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RESONANCE ABSORPTION OF MICROWAVES BY PARAMAGNETIC SUBSTANCES

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RESONANCE ABSORPTION OF MICROWAVES BY PARAMAGNETIC SUBSTANCES

SECTION I

1-INTRODUCTION

The phenomenon of resonance absorption of electromagnetic waves of microwave frequencies by paramagnetic substances was first observed in hydrated crystals of ions of the elements in the iron transition group by Zavisky (1) in 1945. Since that time the experimental technique of microwave absorption, accompanied by successful quantum theoretical interpretation of the phenomenon, has proved to be an important tool for throwing additional light on the properties of paramagnetic crystals beyond that which had been shed on the matter previously by means of infrared, magnetic susceptibilities, the X-ray, and specific heat measurements. The refinement of the experimental technique in subsequent years has eventually led to the discovery of nuclear effects upon the resonance absorption in the form of the hyperfine structure in the absorption curve. Since the first discovery of this effect by Penrose (2) in copper ions of sulphate crystals similar effects have been observed in several other paramagnetic crystals, leading to the determination of the spin and the magnetic moments of some of the nuclei of the paramagnetic atoms. Recently Bleaney was able to determine the ratio of the nuclear electric quadrupole moments of the copper isotopes from experimental observations of the hyperfine effects.

The potentialities of the paramagnetic absorption technique have been explored in other directions. A great deal of interest has been aroused in recent years in the absorption properties of certain organic compounds known as free radicals in organic chemistry. These substances exhibit resonance absorption curves of the width of a few oersteds, which are exceedingly narrow in comparison to the width of several hundred oersteds associated with the ions of the transition elements. It has been found also that the width can be further reduced by modifying the molecular structure of the organic compound.

The investigations of phosphors initiated by Schneider and England (3) revealed the resonance of divalent manganese in the manganese-activated zinc sulfide phosphor. At this Laboratory, Spencer has investigated the

absorption properties of manganese-activated zinc orthosilicate phosphors at various concentrations of manganese. Undoubtedly, there are other phosphors whose absorption properties may be of great interest. The paramagnetic absorption of crystals having F-centers and lattice defects produced by irradiation has been reported by Hutchison and Tinkman and Kip. At this Laboratory preliminary investigations are being made of glasses containing paramagnetic ions.

Among other areas in which the paramagnetic absorption methods may prove to be useful as a means of investigation, the field of photosensitive compounds may be mentioned as a possibility. According to current theories, neutral silver atoms are produced in one of the intermediate stages in the development of photosensitive silver bromide crystals. Since neutral silver atoms are paramagnetic, it should then be possible to detect their presence, provided an appreciable amount of silver in the atomic form is present at any particular time.

In view of these potentialities and also in view of the fact that the experimental results obtained so far in the fields mentioned above are not in every case thoroughly understood, we thought it worthwhile to reconsider the fundamentals of the theory of paramagnetic absorption. In the present report we shall be primarily concerned with the factors that determine the energy levels of paramagnetic ions in crystals, leaving other aspects in the theory of paramagnetic resonance to a later report.

In order to formulate the problem of paramagnetic absorption theoretically, it is necessary for us to obtain a clear picture of the structure of paramagnetic crystals, the facts which are often revealed by X-ray studies. Figure 1 depicts schematically a typical distribution of the diamagnetic and magnetic ingredients in a paramagnetic crystal. The magnetic ions are designated by the symbol i, with their associated electron more or less localized in the vicinity of each atom. The diamagnetic ions which surround each magnetic ion are usually distributed with respect to the latter with some degree of symmetry and are endowed with electric dipole moments. We shall designate these by α.

