results up to about 90°K. in MgO using a saturation-inversion technique. To date, this is the most comprehensive

high temperature relaxation study in crystal salts. This is the situation at the present time: theories predicting higher temperature results have been formulated but still await direct experimental evidence before they can be expanded and/or corrected.[104]

Our experiment contrasts the relaxation time of an S state ion, $Fe^{+++}(^6S_{5/2})$, and a non-S state ion, Cr^{+++} $(^4F_{3/2})$, in the same host lattice $AlCl_3 \cdot 6H_2O$ over a temperature range of 1.1° to $80^{\circ}K$. In order to enhance the value of the data two dissimilar methods were used to check the validity of the results.

Summary of Theory

In order to understand relaxation time measurements, one must consider the theory of lattice vibrations[111, 48] and the theory of paramagnetic resonance.[43, 88, 97] The overall aim is to calculate the characteristic time (relaxation time) for electron spins that have absorbed energy to relinquish the energy to the thermal bath.

The absorption of energy by a paramagnetic electron is governed by the resonance equation,

$$h\nu = E_1 - E_2 \sim g\beta H \qquad (1.1)$$

where ν is the frequency of the incoming r.f., h is Planck's constant, E_1 is the final energy of the electron, E_2 is the

initial energy, g is a parameter for the paramagnetic system called the spectroscopic splitting factor, β is the Bohr magneton, and H is the applied magnetic field. Assume a certain group of spins with $g = g_1$ have their resonance condition met (1.1). If the r.f. field is turned off, then the spins will be in a non-equilibrium state. There are two processes that may occur. The first process is called cross-relaxation and has two aspects. The spins with $g = g_1$ can exchange energy among themselves in a characteristic time τ_2; also if there exists another set of spins with $g_2 \neq g_1$, the spins with g_1 may undergo mutual spin flips with them in a characteristic time denoted τ_{12}. The second process is termed the spin-lattice relaxation. The spins dispose of their energy to the lattice heat sink by means of the coupling between their orbital magnetic moment and the time varying electric field. The relaxation time for this process is labeled τ_1.

It is the latter process that shall be of concern to us. In order to calculate τ_1, the crystal field must be expanded in terms of the strain. Knowledge of the "exact" wavefunctions of the paramagnetic system is necessary in order to calculate the required matrix elements. These wavefunctions must reflect the symmetry of the crystal field. The "exact" wavefunctions would be calculated by

expansion in terms of d electron wavefunctions (and if need be admixtures of wavefunctions of the bonding electrons) which have been corrected for spin-orbit coupling by means of perturbation theory. The expansion coefficients are the Clebsh-Gordon coefficients (or their equivalents) which are arrived at by group theoretical arguments. However the coefficients and the correct wavefunctions for the expansions require a detailed knowledge of magnetic energy levels of the system under study, which, for our case, unfortunately is not available. One can write down the Spin Hamiltonian, which is a highly specialized form of the Hamiltonian used to describe only the states that participate in the resonance phenomena.

In spite of our difficulties in writing an exact expression for τ_1, it is still possible to extract the theoretical temperature dependence of τ_1 and compare it with our measured values. By writing down the lattice waves of a crystal in a simple classical form, one can obtain several quantum mechanical operators. These operators have the effect of creating and destroying a phonon, a process which takes place when an electron spin absorbs energy from or relinquishes energy to the lattice. Two systems of ions must be considered:

1) those which have an even number of electrons

(non-Kramers' systems), and

2) those with an odd number of electrons (Kramers' systems). Two types of relaxation can occur for each system: one which involves one phonon (the direct process) and one which involves two phonons (the Raman process). The direct process occurs at lower temperatures while the Raman is dominant at higher temperatures. For non-Kramers' systems we find $\frac{1}{\tau_1} \propto T$ for the direct process and $\frac{1}{\tau_1} \propto T^7$ for the Raman process. The situation for Kramers' systems is not so simple. If zero order wavefunctions are used in the computation of the necessary matrix elements, the direct process will vanish and the Raman process will have a T^9 dependence. If the zero order wavefunctions, however, are admixed with higher levels a direct process that again is proportional to T and a Raman process proportional to T^7 are obtained. However, if there are energy levels that lie low enough, the Raman process may go as T^5.

One can also consider the situation in which the thermal bath does not remain in equilibrium during the absorption of energy from the electrons. This is found to give an additive term proportional to T^2. The concentration of the impurity ions ($< .03\%$) is low enough so that this effect is negligible in our experiment.

Terms proportional to T^3 and T^{11}, for Kramers' case, and T^5 and T^{13}, for non-Kramers' case, arise from the effect of the impurity on the lattice modes. The results are obtained from the consideration of damped vibrational modes which are localized around the site of an impurity. These modes produce a spike in the frequency spectrum centered around a frequency which is termed the local mode frequency. For lattice frequencies above the local mode frequency, the impurity mass will not follow the lattice vibration and the resulting strain will be proportional to wave amplitude (in the normal situation the strain is proportional to the derivative of wave amplitude).

Outline of Mathematical Theory

In Chapter 2 we have indicated the calculations that are pertinent to our problem. In the first section, the group theory concepts applicable to paramagnetic resonance are set forth. The groups used in the examples are those which are directly applicable to our problem. In the second section we derive the local electric field at the Al^{+++} site and the Spin Hamiltonian. The construction of the "exact" wavefunctions and Hamiltonians is outlined using the Koster-Statz formalism. In the third section the normal mode relations are obtained and related to the creation and

annihilation operators. A discussion of the approximations that are made in the dispersion law is also included. Finally the relation of the Debye θ to other measured parameters is examined. In the fourth section relaxation times of the direct and Raman processes are determined in terms of transport integrals. In addition a brief discussion of cross-relaxation has been included.

CHAPTER 2

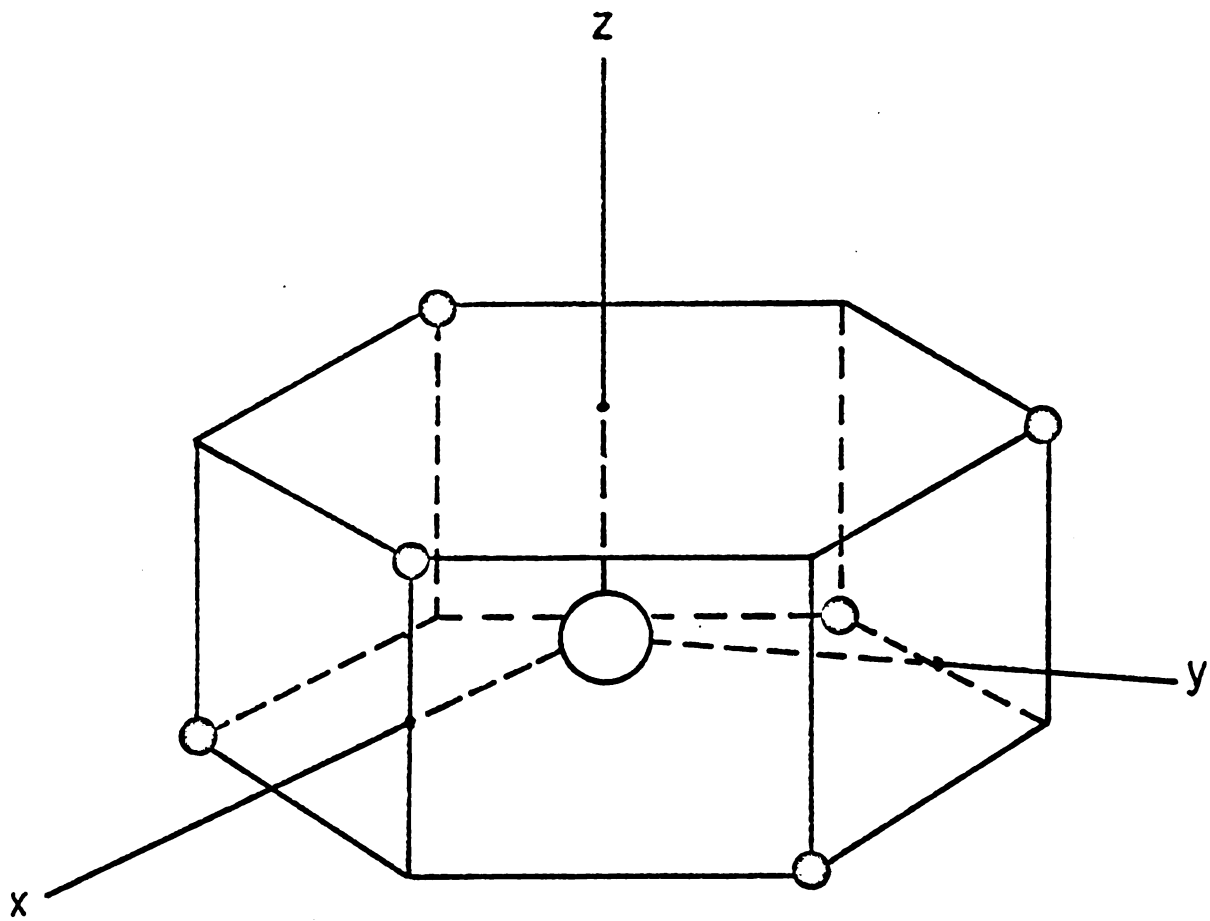
MATHEMATICAL THEORY

Introduction to Crystal Symmetry

In any discussion of the properties of a crystalline solid a definition of the geometric structure must be established. A perfect single crystal consists of a regular array of lattice sites (atom positions) with some periodic arrangement. Real crystals possess impurity atoms, vacant sites, and localized departures from the regular array extending over many sites.

The periodicity of the array of sites is commonly termed symmetry. If only the symmetry about each lattice site is considered, there are just 32 different point symmetries found in nature. A cross reference for notation of point-groups is given in the appendix. The addition of translational operations gives 230 space groups.

A resonance experiment, however, can only sample the point symmetry. The local point symmetry about the Al^{+++} site in $AlCl_3 \cdot 6H_2O$ is C_{3i}.[110] (See Figure 1.) This implies that the Al^{+++} site is a center of inversion and lies on a three-fold axis (the z-axis). Hence the neighboring atoms



H_2O

Al^{+++}

Figure 1. Local Symmetry of Al^{+++} Site.

lie at vertices of pairs of equilateral triangles whose planes are perpendicular to the three-fold axis. If one of the triangles lies in a plane at -z, the other is reflected through the inversion center to +z. The nearest neighbors are two sets of three water molecules located 1.8 Å from the Al^{+++} site. The two triangular planes are nearly coincident, being separated by less than .2 Å. The next nearest neighbors are two sets of three Cl^{-} atoms which lie at 3 Å and whose planes are separated by only .4 Å. Another group of three Cl^{-} also lies 3 Å from the Al^{+++} site but in a plane midway (2.1 Å) between two Al^{+++} sites.

It is useful to think of C_{3i} symmetry as a "distortion" of one of the body diagonals of a cube, since it is this "distortion" which changes upon substitution of an impurity for the Al^{+++} such as Fe^{+++} or Cr^{+++}. Thus the local symmetry can still be described as C_{3i},[109] but with a different distortion.

We shall now develop the basic ideas of group theory and use them to investigate the C_{3i}, distorted cubic, type of symmetry and apply the results to our resonance problem.

Group and Representation Theory

Groups. Group theory is an extensive topic in modern algebra. Most of the literature is highly mathematical in nature, the physical application aspect having been somewhat neglected. Wigner[107] and Lamont[68] are two of the best standard references combining a good mathematical introduction with physical applications. Several other texts[5, 33, 34, 62] and articles[6] referenced in the bibliography were invaluable aids in the following discussions.

A group G consists of a set of elements, A,B,C,.... which may be real or complex scalar functions, vectors, matrices, or any type of operator. The elements may be combined according to certain rules of "multiplication."

(1) Multiplication is closed (i.e., the product of any two elements is always in the group) and single valued.

(2) Multiplication is associative.

(3) Every group contains the identity element E (e.g. $EA = AE = A$).

(4) Every element has an inverse (e.g. $AA^{-1} = E$ where A^{-1} is the inverse of A).

The elements of a group do not necessarily commute. If the elements do, the group is termed Abelian.

The group multiplication properties can be exhibited

in a table form. Consider the group of six elements, E, A, B, C, J, F with the multiplication table:

	E	A	B	C	J	F
E	E	A	B	C	J	F
A	A	E	J	F	B	C
B	B	F	E	J	C	A
C	C	J	F	E	A	B
J	J	C	A	B	F	E
F	F	B	C	A	E	J

Example: BA = F and AB = J. The group is not Abelian. (2.1)

The table may be rewritten so that E's appear on the diagonal.

	E	A	B	C	J	F
E	E	A	B	C	J	F
A	A	E	J	F	B	C
B	B	F	E	J	C	A
C	C	J	F	E	A	B
F	F	B	C	A	E	J
J	J	C	A	B	F	E

(2.2)

Some basic terms must be defined:

1) g = the order of the group (i.e. the number of elements in the group).

2) n = the order of the element (i.e. $A^n = E$ where no number less than n satisfies the equation. The order of an element is always a divisor of the order of the group.).

3) A subgroup is a subset of G which itself forms a group.

4) A' is conjugate to A if $SAS^{-1} = A'$ and A and S belong to G.

5) The set of all elements conjugate to an element of G forms a subset of G known as a <u>class</u>. It follows that all the elements of a class have the same order. An invariant

subgroup is one that is made out of self-conjugate elements.

Representations. Given a group G, a matrix representation of the elements of G may be constructed. For each group element one matrix is chosen such that the multiplication table is the same as that of the group elements. Such a one to one correspondence is called an isomorphism. Denote the matrix corresponding to the group element A by D(A), B by D(B), etc. For the group described by (2.1), a matrix representation then is (it is not unique):

$$D(A) = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad D(B) = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix} \quad D(C) = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ -\sqrt{3}/2 & 1/2 \end{pmatrix} \tag{2.3}$$

$$D(J) = \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ -\sqrt{3}/2 & -1/2 \end{pmatrix} \quad D(F) = \begin{pmatrix} -1/2 & -\sqrt{3}/2 \\ \sqrt{3}/2 & -1/2 \end{pmatrix} \quad D(E) = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix}$$

Once a representation has been found, it is possible to generate "new" representations that obey the multiplication tables by using matrix transforms known as similarity transformations. These "new" matrices, since they are not unique, are termed equivalent matrices. If R is a general element of a group and D(R) is its matrix representation, the transformation is

$$\left(S\right) \; D(R) \quad \left(S\right)^{-1} \quad = D'(R) \tag{2.4}$$

and is carried out for all the elements of the group. $\left(S\right)$ does not have to be a matrix in the representation. It is

always possible to transform a matrix representation so that all the representation matrices of the group elements are simultaneously unitary, that is the complex conjugate transpose of the matrix is equal to the inverse of the matrix.

$$\left(P\right)^{-1} = \left(\tilde{P}\right)^{*} = \left(P\right)^{\dagger} \tag{2.5}$$

The sum of the diagonal elements of a matrix is called the trace, spur, or, in group theory, the character of the matrix. A similarity transformation leaves the character of a matrix invariant; the determinant is also left invariant.

There is a method other than inspection for writing a matrix representation of a group by just using the multiplication table. This representation is constructed by first rewriting the multiplication so that E's appear on the diagonal. Then the representation matrix of the element is obtained by replacing that element in the table by 1 and every other element by zero. From (2.2), the representation for A is:

$$\left(A\right) = \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \end{pmatrix}. \tag{2.6}$$

This is called the regular representation of A. The other elements can be written down in a similar fashion. By the

proper similarity transformation, it might be possible to completely diagonalize this matrix. Failing in this we try to form blocks along the diagonal, then try to diagonalize each block. In (2.6) there is already a small block of 2x2 elements in the left hand upper corner and a large block of 4x4 elements in the lower corner. Let us diagonalize the 2x2 block:

$$\begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \longrightarrow \begin{vmatrix} 0-\lambda & 1 \\ 1 & 0-\lambda \end{vmatrix} = \lambda^2 - 1 = 0 \qquad (2.7)$$

$$\therefore \lambda = \pm 1$$

Construction of the similarity transformation can be done immediately. The secular equation[23] is

$$\begin{aligned} (0-\lambda)\,\xi' + \eta' &= 0 \\ \xi' + (0-\lambda)\,\eta' &= 0 \end{aligned} \qquad (2.8)$$

and we are free to pick a normalizing condition

$$\xi^2 + \eta^2 = 1. \qquad (2.9)$$

For $\lambda = 1$ $\quad \begin{pmatrix} \xi' \\ \eta' \end{pmatrix} = \begin{pmatrix} 1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} \equiv |x'\rangle \qquad (2.10)$

For $\lambda = -1$ $\quad \begin{pmatrix} \xi' \\ \eta' \end{pmatrix} = \begin{pmatrix} -1/\sqrt{2} \\ 1/\sqrt{2} \end{pmatrix} \equiv |y'\rangle \qquad (2.11)$

(2.10) and (2.11) are called the basis vectors. Notice they are orthogonal and hence span a two-dimensional subspace. The diagonalization just performed can be interpreted as

a rotation of the basis vectors in two-dimensional subspace. If S is the unitary matrix (that is a rotation matrix which keeps an orthogonal system orthogonal) that transforms $\begin{pmatrix}\xi\\ \eta\end{pmatrix}$ to $\begin{pmatrix}\xi'\\ \eta'\end{pmatrix}$, then

$$\begin{pmatrix}S\end{pmatrix}\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix}\begin{pmatrix}S\end{pmatrix}^{-1} = \begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}$$

will transform A to a diagonalized form. S^{-1} can be shown[24] to be a matrix made from the transformed column basis vectors.

$$S^{-1} = \begin{pmatrix}|x'\rangle & |y'\rangle\end{pmatrix} = \begin{pmatrix}1/\sqrt{2} & -1/\sqrt{2}\\ 1/\sqrt{2} & 1/\sqrt{2}\end{pmatrix} \qquad (2.12)$$

Since S is unitary, $S^{-1} = \tilde{S}^*$ ($\sim$ indicates transpose) and thus

$$S = \begin{pmatrix}1/\sqrt{2} & 1/\sqrt{2}\\ -1/\sqrt{2} & 1/\sqrt{2}\end{pmatrix} \qquad (2.13)$$

By permuting the elements B,C,J,F, in the multiplication table, still keeping the E's on the diagonal, the 4x4 matrix can be reduced into smaller blocks.

$$\begin{pmatrix}0 & 0 & 0 & 1\\ 0 & 0 & 1 & 0\\ 0 & 1 & 0 & 0\\ 1 & 0 & 0 & 0\end{pmatrix} \Rightarrow \begin{pmatrix}0 & 1 & 0 & 0\\ 1 & 0 & 0 & 0\\ 0 & 0 & 0 & 1\\ 0 & 0 & 1 & 0\end{pmatrix} \qquad (2.14)$$

This allows us to work with two two-dimensional parts of the '4' dimensional subspace. Then the similarity transformation for A in block form of (2.7) and (2.14) is, if

$$\begin{pmatrix} 1/\sqrt{2} & 1/\sqrt{2} & 0 & 0 & 0 & 0 \\ -1/\sqrt{2} & 1/\sqrt{2} & 0 & 0 & 0 & 0 \\ 0 & 0 & 1/\sqrt{2} & 1/\sqrt{2} & 0 & 0 \\ 0 & 0 & -1/\sqrt{2} & 1/\sqrt{2} & 0 & 0 \\ 0 & 0 & 0 & 0 & 1/\sqrt{2} & 1/\sqrt{2} \\ 0 & 0 & 0 & 0 & -1/\sqrt{2} & 1/\sqrt{2} \end{pmatrix} = (S) \qquad (2.15)$$

then

$$(S) \begin{pmatrix} 0 & 1 & 0 & 0 & 0 & 0 \\ 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} (S)^{-1} = \begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & -1 \end{pmatrix} \qquad (2.16)$$

This similarity transformation is then applied to the regular representation of each of the other elements. The direct sum rule may be illustrated for $(B)_{reg}$:

$$\begin{pmatrix} -1/2 & \sqrt{3}/2 & & & & \\ \sqrt{3}/2 & 1/2 & & & & \\ & & -1/2 & \sqrt{3}/2 & & \\ & & \sqrt{3}/2 & 1/2 & & \\ & & & & 1 & \\ & & & & & -1 \end{pmatrix} \equiv$$

$$\begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix} \oplus \begin{pmatrix} -1/2 & \sqrt{3}/2 \\ \sqrt{3}/2 & 1/2 \end{pmatrix} \oplus (1) \oplus (-1) \qquad (2.17)$$

Inspecting the results of (2.15) and (2.17) shows that the same two-dimensional matrix occurs twice; two different one-dimensional matrices occur once. The reason for not interpreting (2.15) as six one-dimensional matrices is that it is impossible to completely diagonalize all the regular

representations simultaneously as (2.17) clearly shows. If we were to write the regular representations for all the elements and then perform the similarity transformation as shown above, each matrix would have at most two two-dimensional matrices, the remainder being one-dimensional. These matrices then are said to be irreducible matrix representations, that is their dimension cannot be reduced. It can be shown[33] that the regular representation contains each possible irreducible representation a number of times equal to the dimension of the irreducible representation. Our example group has two one-dimensional irreducible representations and one two-dimensional irreducible representation. A by-product of this result is

$$\sum_{\lambda} \ell_{\lambda}^{2} = g \qquad (2.18)$$

where ℓ_{λ} is the dimension of the λ^{th} irreducible representation and g is the order of the group. Schur's lemma[33] states that if D(R) is an irreducible representation, then if and only if for all R, AD(R) = D(R)A, then A = constant · 1.

Hilbert Space. A complete unitary space is called a Hilbert space. The unitary spaces of a finite dimension are always complete. In our example the basis vectors of the entire group span a four-dimensional Hilbert Space. By finding the irreducible matrices and the corresponding basis vectors

the space was subdivided into one two-dimensional subspace and two one-dimensional subspaces. (This is the equivalent of subdividing relativistic four-dimensional space [Minkowski space] into an x-y plane, the z-axis, and the time axis.) Each of these spaces is invariant under the action of the group.

Among the irreducible representations there is always a trivial one, the unit representation, given by a single base function invariant under transformations of the group. In the unit representation all the elements of the group are represented by the one-dimensional unit matrix and hence all the characters equal one.

The Character Table. The fact that the character of a matrix is invariant under a similarity transformation suggests it might be seen that the character of the irreducible representations is significant; in fact a great deal of information may be gleaned in this way. The table of the characters of our example, which is commonly called Group 32, is now listed.

	E	ABC	JF
Γ_1	1	1	1
Γ_2	1	-1	1
Γ_3	2	0	-1

(2.19)

Since elements in the same class have the same character,

only the characters for each class are listed. (Elements in the same class are related by a similarity transformation.) Γ_1 refers to one of our one-dimensional representations, Γ_2 to the other. Γ_3 is the notation of the two-dimensional representation. (The notation is that of Bethe. There is another common notation, the Mulliken notation. The two notations are cross referenced in Table 1 of the appendix.)

Several important relations between group characters can now be written.[108] Remembering k is the number of classes, ℓ is the dimension of the irreducible representations, g is the order of the group, h_i is the number of elements in the class C_i, and $X^{\alpha}(C_i)$ is the character of the α^{th} representation, i^{th} class, we have

$$g\delta_{\alpha\beta} = (\underline{X}^{\alpha}, \underline{X}^{\beta}) = \sum_{i=1}^{k} h_i X^{\alpha *}(C_i) X^{\beta}(C_i) \qquad (2.20)$$

$$g\delta_{ij} = (\underline{X}(C_i), \underline{X}(C_j)) = \sum_{\alpha=1}^{k} h_i X^{\alpha *}(C_i) X^{\alpha}(C_j) \qquad (2.21)$$

These relations are known as the orthogonality relations. Relation (2.20) implies that if each element in a row of a character table is considered as a vector component, then the rows are mutually orthogonal with respect to one another. These vectors are normalized to one by the appearance of the g's and h's in the formula. Relation (2.21) is a similar orthogonality condition on the columns. Any general

representation of the group with the vector character $\underline{X}$ of the group can be resolved into its component irreducible representations by the same device as used in vector algebra, the scalar product:

$$a_\alpha = (\underline{X}^\alpha , \underline{X}) = \frac{1}{g} \sum_{i=1}^{k} h_i X^{\alpha *}(C_i) X (C_i) \qquad (2.22)$$

One other orthogonality relation is important. For irreducible representations, G, of the same group

$$\sum_G G^\alpha_{ik} G^\beta_{\ell m} = \frac{g}{h_\alpha} \delta_{i\ell} \delta_{km} \delta_{\alpha\beta} \qquad (2.23)$$

Projection Operators.[42, 35] If there exists a particular vector in the Hilbert space spanned by the basis vectors of the irreducible representations, then it is reasonable to ask for the components of that vector along each of the basis vectors. If the α^{th} irreducible matrix representation is $\left(D^\alpha(A)\right)$ for an element A, then the component of Φ along the i^{th} basis vector in the subspace of the α^{th} representation is

$$\phi^\alpha_i = \sum_A^g D^\alpha(A)^*_{ij} A\Phi \qquad (2.24)$$

where j is fixed at any value. If, as is usually the case, only a character table is available, we must settle for the total component of Φ in the α^{th} subspace.

$$\phi^\alpha = X^\alpha(A)^* A\Phi \qquad (2.25)$$

Direct Product of Representations. Consider the vectors spanning the subspaces of two irreducible representations of the same group, $|\psi^{\alpha}\rangle$ and $|\psi^{\beta}\rangle$. The products $\psi_i^{\alpha}\psi_j^{\beta}$ can serve as basis functions of a new representation equal in dimension to the product of the dimensions of the irreducible representations. The characters of the new representation are equal to the products of the characters of the two component representations, that is $X^{\alpha}\times X^{\beta}(G) = X^{\alpha}(G)X^{\beta}(G)$. The product of a representation with itself can immediately be decomposed into two representations, one with symmetric, the other with antisymmetric functions. The character for the symmetric product is

$$[X^2](G) \equiv \frac{1}{2}\left\{[X(G)]^2 + X(G^2)\right\} \tag{2.26}$$

and that for the antisymmetric product is

$$\left\{X^2\right\}(G) \equiv \frac{1}{2}\left\{[X(G)]^2 - X(G^2)\right\} . \tag{2.27}$$

No antisymmetric product can be formed if the $|\psi^{\alpha}\rangle$ and the $|\psi^{\beta}\rangle$ are the same functions.