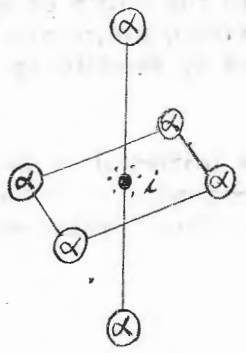


Figure 1 - Distribution of diamagnetic and magnetic ingredients in a paramagnetic crystal

When a crystal of such a structure is placed in the external magnetic field the total Hamiltonian or the energy of the crystal may be written in the form

$$\mathcal{H} = \mathcal{H}(\text{ion}) + \mathcal{H}(\text{elect. int.}) + \mathcal{H}(\text{Zeeman int.}) + \mathcal{H}(\text{mag. int.})$$

where $\mathcal{H}$(ion) designates the sum of the Hamiltonian of the individual free ion, $\mathcal{H}$(Zeeman int.) that due to the interaction of each ion with the external magnetic field, $\mathcal{H}$(electric int.) that which arises from the electrostatic interactions between each pair of ions, and $\mathcal{H}$(magnetic int.) that which originates from the magnetic interactions between each pair of ions.

The term $\mathcal{H}$(electric) may further be decomposed into three groups of terms--namely, those between diamagnetic ions, those between paramagnetic ions, and those between paramagnetic and diamagnetic ions. Under the assumption, however, that the nearest neighborhood interactions are predominant over others, we may safely consider only those between the paramagnetic ions and the surrounding diamagnetic ions in the immediate vicinity, so far as the influence of crystal structure upon each paramagnetic ion is concerned. We then have

$$\mathcal{H}(\text{elect. int.}) = -\sum_{\alpha,i} \frac{e Q_\alpha}{|\vec{R}_\alpha - \vec{r}_{ei}|} + \sum_{\alpha,n} \int \frac{Q_\alpha \rho_n \, d\tau_n}{|\vec{R}_\alpha - \vec{r}_{ni}|} + \sum_{\eta} \frac{e^2}{|\vec{r}_{\eta\eta'}|} \qquad (1)$$

where each term in the first sum designates the electrostatic interaction between the electrons of the paramagnetic ions and the neighboring diamagnetic ion, and that in the second sum signifies the electrostatic interaction between nuclei of the paramagnetic ions and the neighboring diamagnetic ions. Here Q_α and R_α refer respectively to the charge and the position vector of a diamagnetic ion, ρ_n is the nuclear charge density, and $\vec{r}_{ni}$ is the position vector of the nuclear volume element $d\tau_n$. The symbols e and r_{ei} stand respectively for the charge and the position vector of a particular electron. At temperatures other than absolute zero, the position vection R_γ, r_{ei}, and r_{ni} will undergo periodic changes due to the thermal motions of the lattice. These variations, however, are small. Consequently, it is possible to make a Taylor expansion of Equation (1) in powers of the thermal displacements; in which case Equation (1) resolves into two types of terms--namely, "static" and "dynamic" terms.

The static part of the first expression in Equation (1) may be called "crystalline electric field" and gives rise to the Stark effect upon the electronic energy level of the paramagnetic ions; whereas the corresponding term in the second expression tends to modify the nuclear energy levels of the paramagnetic ions through their nuclear quadrupole moments. The dynamic part of the first expression in Equation (1) leads to the spin-lattice relaxation effects as discussed in the papers by Kronig (4) and Van Vleck (5). On the other hand, the dynamic part of the second expression

in Equation (1) is important only in nuclear magnetic dipole and electric quadrupole resonance experiments. The last term is responsible for the exchange interaction which gives rise to the narrowing of the resonance lines (6).

The term $\mathcal{H}$ (magnetic int.) consists of a term giving the interactions among the paramagnetic ions,

$$\sum_{i,j} \frac{1}{|\vec{r}_{ij}|^3}\left[\frac{3(\vec{\mu}_{ei}\cdot\vec{r}_{eij})(\vec{\mu}_{ej}\cdot\vec{r}_{eij})}{|\vec{r}_{eij}|^2} - (\vec{\mu}_{ei}\cdot\vec{\mu}_{ej})\right]$$

where $\vec{r}_{eij}$ is the distance between two electrons having magnetic moments $\vec{\mu}_{ei}$ and $\vec{\mu}_{ej}$. The static part of this term is responsible for the dipolar broadening of the resonance lines; whereas the dynamic part provides the mechanism for the spin-lattice relaxation effects (Waller relaxation effect (7)).