As an example of representation products consider the integral $\int\psi_i^{\alpha}dq$ where ψ_i^{α} is the basis vector of the α^{th} representation of G. The integral is taken over all space and hence is invariant to any symmetry transformations. Then

$$\int\psi_i^{\alpha}dq = \int\hat{G}\psi_i^{\alpha}dq = \int\sum_k G_{ik}{}^{\alpha}\psi_k^{\alpha}dq$$

and if we sum over all members of the group

$$g\int \psi_i^{\alpha} dq = \sum_k \int \sum_G G_{ik}^{c} \psi_k^{\alpha} dq, \tag{2.28}$$

but by (2.23) this is zero is α is not the unit representation. Hence the product of an integral of three functions must also transform as the unit representation to be different from zero. Since the product of a representation with itself contains a unit representation, then for the integral $\int \psi_i V \psi_j$, the product representations according to which ψ_i and ψ_j transform must contain a representation under which V transforms.

Direct Product of Groups. If functions $|\psi^{\alpha}\rangle$ span the α^{th} representation of the group G and $|\phi^{\beta}\rangle$ span the β^{th} representation of group H, the products of the form $\phi_i^{\beta}\psi_j^{\alpha}$ are the basis functions of a $\lambda_{\alpha} \cdot \lambda_{\beta}$ dimensional irreducible representation of the group G $\otimes$ H. The characters of this representation are obtained by multiplying together the characters of the original representations so that if element C belongs to G $\otimes$ H, G' belongs to G, and H' belongs to H and C = G'H', then

$$\psi^{\sigma}(C) = \psi^{\alpha}(G')\psi^{\beta}(H') \tag{2.29}$$

where σ will be an irreducible representation of G $\otimes$ H.

An example of a product group is

$$C_{3i} = C_3 \otimes C_i . \tag{2.30}$$

The corresponding character tables[54] for C_i and C_3 are:

C_i	E	I
A_g	1	1
A_u	1	-1

C_3	E	C_3	C_3^2
A	1	1	1
E	1	ϵ^2	$-\epsilon$
	1	$-\epsilon$	ϵ^2

(2.31)

$\epsilon = \exp \pi i/3$

where I is the inversion operator, C_3 is a rotation of 120° around the three-fold axis, C_3^2 is the rotation of 240° around the same three-fold axis. All the representations are one-dimensional since the representations of E are all one. From $g = \Sigma \ell_2^{\,2}$, the classes all contain only one element; the two groups are thus Abelian. The product group is:

C_{3i}	E	C_3	C_{2y}	I	$\underbrace{C_3 I}_{5}$ S_6	$\underbrace{C_3^2 I}$ S_6
A_{1g}	1	1	1	1	1	1
E_g	1	ϵ^2	$-\epsilon$	1	ϵ^2	$-\epsilon$
	1	$-\epsilon$	ϵ^2	1	$-\epsilon$	ϵ^2
A_{1u}	1	1	1	-1	-1	-1
E_u	1	ϵ^2	$-\epsilon$	-1	$-\epsilon^2$	ϵ
	1	$-\epsilon$	ϵ^2	-1	ϵ	$-\epsilon^2$

(2.32)

Double Valued Representations. Since the group elements of the axial rotational group are Abelian the representations are one-dimensional and thus $X(\Phi_1)X(\Phi_2)$ must equal $X(\Phi_1+\Phi_2)$.[34] We also must have $X(2\pi) = X(0)$; thus $X(\Phi) = e^{im\Phi}$ where m is an integer corresponding to the m^{th} representation. The rotations by an angle Φ about different axes belong to the same class of the full rotation group. Thus[36]

$$X^j(\Phi) = \sum_{m=-j}^{j} e^{im\Phi} = \frac{\sin (j + 1/2)\Phi}{\sin(1/2)\Phi}. \qquad (2.33)$$

Frequently the total angular momentum j takes on nonintegral values, for example $j = 1/2$. Using equation (2.33) for the character of the full rotation group,

$$X^j(\Phi + 2\pi) = (-1)^{2j} \frac{\sin (j + 1/2)\Phi}{\sin (1/2)\Phi} \qquad (2.34)$$

$$X^{1/2}(\Phi + \pi) = -X^{1/2}(\Phi). \qquad (2.35)$$

This does not correspond to the effect that is expected by a rotation of 360°. The introduction of spin has made the characters double valued. If a spin system corresponding to half integral values is to be used, double groups must be employed. In order to do this a new element $R = -E$ is introduced to the old groups. Koster[54] has tabulated the double groups for all the crystal point-groups. Several rules have been written down for calculating the double groups.[38] These rules and the character orthogonality

relations allow us to construct the double-point group of C_{3i}.

Application. The group and representation theory can be applied to determine the energy level degeneracies of a paramagnetic ion in an electric field of a specified symmetry. Consider Fe^{+++}, $^6S_{5/2}$, ion as a substitutional ion for Al^{+++} in $AlCl_3 \cdot 6H_2O$. The local symmetry in such a site is C_{3i}.[109, 5] Using (2.33) to find the characters of the rotation group corresponding to the group elements of C_{3i}, it is seen that

	E	C_3	C_3^2	I	S_6^5	S_6	R	RC_3	RC_3^2	RI	RS_6^5	RS_6
$D_{5/2}$	6	0	0	6	0	0	-6	0	0	-6	0	0 .

(2.36)

The identity character is 6 because of the dimensionality of the 5/2 manifold. We have used the fact that the electrons of interest are d electrons, and the inversion operation shows no effect on the characters of the rotation group whose corresponding basis functions display even parity. The decomposition (2.22) of the reducible representation yields

$$D_{5/2} = 2\Gamma_{4g} \oplus 2\Gamma_{5g} \oplus 2\Gamma_{6g}. \qquad (2.37)$$

This is shown in Figure 2.

The case for Cr^{+++}, $^4F_{3/2}$, substituting for Al^{+++},

CHARACTER TABLE FOR $\bar{3}$

	E	C_3	C_3^2	I	S_6^5	S_6	R	RC_3	RC_3^2	R	RS_6^5	RS_6
Γ_{1g}	1	1	1	1	1	1	1	1	1	1	1	1
Γ_{2g}	1	ϵ^2	$-\epsilon$	1	ϵ^2	$-\epsilon$	1	ϵ^2	$-\epsilon$	1	ϵ^2	$-\epsilon$
Γ_{3g}	1	$-\epsilon$	ϵ^2	1	$-\epsilon$	ϵ^2	1	$-\epsilon$	ϵ^2	1	$-\epsilon$	ϵ^2
Γ_{4g}	1	ϵ	ϵ^2	1	ϵ	ϵ^2	-1	$-\epsilon$	$-\epsilon^2$	-1	$-\epsilon$	$-\epsilon^2$
Γ_{5g}	1	$-\epsilon^2$	$-\epsilon$	1	$-\epsilon^2$	$-\epsilon$	-1	ϵ^2	ϵ	-1	ϵ^2	ϵ
Γ_{6g}	1	-1	1	1	-1	1	-1	1	-1	-1	1	-1
Γ_{1u}	1	1	1	-1	-1	-1	1	1	1	-1	-1	-1
Γ_{2u}	1	ϵ^2	$-\epsilon$	-1	$-\epsilon^2$	ϵ	1	ϵ^2	$-\epsilon$	-1	$-\epsilon^2$	ϵ
Γ_{3u}	1	$-\epsilon$	ϵ^2	-1	ϵ	$-\epsilon^2$	1	$-\epsilon$	ϵ^2	-1	ϵ	$-\epsilon^2$
Γ_{4u}	1	ϵ	ϵ^2	-1	$-\epsilon$	$-\epsilon^2$	-1	$-\epsilon$	$-\epsilon^2$	1	ϵ	ϵ^2
Γ_{5u}	1	$-\epsilon^2$	$-\epsilon$	-1	ϵ^2	ϵ	-1	ϵ^2	ϵ	1	$-\epsilon^2$	$-\epsilon$
Γ_{6u}	1	-1	1	-1	1	-1	-1	1	-1	1	-1	1

Note here that $\epsilon = e^{\pi i/3}$.

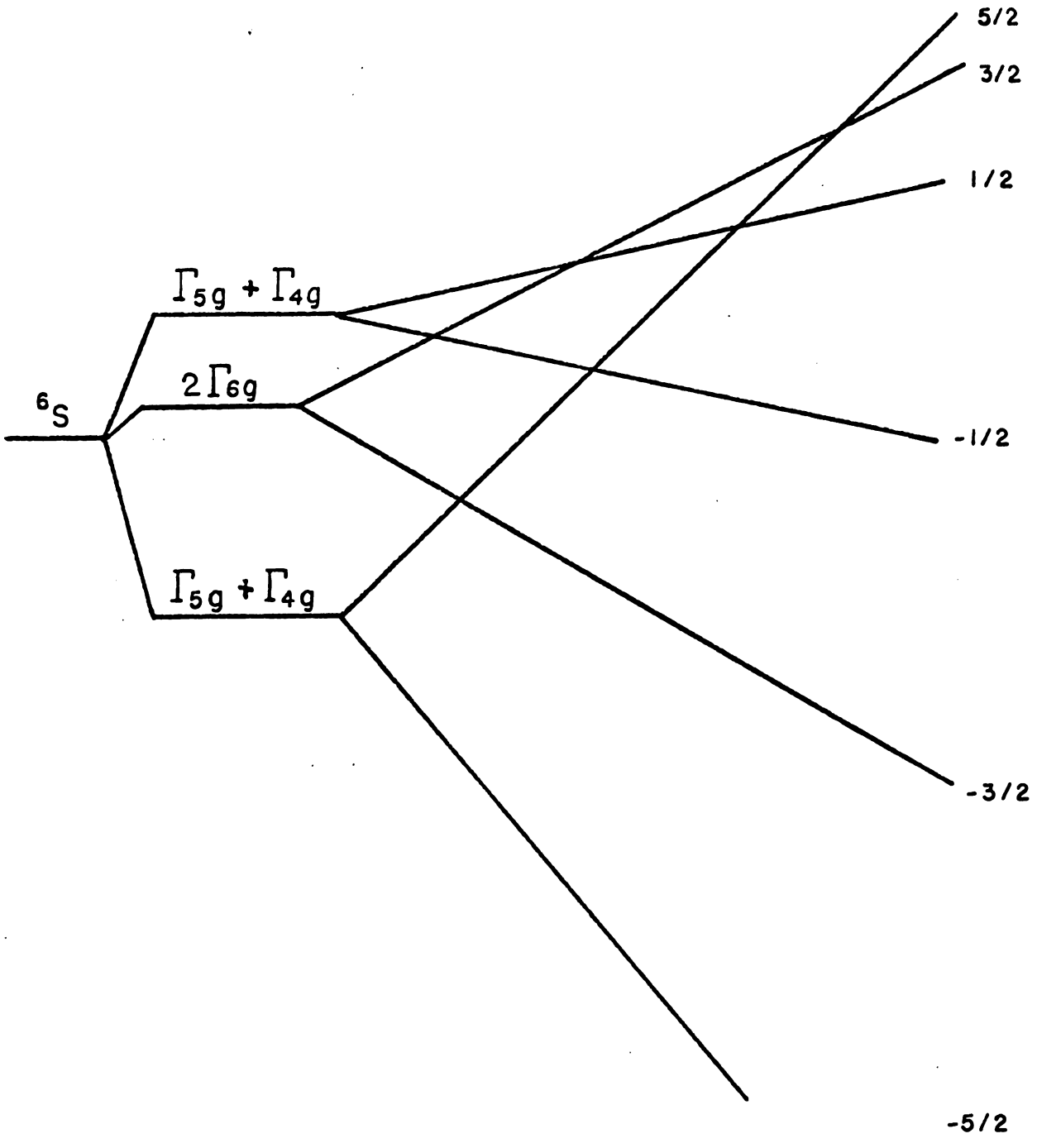


Figure 2. Fe^{+++} Energy Diagram.

can be handled in a similar manner. One must remember that the values of the characters of the rotation group for half integral angular momentum (58.1) are double valued.

	E	C_3	C_3^2	I	S_6^5	S_6	R	RC_3	RC_3^2	RI	RS_6^5	RS_6
$D_{3/2}$	4	-1	1	4	-1	1	-4	1	-1	-4	1	-1

(2.38)

Then

$$D_{3/2} = 2\Gamma_{6g} \oplus \Gamma_{5g} \oplus \Gamma_{4g} \tag{2.39}$$

The same results may be obtained for either Cr^{+++} or Fe^{+++} by assuming an axially distorted cubic symmetry. We shall illustrate this for Cr^{+++}. First a cubic field is considered; then an axial distortion along one of the body diagonals of the cube is carried out. The complete character table can be found for the cubic group in Bethe's article[6] or Koster's compilation.[54] From Table 12 of Bethe's article (or by computing in a similar manner as we did for Fe^{+++} and Cr^{+++})

$$D_3 = \Gamma_2 \oplus \Gamma_4 \oplus \Gamma_5 \qquad D_{3/2} = \Gamma_8 \tag{2.40}$$

where Γ_2 is one-dimensional, Γ_4 is three-dimensional, and Γ_5 is three-dimensional. (We note that D_3 is seven-dimensional which serves as a check to see if the reduction is correct.) The ground state, which must be identified by some means other than group theory, is Γ_2. The product

representation $\Gamma_2 \times \Gamma_8$ is the representation of an LS coupled state for the ground multiplet. However, the product may be reduced into irreducible representation, $\Gamma_2 \times \Gamma_8 = \Gamma_J$. From Hund's rule we note that the lowest j multiplet is j = 3/2 which indicates directly that the ground multiplet transforms as Γ_8. These results are indicated in Figure 3. For reference we note also that

$$\Gamma_8 \times \Gamma_4 = \Gamma_6 \oplus \Gamma_7 \oplus 2\Gamma_8 \tag{2.41}$$

$$\Gamma_8 \times \Gamma_5 = \Gamma_6 \oplus \Gamma_7 \oplus 2\Gamma_8 \tag{2.42}$$

which gives the splitting of the higher multiplets.

Now the cube is distorted along one of its body diagonals. This gives the symmetry of double group 32, which has the following character: (Note the group 32 multiplication tables and irreducible representation have been derived (2.1), (2.3) and (2.19).)

	E	RE	$2C_3$	$2RC_3$	$3C_2$	$3RC_2$
Λ_1	1	1	1	1	1	1
Λ_2	1	1	1	1	-1	-1
Λ_3	2	2	-1	-1	0	0
Λ_4	1	-1	1	-1	i	-i
Λ_5	1	-1	1	-1	-i	i
Λ_6	2	-2	-1	1	0	0

(2.43)

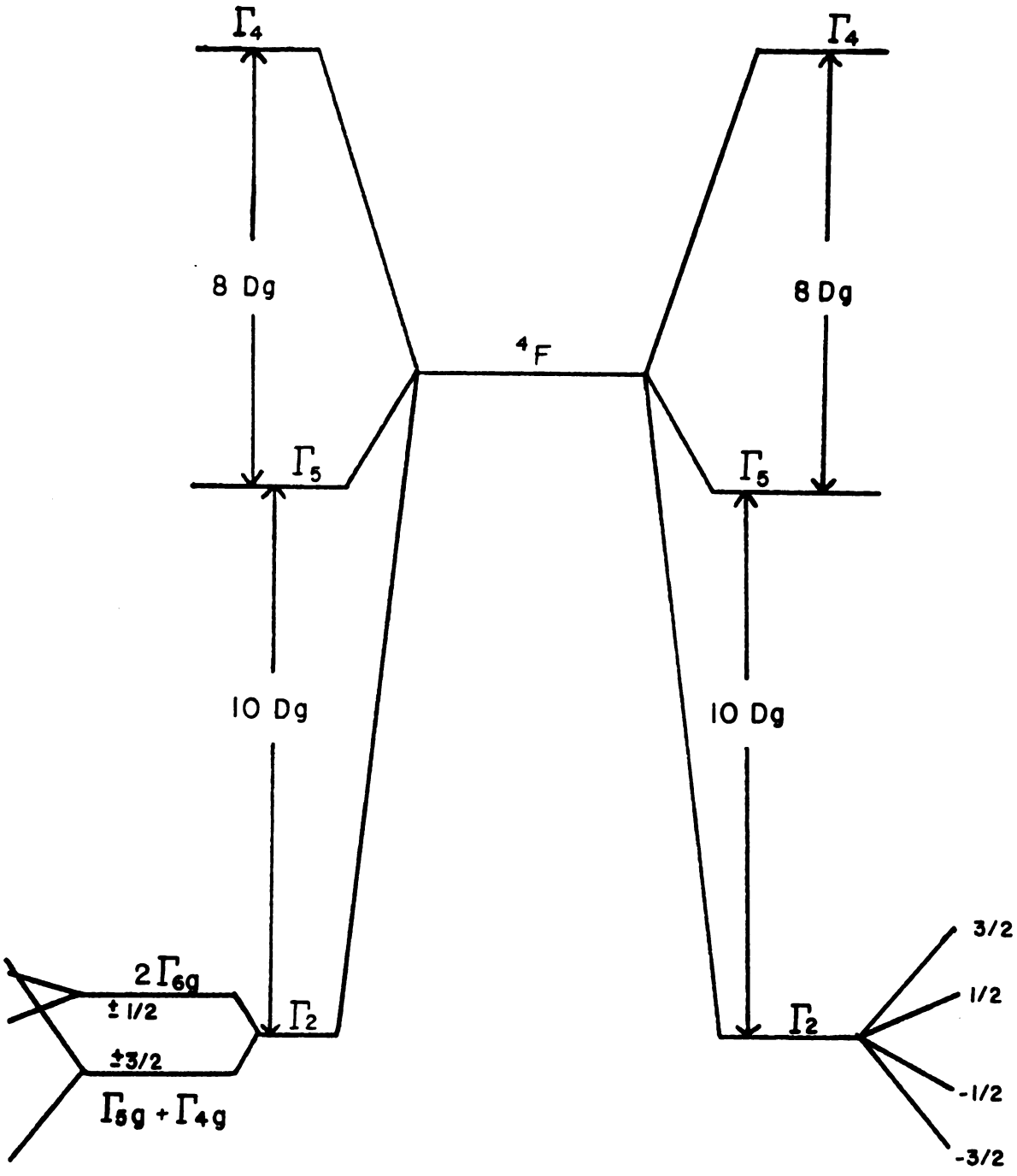


Figure 3. Cr^{+++} Energy Diagram.

Those of the corresponding cubic operators are:

Γ_1	1	1	1	1	1	1
Γ_2	1	1	1	1	-1	-1
Γ_3	2	2	-1	-1	0	0
Γ_4	3	3	0	0	1	1
Γ_5	3	3	0	0	-1	-1
Γ_6	2	-2	1	-1	0	0
Γ_7	2	-2	1	-1	0	0
Γ_8	4	-4	-1	1	0	0

(2.44)

C_2 is the two-fold rotation operator along a cube face;

C_3 is the three-fold rotation operator along a cube diagonal.

Thus

$$\Gamma_8 = \Lambda_4 + \Lambda_5 + \Lambda_6 ,$$

since again the character of the rotations forming a reducible representation are double valued. Note that $\Lambda_6 \longrightarrow \Gamma_{6g}$, $\Lambda_5 \longrightarrow \Gamma_{5g}$, and $\Lambda_4 \longrightarrow \Gamma_{4g}$ on the diagram.

<u>Coupling Coefficients</u>.[90, 107, 31] The product of two representations in general is reducible. Consider a general representation product

$$\chi^{(\alpha \times \beta^*)}(C_i) \equiv \chi^{\alpha}(C_i)\, \chi^{\beta^*}(C_i) \qquad (2.45)$$

then using (2.20)

$$\alpha_\sigma = \frac{1}{g} \sum_{i=1}^{k} h_i \, X^{(\alpha \times \beta^*)}(C_i) X^{\sigma *}(C_i). \tag{2.46}$$

The number of times the identity representation appears then is just

$$\alpha_1 = \frac{1}{g} \sum_{i=1}^{k} h_i \, X^{\alpha}(C_i) X^{\beta *}(C_i) \tag{2.47}$$

$$= \delta_{\alpha\beta} \tag{2.48}$$

The last statement is just (2.20). The α_σ of (2.46) are the expansion coefficients of $D^{\alpha}(C_i) \times D^{\beta}(C_i)$, that is

$$D^{\alpha} \times D^{\beta} = \sum_{\sigma} \alpha_\sigma D^{\sigma} = \sum_{\sigma} (\alpha\beta\sigma) D^{\sigma}. \tag{2.49}$$

(The matrix multiplication here is the same as that used in multiplying the character tables of C_i and C_3 together (2.30).) Equation (2.49) is called the Clebsch-Gordon series. As previously indicated the products of the vectors spanning the two subsets of the α^{th} and β^{th} representation can serve as a basis of space spanned by the product representations. The question is how to pick out the orthonormal set which spans each irreducible subspace by taking the proper linear combination of the product functions. Calling the correct set Φ, then we have (summing over repeated indices)

$$\Phi_{\mathbf{s}}^{\lambda\tau(\lambda)} = \psi_j^{\alpha} \psi_k^{\beta} \langle \alpha j, \beta k | \lambda\tau(\lambda) \; \mathbf{s} \rangle \tag{2.50}$$

as the correct linear combination. The coefficients are Clebsch-Gordon coefficients. λ refers to the λ^{th} representation

spanned by $D^{\alpha} \times D^{\beta}$; s is the s^{th} vector necessary to span the subspace of D^{λ}. If the product representation contains the λ^{th} representation m times, then there will be m 'correct linear combinations' which we distinguish by $\tau(\lambda)$ labeling. (The total number of 'correct combinations' must equal the product of the dimensionality of the α^{th} and β^{th} representations.) The inverse relation,

$$\psi_j^{\alpha}\psi_k^{\beta} = \phi_s^{\lambda\tau(\lambda)} \langle \lambda\tau(\lambda) | \alpha j, \beta k \rangle \tag{2.51}$$

implies that

$$\langle \lambda'\tau'(\lambda')s' | \alpha j, \beta k \rangle \langle \alpha j, \beta k | \lambda\tau(\lambda)s \rangle = \delta_{\lambda\lambda'}\delta_{\tau(\lambda)\tau'(\lambda')}\delta_{ss'} \tag{2.52}$$

and

$$\langle \alpha j', \beta k' | \lambda\tau(\lambda)s \rangle \langle \lambda\tau(\lambda)s | \alpha j, \beta k \rangle = \delta_{jj'}\delta_{kk'} . \tag{2.53}$$

The transformations are again a rotation in Hilbert space and the Clebsch-Gordon coefficients are hence chosen to be unitary, that is

$$\langle \lambda\tau(\lambda) | \alpha j, \beta k \rangle = \langle \alpha j, \beta k | \lambda\tau(\lambda) \rangle^{*} . \tag{2.54}$$

Letting a member of the group G act on $\phi_s^{\lambda\tau(\lambda)}$, we have

$$G\phi_s^{\lambda\tau(\lambda)} = \phi_{s'}^{\lambda\tau(\lambda)} D_{s's}^{\lambda\tau(\lambda)}(G) . \tag{2.55}$$

We can pick $D_{s's}^{\lambda\tau(\lambda)}$ to be independent of $\tau(\lambda)$. Then

$$G\phi_s^{\lambda\tau(s)} = \phi_{s's}^{\lambda\tau(\lambda)} \quad D_{s's}^{\lambda\tau(\lambda)}$$

$$= \psi_j^{\alpha}\psi_k^{\beta} \langle \alpha j, \beta k | \lambda\tau(\lambda)s' \rangle \; D_{s's}^{\lambda\tau(\lambda)}(G) \tag{2.56}$$

also

$$G\phi_{s}^{\lambda\tau(s)} = G[\psi_{i}^{\alpha}\ \psi_{\ell}^{\beta}]\langle\alpha i,\beta\ell|\lambda\tau(\lambda)s\rangle$$

$$= \psi_{j}^{\alpha}\, D_{ji}^{\alpha}(G)\ \psi_{k}^{\beta}\, D_{k\ell}^{\beta}(G)\ \langle\alpha i,\beta\ell|\lambda\tau(\lambda)s\rangle. \quad (2.57)$$

Since the $\psi_{j}^{\alpha}\psi_{k}^{\beta}$ are independent, from (2.56) and (2.57)

$$D_{ji}^{\alpha}(G)D_{k\ell}^{\beta}(G)\langle\alpha i,\beta\ell|\lambda\tau(\lambda)s\rangle = \langle\alpha j,\beta k|\lambda\tau(\lambda)s\rangle\ D_{s's}^{\lambda\tau(\lambda)}(G). \quad (2.58)$$

We can then write the irreducible representation in terms of the product representation by using (2.52).

$$\langle\lambda'\tau'(\lambda')s''|aj,\beta k\rangle\ D_{ji}^{\alpha}(G)D_{k\ell}^{\beta}(G)\langle\alpha i,\beta\ell|\lambda\tau(\lambda)s\rangle =$$

$$D_{s's}^{\lambda\tau(\lambda)}\ \delta_{\lambda\lambda'}\ \delta_{\tau(\lambda)\tau'(\lambda')}\delta_{s's''} \quad (2.59)$$

The inversion of (2.59) can also be written using (2.58) with (2.53).

The more familiar Clebsch-Gordon coefficient is a specialized case. The characters are assumed to be real. This implies that each representation is equivalent to its complex conjugate and that the Clebsch-Gordon coefficients will be real. We have also pointed out that there are 'several correct linear combinations' if the product representation contains any certain irreducible representation more than once. As a result, such coefficients will vary by an arbitrary phase factor. Equation (2.50) then can be rewritten

in a more standard form.

$$|j_1 j_2 JM\rangle = |j_1 m_1\rangle |j_2 m_2\rangle \langle j_1 j_2 m_1 m_2 | \mathbf{s} JM\rangle \tag{2.60}$$

$$= |j_1 j_2 m_1 m_2\rangle \langle j_1 j_2 m_1 m_2 | \mathbf{s} JM\rangle \tag{2.61}$$

($\mathbf{s} = j_1 j_2$ and is sometimes not written on the right side.)

where the phase is fixed by the relations:

$\langle j_1 j_2 j_1 (j_1 - J) | JJ\rangle$ is real

and $J_{\pm} |\mathbf{s} JM\rangle = \sqrt{J(J+1) - M(M\pm 1)}\ |\mathbf{s}, J, M\pm 1\rangle$. (2.62)

Clebsch-Gordon coefficients are tabulated in a publication of the Atomic Energy Commission.[20]

Wigner coefficients, or the '3j' symbols, are related directly to the Clebsch-Gordon coefficients by:

$$\begin{pmatrix} j_1 & j_2 & J \\ m_1 & m_2 & -M \end{pmatrix} = \frac{(-1)^{j_1 - j_2 + M}}{\sqrt{2J+1}} \langle j_1 j_2 m_1 m_2 | JM\rangle \tag{2.63}$$

By consideration of the possible dimensionalities of a product representation, it is seen that

$$|j_1 - j_2| \leq J \leq j_1 + j_2$$

and by the orthogonality of the Hilbert space (or of the spherical harmonics) that

$$m_1 + m_2 = M$$

The Wigner coefficients are:

a) invariant under a circular permutation of the columns,

b) multiplied by $(-1)^{j_1 j_2 J}$ by a permutation of two columns or under a sign change of all the m's.

Racah coefficients V(abc,$\alpha\beta\gamma$) are defined in the following manner:

$$V(abc,\alpha\beta\gamma) = (-1)^{a-b-c} \begin{pmatrix} a & b & c \\ \alpha & \beta & \gamma \end{pmatrix} - \frac{(-1)^{c-\gamma}}{\sqrt{2c+1}} \langle ab\alpha\beta | c,-\gamma \rangle$$

Coupling of the product of more than two representations follows in a similar fashion. A table of recursion relations can be found in Messiah[77] for Racah W coefficients and 6j symbols (for the product of three irreducible representations) and 9j symbols (for the product of four irreducible representations).

General Hamiltonian

Introduction. For an exact solution of the Schroedinger equation, one must know the Hamiltonian which expresses the interaction of all the electrons with themselves and their environment. At the present time such a Hamiltonian cannot be written in closed form. Instead the Hamiltonian is separated into component parts expressing various interactions; the magnitude of each term is estimated and perturbation theory is applied accordingly.

One problem arises in such a separation: Is the paramagnetic ion to be considered 'free', residing in a crystalline field laid down by its neighbors (crystal field theory) or must the local bonding be considered, that is, must we treat in detail the interaction between the paramagnetic center and its neighbors (ligand field theory)? The latter approach is usually too difficult for exact solution. The problem reduces to the question whether the bonding is ionic or co-valent.[5,26,43] Usually it is a mixture of both.

Using the former approach, in the absence of magnetic field, where the summation is over the paramagnetic sites

$$H = \sum_{ij}^{j<i} [(P_i^2/2m) - (Ze^2/r) + (e^2/r_{ij})]$$

$$+ [\lambda_{ij}\underline{\ell}_i \cdot \underline{s}_j + b_{ij}\underline{\ell}_i \cdot \underline{\ell}_j + c_{ij}\underline{s}_i \cdot \underline{s}_j] \qquad (2.64)$$

$$+ [(\underline{s}_i \cdot \underline{s}_j / r_{ij}^3) - 3(\underline{s}_i \cdot \underline{r}_{ij})(\underline{s}_j \cdot \underline{r}_{ij})/r_{ij}^5] - [e_i \phi(r_i)].$$

Inside the first set of brackets is the expression for the kinetic energy, the coulomb interaction between the nucleus and the electrons, and the coulomb interaction between the electrons. It is called the free ion term. The second bracketed term contains the interaction between the electrons' orbital and spin magnetic moment, the orbit-orbit interaction, and the exchange effect for the electrons. The term contained in the third bracket is the magnetic dipole interaction between the spins. The term in the fourth bracket is the crystal field interaction where $\nabla^2\phi = 0$ (Laplace's homogeneous equation) for the region around the paramagnetic ion.

<u>The Crystal Field</u>. A crystalline electric field of a definite symmetry will cause splitting of the terms of the unperturbed ion. The number of components into which a term of a free ion is split will increase with decreasing local symmetry of the electric field.

We shall first expand the crystalline field in a

series of spherical harmonics. The solution to Laplace's equation $\nabla^2\Phi = 0$ is

$$\Phi = \sum_{\ell m} A_{\ell m} r^{\ell} Y_{\ell m} + B_{\ell m} r^{-\ell-1} Y_{\ell m} \tag{2.65}$$

$A_{\ell m}$ and $B_{\ell m}$ are expansion coefficients; r is the radius about the origin of the paramagnetic ion. For solutions finite at the origin, $B_{\ell m} = 0$. $Y_{\ell m}$ are spherical harmonics, with phase factors chosen in the Slater manner, that is $Y_{\ell m} = (-1)^m Y_{\ell,-m}$. Only the effect of the crystalline field on d electrons is of interest. Since the wavefunctions of these electrons can be expanded in a series of d wavefunctions and the product of two d representations is four-dimensional, then only terms up to $\ell = 4$ need be included. The reason for this is that matrix elements of the form $\langle \ell j | A_{\ell m} r^{\ell} Y_{\ell m} | \ell j' \rangle$ will vanish for $\ell > 4$ because of (2.28). All terms of odd ℓ must vanish since in order for the integral of the product of three spherical harmonics not to vanish, the sum of the ℓ's must be even. (If the crystal has no inversion center, other configurations may be admixed allowing odd ℓ's.) The series must also transform according to the symmetry of the site under consideration, C_{3i} in our problem. The group operator C_3 (120° rotation) implies that

$$Y_{\ell,m} = Y_{\ell,m} e^{im2\pi/3},$$

but the group element C_3^2 (-120° rotation) implies that

$$Y_{\ell,m} = Y_{\ell m} e^{-im2\pi/3}.$$

Therefore m=3t, where t is an integer.

Since Φ is real and $Y_{\ell m} = (-1)^m Y_{\ell,-m}$, then $A_{\ell m} = (-1)^m A^*_{\ell m}$.

Thus, neglecting the constant energy term, we have

$$\Phi = A_{20} r^2 Y_{20} + A_{40} r^4 Y_{40} + A_{43} r^4 Y_{43} - A^*_{43} r^4 Y_{4,-3} \qquad (2.66)$$

The coefficients must be determined by calculating the electrostatic potential produced by the nearest neighbors (in our case, the dipoles of the $6H_2O$ molecules) expressing this potential in terms of spherical harmonics. To do this, one uses the expansion for the dipole (the dipole being the origin and the z-axis being directed along the direction of the dipole)

$$e\Phi = \frac{e}{4\pi\epsilon h} p Y_{10}(\theta,\Phi) \qquad (2.67)$$

where p is the dipole moment. Each of the six expansions can be transformed to the origin corresponding to the paramagnetic site such that the z-axis is as shown in figure 1. Further calculation of Φ is difficult since the orientation of the dipole is unknown. If an impurity is located at the C_{3i} symmetry center, actual distortion must also be known.

<u>Interaction Terms</u>. The second and third bracketed terms of equation (2.64) represent interactions of the spin ensemble with itself. They are typically about 10^2 and 1 cm^{-1}

respectively for the transition elements. These terms are more fully discussed under the consideration of τ_2 processes in which their action is of large importance. In general only the spin-orbit interaction term will dominate. It should be noted that all interactions between our electron spin ensemble and any nuclear ensemble have been ignored.

Coulomb Term. The first bracketed term is of the order of $10^5 cm^{-1}$. Besides the coulomb interaction it contains the kinetic energy of the electrons. Its effect is to shift all energy levels by a constant energy and hence it will be ignored.

Zeeman Energy. Upon application of a magnetic field, the interaction of the field and the magnetic moment of electrons produces what is called the Zeeman term of the Hamiltonian:

$$g\beta \sum_i \underline{H}_i \cdot \underline{S}_i + \beta \sum_i (\underline{L}_i \cdot \underline{H}_i). \qquad (2.68)$$

Here g is the spectroscopic splitting factor and is ~ 2. H is the applied magnetic field, and β is the Bohr magneton. The Bohr magneton is defined in the m.k.s. system as $e\hbar/2mc$. Here again it has been assumed that only one 'type' of spin is present, and hence no nuclear spin term is included.

Calculation of the Hamiltonian. The problem now is to

construct a plan for perturbing the free ion Hamiltonian. One must know the order of magnitude of the various terms of (2.64). Since they cannot be calculated, as yet, from first principles, one must rely on experimental observations. Such observations reveal that the problem usually falls into one of three categories.

1) The crystal fields are very large ($\sim 10^{-4}$ cm^{-1}). The coupling between the orbit and electron is overcome. The spin-orbit term then is ignored.

2) The crystal fields are of the order of magnitude of the spin-orbit coupling. The field and the spin-orbit coupling are then considered as simultaneous perturbations.

3) The crystal field is small compared to spin-orbit coupling. J is a good quantum number in this case. The crystalline field is applied as the final perturbation.

Cr^{+++}, like most iron transition elements, falls between cases 1) and 2). Fe^{+++}, being an S state ion, is an exceptional case. Both Cr^{+++} and Fe^{+++} can be handled in one of two general approaches that are commonly used in constructing transition ion Hamiltonians. The first method, the Koster-Statz Hamiltonian,[55] is a more fundamental approach. Here one must consider various possible models of crystalline environments and then check the calculations against empirical results. Unfortunately, the experimental

results compiled at the present are usually insufficient to complete the calculation in full. One must settle for some approximation.

An alternate method is the Spin Hamiltonian approximation. This method represents a phenomenological approach to the problem. Most resonance data can be described with Spin Hamiltonians in a relatively simple way without requiring a detailed knowledge of complicated effects such as crystalline field and spin-orbit coupling, since the parameters involved are directly measurable. The danger in the last approach is that the picture may be grossly oversimplified.[54] We shall outline the two methods using our paramagnetic systems.

Koster-Statz Hamiltonian. The Koster-Statz Hamiltonian being a more 'exact' form in return requires more information. In this form of the Hamiltonian, the exact perturbations appear (e.g., g, λ, and A appear as scalars in the perturbations $g\beta\underline{H}\cdot\underline{S}$, $\lambda\underline{L}\cdot\underline{S}$, and $A\underline{I}\cdot\underline{S}$, where the $A\underline{I}\cdot\underline{S}$ term represents an interaction between the nuclear and electron spins.). The actual wavefunctions, or in lieu of these the best approximation to them, are used. The wavefunctions are associated with the irreducible representations under which they transform. This approach to the Hamiltonian involves

the use of the projection operator of equation (2.25). Consider Fe^{+++} which has a spin of 5/2. We shall need to know how H_z, S_z and $H_{\pm}, S_{\pm}$ transform to evaluate the terms

$$g\beta \underline{H}\cdot\underline{S} = g\beta[\frac{1}{2}(H_+S_- + S_-H_+) + H_zS_z]. \tag{2.69}$$

Using the projection operator (2.25) and the character table for C_{3i}, we find the projections of H_z to within a multiplicative constant are

$$\phi^1(H_z) = \sum_{A=1}^{g} X^1(A)^* A\phi = \sum_{A=1}^{g} X^1(A)^* H_z$$

$$= \sum_{A=1}^{g} X^1(A) H_z = gH_z \tag{2.70}$$

$$\phi^2(H_z) = \sum_{A=1}^{g} 4(1 + \epsilon^2 - \epsilon) H_z = 0 \tag{2.71}$$

In this manner it is seen that H_z transforms as Γ_1 only. These projections can also be seen by inspecting character tables[64] that contain the basis functions for the various representations. Thus S_z and H_z transform as Γ_{1g}; H_-, S_- transform as Γ_{2g}; and H_+, S_+ transform as Γ_{3g}.

The wavefunctions transform (2.37) as $(\Gamma^1_{4g}, \Gamma^1_{5g})$, $(\Gamma^2_{4g}, \Gamma^2_{5g})$, $(\Gamma^1_{6g}, \Gamma^2_{6g})$ where the 1 and 2 are used to separate the levels since each representation occurs twice. The Kramers' degeneracies are easily identified since the characters are complex conjugates of one another, which is the necessary

condition for time conjugate states,[39] and they are paired in the parentheses. Applying the time conjugate operations [(A.9) and (A.10)] to a Kramers' conjugate pair, we see

$$K\Gamma^2_{4g} = \Gamma^2_{5g} \qquad K\Gamma^1_{4g} = \Gamma^1_{5g} \qquad K\Gamma^1_{6g} = \Gamma^2_{6g}$$

and (2.72)

$$K^2\Gamma^2_{4g} = K\Gamma^2_{5g} = -\Gamma^2_{4g} \quad K^2\Gamma^1_{4g} = K\Gamma^1_{5g} = -\Gamma^1_{4g} \quad K^2\Gamma^1_{6g} = K\Gamma^2_{6g} = -\Gamma_{6g}$$

and since $(g\beta\underline{H}\cdot\underline{S})$ under time inversion changes sign, then typically

$$\langle\Gamma^1_{4g}|g\beta\underline{H}\cdot\underline{S}|\Gamma^1_{6g}\rangle = -\langle\Gamma^1_{5g}|g\beta\underline{H}\cdot\underline{S}|\Gamma^2_{6g}\rangle^* \tag{2.73}$$

Following on with the use of (2.72) to establish relations between as many matrix elements as possible and remembering that any matrix element which transforms like $\langle\Gamma_a|\Gamma_b|\Gamma_c\rangle$ will be zero if $\Gamma^*_a \times \Gamma_c$ does not contain Γ_b [equation (2.28)], we write down the matrix Hamiltonian in as exact a form as possible without the knowledge of the actual eigenfunction of the problem. It should also be noted that the matrix is Hermetian. The remaining matrix elements are then evaluated with wavefunctions that best approximate the given problem. They, of course, must transform according to the correct irreducible representations. The method can be adapted to the use of molecular orbitals as is done in ligand field theory.[5]

Spin Hamiltonian. The second approach is the one which has been used most extensively for fitting experimental results. Its success justifies its use although the approximation might seem severe. Even though higher lying energy levels which do not participate in paramagnetic resonance may influence those that do, those levels which participate in magnetic resonance are treated as if they were isolated. An effective spin S is assigned to the 'isolated' levels such that 2S+1 equals the number of levels participating in the resonance. For our system the 2S+1 levels arise from an orbital singlet, that is they have a common orbital quantum number, $\langle L \rangle = 0$. This is true for most transition ions, and it is the usual case treated by the Spin-Hamiltonian formalism. (Several methods for handling the exceptions have been proposed.[70])

Instead of the 'exact' wavefunctions which are called for in the Koster-Statz formalism, a set of free ion wavefunctions which transforms according to the irreducible representations of the 2S+1 levels, namely the ground status in Figures 2 and 3 are chosen. Since, in fact the ion is not free, the various perturbations must be written in the most general form possible to account for the effects of its actual local surroundings. Thus no longer will λ and g

(nor A in $A\underline{I}\cdot\underline{S}$) appear as scalars, and tensor forms take their place. The whole Hamiltonian must transform according to group symmetry. In fact for C_{3i} symmetry the approximation is made that the local symmetry is actually axial.[7] The Spin-Hamiltonian then will consist of a Zeeman term,

$$g_{\parallel}\,\beta H_z + \frac{g_{\perp}\beta}{2}\,(H_+S_- + H_-S_+), \tag{2.74}$$

where $H_{\pm} = H_x \pm iH_y$ and $S_{\pm} = S_x \pm iS_y$

and the contribution from terms involving L. We must select terms similar to those in (2.66)which will be the leading terms in the contribution of the perturbation involving L. This can be done by perturbation theory; the leading terms, as in the usual case, come from the lower order perturbation theory. Since $\langle 0|\underline{L}|0\rangle = 0$, the first contribution comes from second order perturbation theory. Here we expect no terms in S higher than S^2. Higher order perturbation terms must be found if the Hamiltonian does not agree with experimental data as is the case with Fe^{+++}. Cr^{+++} however can be fit with only terms up to quadratic. (The actual perturbation calculation is carried out in full in Slichter[98] for the second order. It should be noted that terms like S(S+1) shift all the levels by a constant amount.)

The crystal field Hamiltonian for C_{3i} symmetry is taken into the operator equivalent form as outlined in the

method for writing equation (2.66). This calculation can be facilitated by the use of the irreducible tensor operators of Racah, $T_{\ell m}$, which transform in the same way as $Y_{\ell m}$.[97] The $T_{\ell m}$ establish the relationship to the J_x, J_y, J_z or S_x, S_y, S_z. Using the following commutation results:

$$[S_x, S_y] = iS_z \qquad [S_y, S_x] = iS_y \qquad [S_x, S_z] = iS_x$$

$$[S^2, S_\pm] = 0 \qquad [S_z, S_\pm] = \pm S_\pm \qquad [S_+, S_-] = 2S_z \tag{2.75}$$

$$[S_z, S_+] = S_+ + S_+S_z.$$

and the necessary definitions:

$$[S_\pm, T_{\ell m}] = \sqrt{\ell(\ell+1)-m(m\pm1)}\ \ T_{\ell,\ m\pm1} \tag{2.76}$$

$$[S_z, T_{\ell m}] = MT_{\ell m}$$

$$S_+^n \propto T_{nn}.$$

Thus, equation (2.66) becomes

$$e\Phi = B_{10}(3S_z^2-S^2) + B_{40}(35S_z^4-30S^2S_z^2 + 25S_z^2-6S^2 + 3S^4) + B_{43}[S_+^3(2S_z+3) + S_-^3(2S_z-3)]. \tag{2.77}$$

This result can be obtained in another way which by invoking the Wigner-Eckart theorem that operators which transform in the same way have proportional matrix elements.[78] The proportionality constants are called reduced matrix elements and depend upon the operator and the initial and

and final total angular momentum and are indicated by $\langle J_{final} \| \text{Operator} \| J_{initial} \rangle$. These are tabulated[69] for some operators and J manifolds. One then proceeds to replace the cartesian co-ordinates in the potential function by equivalent operators, that is x by J_x, y by J_y, and z by J_z. Care must be taken to proceed with proper regard for the commutation rules of J operators, such as replacing xy by $\frac{1}{2}(J_xJ_y+J_yJ_x)$.

Wong's[109] results for spin resonance in $AlCl_3 \cdot 6H_2O$ with the substitution Cr^{+++} for Al^{+++} at C_{3i} site fit the axial spin Hamiltonian

$$H = \beta g_{||} \underline{H} \cdot \underline{S} + D[S_z^2 - \frac{1}{3} S(S+1)] + A_{||} \underline{I} \cdot \underline{S} \quad . \qquad (2.78)$$

At liquid air temperatures, $D = hc(.043)\ cm^{-1}$ and $A = hc(1.7x10^{-3})cm^{-1}$ and $g = 1.977$. The results for Fe^{+++} in the same Al^{+++} site fit the spin Hamiltonian

$$H = \beta g_{||} H + \frac{a}{6}(S_x^4 + S_y^4 + S_z^4) + D(S_z^2 - \frac{35}{12}) + 7(\frac{F}{36})(S_z^4 - \frac{95}{14}S_z^2 + \frac{81}{16}) \qquad (2.79)$$

with $|a| = hc(1.6x10^{-2})cm^{-1}$, $D = hc(.15)cm^{-1}$, and $F = (3.1x10^2)cm^{-1}$. Note for the S state ion it is necessary to carry almost all the crystal field terms.

One should note that D = 0 for cubic symmetry. Thus

D is related to the axial part of the crystalline field. Recently an expression has been presented for D in terms of the actual crystalline parameters and wavefunctions.[27]

Lattice Vibration Theory

Introduction. Our difficulty with the Hamiltonian prevents us from theoretically obtaining numerical expressions for the spin-lattice relaxation times for our particular experiment; however, it is possible to extract both the temperature and field dependence from our final expressions. Before making these calculations, we must discuss lattice vibration theory in order to fully display the concepts and approximations which must be used.

We begin by defining a set of three fundamental translational vectors $\underline{a}_1, \underline{a}_2, \underline{a}_3$ such that the atomic arrangement appears identical whether viewed from an arbitrary origin in the crystal or viewed from any point related to this origin by

$$\underline{\ell} = \ell_1\underline{a}_1 + \ell_2\underline{a}_2 + \ell_3\underline{a}_3 \qquad (2.80)$$

where ℓ_1, ℓ_2, and ℓ_3 are integers and the '$\underline{a}$' are not necessarily orthogonal. The choice of these vectors is somewhat arbitrary. The lattice vectors are termed primitive if all points, whose atomic arrangement appears the same, satisfy equation (2.80) so that ℓ_1, ℓ_2, and ℓ_3 are integers. The unit cell is defined as the polyhedra bounded by the fundamental translational vectors. We shall use primitive translational vectors and the unit cell they define in

order to avoid any ambiguity. If the unit cell contains more than one atom, an origin must be taken in the unit cell and a vector is prescribed from the origin to each atom in the cell.

Lattice Modes. Consider the general 3-dimensional lattice. Arbitrarily choose an origin. Let $\underline{\ell}$ be the vector to the ℓ^{th} unit cell and $\underline{b}$ be the basis vector to the b^{th} atom in the cell. The displacement of this atom from equilibrium is just

$$\underline{\alpha}_{\ell,b} = \underline{x}_{\ell b} - (\underline{\ell} + \underline{b}) \tag{2.81}$$

where $\underline{x}_{\ell,b}$ is the actual position of the atom. Now the potential V in a Taylor series in terms of the displacement is

$$V(\alpha_{\ell,b}) = V_0 + \sum_{\ell b} \frac{\partial V}{\partial \underline{\alpha}_{\ell b}} \cdot \underline{\alpha}_{\ell b} + \frac{1}{2} \sum_{\substack{\ell b \\ \ell' b'}} \underline{\alpha}_{\ell b} \cdot \frac{\partial^2 V}{\partial \underline{\alpha}_{\ell b} \partial \underline{\alpha}_{\ell' b'}} \cdot \underline{\alpha}_{\ell' b'} \tag{2.82}$$

The derivatives are evaluated at the equilibrium position of the atom, for by the definition of equilibrium position,

$$\left.\frac{\partial V}{\partial \alpha_{\ell b}}\right|_{x_{\ell b} = \underline{\ell} + \underline{b}} = 0$$

V_0 can be arbitrarily chosen equal to zero since we are free to choose the zero of the

potential energy. This equation corresponds to Hooke's Law, $V = \frac{1}{2} kx^2 \rightarrow \underline{F} = -k\underline{x}$, and thus it can be said that only the harmonic terms are being carried in this calculation. Following the Hooke's Law analogy further:

$$k \rightarrow \underline{\underline{G}}_{\substack{\ell b \\ \ell' b'}} = \frac{\partial^2 V}{\partial \underline{\alpha}_{\ell b} \partial \underline{\alpha}_{\ell' b'}} \tag{2.83}$$

The Hamiltonian can now be written

$$H = \frac{1}{2} \sum_{\substack{\ell b \\ \ell' b'}} \frac{1}{m_b} \underline{P}_{\ell' b'} \cdot \underline{P}_{\ell b} + \frac{1}{2} \sum_{\substack{\ell b \\ \ell' b'}} \underline{\alpha}_{\ell b} \cdot \underline{\underline{G}}_{\substack{\ell b \\ \ell' b'}} \cdot \underline{\alpha}_{\ell' b'} \tag{2.84}$$

The motion is subject to the Born-vonKármán boundary condition which reflects the fact that the motion, as in an infinite crystal, is subject to no limiting surface condition. This mathematical artifice can be handled easily by considering a one-dimensional linear chain of N atoms. The translation group is Abelian (cf. 2.33) and, we therefore have N one-dimensional representations whose N basis functions differ only by a phase factor. Noting the wave functions for phonons are symmetric if

$$|\alpha_1 \alpha_2 \ldots\ldots \alpha_{N-1} \alpha_N \rangle = e^{iq} \, | \, \alpha_2 \alpha_3 \ldots\ldots \alpha_N \alpha_1 \rangle \tag{2.85}$$

then

$$|\alpha_1 \alpha_2 \ldots\ldots \alpha_{N-1} \alpha_N \rangle = e^{i2q} | \, \alpha_3 \alpha_4 \ldots\ldots \alpha_N \alpha_1 \alpha_2 \rangle \tag{2.86}$$

and so on until

$$|\alpha_1\alpha_2.....\alpha_{N-1}\alpha_N\rangle = e^{i(N-1)q}|\ \alpha_N\alpha_1.....\alpha_{N-2}\alpha_{N-1}\alpha_N\rangle. \quad (2.87)$$

The trick is to go one step further as if the chain formed a large circle with no boundaries. Thus

$$|\alpha_1\alpha_2.....\alpha_N\rangle = e^{iNq}|\ \alpha_1\alpha_2.....\alpha_N\rangle \quad (2.88)$$

which implies $q = 2\pi n/N$. Since $e^{iq\ell} = e^{i2\pi n/N}$ $= e^{i2\pi(n+N)/N}$ the <u>distinct values</u> of q are said to be those for which $0 \leq n \leq N$. Note q, called the wave vector, is often written as k and equals $2\pi/\lambda$. A linear function which transforms as (2.85), (2.86), and (2.87) is

$$A_q = \frac{1}{\sqrt{N}} \sum_{\ell} \alpha_\ell e^{iq\ell} = \frac{1}{\sqrt{N}} (\alpha_1 e^{iq} + \alpha_2 e^{12q} + \ldots + \alpha_N e^{iNq}) \quad (2.89)$$

where N is the total number of atoms.

These functions and their conjugates are the normal coordinates of the one-dimensional problem. The analog in three dimensions will give a normal coordinate for each unit cell.