In the present report we shall be concerned primarily with the effects on the electronic energy levels of the paramagnetic ions produced by the crystalline electric field, the external magnetic field, and the nuclear electric and magnetic fields. These effects give rise to the fine structure and hyperfine structure in the resonance absorption curves.

HAMILTONIAN FOR PARAMAGNETIC IONS IN CRYSTALS

SECTION II

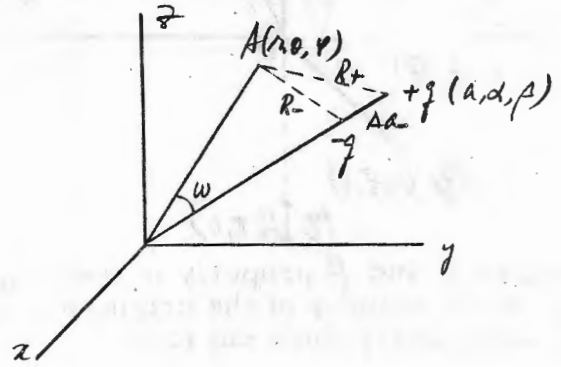
It was pointed out in the last section that an important modification of the electron and nuclear energy levels of the ion is produced by the crystalline electric field. Consequently we shall consider this field in detail. Other electric and magnetic interactions that are of importance in the nuclear effects on paramagnetic absorption will be discussed in later sections.

1-CRYSTALLINE ELECTRIC FIELD

This field arises from the spatial arrangement of the diamagnetic constituents of the crystal. The electrostatic potential produced by these ions or electric dipoles will have cubic, tetragonal, or lower symmetry, depending upon the arrangement of these constituents. For sake of definiteness, consider the crystalline electric field about the Cu^{++} ion in $CuK_2(SO_4)_2 \cdot 6H_2O$. This is known to have tetragonal symmetry, which

arises from a square arrangement of water molecules, with the Cu^{++} ion at the center, and two polarized oxygen atoms lying on an axis perpendicular to the plane of the water molecules and passing through the center. The distances of the oxygen molecules from the Cu^{++} ion are not equal to those of the water molecules.

To compute the electric potential in the vicinity of the paramagnetic ion due to these dipoles, let us first derive a general expression for the potential of a dipole whose axis lies on the radial vector.



From the diagram we may write

$$V(r,\theta,\varphi) = V_+ + V_- = \frac{q}{R_+} - \frac{q}{R_-} ;$$

and since by definition

$$V_{dip}(r,\theta,\varphi) = \lim_{\substack{q\to\infty \\ \Delta a\to 0 \\ q\Delta a\to\mu}} (V_+ + V_-),$$

we obtain

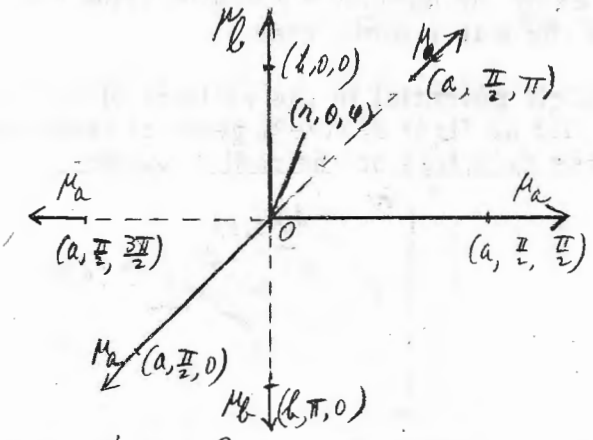
$$V_{dip} = \lim \left[\frac{q}{\sqrt{r^2+a^2-2ar\cos\omega}} - \frac{q}{\sqrt{r^2+(a-\Delta a)^2-2(a+\Delta a)r\cos\omega}} \right]$$

$$= \lim \frac{q}{a} \sum_{l=0}^{\infty} \frac{1}{r} P_l(\cos\omega) \left[\left(\frac{r}{a}\right)^{l+1} - \left(\frac{r}{a-\Delta a}\right)^{l+1} \right]$$

$$= \lim \frac{q}{a} \sum_{l=0}^{\infty} P_l(\cos\omega) r^l \left[a^{-l-1} - a^{-l} \left\{ 1 + \frac{l\Delta a}{a} + \cdots \right\} \right]$$

$$= -\frac{\mu^2}{a^2} \sum_{l=0}^{\infty} (l+1) \left(\frac{r}{a}\right)^l \sum_{m=0}^{\infty} (2-\delta_{m0}) \frac{(l-m)!}{(l+m)!} P_l^m(\cos\theta) P_l^m(\cos\alpha) \cos m(\varphi-\beta$$

Here the last expression is obtained by the use of the addition theorem for Legendre polynomials. For the case of Cu^{++} of copper sulfate, the polar coordinates of the water and oxygen molecules are shown in the following diagram.



By identifying angles α and β properly in the diagram, the electric potentials V_a and V_b, in the vicinity of the origin, due to the electric dipoles μ_a and μ_b, respectively, turn out to be

$$V_a(r,\theta,\varphi) = \text{const.} + 3\frac{\mu_b}{a^4} r^2 P_2^0(\cos\theta) - \frac{\mu_b}{a^6}\left\{\frac{15}{2} r^4 P_4^0(\cos\theta) + \frac{5}{48} r^4 P_4^4(\cos\theta)\cos 4\varphi + \cdots\right\}$$

$$V_b(r,\theta,\varphi) = \text{const.} - \frac{6\mu_a}{b^4} r^2 P_2^0(\cos\theta) - 10\frac{\mu_a}{b^6} r^4 P_4^0(\cos\theta) + \cdots.$$

It is also possible to obtain the expression for the crystal electric field by slightly different arguments. In the close vicinity of the origin we may make a Taylor expansion of the potential due to distant electric dipoles in the following manner

$$V(x,y,z) = V(0,0,0) + \left(\frac{\partial V}{\partial x}\right)_0 x + \left(\frac{\partial V}{\partial y}\right)_0 y + \left(\frac{\partial V}{\partial z}\right)_0 z + \left(\frac{\partial^2 V}{\partial x^2}\right)_0 \frac{x^2}{2} + \left(\frac{\partial^2 V}{\partial y^2}\right)_0 \frac{y^2}{2} + \left(\frac{\partial^2 V}{\partial z^2}\right)_0 \frac{z^2}{2}$$
$$+ \left(\frac{\partial^2 V}{\partial x \partial y}\right)_0 xy + \left(\frac{\partial^2 V}{\partial y \partial z}\right)_0 yz + \left(\frac{\partial^2 V}{\partial z \partial x}\right)_0 zx + \cdots.$$

Because of the prescribed symmetry, however, the nonvanishing terms in the Taylor expansion turn out to be

$$V(x,y,z) = \text{const.} + \frac{1}{2}\left\{\left(\frac{\partial^2 V}{\partial x^2}\right)_0 x^2 + \left(\frac{\partial^2 V}{\partial y^2}\right)_0 y^2 + \left(\frac{\partial^2 V}{\partial z^2}\right)_0 z^2\right\} + \text{higher-order terms}.$$

Since the potential function satisfies Laplace's equation

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) V(x,y,z) = 0,$$

the first set of terms in the above expression become

$$V(x,y,z) = \text{const.} + \left[Ax^2 + By^2 - (A+B)z^2\right].$$

This corresponds to the crystal potential of <u>rhombic symmetry</u>.