Rather than find the P conjugate to A in classical mechanics, it is advantageous to go directly to the operator equivalents for quantum mechanics since quantum mechanical results are desired. If $\hat{A}$ is a 'spatial position' operator, the $\hat{P}$ is the proper momentum operator conjugate to $\hat{A}$ if and only if

$$[A, P] = i\hbar\ ,$$

where $\hbar = h/2\pi$.

$$\text{Then } \hat{P}_q = \frac{1}{\sqrt{N}} \sum_{\ell} \hat{p}_{\ell}^{-iq\ell} \text{ where } [\hat{a}_t p_{\ell}] = \delta_{t\ell}\, i\hbar \tag{2.90}$$

for

$$[\hat{A}_q, \hat{P}_q] = \Sigma_{\ell\ell'} \frac{1}{N} [\hat{\alpha}_{\ell'}, \hat{p}_{\ell}]\, e^{i(q\ell - q'\ell')}$$

$$= \frac{1}{N} \Sigma_{\ell} e^{i(q\ell - q'\ell)} = i\hbar\, \delta_{qq'}. \tag{2.91}$$

Also

$$\hat{P}_{\ell} = \frac{1}{\sqrt{N}} \Sigma_q \hat{P}_q e^{+iq\ell} \text{ and } \hat{\alpha}_{\ell} = \frac{1}{\sqrt{N}} \Sigma_q \hat{A}_q e^{-iq\ell}. \tag{2.92}$$

In the above equations implicit use is made of a Fourier inverse theorem, namely

$$\Sigma_q e^{iq(\ell - \ell')} = \sum_{n=0}^{N-1} e^{i2\pi n(\ell-\ell')/N} = \frac{e^{[1 - e^{i2\pi(\ell-\ell')}]}}{1 - e^{i2\pi(\ell-\ell')/N}}$$

$$= 1/N\, \delta_{\ell-\ell'} \qquad n < N \tag{2.93}$$

and

$$\Sigma_{\ell} e^{i(q-q')\ell} = \sum_{\ell=0}^{N-1} e^{i2\pi\ell(n-n')/N} = 1/N\, \delta_{q-q'}. \tag{2.94}$$

Utilizing only the ideas already employed, formulas (2.90), (2.91), and (2.92) can be carried into three dimensions. However, even with the use of a compact vector notation, the symbolism is cumbersome. The three dimensional results are

$$\hat{\underline{A}}_{\underline{q},\underline{b}} = \frac{1}{\sqrt{NV}} \Sigma_{\underline{\ell}} \underline{\alpha}_{\underline{\ell},\underline{b}} e^{i\underline{q}\cdot\underline{\ell}} \qquad \hat{\underline{P}}_{\underline{q},\underline{b}} = \frac{1}{\sqrt{NV}} \Sigma_{\underline{\ell}} \hat{\underline{p}}_{\underline{\ell},\underline{b}} e^{-i\underline{q}\cdot\underline{\ell}} \tag{2.95}$$

$$\hat{\underline{\alpha}}_{\underline{\ell},\underline{b}} = \frac{1}{\sqrt{NV}} \Sigma_{\underline{q}} \hat{\underline{A}}_{\underline{q},\underline{b}} \, e^{-\underline{q}\cdot\underline{\ell}} \qquad \hat{\underline{p}}_{\underline{\ell},\underline{b}} = \frac{1}{\sqrt{NV}} \Sigma_{\underline{q}} \hat{\underline{P}}_{\underline{q},\underline{b}} \, e^{i\underline{q}\cdot\underline{\ell}} \tag{2.96}$$

and

$$[\hat{\underline{A}}_{\underline{q},\underline{b}}, \hat{\underline{P}}_{\underline{q}',\underline{b}'}] = i\hbar \, \underline{\underline{\ell}} \, \delta_{\underline{q}\underline{q}'} \, \delta_{\underline{b}\underline{b}'}. \tag{2.97}$$

where N is the number of unit cells per unit volume V. All that remains now is the substitution into the Hamiltonian (2.84) and the summation over both lattice cells and sites.

$$H = \frac{1}{2} \left(\frac{1}{NV}\right) \Sigma_{\underline{\ell},\underline{b}} \frac{1}{m_{\underline{b}}} \Sigma_{\underline{q},\underline{q}'} P_{\underline{q},\underline{b}} \, e^{-i\underline{q}\cdot\underline{\ell}} \cdot P_{\underline{q},\underline{b}} \, e^{-i\underline{q}'\cdot\underline{\ell}}$$

$$+ \frac{1}{2} \left(\frac{1}{NV}\right) \Sigma_{\substack{\underline{\ell},\underline{b} \\ \underline{\ell}',\underline{b}'}} \Sigma_{\underline{q}\underline{q}'} A_{\underline{q},\underline{b}} \cdot \underline{\underline{G}}_{\substack{\underline{\ell},\underline{b} \\ \underline{\ell}',\underline{b}'}} \cdot A_{\underline{q}',\underline{b}'} \, e^{-i(\underline{q}\cdot\underline{\ell} + \underline{q}'\cdot\underline{\ell}')} \tag{2.98}$$

Yet $\sum_{\underline{\ell}} e^{i(\underline{q} + \underline{q}')\underline{\ell}} = NV\delta_{\underline{q},-\underline{q}'}$ from Fourier theory [cf. (2.94)].

therefore

$$H = \frac{1}{2} \Sigma_{\underline{q},\underline{b}} \frac{1}{m_{\underline{b}}} P_{\underline{q},\underline{b}} \cdot P_{-\underline{q},\underline{b}} + \frac{1}{2NV} \Sigma_{\substack{\underline{q},\underline{q}' \\ \underline{b},\underline{b}'}} \underline{A}_{\underline{q},\underline{b}} \cdot$$

$$\left\{ \Sigma_{\underline{\ell},\underline{\ell}'} \underline{\underline{G}}_{\substack{\underline{\ell},\underline{b} \\ \underline{\ell}',\underline{b}'}} e^{i\underline{q}\cdot(\underline{\ell} - \underline{\ell}')} \, e^{-i(\underline{q} + \underline{q}')\cdot\underline{\ell}} \right\} \cdot \underline{A}_{\underline{q}',\underline{b}'}. \tag{2.99}$$

Since $\underline{\underline{G}}_{\substack{\underline{\ell},\underline{b} \\ \underline{\ell}',\underline{b}'}}$ depends only on the separation of the two lattice cells rather than the absolute position of the cells, it is only a function of $\underline{\ell} - \underline{\ell}' \equiv \underline{h}$ and of $\underline{b},\underline{b}'$. Thus the sum over $\underline{\ell}'$ is the same as a sum over $\underline{h}$ and each $\underline{\ell}$ contributes

$$\Sigma_{\underline{h}}\, e^{-i\underline{q}'\underline{h}} G_{\underline{b},\underline{b}'}(\underline{h}) \equiv E_{\underline{b},\underline{b}'} \quad . \tag{2.100}$$

Using

$$\Sigma_{\underline{\ell}}\, e^{i(\underline{q}+\underline{q}')\cdot\underline{\ell}} = NV\delta_{\underline{q},-\underline{q}'} \tag{2.101}$$

(2.99) reduces to

$$H = \frac{1}{2}\Sigma_{\underline{q}} \left\{ \Sigma_{\underline{b}} \frac{1}{m_{\underline{b}}} P_{\underline{q},\underline{b}} \cdot P^{*}_{\underline{q},\underline{b}} + \Sigma_{\underline{b},\underline{b}'} A_{\underline{q},\underline{b}} \cdot \underline{\underline{E}}_{\underline{b},\underline{b}'} \cdot A^{*}_{\underline{q},\underline{b}'} \right\} \tag{2.102}$$

Inspection of the above equation reveals that our choice of coordinates is only normal up to the interaction inside of unit cell. In order to complete the problem, the usual normal mode method must be applied.[29] Thus the Hamiltonian can be reduced to a form which has no cross terms. If p is the correspondence label connecting the p^{th}-type branch mode to the p^{th}-root of the resulting secular equation, and if we assume

$$A_{\underline{q},\underline{b}} = (m_{\underline{b}})^{-1/2}\, \beta_{\underline{q},\underline{b}}\, e^{i\omega t} \tag{2.103}$$

then

$$H = \frac{1}{2}\Sigma_{p}\, C_{\underline{q},p}\, C^{*}_{\underline{q},p} + \omega^{2}_{\underline{q},p}\, B_{\underline{q},p}\, B^{*}_{\underline{q},p} \tag{2.104}$$

where

$$C_{\underline{q},p} = \Sigma_{\underline{b}}\, (m_{\underline{b}})^{-1/2}\, \beta^{*}_{\underline{q},\underline{b},p} \cdot P_{\underline{q},\underline{b}} \tag{2.105}$$

$$\underline{B}_{\underline{q},p} = \Sigma_{\underline{b}} (m_{\underline{b}})^{-1/2} \beta_{\underline{q},\underline{b},p} \cdot \underline{A}_{\underline{q},\underline{b}} \tag{2.106}$$

with the normalization

$$\Sigma_{\underline{b}} \beta^{*}_{\underline{q},p} \cdot \beta_{\underline{q},\underline{b},p'} = \delta_{p,p'} \cdot \tag{2.107}$$

The creation and annihilation operators can now be expressed in terms of the normal coordinates:

$$\underline{a}_{\underline{q},p} \equiv (2\hbar\omega_{\underline{q},p})^{-1/2} \underline{C}_{\underline{q},p} - i(\omega_{\underline{q},p}/2\hbar)^{1/2} \underline{B}^{*}_{\underline{q},p} \tag{2.108}$$

$$\underline{a}^{*}_{\underline{q},p} = (2\hbar\omega_{\underline{q},p})^{-1/2} \underline{C}^{*}_{\underline{q},p} + i(\omega_{\underline{q},p}/2\hbar)^{1/2} \underline{B}_{\underline{q},p}. \tag{2.109}$$

<u>Creation and Annihilation Operators</u>. At this point some of the important properties of $\hat{a}$ and $\hat{a}^*$ should be discussed. To do this, consider once again, for simplicity, the case of one atom per unit cell. The mass will appear explicitly and $[\hat{A},\hat{P}] = i\hbar$. Then for each mode and polarization

$$\hat{a} = (2m\hbar\omega)^{-1/2} [\hat{P} - im\omega\hat{A}] \tag{2.110}$$

$$\hat{a}^* = (2m\hbar\omega)^{-1/2} [\hat{P} + im\omega\hat{A}] \tag{2.111}$$

Some of the more important relationships are derived in the following paragraphs.

A) $a^*a = N$ the number of phonons (2.112)

This follows from a rather interesting line of reasoning.

Since $H = (2m)^{-1} (P^2 + m\omega^2 A^2) = E$ classically, and the corresponding operator equivalents obey the quantum mechanical commutation brackets $[\hat{A}, \hat{P}] = i\hbar$, then the operator equivalent of the classical Hamiltonian is the correct quantum mechanical Hamiltonian which has the energy eigen values $E = (N + \frac{1}{2})\hbar\omega$.

Then
$$N = \frac{1}{\hbar\omega} E - \frac{1}{2}$$

$$= \frac{1}{\hbar\omega} \left(\frac{1}{2m} \right] P^2 + m^2\omega^2 A^2]) - \frac{1}{2}$$

$$= \frac{1}{2m\hbar\omega} (\hat{P} + im\omega \hat{A})(\hat{P} - im\omega \hat{A})$$

$$= \hat{a}^* \hat{a} \qquad (2.113)$$

B) $$[\hat{a}, \hat{a}^*] = 1 \qquad (2.114)$$

This follows from the relation $[\hat{A}, \hat{P}] = i\hbar$

C) $$[\hat{a}, \hat{a}^{*n}] = n\hat{a}^{*(n-1)} \qquad (2.115)$$

D) $$\hat{P} = (2m\hbar\omega)^{1/2} \frac{(\hat{a} + \hat{a}^*)}{2} \qquad (2.116)$$

$$\hat{A} = \frac{i(2m\hbar\omega)^{1/2}}{m\omega} \frac{(\hat{a} - \hat{a}^*)}{2} \qquad (2.117)$$

Assume that there exists a state such that

$$\hat{a}|0\rangle = 0 \qquad (2.118)$$

Interpreting $\hat{a}$ as the annihilation operator, equation (2.118) means physically that $|0\rangle$ contains no phonons and the state

with fewer phonons is non-existent.

We then define the property of $\hat{a}^*$ by the following equation:

$$|n\rangle = \frac{1}{\sqrt{n!}} \hat{a}^* |0\rangle .$$

E) $$N|n\rangle = n|n\rangle \tag{2.119}$$

Since

$$N|n\rangle = \hat{a}^*\hat{a}|n\rangle = \frac{1}{\sqrt{n!}} \hat{a}^*\hat{a}\,\hat{a}^{*n}|0\rangle = \frac{1}{\sqrt{n!}} \hat{a}^*(n\hat{a}^{*(n-1)}$$

$$+ \hat{a}^{*n}\hat{a}|0\rangle) = \frac{1}{\sqrt{n!}} \hat{a}^* n\hat{a}^{*(n-1)}|0\rangle = \frac{1}{\sqrt{n!}} n\hat{a}^{*n}|0\rangle$$

F) $$H|n\rangle = (N + \tfrac{1}{2})\hbar\omega = (n + \tfrac{1}{2})\hbar\omega \tag{2.120}$$

Since n is the same as the number of phonons present, the $|n\rangle$ correspond to the Hermite polynomial eigen functions which are the solutions for the quantum mechanical oscillator.[59]

G) $$\langle m|\hat{a}|n\rangle = \sqrt{n}\,\delta_{m,n-1} \tag{2.121}$$

H) $$\langle m|\hat{a}^*|n\rangle = \sqrt{n+1}\,\delta_{m,n+1} \tag{2.122}$$

(Note the matrix element corresponding to an increase in phonons exceeds that for a decrease.) From (2.121) and (2.122) it is easy to deduce that the matrix elements connecting two phonon states are zero everywhere except adjacent to the diagonal.

The Dispersion Law. In order to be able to understand some of the problems encountered in the calculations pertinent to this thesis, it will be necessary to discuss the dispersion law. Inspection of the equations derived so far seems to imply that the basis vectors are orthogonal. This is not necessarily so. Mathematically all that has been said will hold for a non-orthogonal system if the meaning of the scalar product can be preserved. In order to do this, the reciprocal lattice must be introduced. If $\underline{a}_1$, $\underline{a}_2$, and $\underline{a}_3$ are unitary basis vectors in the regular lattice (or direct lattice), then basis vectors of the reciprocal space are constructed such that the vector reciprocal to $\underline{a}_1$, that is $\underline{a}_1^*$, is perpendicular to $\underline{a}_2$ and $\underline{a}_3$ and $\ni\ \underline{a}_1 \cdot \underline{a}_1^* = 1$. Reciprocal lattice vectors with these properties are defined by:

$$\underline{a}_1^* = \frac{\underline{a}_2 \times \underline{a}_3}{\underline{a}_1 \cdot (\underline{a}_2 \times \underline{a}_3)} \tag{2.123}$$

$$\underline{a}_2^* = \frac{\underline{a}_3 \times \underline{a}_1}{\underline{a}_2 \cdot (\underline{a}_3 \times \underline{a}_1)} \tag{2.124}$$

$$\underline{a}_3^* = \frac{\underline{a}_1 \times \underline{a}_2}{\underline{a}_3 \cdot (\underline{a}_1 \times \underline{a}_2)} \tag{2.125}$$

(Note the reciprocal and direct lattices coincide for the orthogonal case.) In the scalar products $\underline{q} \cdot \underline{\ell}$ (cf. (2.95) and (2.96)), $\underline{q}$ is assumed to be written in reciprocal space. It also should be noted that all the physically distinguishable

values of $\underline{q}$ lie inside the region in reciprocal space defined by the vectors $2\pi\underline{a}_1^*$, $2\pi\underline{a}_2^*$, $2\pi\underline{a}_3^*$. This region is called a reciprocal lattice unit cell or the unit cell in q-space.

It should be mentioned in passing that if non-orthogonal coordinate systems are utilized, tensors must be expressed in two forms (co-variant and contra-variant) corresponding to the two-coordinate systems reciprocal to one another. The reciprocal and direct lattice vectors are physical examples of co-variant and contra-variant tensors. The same ideas also apply when writing bras and kets in non-orthogonal systems.

The next step is to write down the distribution of modes $p(\omega)$. Consider for simplicity a primitive lattice, although the argument is easily extended to the general case. If the number of modes in a volume $d\tau_q$ in q-space is m, then

$$\frac{m}{d\tau_q} = \frac{N_1 N_2 N_3}{(2\pi)^3 (\underline{a}_1^* \times \underline{a}_2^* \times \underline{a}_3^*)} \tag{2.126}$$

where the ratio on the right is just the number of modes per unit volume in q-space. Hence

$$m = \frac{d\tau_q V}{(2\pi)^3} \tag{2.127}$$

where V is the volume in direct space. The volume $d\tau_q$

between two constant ω surfaces in q-space is

$$d\tau_q = \left(\int \frac{1}{|\underline{\nabla}_q \omega|} dA_g\right) d\omega \tag{2.128}$$

where $\underline{\nabla}\omega$ is the gradient in q-space and the integral is over a constant ω surface. It is evident that both the constant ω surface and the group velocity, $|\underline{\nabla}_q \omega| = \underline{v}_g$, are required to evaluate this expression. Both can be determined from the dispersion law, which is the relationship between ω and q. Such a relationship is usually semiempirical. It is not known for the crystal being studied. For a one-dimensional chain, the relationship can be arrived at easily:

$$\omega = \pm (4\beta/M)^{1/2} \sin (qa/2) \quad [48] \tag{2.129}$$

$$\therefore v_g = v_0 \left(\sqrt{1-(\omega/\omega_{max})}\right) \text{ for } \omega \longrightarrow 0 \tag{2.130}$$

where 'a' is the lattice spacing and $v_0 \equiv \omega/q$.

Since the problem of calculating the density of states for an anisotropic distribution is sometimes confused, two different derivations will be presented.

More often than not, it is necessary to introduce a very simple dispersion relation

$$\omega = v_0 q \tag{2.131}$$

In this type of relation v_0 is an 'average' velocity

characteristic of the crystal. This relation produces no distinction between the group velocity ($v_g = d\omega/dq$) and the phase velocity ($v_p = \omega/q$). This dispersion law will be used in the following discussion.

The first method for obtaining the density of states uses the basic idea of the relation of phase space to the number of quantum mechanical states, $\Delta\Gamma$.

$$\Delta\Gamma = \frac{\Delta p \Delta q}{(2\pi\hbar)^s} \quad \text{where } s \text{ is the number of degrees of freedom of a given subsystem.} \tag{2.132}$$

$$\sum_i \Delta\Gamma_i \longrightarrow \frac{1}{(2\pi\hbar)^s} \int dp_x dp_y dp_z dq_x dq_y dq_z = \text{total number of states} \equiv \int d\Gamma \tag{2.133}$$

The probability of occupancy in a particular volume of phase space then is

$$w = \int \rho d\Gamma \quad \text{where } \rho \text{ is the distribution or density function.} \tag{2.134}$$

Assuming $\rho = \rho(q)$, then

$$\int \rho(q) d\Gamma = \frac{V}{(2\pi h)^3} \int \rho(\underline{q}) dp_x dp_y dp_z \tag{2.135}$$

If

$$p = h/\lambda \qquad \text{and } \omega \equiv qv$$

$$q \equiv 2\pi/\lambda \qquad \text{or } q = p/\hbar \tag{2.136}$$

and ρ ($\underline{q}$) has spherical symmetry,

$$w = \frac{V}{(2\pi\hbar)^3} \int \rho(q)\ 4\pi p^2 dp \tag{2.137}$$

where

$$p^2 dp = \hbar^3 q^2 dq. \tag{2.138}$$

Thus

$$w = \frac{2V}{2\pi^2} \int \rho(q) q^2 dq\ . \tag{2.139}$$

Therefore

$$\Delta\Gamma = \frac{V}{(2\pi)^3} \quad 4\pi q^2 dq \tag{2.140}$$

for one mode.

A more physical way of formulating the same result is to consider running waves in a crystal. Choose a crystal with a cubic lattice of one type of atom with the dimensions ℓ_x, ℓ_y, ℓ_z. The assumed Born-von Kármán boundary condition on which polarization of the wave then implies $q_x = 2\pi n/\ell_x$, etc. For each point in the real lattice there corresponds a point in a reciprocal q lattice such that each lattice cell has sides $2\pi/\ell_x$, $2\pi/\ell_y$, $2\pi/\ell_z$, and each such point corresponds to a mode. Then each volume $(2\pi)^3(1/\ell_x\ell_y\ell_z)$ corresponds to one mode. Then in the volume $4\pi q^2 dq$ there are $\frac{V}{(2\pi)^3} \cdot 4\pi q^2 dq$ modes per polarization, that is

$$\Delta\Gamma \longrightarrow \frac{V}{(2\pi)^3} \quad 4\pi q^2 dq \tag{2.141}$$

the total number of states in the interval dq.

The total number of states is always equal to three times the number of atoms. Thus the integral that totals up the number of states must be cut off at 3N regardless of the dispersion law used. From (2.141) for three polarizations

$$3N = \frac{V4\pi}{(2\pi)^3} \int_0^{q_{max}} 3q^2 dq \tag{2.142}$$

$$3N = \frac{V4\pi}{(2\pi)^3} \quad q_{max}^3. \tag{2.143}$$

Assume for the dispersion law [eq. (2.131)]

$$\omega = v_0 q$$

then

$$\hbar^3 \omega_{max}^3 = \frac{\hbar^3 (2\pi)^3 3Nv_0^3}{4\pi V} = (k\theta)^3 \tag{2.144}$$

where

$$\frac{3}{v_0^3} \sim \frac{2}{v_t^3} + \frac{1}{v_\ell^3} \tag{2.145}$$

v_t = transverse velocity

v_ℓ = longitudinal velocity

k = Boltzman constant

θ = a characteristic constant of the crystal, termed the Debye temperature.

The velocity is related to the elastic constants of Hooke's law.

$$(X) = (C)\,(e)$$

$$(\text{Stress}) = (C)\,(\text{Strain}) \qquad (2.146)$$

For a crystal with tirgonal symmetry

$$(C) = \begin{pmatrix} c_{11} & c_{12} & c_{13} & c_{14} & 0 & 0 \\ c_{12} & c_{11} & c_{13} & -c_{14} & 0 & 0 \\ c_{13} & c_{13} & c_{33} & 0 & 0 & 0 \\ c_{14} & -c_{14} & 0 & c_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & c_{44} & 2c_{14} \\ 0 & 0 & 0 & 0 & 2c_{14} & 2(c_{11} - c_{12}) \end{pmatrix} \qquad (2.147)$$

and $v_l = \sqrt{c_{33}/\rho}$ along the c axis where ρ is the density.[30]

Combining this with the experimental guide that $v_l \sim \frac{3v}{2t}$,

$$\frac{3}{v_0^3} \sim \frac{2}{v_t^3} + \frac{1}{v^3} \sim \frac{27}{16v^3} + \frac{1}{v^3} = \frac{43}{16}\left(\frac{\rho}{c_{33}}\right)^{3/2}$$

$$\text{or} \quad v_0^3 \sim \left(\frac{c_{33}}{\rho}\right)^{3/2} \qquad (2.148)$$

Solving for θ^3 in terms of c_{33}:

$$\theta^3 \sim \frac{\hbar^3 (2\pi)^3}{4\pi} = \frac{3N}{Vk^3}\left(\frac{c_{33}}{\rho}\right)^{3/2} \qquad (2.149)$$

The Debye θ can also be related to the specific

heat (C_v) since the ensemble average of a function is just

[cf. (2.132) to (2.139)]

$$\bar{A} = \int_{d\Gamma} \rho \, A \, d\Gamma \tag{2.150}$$

where the distribution function for phonons is the Einstein distribution.[65]

$$\rho = \frac{1}{e^{\hbar\omega/kT}-1} \tag{2.151}$$

Therefore

$$E = \int_0^{q_m} \left(\frac{1}{e^{\hbar\omega/kT}-1}\right) \quad (\hbar\omega) \quad \left(\frac{V}{2\pi^2} 3q^2 \, dq\right) \tag{2.152}$$

Let the energy per unit volume $E/V \equiv U$. Then

$$U = \frac{3\hbar}{2\pi^2 v_0^2} \int_0^{\omega_m} \frac{\omega^2 d\omega}{e^{\hbar\omega/kT}-1} \tag{2.153}$$

Extracting the temperature dependence by letting $\hbar\omega/kT = x = \theta/T$

$$U = \frac{3k^4T^4}{2\pi^2\hbar^3 v_0^3} \int_0^{x_m} \frac{x^3 dx}{e^x-1} \tag{2.154}$$

Differentiating with respect to T (note the limits of the integral depend upon T):

$$\left(\frac{\partial U}{\partial T}\right)_v \equiv C_v = 9Nk(T/\theta)^3 \int_0^{x_m} \frac{e^x x^4 dx}{(e^x-1)^2} \tag{2.155}$$

$$C_v = 9Nk(T/\theta)^3 J_4 \tag{2.156}$$

The integral is one of a class of integrals known as

transport integrals. The integrals are defined as follows:

$$J_n(x) \equiv \int_0^{x_m} \frac{x^n e^x}{(e^x-1)^2}\, dx = \int_0^{x_m} \frac{x^n}{e^x+e^{-x}-2}\, dx \qquad (2.157)$$

The transport integrals cannot be evaluated in a closed form; however, they are well tabulated.[91]

Relaxation Theory

Introduction. A discussion of the phonon distribution as a function of frequency or energy will provide a basis for the organization of the discussion of relaxation theory. It is assumed that the energy sink for the spin energy is the phonon bath.