In the case of tetragonal symmetry it is further required that

$$\left(\frac{\partial^2 V}{\partial x^2}\right)_0 = \left(\frac{\partial^2 V}{\partial y^2}\right)_0 \quad \text{or} \quad A = B.$$

Then the potential function becomes

$$V(x,y,z) = A(x^2 + y^2 - 2z^2). \tag{2.1}$$

If the crystalline electric field has cubic symmetry, from the Laplace's equation we have

$$\left(\frac{\partial^2 V}{\partial x^2}\right)_0 = \left(\frac{\partial^2 V}{\partial y^2}\right)_0 = \left(\frac{\partial^2 V}{\partial z^2}\right)_0.$$

The first nonvanishing terms in the Taylor expansion for this case turn out to be

$$V(x,y,z) = \frac{1}{4!}\left(\frac{\partial^4 V}{\partial z^4}\right)_0 (x^4 + y^4 + z^4) = D_4(x^4 + y^4 + z^4). \tag{2.2}$$

2-SPIN-ORBIT COUPLING ENERGY

Next to the crystalline electric field, the term of importance is for the elements in the iron group is the spin-orbit coupling term $\lambda(\vec{L}\cdot\vec{S})$. The constant λ is known from spectroscopic data for various elements, but in any case its values can be determined through the work of Laporte (8). On the other hand, for the rare earth group, $\lambda(\vec{L}\cdot\vec{S}) > V_{\text{crystal}}$.

The following statements are true in general:

$$V_{\text{crystal}} > \lambda(\vec{L}\cdot\vec{S}) \text{ for the iron group}$$

$$V_{\text{crystal}} < \lambda(\vec{L}\cdot\vec{S}) \text{ for the rare earth group.}$$

Hence, the terms in the Hamiltonian which must be successively diagonalized in order to discuss the paramagnetic resonance absorption of the elements of the iron group are as follows:

$$\mathcal{H} = \mathcal{H}_0 + V_{\text{cryst.}} + \lambda(\vec{L}\cdot\vec{S}) + \mu_B((\vec{L} + 2\vec{S})\cdot\vec{H})$$

where μ_B is the Bohr magneton. The orders of magnitude of these terms are:

$$\mathcal{H}_0(\text{free ion}) \approx 10 \text{ ev.}$$

$$V_{\text{cryst.}} \approx 10{,}000 \text{ cm}^{-1}$$

$$\lambda(\vec{L}\cdot\vec{S}) \approx 10 - 1{,}000 \text{ cm}^{-1}$$

$$\mu_B((\vec{L} + 2\vec{S})\cdot\vec{H}) \approx 1 \text{ cm}^{-1}.$$

GROUP THEORY

SECTION III

1-INTRODUCTION

The diagonalization of the crystalline electric field can be executed by a straightforward perturbation calculation. However, since a great deal of qualitative information can be obtained by group theory arguments, we shall present as much of the elements of group theory as needed for our purpose.

The usefulness of group theory stems from the fact that the wave functions that will diagonalize the Hamiltonian are representations of the particular group of operations that leave the Hamiltonian invariant. For example, if the Hamiltonian is invariant under arbitrary rotations, finite and infinitesimal, the appropriate wave functions will be representations of the spherical group; if the Hamiltonian is invariant under the operations of the cubic group, the appropriate wave functions are representations of the cubic group.

In the free-ion state the electron wave functions are the representations of the rotation group of $2\ell + 1$ dimensions, i.e., there are $2\ell + 1$ linearly independent wave functions belonging to the same energy level. For an arbitrary rotation, any one of these functions will, in general, transform into a linear combination of $2\ell + 1$ functions referred to the new axes. If the ion is now placed in a crystalline electric field, the potential field in which the electrons find themselves will no longer be a function of the distance from the nucleus only; i.e., the potential field will no longer be invariant under an arbitrary rotation, but invariant only for a finite number of finite rotations. For these rotations, one might suspect that the original set $2\ell + 1$ functions will break up into sets of functions, such that the functions of each set will transform among themselves under the operations of the reduced group. These sets into which the original $2\ell + 1$ dimensional representation can be decomposed are called the irreducible representations of the particular symmetry group. Since each such set of functions belong to an energy level, the splittings produced by the crystalline electric field can be determined by finding the irreducible representations contained in the representation of the rotation group.