Equation (2.134) gives the probability of finding a particle in a particular section of phase space. By rewriting (2.134) using $\omega = v_0 q$, an expression for the distribution as a function of energy may be obtained.

$$\begin{aligned} w &= \int \rho d\Gamma \\ &= (V/2\pi^2) \int \rho(q) q^2 dq \\ &= \int [\rho(\omega)] \left(\frac{V}{2\pi^2 v^3}\right) \omega^2 d\omega \end{aligned} \tag{2.158}$$

where $\rho(\omega)$ is the occupation number and the remaining terms represent the density of states. For phonons

$$\rho(\omega) = \frac{1}{e^{\hbar\omega/kT} - 1} \tag{2.159}$$

is the Bose-Einstein distribution with the chemical potential (Fermi energy) equal to 0. A factor of three should also be included to account for the two transverse and one longitudinal modes of vibration.

The functional dependence of (2.158) is depicted graphically in Figure 4. In general, the maximum for such distributions occurs at $E \sim kT$, that is, at about the energy associated with the temperature of the crystal. The resonant energy of an electron in a field of 3,000 gauss corresponds to about $1/2^{\circ}K.$, the maximum for the distribution shifts to the right, and thus, as the temperature of the crystal increases there are decreasingly fewer phonons at the resonant energy. In Figure 4, the shaded area represents those phonons capable of interacting in a direct exchange of energy with the electrons.

It becomes evident then for high temperatures that perhaps some other process than the direct interaction will be important. Such a process is the Raman interaction. In a Raman interaction an incoming phonon is inelastically scattered by an electron and an outgoing phonon departs with an energy different by just the resonant electron energy. Since the Raman effect involves the creation and annihilation of a phonon in one process, the probability is more unlikely than one involving only one phonon; however, at elevated temperatures the number of likely phonon candidates for such a process is large enough to make the process become important. Although all the phonons in the spectrum participate

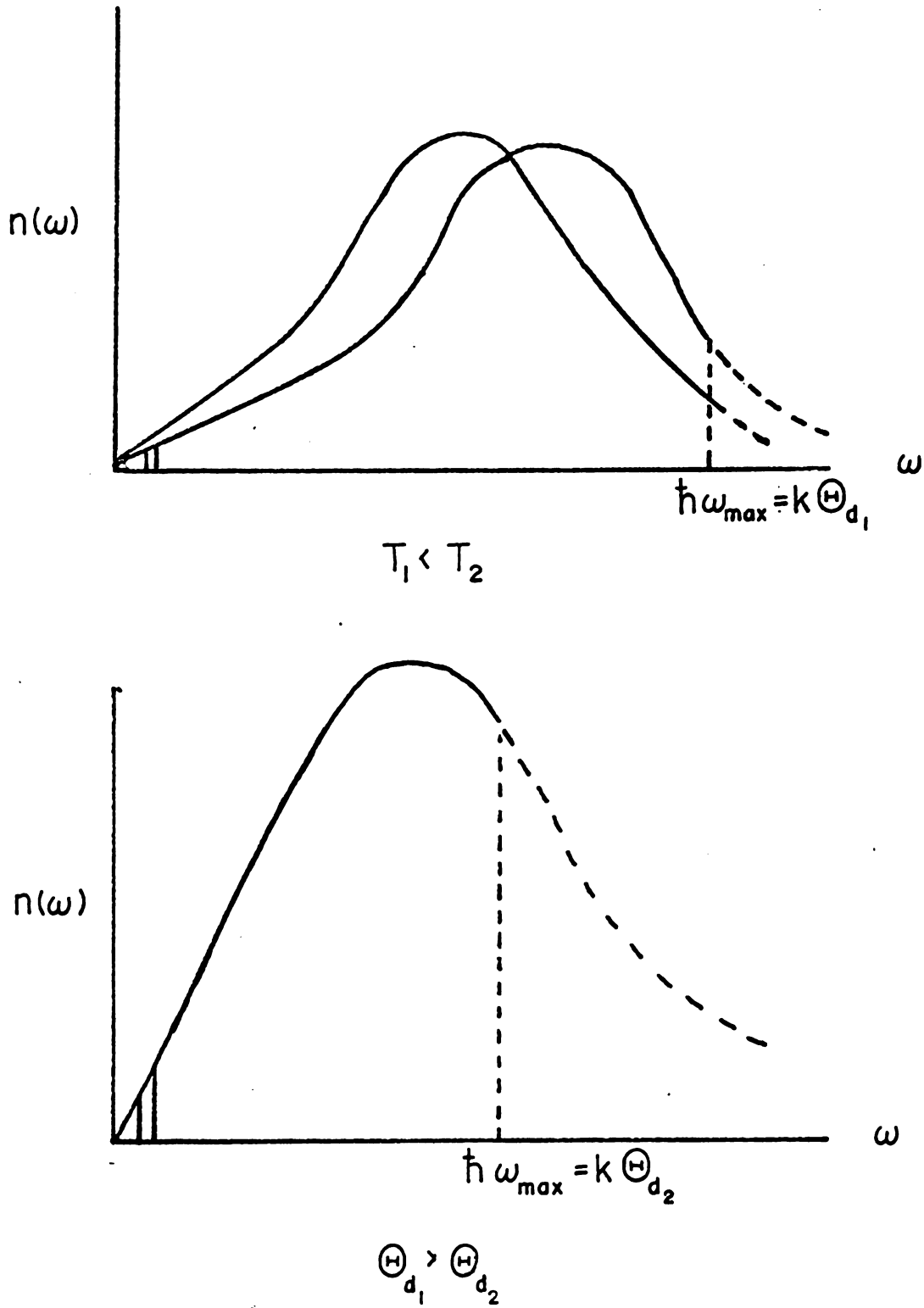


Figure 4. Phonon Distribution. This figure illustrates the effect of lowering the Debye θ_d for a distribution. The occupation number contribution will remain the same; however, the maximum in the density of states is shifted to the left for a lower Debye θ_d.

in the Raman process, the most important contribution comes from phonons at the energy corresponding to the temperature of the crystal.

Since the electrons that are of interest are non-interacting, they obey Boltzman statistics. If all the spins are either in state $|a\rangle$ or $|b\rangle$, then $n_b/n_a = \exp(-E_{ab}/kT)$ When the distribution varies from equilibrium we speak of spin temperature, T_s, defined by $n_b/n_a = \exp(-E_{ab}/kT_s)$.

The time it takes for a spin system to return from some non-equilibrium state to a state of thermal equilibrium with the surrounding heat bath is referred to as the spin lattice relaxation time τ_1, defined as

$$\frac{d(n_b-n_a)}{dt} \equiv \frac{-1}{\tau_1}\left[(n_b-n_a) - (n_b-n_a)_\infty\right] \qquad (2.160)$$

or

$$(n_b-n_a) - (n_b-n_a)_\infty = (n_b-n_a)_0 - (n_b-n_a)_\infty e^{-t/\tau_1} \qquad (2.161)$$

It is necessary to consider the rate equations under the condition that our ensemble is in contact with a phonon bath. Consider a displacement α whose time dependence we shall, for the moment, disregard. From the solution of the lattice mode problem

$$\underline{\alpha} = \left(\underline{A} / \sqrt{N}\right) e^{i\underline{q}\cdot\underline{\ell}}.$$

The matrix element for annihilation of a phonon is

(cf. (2.121) and (2.122)).

$$\langle n_{\underline{q}} - 1 | \underline{A}(\underline{q}) | n_{\underline{q}} \rangle = \langle n_{\underline{q}} - 1 | \frac{(2m\hbar\omega_q)^{1/2}}{\sqrt{N}m\omega_q} \frac{\hat{a} - \hat{a}^*}{2} e^{-i\underline{q}\cdot\underline{\ell}} | n_{\underline{q}} \rangle \tag{2.162}$$

$$= \langle n_{\underline{q}} - 1 | \frac{(2m\hbar\omega_q)^{1/2}}{\sqrt{N}\, m\omega_q} \frac{\hat{a}}{2} e^{-i\underline{q}\cdot\underline{\ell}} | n_{\underline{q}} \rangle \tag{2.163}$$

$$= \sqrt{\frac{\hbar n_{\underline{q}}}{2M\omega_q}}\, e^{-i\underline{q}\cdot\underline{\ell}}\, \underline{f}(\underline{q}) \tag{2.164}$$

and for creation

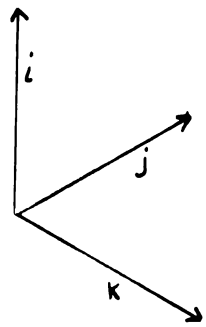
$$\langle n_{\underline{q}} + 1 | \underline{A} | n_{\underline{q}} \rangle = \sqrt{\frac{\hbar n_{\underline{q}} + 1}{2M\omega_q}}\, e^{-i\underline{q}\cdot\underline{\ell}}\, \underline{h}(\underline{q}) \tag{2.165}$$

and $\underline{f}$ is the unit vector in the direction of the polarization and $\sqrt{mN} = \sqrt{M}$, the total mass of the crystal.

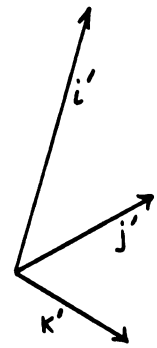
Rather than displacements, elements of the strain tensor will be used [cf. equations (2.146) and (2.147)]. A brief review of the facts in reference[30] is in order. The fractional changes per unit length, are ℓ_{xx}, ℓ_{yy}, and ℓ_{zz} where x,y, and z are the three orthogonal axes. The off-diagonal terms represent shear type forces and represent the angular change between the principal axes indicated by the subscript.

Let $\underline{\alpha} = u\underline{i} + v\underline{j} + w\underline{k}$ ($\underline{i},\underline{j},\underline{k}$ are cartesian basis vectors) be

the displacement of a point at $\underline{r} = x\underline{i}+y\underline{j}+z\underline{k}$ before the strain



before strain



after strain

and $\underline{r}' = x\underline{i}'+y\underline{j}'+z\underline{h}'$ ($\underline{i}', \underline{j}', \underline{h}'$ are not necessarily orthogonal or unit vectors) after the strain. If

$$\underline{i}' - \underline{i} \equiv \ell_{xx}\underline{i} + \ell_{xy}\underline{j} + \ell_{zx}\underline{k} \tag{2.166}$$

$$\underline{j}' - \underline{j} \equiv \ell_{yx}\underline{i} + \ell_{yx}\underline{j} + \ell_{yz}\underline{k} \tag{2.167}$$

$$\underline{h}' - \underline{h} \equiv \ell_{zx}\underline{i} + \ell_{zy}\underline{j} + \ell_{zz}\underline{k} \tag{2.168}$$

and $$\ell_{xy} = \ell_{yx},\ \ell_{zx} = \ell_{xz},\ \ell_{yz} = \ell_{zy}, \tag{2.169}$$

then

$$\epsilon_{xy} = \frac{1}{2}\left(\frac{\partial v}{\partial x} + \frac{\partial u}{\partial y}\right) \tag{2.170}$$

or, in general notation

$$\epsilon_{\gamma\beta} = \frac{1}{2}\left(\frac{\partial u_\gamma}{\partial x_\beta} + \frac{\partial u_\beta}{\partial x_\gamma}\right). \tag{2.171}$$

It should be noted that the off diagonal elements are sometimes written so the 1/2 will not appear in equation (2.170).

Instead of using the strain components, an average strain will be used, ϵ. Then (2.164) and (2.165) become

(with the use of $\partial\alpha_x/\partial x = q_x A_x e^{i\underline{q}\cdot\underline{\ell}}$)

$$|\langle n_{\underline{q}} - 1|\epsilon|n_{\underline{q}}\rangle|^2 \sim q^2\hbar n_{\underline{q}} / 2M\omega_{\underline{q}} \qquad (2.172)$$

$$|\langle n_{\underline{q}}+1|\epsilon|n_{\underline{q}}\rangle|^2 \sim q^2\hbar(n_{\underline{q}}+1)/ 2M\omega_q \qquad (2.173)$$

In 1932, Waller[106] originally pointed out the possibility of two relaxation phenomena: the diffusion of energy among the spins themselves, termed τ_2, and a spin-lattice coupling, termed τ_1. For the latter mechanism he proposed that as the interionic distances are modulated by the lattice motions, the dipoles of the neighboring spins set up an oscillatory magnetic field. The frequency components of the motion at the Larmor frequency, $\hbar\omega = g\beta H$, provided the coupling of spins and the lattice. Waller also introduced the idea of the Raman process.

J. H. Van Vleck[101] showed that the order of magnitude of the Waller coupling is too weak by a factor of 10^2 to 10^4 and that the τ_1 will be too long when compared with the observed values. In 1939, Van Vleck[100] and Kronig [57, 58] established the now accepted theory; the thermal vibrations modulate the crystalline electric field which effects the orbital motion of the electrons and then the spins by way of spin-orbit coupling.

The crystalline electric field arises in ionic salts

from the charges surrounding the paramagnetic ion. A distortion of the surrounding ions due to a strain will result in a change in the electric field. We expand the crystalline field in powers of the strain.

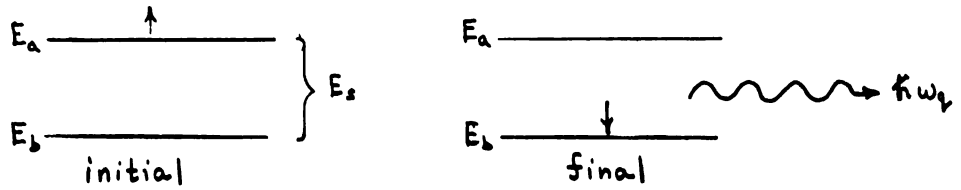
$$V = V_0 + V_1\epsilon + V_2\epsilon\epsilon' + V_3\epsilon\epsilon'\epsilon'' + \ldots \qquad (2.174)$$

The first term in the series is the static term producing a stationary state. The second produces the perturbation on the stationary state which we shall assume is responsible for the spin-lattice relaxation. In this approximation second and higher order terms are temporarily neglected.

The Direct Process. This process involves the creation of one phonon equal in energy to that given up when the electron relaxes. The probability for a spin to relax in such a combination of events can be calculated from first order time dependent perturbation theory.[60,94,75]

$$dw_{if} = \frac{2\pi}{\hbar}|F_{if}|^2\ \delta(E_f - E_i - \hbar\omega)df \qquad (2.175)$$

Here dw_{if} is the probability of transition per unit time to a range of final states df due to a perturbation $\hat{F}$ and E_i and E_f are the initial and final energies of the system as a whole.



The figure depicts a spin in the initial state 'a' relaxing to state 'b' with the emission of one phonon. E_s is the difference in the spin energy levels and $\hbar\omega_q$ is the phonon energy. The collective state function ψ of the system is separable, that is $\psi = \beta(\text{phonons})\alpha(\text{paramagnetic ions})$.

We would like the probability for all phonon states and all lattice sites. The former involves use of the relation (2.132)

$$\Sigma\Delta\Gamma \longrightarrow \frac{3V}{2\pi^2 v_o} \int \omega^2 d\omega \qquad (2.176)$$

which allows one to evade counting the quantum mechanical states and to substitute an integral in the approximation that the states form a continuum. The latter operation is accomplished by summing over those sites with a spin in the desired state, in this case n_a of them in the 'a' state. It should be noted that these are randomly situated; thus the phase factor in (2.164) and (2.165) may be neglected.

Then

$$W_{b \to a} \equiv n_b \int dw_{b \to a} \tag{2.177}$$

Using (2.173) for the creation of a phonon and

$$W_{b \to a} = n_b \frac{2\pi}{\hbar} \frac{3V}{2\pi^2 v^3} \int_0^{\omega_{max}} \omega^2 d\omega |\langle a|V_1|b\rangle|^2 \cdot |\langle n_q+1|\epsilon|n_q\rangle|^2$$

$$\delta(E_s - \hbar\omega) \tag{2.178}$$

then

$$W_{b \to a} = \frac{3(E_s/\hbar)^3 \rho n_b}{\hbar v^5} |\langle a|V_1|b\rangle^2 |n_{\Delta E} \tag{2.179}$$

where $\rho = V/m$. Therefore

$$-dN_b/dt = W_{b \to a} - W_{a \to b} = \frac{3(E_s/\hbar)^3}{2\pi\hbar\rho v^5} |\langle a|V_1|b\rangle|^2$$

$$|(n_{\Delta E}+1)n_b - n_{\Delta E} n_a|^2 \tag{2.180}$$

Since we have assumed a two level system (i.e., only two levels are occupied),

$$dn_b/dt = - dn_a/dt.$$

$$\frac{d(n_b - n_a)}{dt} = \frac{3(E_s/\hbar)^3}{\pi\hbar\rho v^5} |\langle a|V_1|b\rangle|^2 [(n_{\Delta E}+1)n_b - n_{\Delta E} n_a]. \tag{2.181}$$

n_b and n_a are the spin populations at the temperature T_s. At equilibrium $d(n_b - n_a)/dt = 0$ implies $[(n_{\Delta E}+1)n_b - n_{\Delta E} n_a]_{T_s=T} = 0$. It is assumed that the thermal bath remains at the thermal

equilibrium temperature during the process, therefore

$$n_{\Delta E} = \frac{1}{e^{\Delta E/kT}-1} \quad . \tag{2.182}$$

Thus

$$n_b + n_{\Delta E} n_{bT_s} - n_{\Delta E} n_{aT_s} = n_{\Delta E}[(n_{bT_s} - n_{aT_s}) - (n_{bT} - n_{aT})]$$

$$+ n_{bT_s} - n_{bT} \cong (\tfrac{1}{2} + n_{\Delta E})[(n_{bT_s} - n_{aT}) - (n_{bT} - n_{aT})]$$

$$\cong (\tfrac{1}{2})\left(\frac{e^{\Delta E/kT}+1}{e^{\Delta E/kT}-1}\right)[(n_{bT_s} - n_{aT}) - (n_{bT} - n_{aT})] \tag{2.183}$$

Combining the above expressions with equation (2.160),

$$\frac{1}{\tau_1} = \frac{3(E_s)^3}{\hbar^4 2\pi\rho v^5} |\langle a|V_1|b\rangle|^2 \left(\frac{e^{E_s/kT}+1}{e^{E_s/kT}-1}\right) \tag{2.184}$$

or assuming $E_s << kT$

$$\frac{1}{\tau_1} = \frac{3(E_s)^3}{\hbar^4 2\pi\rho v^5} |\langle a|V_1|b\rangle|^2 \frac{(2)}{(E_s/kT)} \tag{2.185}$$

$$\frac{1}{\tau_1} = \frac{3(E_s)^2 kT}{\hbar^4 \pi\rho v^5} |\langle a|V_1|b\rangle|^2 \tag{2.186}$$

If $|a\rangle$ and $|b\rangle$ are time conjugate states, then the matrix element in (2.186) will be zero by Kramers' theorem. Kramers' theorem holds for the case of an odd number of electrons. This also can be seen by applying the idea of time reversal (see Appendix, Section A). Thus

$$\langle a|V_1\epsilon|b\rangle = \langle Kb|V_1|b\rangle \tag{2.187}$$

$$= K\langle b|K_0V_1|Kb\rangle$$

$$= \langle Kb|K_0K_0V_1|KKb\rangle$$

$$= -\langle a|V_1|b\rangle \tag{2.188}$$

since KK = -1 for an odd number of electrons. The only way for (2.188) to be true is for the matrix element to vanish.

Non-time conjugate states, however, can be admixed by the magnetic dipole-magnetic field interaction to the wavefunctions $|a\rangle$ and $|b\rangle$ by use of perturbation theory to produce a non-zero result. The admixed wavefunctions correct to first order, then are[63]

$$|b'\rangle = |b\rangle + \sum_m{}' \frac{\langle m|\underline{\mu}.\underline{H}|b\rangle}{E_b-E_m} |m\rangle \tag{2.189}$$

$$|a'\rangle = |a\rangle + \sum_m{}' \frac{\langle m|\underline{\mu}.\underline{H}|a\rangle}{E_a-E_m} |m\rangle \tag{2.190}$$

where $\underline{\mu}$ is the magnetic dipole and $\underline{H}$ is the magnetic field. The only terms that contribute are those which lie near to the ground state (see Figure 5). If c and d are the nearest lying time conjugate states, then

$$|b'\rangle = |b\rangle + \frac{\langle c|\underline{\mu}.\underline{H}|b\rangle}{E_a-E_c} |c\rangle + \frac{\langle d|\underline{\mu}.\underline{H}|b\rangle}{E_b-E_d} |d\rangle. \tag{2.191}$$

Since $|\Delta m|$ is at most equal to one, both bra-kets cannot be different from zero. Thus if

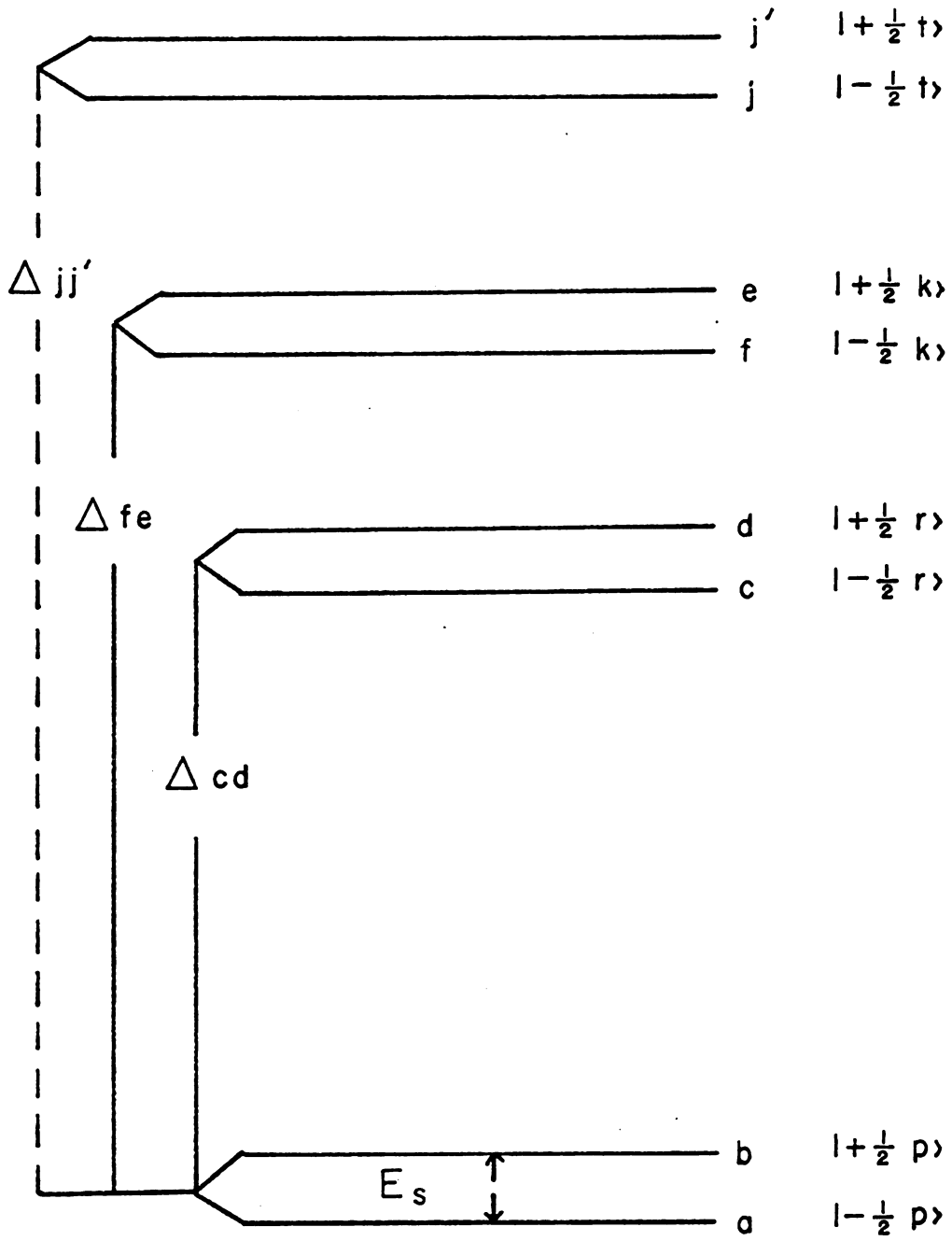


Figure 5. Typical Energy Diagram.

$$|b'\rangle = |b\rangle + \frac{\langle c|\underline{\mu}.\underline{H}|b\rangle}{\Delta_{cd}} |c\rangle$$

then

$$|a'\rangle = |a\rangle + \frac{\langle d|\underline{\mu}.\underline{H}|a\rangle}{\Delta_{cd}} |d\rangle \qquad (2.192)$$

where Δ_{cd} is the energy difference between the unsplit

$\binom{a}{b}$ and $\binom{c}{d}$ levels and $E_c - E_b \sim \Delta_{cd} \sim E_a - E_d$ (2.193)

Following the notation of Figure 5, then

$$\frac{1}{\tau_1} = \frac{3(E_s)^2 H^2 kT}{\hbar^4 \pi \rho v^5 \Delta_{cd}^2} |\langle c|\mu|b\rangle\langle a|V_1|c\rangle + \langle a|\mu|d\rangle\langle d|V_1|b\rangle|^2 \qquad (2.194)$$

This can be put into a slightly more compact form by a time reversal argument.[83]

$$\frac{1}{\tau_1} = \frac{12(E_s)^2 H^2 kT}{\hbar^4 \pi \rho v^5 \Delta_{cd}^2} |\langle c|\mu|a\rangle \langle d|V_1|b\rangle|^2 \qquad (2.195)$$

where μ is the magnetic moment in the direction of H.

The Two Phonon Process. There are many mathematical approaches to the Raman process. The two different methods used here follow the two basically dissimilar physical approaches.

The first method consists of using the second order term in equation (2.174), that is $V_2\epsilon^2$, and applying first order perturbation theory.

$$w_{v\to a} = \frac{2\pi}{\hbar}\int |\langle a, n_{q_1}+1, n_{q_2}-1|V_2\epsilon_1\epsilon_2|b, n_{q_1}, n_{q_2}\rangle|^2 \cdot$$

$$\frac{3V}{2\pi^2 v^3}\,\omega_1^2 d\omega_1\,\frac{3V}{2\pi^2 v^3}\,\omega_2^2 d\omega_2\,\delta[\hbar(\omega_2-\omega_1)-E_s] \qquad (2.196)$$

where $dE_s = \hbar(\omega_2-\omega_1)$ and $\hbar\omega_1$ is the energy of the incident phonon and $\hbar\omega_2$ is the energy of the scattered phonon.

Then

$$w_{b\to a} = \frac{9|\langle a|V_2|b\rangle|^2}{8\rho^2\pi^3 v^{10}\hbar^7}\int (\hbar\omega_1)^3 d(\hbar\omega_1)\,(\hbar\omega_2)^3 d(\hbar\omega_2)\,\delta[\hbar(\omega_1-\omega_2)-E_s]$$
$$(n_{q_1}+1)n_{q_2} \qquad (2.197)$$

and

$$\dot{n}_b = -\dot{n}_a = \frac{9|\langle a|V_2|b\rangle|^2}{8\rho^2\pi^3 v^{10}\hbar^7}\int [n_a n_{q_2}(n_{q_1}+1)\frac{(\hbar\omega_1)^3}{\exp(\hbar\omega_1/kT)-1}$$
$$-\frac{(\hbar\omega_2)^3}{\exp(\hbar\omega_2/kT)-1}\,n_b n_{q_1}(n_{q_2}+1)]$$
$$d\omega_1 d\omega_2[\delta(\hbar\omega_2-\omega_1-E_s)] \qquad (2.198)$$

The n_q, the phonon occupation numbers, are assumed to have thermal equilibrium values. If $E_s \ll kT$ and $E_s \ll \hbar\omega_1$, then $\hbar\omega_1 \sim \hbar\omega_2$. Equating $\frac{\hbar\omega_1}{kT}$ and $\frac{\hbar\omega_2}{kT}$ to x, then (2.198) yields [cf. (2.181)]

$$\frac{1}{\tau_1} = (kT)^7\,\frac{9|\langle a|V_2|b\rangle|^2}{4\rho^2\pi^3 v^{10}\hbar^7}\int_0^{\theta/T}\frac{x^6 e^x dx}{(e^x-1)^2} \qquad (2.199)$$

Since the transport integral is nearly constant for $\theta/T > 30$

$$\frac{1}{\tau_1} \propto T^7. \tag{2.200}$$

The bra-ket will vanish if a and b are time conjugate states [cf. (2.187) and (2.188)]; however, as in the direct case, higher order states may be admixed. By comparing (2.194), (2.195), and (2.186) to our present case, we find

$$\frac{1}{\tau_1} = \frac{9T^7H^2J_6}{\rho^2\pi^3v^{10}\hbar^7\Delta_{cd}^2}|\langle c|\mu|a\rangle\langle d|V_2|b\rangle|^2 \tag{2.201}$$

The second method used first order strain terms in second order perturbation theory. Mathematically, the only major difference from the direct process is in calculating the new $|F_{if}|^2$. Here an appeal is made to second order time dependent perturbation theory.[60]

$$F_{if} = \sum_j \frac{\langle f|A|j\rangle\langle j|A|i\rangle}{E_i - E_j} \qquad j \neq i \neq f \tag{2.202}$$

j = all the intermediate states (and is not equal to either i or f). We use equation (2.175) in the same fashion as before, letting the initial state consist of a phonon and the electron in state b, the intermediate state consists of only an electron in a virtual level j. Denoting Δ as the difference in initial and intermediate magnetic states (see Fig. 5), we find

$$W_{b\to a} = n_b \frac{2\pi}{\hbar} \int \left| \sum_{jj'} \frac{\langle a, n_{q_1}+1 | V_1(2)\epsilon_2 | j, n_{q_1}\rangle\langle j, n_{q_2}-1}{h\omega_2-\Delta_j} \right.$$

$$\underline{|V_1(1)\epsilon_1|b, n_{q_2}\rangle}$$

$$\left. + \frac{\langle a, n_{q_1}+1 | V_1(1)\epsilon_1 | j', n_{q_1}\rangle\langle j', n_{q_2}-1 | V_1(2)\epsilon_2 | b, n_{q_2}\rangle}{-h\omega_1-\Delta_{j'}} \right|^2 .$$

$$\frac{3V_1}{2\pi^2 v^3}\omega_1^2 d\omega_1 \frac{3V_2}{2\pi^2 v^3}\omega_2^2 d\omega_2 \quad \delta[E_s-\hbar(\omega_2-\omega_1)]. \quad (2.203)$$

If we were dealing with a non-Kramers' system there would be only one term inside the absolute value signs. The phonon contribution can be separated from the spin terms giving an expression multiplying the spin contributions as in the direct case, as in(2.196) and (2.197), namely

$$P \equiv n_b \frac{2\pi}{h}\left[\frac{q_1^2 \hbar(n_{q_1}+1)}{2M\omega_1}\right]\left[\frac{q_2^2 \hbar n_{q_2}}{2M\omega_2}\right]\frac{9V}{4\pi^4 v^6}\omega_1^2\omega_2^2 d\omega_1 d\omega_2 \cdot$$

$$\delta[E_s-\hbar(\omega_2-\omega_1)]. \quad (2.204)$$

Subtracting $W_{a\to b}$ and remembering $\dot{n}_a=-\dot{n}_b$, $1/\tau_1$ can be found as in the previous calculations.

$$\frac{1}{\tau_1} = 2\int P \left|\sum_j \frac{\langle a|V(1)|j\rangle\langle j|V(2)|b\rangle}{h\omega-\Delta_j}\right|^2 \quad (2.205)$$

Assuming as before that $\omega_1 \sim \omega_2$, $\hbar\omega \ll \Delta$, and noting that the

same form appears as in (2.198) and (2.199), we have

$$\frac{1}{\tau_1} = \frac{9(kT)^7}{4\pi^3 \rho v^{10} \hbar^7} \left| \sum_j \frac{\langle a|V(1)|j\rangle\langle j|V(2)|b\rangle}{\Delta_j} \right|^2 J_6 \qquad (2.206)$$

In the special case where Δ_j corresponds to an energy difference between a non-Kramers' ground state and a non-Kramers' first excited state, the denominator of (2.205) will display a resonance. For this resonance to be operative, Δ_j must be less than the Debye cut-off energy. If this condition is met, then the relaxation time may display an exponential dependence.[22]

$$\tau_1 = Ae^{-\Delta_j/kT} \qquad (2.207)$$

This is known as the Finn-Orbach-Wolf process.

Our discussion will now be limited to systems which display a Kramers' degeneracy. We shall temporarily fix our attention on the term inside the absolute value signs in (2.203). Let us expand V [eq. (2.174)] in a series of spherical harmonics.

$$V = \sum_{\ell m} a_{\ell m} Y_{\ell m}$$

where $$a_{\ell m} = r^{\ell} B_{\ell m}(\alpha_0) + \epsilon\alpha \left(\frac{\partial B_{\ell m}}{\partial \alpha}\right)\Big|_0 + \frac{1}{2}\epsilon\epsilon'\alpha\alpha' \left(\frac{\partial^2 B_{\ell m}}{\partial \alpha \alpha'}\right)\Big|_0 \qquad (2.208)$$

Upon rewriting we can express V in terms of $\epsilon_{\ell m}$.

$$V = \sum_{\ell m} V_{\ell m} \epsilon_{\ell m} \qquad (2.209)$$

The factor in the absolute value signs [eq. (2.203)] becomes, when considering only a particular term in the expansion of V,

$$\left|\frac{\langle a|V_{\ell' m'}|j\rangle\langle j|V_{\ell m}|b\rangle}{-\Delta_j+\hbar\omega_{\ell m}} + \frac{\langle a|V_{\ell m}|j'\rangle\langle j'|V_{\ell' m'}|b\rangle}{-\Delta j-\hbar\omega_{\ell' m'}}\right|^2 \qquad (2.210)$$

Consider the second term. The matrix elements must be invariant under a time inversion. Let

$$\begin{pmatrix} a \\ b \end{pmatrix} \equiv \begin{pmatrix} -\frac{1}{2}\,p \\ +\frac{1}{2}\,p \end{pmatrix} \text{ and } \begin{pmatrix} j' \\ j' \end{pmatrix} \equiv \begin{pmatrix} -\frac{1}{2}\,r \\ +\frac{1}{2}\,r \end{pmatrix} \quad \text{(Figure 5),}$$

then from the orthogonality of the spherical harmonics

$$m' = \frac{1}{2}(p-r) \quad \text{and} \quad m = \frac{1}{2}(r+p).$$

Hence m + m' is odd since, by assumption, p and r are Kramers' states and therefore odd. Then, since this term is invariant under time reversal

$$\langle a|V_{\ell m}|j'\rangle\langle j'|V_{\ell' m'}|b\rangle = (-1)^{m+m'}\langle b|V^*_{\ell' m'}|j\rangle\langle j|V^*_{\ell' m}|a\rangle \qquad (2.211)$$

$$= (-1)\,\langle a|V_{\ell' m'}|j\rangle\langle j|V_{\ell m}|b\rangle \qquad (2.212)$$

since the term is also invariant under Hermetian conjugation . Note also, since

$$\left|\langle a|V_{\ell' m'}|j\rangle\langle j|V_{\ell m}|b\rangle\left(\frac{1}{-\Delta_j+\hbar\omega_{\ell m}} - \frac{1}{-\Delta_j-\hbar\omega_{\ell' m'}}\right)\right|^2 \sim$$

$$\frac{\hbar(\omega_{\ell m}+\omega_{\ell' m'})}{\Delta_j^2}\,\langle a|V_{\ell' m'}|j\rangle\langle j|V_{\ell m}|b\rangle^2 \qquad (2.213)$$

where the left hand side is in the approximation that

$\Delta_j >> \hbar\omega_{\ell m}$

that

$$\frac{1}{(-\Delta_j + \hbar\omega_{\ell m})} + \frac{1}{(\Delta_j + \hbar\omega_{\ell' m'})} = - \frac{\Delta_j + \hbar\omega_{\ell' m'} - \Delta_j + \hbar\omega_{\ell m}}{\Delta_j^2 + (\hbar^2 \omega_{\ell m} \omega_{\ell' m'}) + \Delta_j \hbar(\omega_{\ell m} - \omega_{\ell' m'})}$$

$$\sim \frac{\hbar(\omega_{\ell' m'} + \omega_{\ell m})}{\Delta_j^2} \quad . \qquad (2.214)$$

This is the Van Vleck[10] cancellation and is based upon the assumption that the splitting of j and j' levels by the magnetic field is small compared to Δ_j. The effect of the cancellation is to raise the power of $\hbar\omega$ in the integrand of equations (2.203) and (2.205) by a factor of two. Using the definition of transport integrals (2.157), then

$$\frac{1}{\tau_1} = \frac{9h^2}{4\pi^3 \rho^2 v^{10}} \left(\frac{kT}{\hbar}\right)^9 J_8(\theta/T) \qquad (2.215)$$

and for $\frac{\theta}{T} > 35$ $\qquad \frac{1}{\tau_1} \propto T^9$.

Cancellation of the Van Vleck type may be inhibited by application of a magnetic field. Admixture of adjacent Kramers' levels to the ground states $\begin{pmatrix} a \\ b \end{pmatrix}$ and/or the excited states $\begin{pmatrix} j \\ j' \end{pmatrix}$ can destroy the time conjugate nature of these

states. The admixture enters again as in (2.194) and (2.195) giving an equation comparable to (2.201).

Orbach and Blume[86] have considered the Van Vleck cancellation term further. In the above arguments we assumed that j and j' were split apart from the ground state by a large energy, but there is no reason to demand this a priori. Now cancellation [(2.210) and (2.213)] gives for $\Delta_j \ll \hbar\omega_{\ell m}$ and $\hbar\omega_{\ell m} = \hbar\omega_{\ell' m'}$

$$\langle a|V_{\ell' m'}|j\rangle\langle j|V_{\ell m}|b\rangle\left(\frac{2}{\hbar\omega_{\ell m}}\right) \tag{2.216}$$

The absolute value squared of (2.216) replaces the absolute value squared in equation (2.206). The effect is to multiply the previously determined absolute value of the relaxation time in equation (2.206) by

$$\left(\left(\frac{2}{\hbar\omega_{\ell m}}\right)^2 \Delta_j^2\right)^{1/2} \text{ or } \left(4\left(\frac{kT}{\hbar\omega_{\ell m}}\right)^2\left(\frac{1}{kT}\right)^2 \Delta_j^2\right)^{1/2}. \quad \text{Thus}$$

$$\frac{1}{\tau_1} \sim \frac{9(kT)^5}{\rho\pi^3 v^{10}\hbar^7} J_4(\theta/T) \tag{2.217}$$

and for $\theta/T > 25$ $\quad \frac{1}{\tau_1} \propto T^5$.

A rough order of magnitude criterion for the above process to dominate in the Raman region is given by Orbach and Blume as

$$\lambda\left(\frac{\lambda}{\Delta}\right) > kT \tag{2.218}$$

where Δ is the appropriate crystal field splitting and λ is the spin-orbit coupling constant.

Phonon Bottleneck. In all the preceding derivations the phonon bath was assumed to remain in equilibrium during the relaxation process. Our measurements actually measure spin-bath relaxation time, τ_b, which is identical to τ_1 if our equilibrium assumption remains valid. The non-equilibrium case has been debated by many authors.[102, 28, 10, 17] The most recent theoretical and experimental effort of note has been carried out by Scott and Jeffries.[99] They envision a strong 'localized heating' in the phonon spectrum at the resonant electron energy. In the direct region this process can be dominant. The solution of the rate equations for this process yields two time constants. One of these would be of the order of one microsecond for a ten gauss wide line. The other should be larger and have the predicted temperature dependence of

$$\frac{1}{\tau_b} = \frac{ADT^3}{DT^2+AT} \qquad (2.219)$$

where D is related to (density of spins) (average linear dimension of crystal)$^{-1}$ (line width), and A is an empirical constant. Then for $DT^2 \gg AT$ (no bottleneck)

$$\frac{1}{\tau_b} = \frac{1}{\tau_1} = AT \tag{2.220}$$

and for $DT^2 \ll AT$ (bottleneck)

$$\frac{1}{\tau_b} = DT^2. \tag{2.221}$$

Localized Modes. It has been assumed that the phonon spectrum with which the spins are on speaking terms is the phonon spectrum characteristic of the crystal. The effects on the phonon spectrum introduced by an impurity or defect site have been studied theoretically by I. M. Lifshitz,[67] E. Montroll and R. Potts,[81] P. Klemens[50, 51, 52, 53] B. I. Kocheleav,[56] and R. Brout and W. Vissher.[14] Castle, Feldman, and Klemens have applied their theory to paramagnetic relaxation experiments.[17, 18] A brief summary of their theory is given below. The contribution of the strain, ϵ, to the J_6 transport integral in a normal T^7 Raman process is $\epsilon^4 \alpha (\hbar\omega)^4$. The strain introduced by the impurity is:

$$\epsilon' = \left(\frac{a}{a_0}\right)\left(\frac{\omega_i^2}{\omega_i^2 - \omega^2}\right) \tag{2.222}$$

where ω_i is the local mode frequency. Then for $\omega \ll \omega_i$

$$\epsilon' = \left(\frac{\omega}{\omega_i}\right)^2 \frac{a}{a_0} e^{i\omega t} \tag{2.223}$$

and for $\omega \gg \omega_i$

$$\epsilon' = \frac{a}{a_0} e^{i\omega t} \tag{2.224}$$

This leads immediately to the relaxation law for a T^7 Raman process.

$$\frac{1}{\tau_1} = AT^7 J_6 + B(T^3 J_2 - T^3 J_2 \frac{\theta i}{T}) + C(T^{11} J_{10}(\frac{\theta i}{T})) \tag{2.225}$$

The second term arises from the contribution of the modes from $\theta_i(\omega_i)$ to $\theta_D(\omega_D)$. The third term arises from all modes up to $\theta_i(\omega_i)$. The equivalent law for T^9 then is

$$\frac{1}{\tau} = A' T^9 J_8 + B'(T^5 J_4 - T^5 J_4(\frac{\theta i}{T})) + C'(T^{13} J_{12}(\frac{\theta i}{T})). \tag{2.226}$$

Cross Relaxation

Relation to Line Shape. The general theories of line shapes and various cross relaxation processes are intertwined. In theory if the correct interaction Hamiltonian for a spin system can be written down, then all possible cross relaxation interactions will be present and the relaxation time line shapes can then be calculated. A general form of such an interaction Hamiltonian for two spin ensembles is

$$H_{int} = \underline{S}.\underline{\underline{D}}.\underline{S} + \underline{I}.\underline{\underline{P}}.\underline{I}. + \underline{S}.\underline{\underline{A}}.\underline{I} + \underline{L}.\underline{\underline{\lambda}}.\underline{S} \qquad (2.227)$$

which represents the internal interaction between spins in ensemble S and those in ensemble I and the interaction between the two ensembles. The first term can correspond to two physical phenomena, the contribution of the exchange integral[88] and that of dipole-dipole interactions[4] for the ensemble of spins S. The second term has the same interpretation for the ensemble of spins I. The third term is the interaction between the ensembles. The strength of this interaction is determined by the amount of frequency overlap in the Fourier spectrum of individual members of ensemble S and I. The fourth term is the spin orbit coupling. Bloembergen, et al, have written down the dipole interaction plus a pseudo-dipole interaction in terms of raising and lowering operators which is an equivalent of (2.227).[10] (The dipole expansion

is done in detail in reference 4. The discussion in reference 10 provides the basis for much of the work in spin-spin interaction theory at the present time.) The operator form carries a physical significance with each term. S_+I_- or S_-I_+ indicates a mutual spin 'flip'. S_zI_- or S_zI_+ denotes an interaction in which spin I, being coupled to spin S, finds components in the frequency spectrum of S which correspond to frequency components in the Fourier transform of the time dependence of its relaxation. S_+I_+ or S_-I_- corresponds to a simultaneous spin transition of spins S and I. Using a hybrid of perturbation theory and Van Vleck's[103] method for calculating the line moments using traces of the Hamiltonian and spin components, it is possible to evade calculating the repeated perturbation action of H_{int} which would account for the reshuffling of the dipole fields caused by H_{int}. In making the calculations certain terms normally are dropped as being negligible, but these terms have recently been investigated for special systems in which they are important. For example, A. Kiel considers in detail the effect of the exchange terms.[46, 47] An important result of Bloembergen's calculations was to show that even if resonance absorption lines are clearly resolved, there still may be considerable overlap between the lines as calculated from the H_{int} terms since the absorption line

does not represent the effect of all the terms in H_{int}.

Relation to Relaxation Time. The typical resonance line can be thought of as made up of a group of Lorentzian ensembles or lines randomly distributed in a Gaussian-like manner. Each Lorentz packet is said to be a homogeneous line, that is a line made up of an ensemble of spins seeing essentially the same local field. τ_2 is defined as the characteristic time it takes for the transverse components of the spin in a homogeneous line to lose phase coherence, that is, if at time equal to $t = 0, N_0$ of the spins are precessing about the 'z-axis' in a coherent fashion, $N = N_0 e^{-t/\tau_2}$ will still be coherent at a time t and N_0-N of the spins will have had a mutual spin transition with another member of the same ensemble. τ_2 is related to the ensemble width, Δf, through the Heisenberg uncertainty principle.

$$\frac{1}{\tau_2} = 2\Delta f \qquad (2.228)$$

(Note that we have tacitly assumed that none of the N_0 spins will undergo the τ_1 process.) τ_{12} is defined as the characteristic time for a spin in one particular ensemble to exchange energy by a mutual spin 'flip' with a member of another ensemble. The whole line consisting of all the ensembles seeing slightly different local fields is termed

a non-homogeneous line. τ_2^* is defined as the inverse of twice the non-homogeneous line width.

The diffusion time, τ, for a packet of energy to diffuse through a non-homogeneous line can be calculated in the first approximation using a random walk method. τ_2^*/τ_2 is the chance that a neighbor is on 'speaking terms'. Therefore the probable time to cover a step is $\tau_2(\tau_2/\tau_2^*)$. The number of steps to go from boundary to boundary, however, is $(\tau_2/\tau_2^*)^2$. Therefore

$$\tau \sim \tau_2^4/\tau_2^{*3} \tag{2.229}$$

A more accurate expression is derived by Bloembergen:

$$\tau \sim (\langle v_c^2 \rangle^{1/2} \tau_2^4)^{-3} \tau_{12} \tag{2.230}$$

where $\langle v_c^2 \rangle^{1/2}$ is the mean square cross relaxation line width.

One other effect has been observed. Upon the application of an r.f. field there will be a reshuffling of the local dipole fields.[79, 12] Depending upon the system and the magnitude of the r.f. field, the system will take a finite amount of time to come to a quasi-equilibrium.

CHAPTER 3

EQUIPMENT AND TECHNIQUES

General Description

The equipment for this experiment may be divided into two categories, the saturation recovery apparatus (see Figure 6) and the spin echo apparatus (see Figure 7). Both pieces of apparatus are connected to a standard X-band microwave waveguide passing through a vacuum sealed head into a double Helium dewar (Figure 8). The waveguide terminates at a cyclindrical reflection microwave cavity (Figure 8) excited in the TE-011 mode.[80] The frequency of the cavity can be varied with a pair of Teflon rods 1/4" in diameter which enter the cavity at 1/4 and 3/4 the diameter of the cavity. This positioning of the rods allows maximum coupling to the electric field and permits tuning over a range of 150 megacycles. A small bifilar Manganin wire coil was wound around the waveguide just above the cavity. This coil was used to regulate the temperature between 4.2°K. and 80°K. The samples were mounted at the center of the cavity on a polystyrene rod

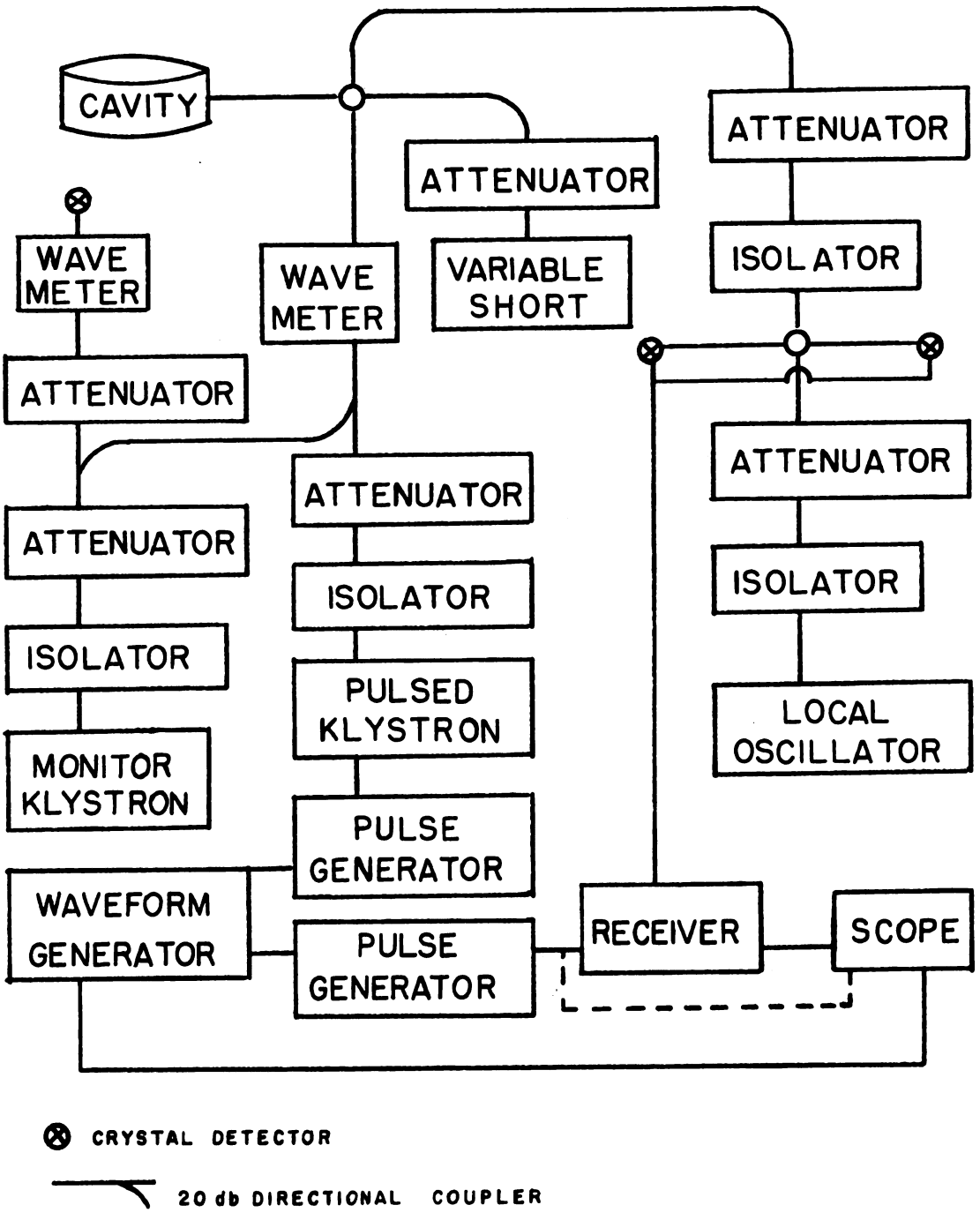


Figure 6. Saturation Equipment.