In order to carry out this process of reducing the $2\ell + 1$ dimensional irreducible representation of the spherical symmetry group to the irreducible representation of the group of lower symmetry, we must rely on the fundamental theorem of group theory which states "Each representation of a group can be reduced into its irreducible components in one and only one possible manner, thereby the character of each group element in the reducible representation class is equal to the sum of the characters of the irreducible components."

2-SYMMETRY TYPES OF CRYSTALLINE POTENTIAL ENERGY

The symmetry types of crystalline potential, which are of importance in our problems, are listed below in decreasing order of symmetry. Also for each type the dimension of the largest irreducible component is given. These numbers correspond to the maximum degeneracy of the energy levels arising from the original $2\ell + 1$ degenerate level.

Symmetry Types of Crystal Potential	Degree of Degeneracy for a Given
1. spherical	$2\ell + 1$
2. cubic	≤ 4
3. tetragonal	≤ 2
4. trigonal	≤ 2
5. rhombic	≤ 2

3-CUBIC GROUP

We shall use cubic symmetry to demonstrate the application of group theory to our problems. This symmetry group contains 24 pure rotation elements in five different classes as follows:

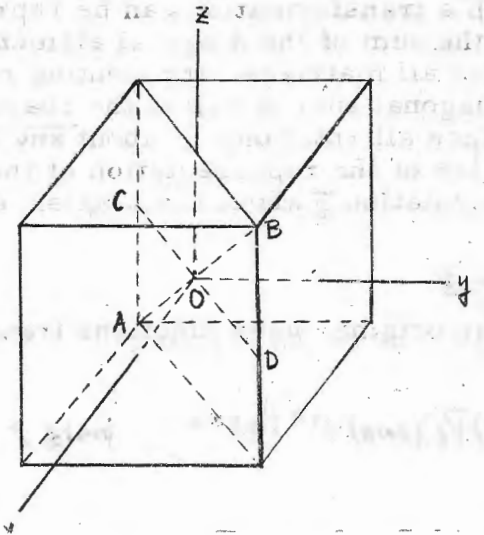
E - identity rotation (1 element)

C_2 - rotation about x, y, z axes by π (3 elements)

C_3 - rotation about x, y, z axes by $\pm\frac{\pi}{2}$ (6 elements)

C_4 - rotation about face-center axes by π (6 elements)

C_5 - rotation about body-center axes by $\pm\frac{2\pi}{3}$ (8 elements)



AB -- body center axis
CD -- face center axis

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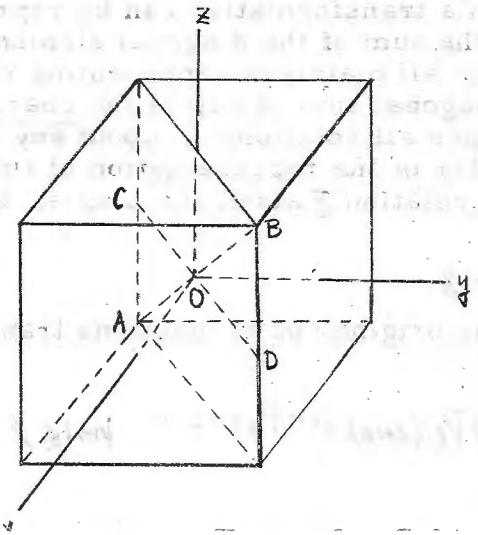


AB -- body center axis
CD -- face center axis

The resulting transformation matrix then becomes:

$$\begin{pmatrix} e^{-i\ell\Phi} & 0 & 0 & \cdots & \\ 0 & e^{-i(\ell-1)\Phi} & 0 & \cdots & \\ 0 & 0 & \ddots & 0 & 0 \\ \cdots & & 0 & e^{i(\ell-1)\Phi} & 0 \\ \cdots & & 0 & 0 & e^{i\ell\Phi} \end{pmatrix}.$$

Let the trace be represented by $\chi(\Phi)$; then

$$\chi(\Phi) = e^{-i\ell\Phi} + e^{-i(\ell-1)\Phi} + \cdots + e^{i(\ell-1)\Phi} + e^{i\ell\Phi}$$

$$= e^{i\ell\Phi} \frac{1-(e^{-i\Phi})^{2\ell+1}}{1-e^{-i\Phi}}$$

$$= \frac{\sin(\ell+\frac{1}{2})\Phi}{\sin\frac{1}{2}\Phi}. \qquad (3.1)$$

From this the characters for finite rotations can be easily obtained

class E $\quad \Phi = 0 \quad$ $\chi(E) = 2\ell+1$

" C_2 & C_4 $\quad \Phi = \pi \quad$ $\chi(C_2) = \chi(C_4) = (-1)^\ell$

" C_3 $\quad \Phi = \frac{\pi}{2} \quad$ $\chi(C_3) = (-1)^{\ell/2}$ for ℓ even
$= (-1)^{\frac{\ell-1}{2}}$ for ℓ odd.

" C_5 $\quad \Phi = \frac{2\pi}{3} \quad$ $\chi(C_5) = 1$ for $\ell = 3m$, 0 for $\ell = 3m+1$, -1 for $\ell = 3m+2$.

The reduction of the $2\ell + 1$ dimensional representation of the rotation group to the irredicible representations of the cubic group has been worked out by Bethe (9) (Table 2, p. 143). We shall show here how this is done for the cases $\ell = 6$ and 7.

$\ell = 6$: $\quad \chi(E) = 13, \ \chi(C_2) = \chi(C_4) = 1, \ \chi(C_3) = -1, \ \chi(C_5) = 1.$

Making use of the fundamental theorems of group theory given at the end of Sabertion, we make the following assumption for the representation D_6

$$D_6 = a\Gamma_1 + b\Gamma_2 + c\Gamma_3 + d\Gamma_4 + e\Gamma_5,$$

and proceed to determine the coefficients a, b, . . . e algebraically.

$$\begin{aligned} a + b + c + d + e &= 13 \\ a + b + 2c - d - e &= 1 \\ a - b \quad\quad + d - e &= -1 \\ a - b \quad\quad - d + e &= 1 \\ a + b - c \quad\quad\quad &= 1 \end{aligned}$$

Hence, we obtain

$$a = 1,\ b = 1,\ c = 1,\ d = 1,\ e = 2$$

$$D_6 = \overset{(1)}{\Gamma_1} + \overset{(1)}{\Gamma_2} + \overset{(2)}{\Gamma_3} + \overset{(3)}{\Gamma_4} + 2\overset{(3)}{\Gamma_5}.$$

The numbers enclosed in parentheses above the Γ's are the dimensions of the irreducible representations. From this result we state that the energy level of an atom in a spherically symmetric potential corresponding to $\ell = 6$ will split into six distinct levels under the influence of a crystal electric potential of cubic symmetry.

From the point of view of degeneracy, there are two levels which are nondegenerate (Γ_1 and Γ_2), one level which is twofold degenerate (Γ_3), and three levels which are individually threefold degenerate (Γ_4, Γ_5', Γ_5''). In the language of degenerate perturbation theory involving an electrostatic potential of cubic symmetry one obtains six distinct eigenvalues in some order of approximation. Since the group theoretical consideration is based on the absolute space symmetry of the potential, its predictions as to the splitting of the energy levels are ultimate.

$$\ell = 7: \quad \chi(E) = 15,\ \chi(C_2) = \chi(C_4) = -1,\ \chi(C_3) = -1,\ \chi(C_2') = 0$$

$$D_7 = a\Gamma_1 + b\Gamma_2 + c\Gamma_3 + d\Gamma_4 + e\Gamma_5$$

These coefficients can be determined similarly. However, we present here another method based on Theorem III, Appendix 3, which states that the characters of different representations are orthogonal,

$$\sum_{\text{all classes } i} h_i \chi_i^{(u)} \chi_i^{(v)} = \delta_{uv}\, g.$$

The left-hand side signifies the operation in which one multiplies the characters of the representations μ and ν under the same symmetry class i, further multiplies the result by the number of elements h_i in the class i, and lastly sums over all the classes i. g on the right-hand side is the total number of elements in the symmetry group. Let us multiply Γ_1 into D_7.