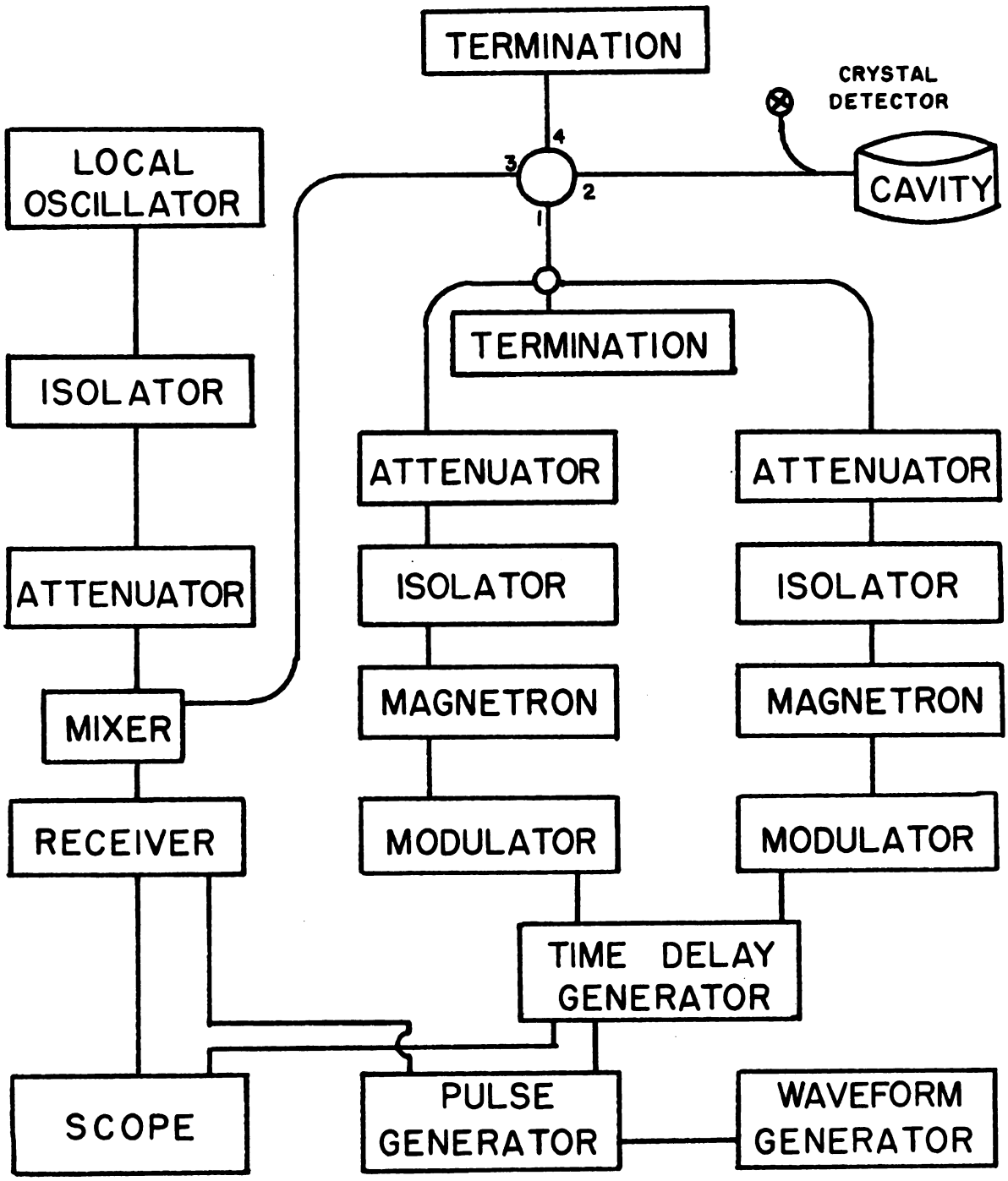
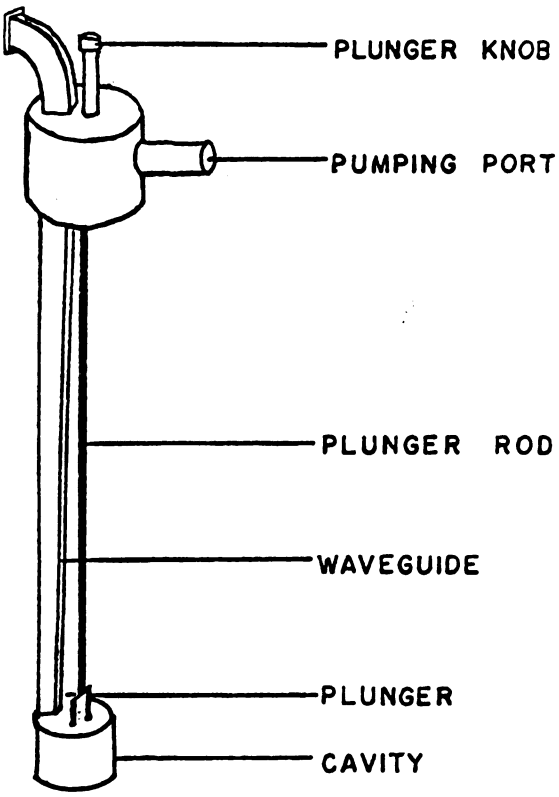


Figure 7. Spin Echo Equipment.



DEWAR CAP ASSEMBLY

SHOWING POSITION OF CAVITY

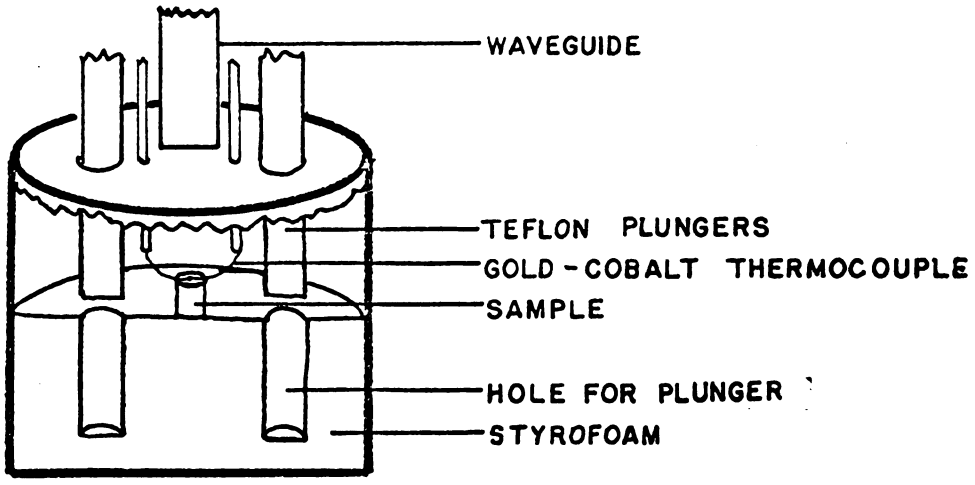


Figure 8. Dewar Cap and Cavity.

embedded in styrofoam which filled the bottom of the cavity. A thermocouple made from 3 mil silver 32 atomic % gold and gold 2.1 atomic % cobalt wire was attached to the crystal with Glyptol. The other junction of the thermocouple was in contact with the liquid Helium. The temperature was monitored with a K-3 potentiometer and a null indicator. This method of measuring temperature was checked by observing the temperature dependence of the splittings of the nuclear resonance lines of the protons in $NiSO_4.6H_2O$. The splittings in this salt are known to obey 1/T Curie law dependence down to 4.2°K. Temperatures were stabilized at boiling Helium (4.2°K.) and Nitrogen (77.2°K.) temperatures as a further check. Temperatures below 4.2°K. were obtained by pumping on liquid Helium with a Kinney vacuum pump at rates up to 230 cu.ft./min. Temperatures as low as 1.1°K. were obtained in this fashion.

Spin Echo

The spin-echo techniques and apparatus used are those developed by D. E. Kaplan.[45,15] A block diagram of the apparatus is shown in Figure 7. The idea of spin echoes, although relatively new in the area of paramagnetic resonance, was originally introduced in nuclear magnetic resonance work by Hahn.[32] The effect can be explained readily on the basis

of a classical model (Figure 9). Consider the spins initially precessing about the z-axis under the influence of a static magnetic field applied in the z direction. At time 0, a linearly polarized magnetic field in the x direction is applied at the resonance frequency of the spins for an extremely short period of time ($\sim 50 \times 10^{-9}$ seconds). The linearly polarized field can be decomposed into two circularly, oppositely polarized components. The component rotating with the spins pulls the spins down toward the xy-plane. If the power is correct, the pulse will pull the spins 90° into the xy-plane. The spins then start to precess coherently in phase in the x-y plane at $\omega = \gamma H \equiv g\beta H/\hbar$, where H is the combined externally applied and local magnetic crystal fields. Due to differences in the local field, the spins will become more and more out of phase as time progresses. This loss of phase coherence because of local field differences is not an irreversible process. By applying a second pulse (of twice as much power) at time T, it is possible to have the spins essentially reverse their angular velocity and retrace their paths back to the phase coherent condition. Actually the second pulse flips the y component of spins a full 180°, but the effect is the same. At a time 2T a pulse may be observed as spins

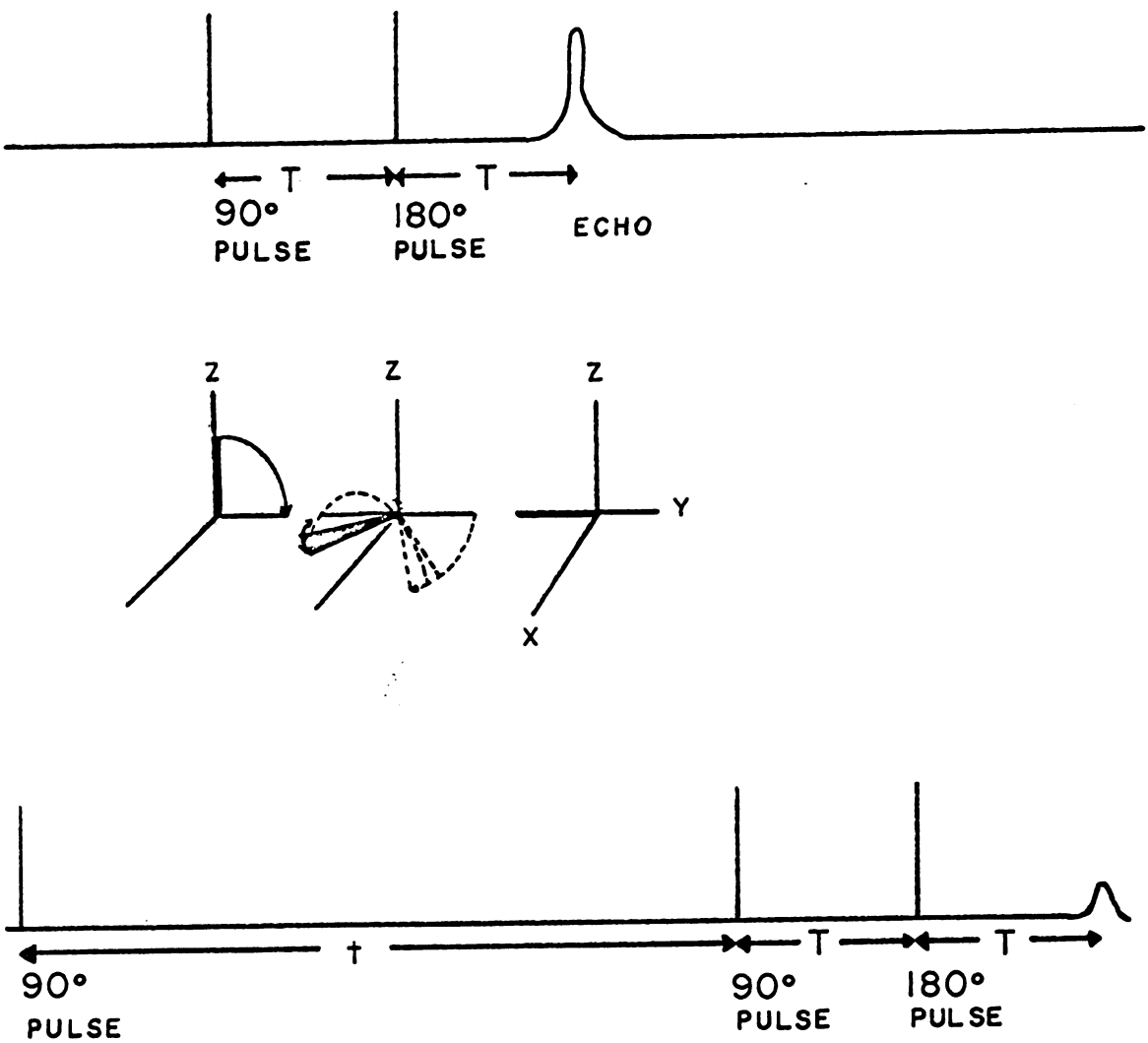


Figure 9. Spin Echo Pulse Sequence.

pass through the phase coherent condition. This process of bringing the spins into coherence can be repeated. However, as time passes it will be observed that the size of the pulse decreases due to various relaxation processes. Normally at low temperatures $\tau_2 \ll \tau_1$, so the decreases in pulse size are due to cross relaxation processes. Although energy is conserved, such a process will destroy the phase coherence. If one wishes to actually measure τ_2, not τ_{12} or τ_2^*, (see cross relaxation section for definitions) it is essential that the whole resonance line be spanned by the Fourier components of the pulse.

Let N_0 be the initial number of spins tipped by the 90° pulse, and N be the number that have not undergone a relaxation process. Then

$$N = N_0 e^{-t/\tau_2}. \tag{3.1}$$

If the system is initially pulsed at time equal to zero, and then at some time $t \gg \tau_2$, the system is inspected for echoes with a 90° and then an 180° pulse. The echo then formed will depend upon the number of spins that have relaxed in the time t, since the relaxed spins are again eligible for a spin echo process (Figure 9).

Thus

$$N = N_0(1 - e^{t/\tau_1}). \tag{3.2}$$

Both equation (3.1) and (3.2) must be written in an operational form. If V is the voltage monitored on the oscilloscope, then $V^k = P$, the power emitted by the echo where k is a characteristic parameter of the equipment. It can be shown[15] directly from Bloch's equations that

$$P = N^2. \tag{3.3}$$

Hence, (3.1) becomes

$$V = V_0 \ e^{-kt/2\tau_2} \tag{3.4}$$

and (3.2) becomes

$$1 - (V/V_0)^{k/2} = e^{-t/\tau_1}. \tag{3.5}$$

In making such a measurement it is essential that the initial pulse tip the spins 90°. The criterion on the line is that it be sufficiently narrow so that it can be spanned by the first 90° pulse. Times down to .1μs can be measured with this technique.

The spin echo equipment is shown in block form, Figure 7. The repetition of the pulse sequence is controlled by a waveform and pulse generators (Tektronix 161, 162, 163). These are used to trigger a General Radio 1392 delay generator and to gate the receiver. The delay generator triggers the magnetron modulators and the oscilloscope. Two sets of magnetrons (Litton 3028D) and modulators are used to allow for the magnetrons to recover in short-time pulse work.

The magnetron lines join at a matched-T. Pulses are distributed through a circulator with 40db isolation to the cavity. Pulses from the cavity are returned through the circulator, mixed with the local oscillator frequency, and detected by a superhetrodyne receiver (Figure 10). The receiver has a bandwidth of 50 megacycles at a center frequency of 350 megacycles.

Saturation Recovery

The saturation recovery technique is similar to that used by Jeffries and Scott.[99] A microwave pulse of 10^{-5} seconds is applied to the microwave system. The pulse is of sufficient power to saturate the signal. The recovery of the cavity and the sample is then monitored at low power level. The monitor is modulated to compensate for any drifts from the cavity frequency. The monitor power must be low enough so that its effect is negligible. The sensitivity of our system is around 80 dbm. The shortest measureable time is about .1 ms. The operational equation for this system is

$$V = V_0 e^{-kt/\tau_1} \qquad (3.6)$$

where V^k represents the response of the saturation apparatus to a power level P, since the power absorbed by the sample is proportional to N, the number of centers.[71]

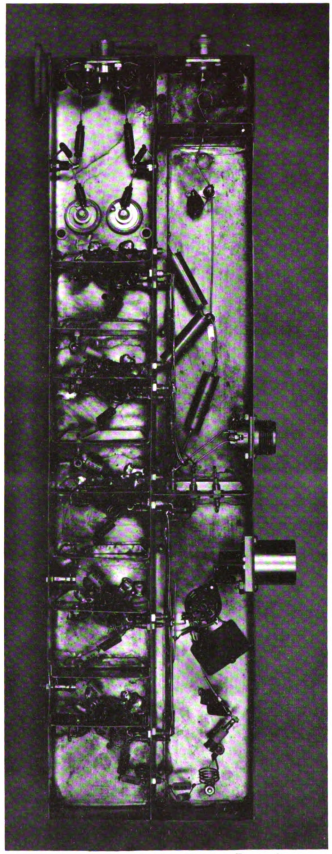


Figure 10. Spin Echo Receiver.

The equipment is shown in block form, Figure 6. The pulse klystron is connected to standard magnetic resonance spectroscopy bridge with reflection cavity. A side arm with 40 db isolation connects the monitor klystron to the pulse klystron arm. The detection arm contains a balanced mixer and local oscillator. The output of the balanced mixer is fed to a superhetrodyne receiver which operates at 150 megacycles with a bandwidth of 10 megacycles.

CHAPTER 4

RESULTS AND CONCLUSIONS

The Experiment

Single crystals of $AlCl_3.6H_2O$ were grown from an aqueous solution. Extremely slow growth produced crystals which were optically clear. The c axis was clearly defined by the intersection of the large crystal faces. When either the chlorides of Fe^{+++} or Cr^{+++} were added to the solution, the impurity ions readily substituted for the Al^{+++}. The actual percentage by weight of the substituted ion was estimated by E.P.R. absorption and checked by chemical analysis. The results showed the percentage of iron to be .009 and the percentage of chromium to be .028.

For the experiment, the crystals were mounted as described in Chapter 3. τ_1 data was taken in the 4.2°K. to 1.1°K. temperature region using the saturation technique. The spin-echo technique was normally used from 4.2°K. to 80°K. since it is more sensitive and can measure shorter times. Temperatures over 4.2°K. were obtained by heating the cavity as indicated in Chapter 3. However, as a check of

the reliability of the data, both sets of apparatus were used interchangeably in the region between 4.2°K. and 15°K. Within the limits of error (10%) both gave the same results. The upper temperature for obtaining data was limited by the combined effects of τ_2, the ultimate time resolution of the spin-echo apparatus, and the Boltzman population factor. This upper limit was at 47°K. for Fe^{+++} and 80°K. for Cr^{+++}.

For each run the equipment was checked to find its response law, namely input power was plotted against output voltage. The response law then was determined in the power region used for obtaining data; that is k in $P = V^k$ was obtained.

Analysis

The saturation recovery data is read directly from the photographs of the oscilloscope traces (Figure 12). The modulation clearly shows when the apparatus is on the cavity frequency. In the photograph shown, we would read the bottoms of the recovery trace. The voltage is then plotted against time on semi-log paper. The spin-echo data must be handled differently (Figure 11). Here we do not see the continuous recovery, but only the pulse corresponding to a particular delay between the first and second pulses. Since the experiment is not continuous, but

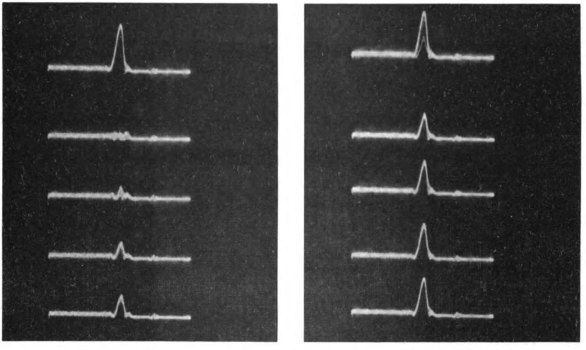


Figure 11. Spin Echo Data. The pictures correspond to elapsed times of V_o, .1, .25, .5, .75 m.s.; and V_o, 1, 2, 3, 4 m.s.

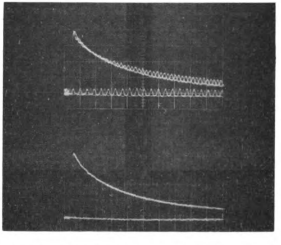


Figure 12. Saturation Recovery Data. The top trace is with modulation. The sweep is 1 m.s. per large division.

actually takes place over a time $\gg\tau_1$, one must be careful to check V_0, the pulse in a spin-echo after the system has had a time $\gg\tau_1$ in which to recover. Thus the top trace in each picture is V_0. For the spin-echo technique, $1 - (V/V_0)^{k/2}$ is plotted against time on semi-log paper (3.4). Using this technique, the best straight line through the data will be a good statistical average for the determination of the relaxation time from the data. Using (3.4) and (3.5) τ_1 is readily interpreted. The initial points (especially in the Cr^{+++} data) probably show a Bowers and Mims effect.[12]

Resonance data was taken on all three lines in the Cr^{+++} spectra between 1.1° and $2^{\circ}K$. No appreciable difference in relaxation times was observed. The relaxation times were also found to be angle independent. Since the 1/2, -1/2 transition was the strongest, it was used for determining the temperature dependence of the relaxation time. All five transitions for iron gave the same relaxation time between 1.1° and $2^{\circ}K$. when the crystal was oriented parallel to the magnetic field. The line at 3800 gauss was strongest and therefore was used in obtaining the temperature dependence.

We have seen in Chapter 2 that two distinct types of temperature dependence are expected. At low temperatures,

equation (2.195) is expected to dominate since it is a single phonon process. At higher temperatures we expect the two-phonon (Raman) process to prevail. The actual temperature dependence of the Raman process depended upon the splitting Δ of the energy levels near to the ground state levels (Figures 2, 3, and 5 and equation (2.218)). Summarizing, we have two processes which occur for transition ions:

$$\frac{1}{\tau_1} = \alpha T + \beta T^7 J_6\left(\frac{\theta_d}{T}\right) \qquad \text{for } \frac{\lambda^2}{\Delta} < kT \tag{4.1}$$

or

$$\frac{1}{\tau_1} = \alpha T + \beta T^5 J_4\left(\frac{\theta_d}{T}\right) \qquad \text{for } \frac{\lambda^2}{\Delta} > kT \tag{4.2}$$

where θ_d, α, β, are experimental parameters. A more specialized process called the Finn-Orbach process which is highly unlikely for transition ions would contribute an additional term (2.207)

$$\gamma e^{-\Delta/kT} \tag{4.3}$$

to equations (4.1) and (4.2), where γ is a constant to be determined.

The relaxation time dependence was plotted against temperature on a log-log plot. The curves were fitted trying various theories as outlined in Chapter 2. A Finn-Orbach process gave a very poor fit. A bottleneck term if present

Figure 13. Cr^{+++} Temperature Dependence of Relaxation.

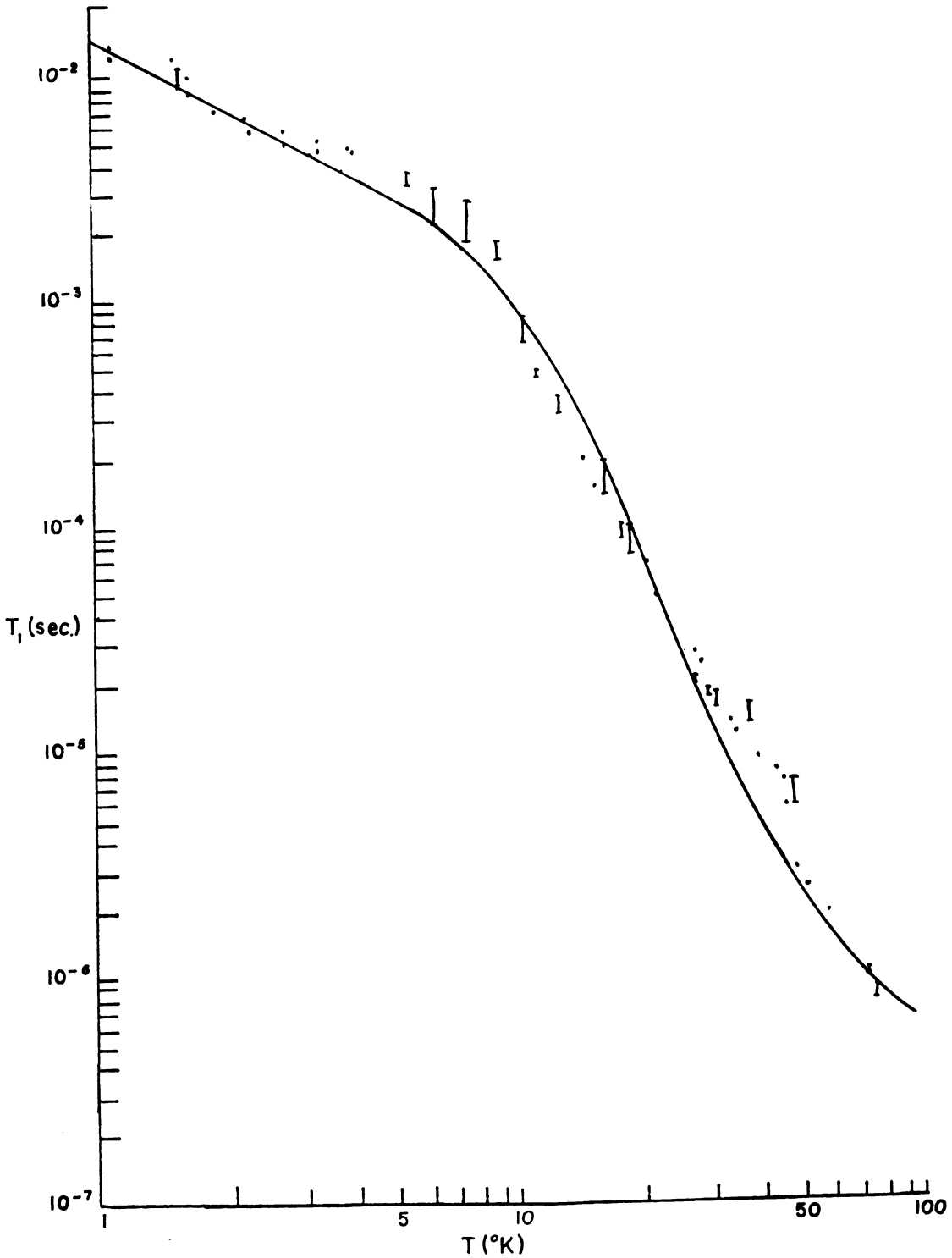
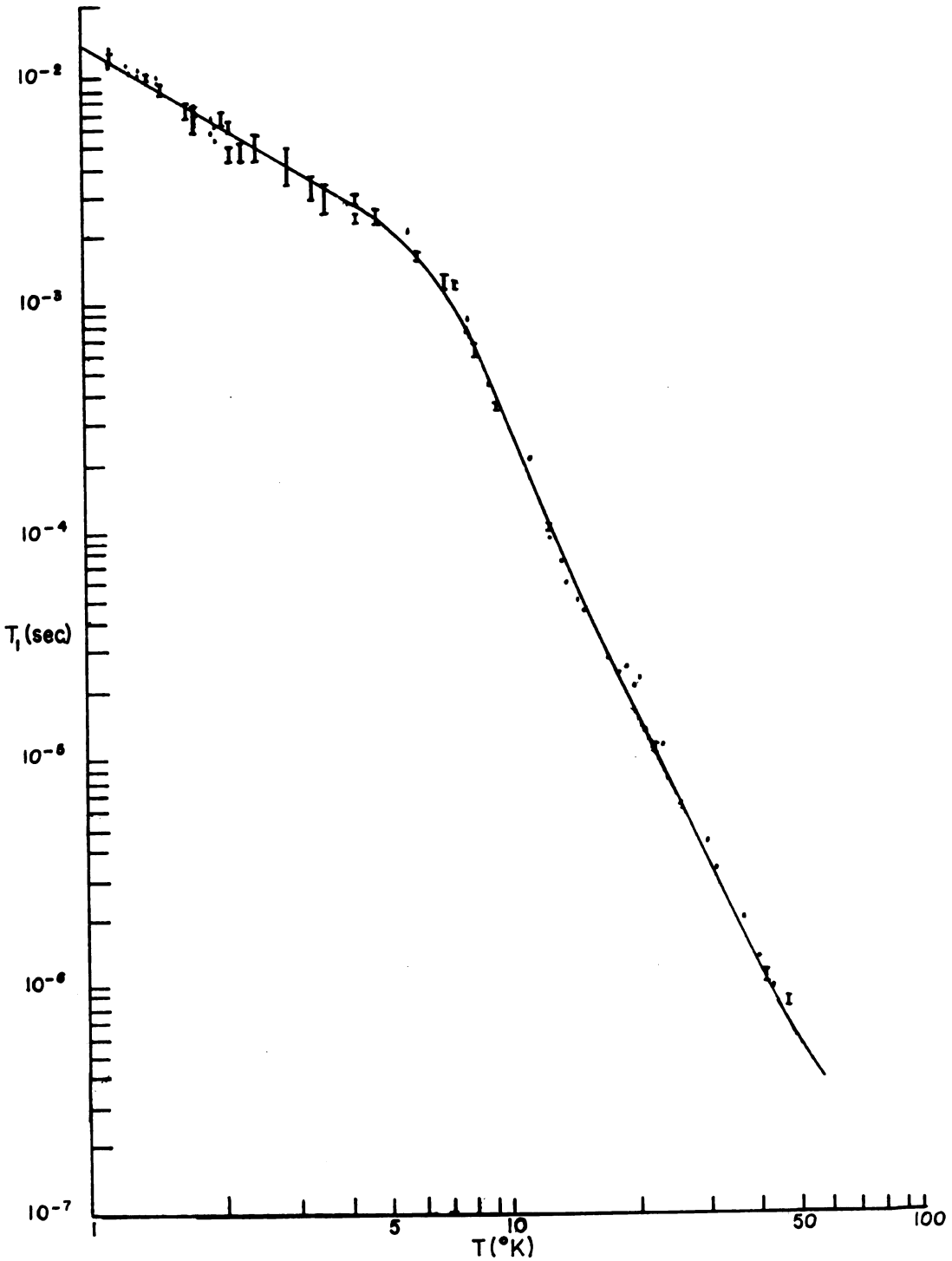

10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
T_1 (sec.)
1
5
10
50
100
T (°K)

Figure 14. Fe^{+++} Temperature Dependence of Relaxation.


10^{-2}
10^{-3}
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T_1 (sec)
10^{-5}
10^{-6}
10^{-7}
1
5
10
50
100
T (°K)

would have to have a negative coefficient if it were to improve the fit. Both of these effects were not expected for our systems. Therefore, they were discarded. The Cr^{+++} data fit well using a T^7 dependence and much more poorly for a T^5 dependence and very badly using a T^9 dependence. The Fe^{+++} data fit extremely well to a T^5 dependence and quite poorly to a T^7 dependence. The results as shown in Figure 13 for Cr^{+++} are

$$\frac{1}{\tau_1} = 67T + 1.20\times10^{-8}T^7J_6\left(\frac{160^\circ}{T}\right) \qquad (4.4)$$

In Figure 14 the results for Fe^{+++} are

$$\frac{1}{\tau_1} = 71T + 7.58\times10^{-4}T^5J_4\left(\frac{160^\circ}{T}\right) \qquad (4.5)$$

It should be noted that in both cases the same Debye θ, 160°, gave the best fit. We should now like to compare these results with the theoretical predictions for the T^7 and T^5 Raman processes.

Discussion

In general for T^5 to be a probable process, $\lambda^2/\Delta \geq kT$.[32] Since $kT = hc/\lambda$, then $1.38\times10^{-16}\times 1^0 = (6.6\times10^{-27})(3\times10^{10})/\lambda$, or each degree Kelvin equals .7 cm^{-1}. Since the roll off of τ_1 occurs at about $4.2^\circ K.$, the criterion is $\lambda^2/\Delta \geq 4$. We now consider our two cases,

Figure 13. Cr^{+++} Temperature Dependence of Relaxation.

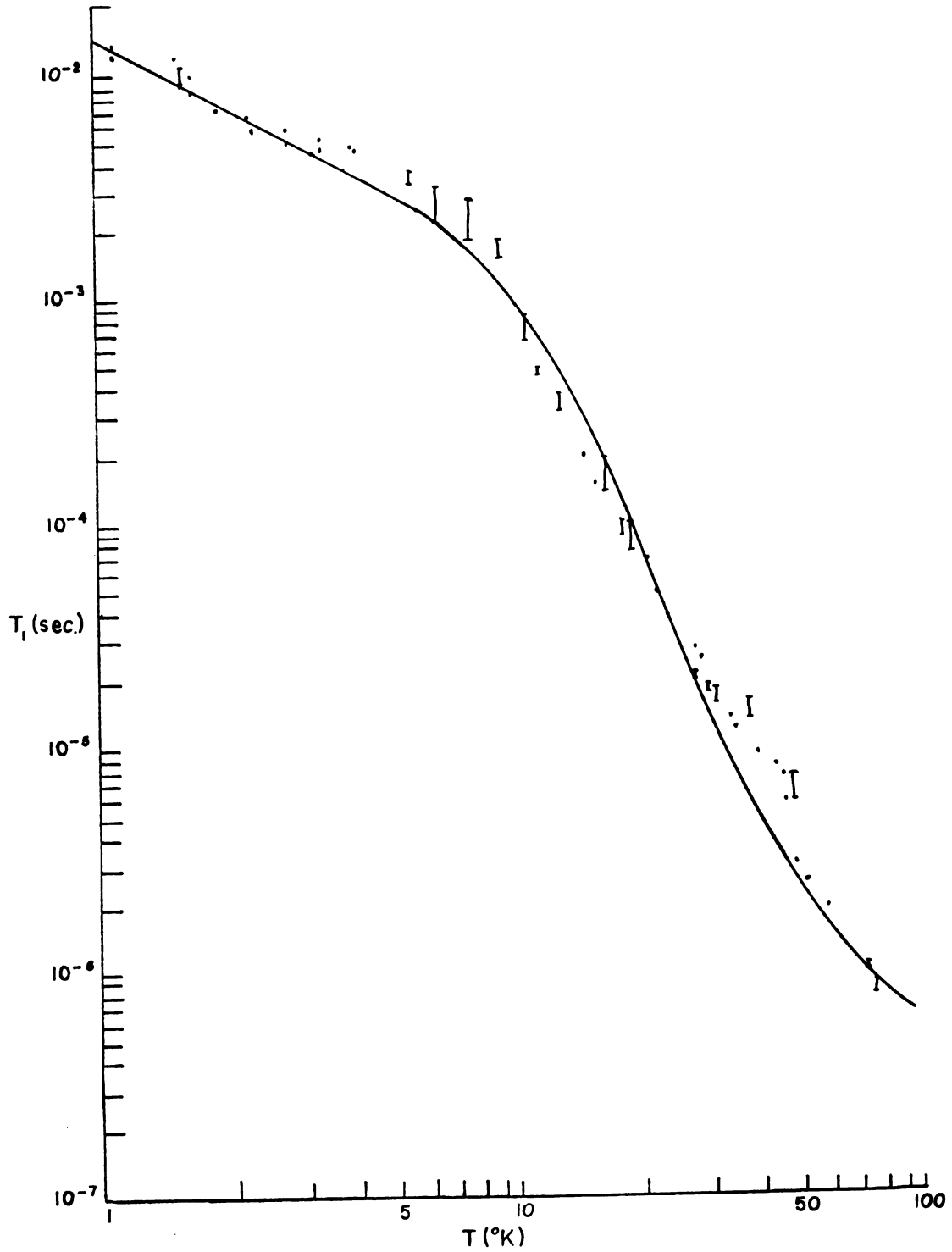
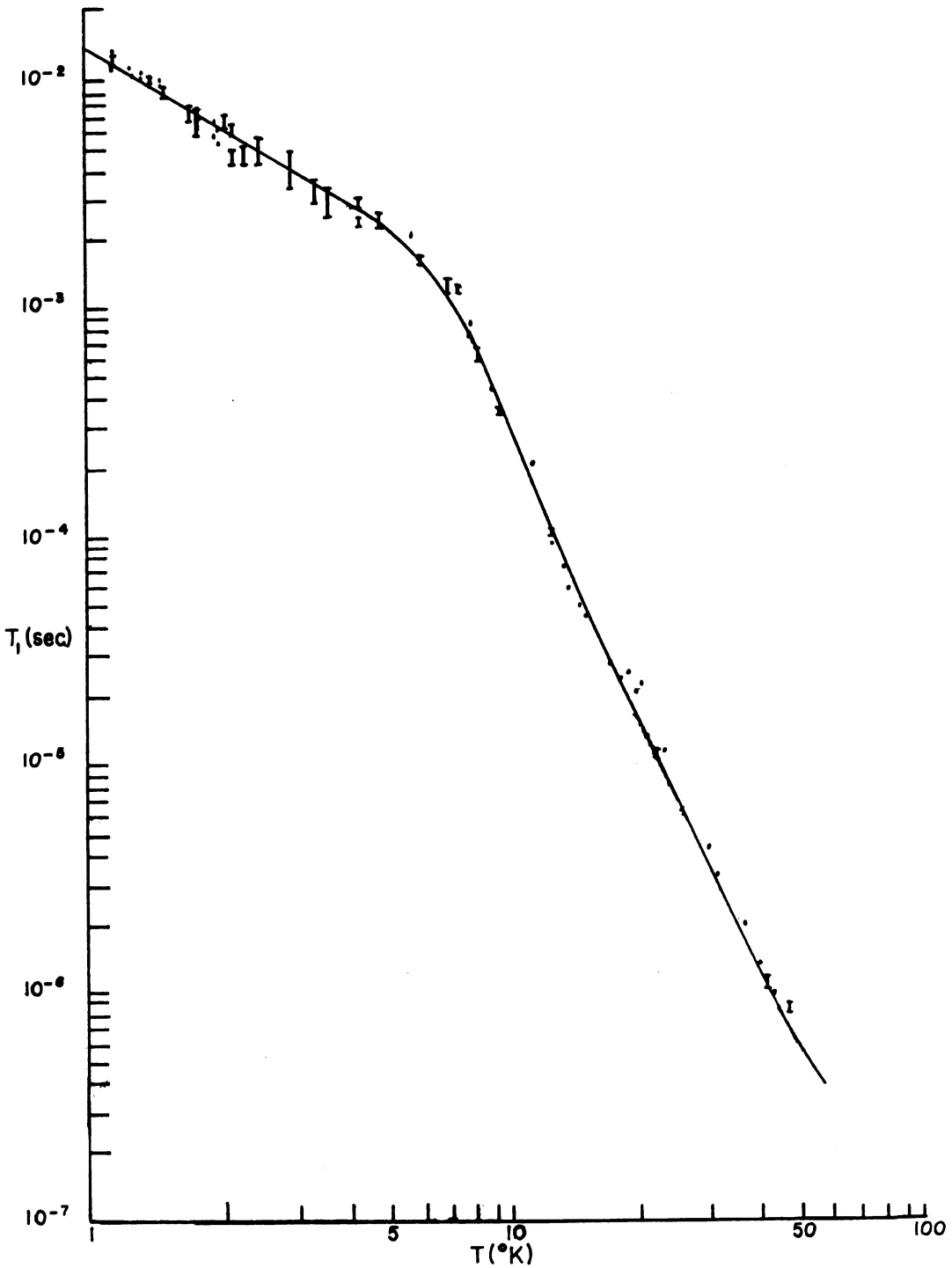

10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
T_1 (sec.)
1
5
10
50
100
T (°K)

Figure 14. Fe^{+++} Temperature Dependence of Relaxation.


10^{-2}
10^{-3}
10^{-4}
T_1 (sec)
10^{-5}
10^{-6}
10^{-7}
III
II
I
I
I
1
5
10
50
100
T(°K)

Cr^{+++} and Fe^{+++}.

<u>Cr^{+++}</u>. The local symmetry of the Al^{+++} is basically C_{3i}. Since the ratio of the ionic radii of the Cr^{+++}/Al^{+++} = .064/.056 and the coordination is in direct correspondence with (radius of metal/radius of ion) = 1.28/.64 = 2 $\longrightarrow$ C.N. = 3, then the Cr^{+++} has the tendency to lend itself to a situation in which it is coordinated by atoms forming a triangle about the Cr^{+++}. This strain will tend to produce an extra axial distortion. However Wong[109] has fit the E.P.R. data to an axial form of the Hamiltonian with a g factor of 1.977. The g factor for Cr^{+++} in an octahedral field is[72]

$$g = 2.0023 - 8\lambda/\Delta.$$

(This expression will vary slightly with axial distortion.) Hence $8(\lambda/\Delta) = .025$ or $\lambda/\Delta \sim .003$ where Δ is the splitting between the Γ_2 and Γ_5 levels.

We assume a λ of 55 cm^{-1} which is the value given by Low,[73] or that of the free ion (λ is certainly less for the non-free ion) given by Dunn,[21] $\zeta = 275$ or $\lambda = 275/2S = 92$. Thus $\lambda^2/\Delta < (92)(.003) = .276$ or, in other words T^5 is important as a Raman process somewhere below $.5^{o}K$. At these temperatures the direct process will be dominant.

We have available one other scheme of attack,

namely using the direct optical observation of $\Delta \rightarrow \Gamma_5 - \Gamma_2$ = 17,400 cm^{-1}.[44] Using the λ of 92, we see λ^2/Δ = $8.1 \times 10^3 / 1.7 \times 10^4 \sim .5^{\circ}K$.

Fe^{+++}. The ratio of the ionic radii of Fe^{+++}/Al^{+++} = .067/.056 and the coordination is given by 1.26/.67 = 1.88 and this also leads to a coordination of 3, but to a greater tendency than does the Cr^{+++}. Thus we would expect a larger axial term, D, than for the Cr^{+++} and indeed the resonance work of Wong[109] bears this out. Therefore, one should be more careful in handling the Fe^{+++} data. This plus the fact that no other spectral data is available for Fe^{+++} in a similar site makes the situation nebulous. However, one would expect that the Δ should be small since the admixture of excited states needed to account for the large splittings seen at zero field in Fe^{+++} is proportional to $(\lambda/\Delta)^2$.[11] Using Dunn's extrapolated values $\sim$ 100 cm^{-1} (and this is but a very crude estimate), Δ would have to be of the order of 200 cm^{-1} if T^5 were to be a dominant process at 50°. This implies a value for the admixture which may be reasonable, $(\lambda/\Delta)^2 \sim .25$.

Final Discussion

The possibility of a local mode dependence should

not be overlooked. The theory for one local mode, however, will not give a very good fit. A priori, there is no reason why more than one mode cannot occur. This could lead to an alternate explanation of the data.

The possibility of cross relaxation has been checked carefully by making relaxation time vs. concentration measurements. These measurements showed no concentration dependence in systems as dilute as we have reported here.

The data are reproducible by two techniques, the temperature measuring techniques have been proven reliable, and the possibility of τ_2 effects have been ruled out. In conclusion, the effects reported are real τ_1 effects in the $AlCl_3.6H_2O$ and do represent departure from the normal Raman process.

APPENDIX

APPENDIX

A. Kramer's Degeneracy

In addition to the usual types of symmetry such as space groups, it is also necessary to consider the symmetry of the time variable. Consider the Schroedinger equation and its complex conjugate.

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\Phi = \frac{\hbar}{i}\frac{\partial\Phi}{\partial t} = E\Phi \qquad \text{(A.1)}$$

$$\left(-\frac{\hbar^2}{2m}\nabla^2 + V(r)\right)\Phi^* = -\frac{\hbar}{i}\frac{\partial\Phi^*}{\partial t} = E\Phi^* \qquad \text{(A.2)}$$

(It is assumed Φ is non-spin dependent.) Two conclusions can be drawn. Φ and Φ^* form a degenerate pair of eigenfunctions and hence (A.2) implies that time inversion (replacing t by -t) is the same as taking the complex conjugate. We will denote the complex conjugate operator as K_0 (K_0 is a non-linear operator.). By taking the proper linear combination of Φ and Φ^* it is always possible to construct a real function. Hence, real operators have real eigenvalues and imaginary operators have imaginary eigenvalues. Since any operator with an odd power of t is imaginary, the expectation value of such operators (e.g. $\hat{p}$, $\hat{L}$) must vanish over the entire set of

degenerate non-spin states.

The addition of spin to the picture necessitates the introduction of a new operator, K, for time reversal. The following properties will enumerate some of the more important features of K.

A) $$K = e^{(-i\pi S_y/\hbar)}K_0 \qquad (A.3)$$

where $\underline{S}$ is the spin of the system.

$$K = -i\sigma_y K_0$$

for one electron where σ_y is a Pauli spin matrix.[34,p.232]

B) $$K^{-1}K = (K_0K_0^{-1})(-\sigma_y\sigma_y^{-1}) = -\sigma_y\sigma_y^{-1} \qquad (A.4)$$

C) $$[K,A] = 0 \qquad (A.5)$$

where A is a real operator.

D) $$KB = -BK \text{ (anticommutation)} \qquad (A.6)$$

where B is an imaginary operator.

E) $$KxK^{-1}\phi = x\phi \quad KpK^{-1}\phi = -p\phi \qquad (A.7)$$

F) $$K = i^n\sigma_{y_1}\sigma_{y_2}\ldots\sigma_{y_n} \quad \text{(for n spins)} \qquad (A.8)$$

G) $$K^2\phi = (-1)^n\phi \quad \text{(for n spins)} \qquad (A.9)$$

H) $$\langle\phi|\psi\rangle = \langle K\psi|K\phi\rangle \qquad (A.10)$$

An inspection of the above equations shows that most of the features of complex conjugation remain. Using the properties of K several important conclusions can be draw.

A) $K\Phi \perp \Phi$ for an odd number of electrons.

$$\langle K\Phi | \Phi \rangle = \langle K\Phi | KK\Phi \rangle = -\langle K\Phi | \Phi \rangle = 0$$

$$\therefore \langle K\Phi | \Phi \rangle = 0 \qquad \text{(A.11)}$$

B) $$\langle K\Phi | A\Phi \rangle = 0 \qquad \text{(A.12)}$$

where A is a real Hermetian operator.

The important theorem of Kramers can now be easily derived: for n odd, every state is at least two fold degenerate in the absence of a magnetic field. In the absence of a magnetic field and even with an electric field present, H is real. If $H\Phi = E\Phi$, then from (A.5) $KH\Phi = EK\Phi$ shows that $K\Phi$ is also an eigenfunction. Kramers' theorem says that it is independent. Assume that this is false. Then

$$K\Phi = a\Phi \quad \text{(where a is a constant)}$$

$$K^2\Phi = a^* K\Phi = a^*a\Phi = |a|^2\Phi$$

But n is odd and $K^2\Phi = -\Phi$, thus

$$|a|^2 = -1$$

Therefore our assumption leads to a false conclusion leaving only the possibility of at least two-fold degeneracy. In the presence of a magnetic field, the Hamiltonian contains terms linear in the angular momentum[95] and is not invariant under time reversal.

B. Definition of a Real Rotation Operator

The rotational operator $R = e^{i(\underline{\alpha}.\underline{I})}$. Here I is the infinitesimal rotation operator and α is the angle through which the rotation is carried. The angular momentum operator $\underline{J}$ can be defined in terms of $\underline{I}$.

$$\underline{J} = \underline{I}\hbar \tag{B.1}$$

Consider a rotation about the y-axis by π radians.

$$K_y = R_y K_0 = e^{(i\pi J_y/h)} K_0 \tag{B.2}$$

The effect of K_y on the spherical harmonic $Y_{\ell m}$ when $j = \ell$ is

$$K_y Y_{\ell m} = e^{-i\pi l_y} Y^*_m = e^{-i\pi \ell_y} (-1)^m Y_{\ell,-m}$$

$$= (-1)^{\ell} Y_{\ell m} \tag{B.3}$$

since

$$(Y_{\ell m})^* = (-1)^m Y_{\ell,-m} \text{ and}$$

$$R_y |\ell m\rangle = (-1)^{\ell - m} |\ell, -m\rangle .^{76} \tag{B.4}$$

$Y_{\ell,-m}$ is termed real if ℓ is even since then it commutes with K_y.

C. Jahn-Teller Effect

In fields of high symmetry, the ground and excited states of an ion may often be degenerate. The Jahn-Teller effect[37] shows that a molecule having an electronic energy level which is degenerate can undergo a nuclear displacement such that the degeneracy is removed. This gives rise to an axial distortion in a cubic lattice which will remove the symmetry causing the degeneracy. Physically this corresponds to the paramagnetic complex seeking the lowest possible energy; for given a small distortion perturbation the energy levels shift so that their center of gravity remains the same which in turn means that there is a higher and a lower energy level possible. There will therefore be a distortion in the molecule to remove the symmetry degeneracy. Several configuration distortions may be stable, giving rise to a new degeneracy. There are two exceptional cases. The Kramers' degeneracy of the lowest level cannot be removed and, in the case of strong spin-orbit coupling, the effect may be overcome.

D. Further Discussion of Crystal Field Calculations

It should be noted that the approach established by Bleaney and Stevens[7] will yield the same results for the expansion of the crystal field (2.65). The local symmetry is axially distorted cubic symmetry. The distortion is along one of the three-fold axes of the cube, which is labeled as the z-axis [cf. (2.43) and (2.44)]. The cubic field is

$$\Phi = A_4^{\theta} Y_4^{\theta} - \left(\frac{10}{7}\right)^{1/2} A_4^{\theta} \left[Y_4^3 + Y_4^{-3}\right] \qquad (D.1)$$

and with axial distortion it is just equation (2.66).

Matrix elements of the potential between two states are needed when one applies the crystal field as a perturbation. These elements take the form $\langle LM|\Phi|\ell_1 m_1\rangle$. Two common techniques are needed. If the potential is expressed in spherical harmonics, Φ reduces immediately to a sum of Wigner coefficients. The ones of interest may be found[69] tabulated. Hence

$$\langle LM|\Phi|\ell_1 m_1\rangle = \alpha_{20}[3M^2 - J(J+1)] + (\alpha_{43} - \alpha_{43}^*) \left[\frac{(L\mp M)!\,(L\pm M+2)!}{(L\mp M)!\,(L\mp M-2)!}\right]^{1/2} (2M\pm 3) \qquad (D.2)$$

where $M = m_1 + m$, $L = \ell'$, and $2L \geq \ell \geq 0$.

Table 1. Cross reference for group notations

Crystal Type	Schoenflies Notation	International Notation
Rhombohedral-trigonal (one 3-fold axis)	C_3	3
	C_{3i}	$\bar{3}$
	C_{3v}	32
	D_3	3m
	D_{3d}	$\bar{3}$m
Hexagonal (one 6-fold axis)	C_{3h}	6
	D_{3h}	$\bar{6}$
	C_6	6/m
	C_{6h}	622
	C_{6v}	6mm
	D_6	$\bar{6}$m2
	D_{6h}	6/mmm
Triclinic (no rotational symmetry)	C_1	1
	$C_i=S_2$	T
Monoclinic (one 2-fold axis)	C_s	2
	C_2	m
	C_{2h}	2/m
Orthohombic (three mutually 2-fold axis)	C_{2v}	222
	$V=D_2$	mm2
	$V_h=D_{2h}$	mmm
Tetragonal (one 4-fold axis)	S_4	4
	$V_d=D_{2d}$	$\bar{4}$
	C_4	4/m
	C_{4h}	422
	C_{4v}	4mm
	D_4	$\bar{4}$2m
	D_{4h}	4/mmm

Table 1.--Continued

Crystal Type	Schoenflies Notation	International Notation
Cubic (four 3-fold axis)	T	23
	T_h	m3
	T_d	432
	O	$\bar{4}$3m
	O_h	m3m

Table 2. Cross reference for irreducible representations.

Dimension	1	1	2	2	2	3	3	4
Bethe	Γ_1	Γ_2	Γ_3	Γ_6	Γ_7	Γ_4	Γ_5	Γ_8
Mulliken	A_1	A_2	E	$E_{1/2}$	$E_{5/2}$	T_1	T_2	G
Variations				B_1		B_2		

Subscripts:

g = gerade (even with respect to inversion)

u = ungerade (uneven with respect to inversion)

Superscripts:

prime indicates double group representation

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