$$\sum_i h_i \chi_i^{(1)} \chi_i^{(7)} = 0 = a \sum_i h_i \chi_i^{(1)} \chi_i^{(1)} = a\,24.$$

Now, multiply Γ_2 into D_7.

$$\sum_i h_i \chi_i^{(2)} \chi_i^{(7)} = 24 = l \sum_i h_i \chi_i^{(2)} \chi_i^{(2)} = l\,24$$

Hence, a = 0, b = 1. Proceeding similarly, one finds c = 2, d = 2, and e = 2.

$$D_7 = \overset{(1)}{\Gamma_2} + \overset{(2)}{\Gamma_3} + 2\overset{(3)}{\Gamma_4} + 2\overset{(3)}{\Gamma_5}$$

The energy level of an atom in a spherically symmetric potential corresponding to $l = 7$ will split into six distinct levels under the influence of a crystal electric potential of cubic symmetry.

5-TETRAGONAL GROUP

Here, the group consists of 8 elements in the following classes:

C_2 - rotation about z-axis by	π	(1 element)
C_3 - rotation about z-axis by	$\pm\pi/2$	(2 elements)
C_4 - rotation about x,y axes by	π	(2 elements)
C_5 - rotation about xoy by	π	(2 elements)

TABLE 2
Character Table of Tetragonal Group

	E	C_2	C_3	C_4	C_5
Γ_1	1	1	1	1	1
Γ_2	1	1	1	-1	-1
Γ_3	1	1	-1	1	-1
Γ_4	1	1	-1	-1	1
Γ_5	2	-2	0	0	0

TABLE 3
Reduction Table

Character of the classes of tetragonal rotation group in the $2\ell + 1$ dimensional representation of the spherical rotation group.

Decomposition of the $2\ell + 1$ dimensional representation of the spherical rotation group into the irreducible representations of the tetragonal rotation group.

ℓ	E	C_2	C_3	C_4	C_5		Number of terms
0	1	1	1	1	1	Γ_1	1
1	3	-1	1	-1	-1	$\Gamma_2 + \Gamma_5$	2
2	5	1	-1	1	1	$\Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$	4
3	7	-1	-1	-1	-1	$\Gamma_2 + \Gamma_3 + \Gamma_4 + 2\Gamma_5$	5
4	9	1	1	1	1	$2\Gamma_1 + \Gamma_2 + \Gamma_3 + \Gamma_4 + 2\Gamma_5$	7
5	11	-1	1	-1	-1	$\Gamma_1 + 2\Gamma_2 + \Gamma_3 + \Gamma_4 + 3\Gamma_5$	8
6	13	1	-1	1	1	$2\Gamma_1 + \Gamma_2 + 2\Gamma_3 + 2\Gamma_4 + 3\Gamma_5$	10

6-DOUBLE GROUPS

When an atom possesses a half-integral total angular momentum quantum number j, the character of rotation through an angle Φ will be given by Equation (3.1), where ℓ is replaced by j

$$\chi(\Phi) = \frac{\sin(j+1/2)\Phi}{\sin 1/2\Phi} . \qquad (3.2)$$

However, $\chi(\Phi \pm 2\pi) = -\chi(\Phi)$, contrary to the previous cases (simple group), and one must rotate through 2π before the characters get back to the original values,

$$\chi(\Phi) = \chi(4\pi - \Phi) .$$

Under a rotation through an angle of 2π each character changes it sign, which implies that the character is double-valued. Also the characters of the identity rotation are double-valued. Only the characters of rotation through an angle of π are single-valued,

$$\chi(\pi) = \chi(3\pi) = 0 .$$

The larger double group is obtained by introducing another element R which satisfies $A^4 = B^4 = R$, $R^2 = E$. Then C_2 stays the same with the number of elements doubled, C_3 splits into two classes C_3' (rotation $4\pi/3$)

and C_3'' (rotation by $-\frac{\pi}{2}$) with 6 elements in each, C_4 remains the same with the number of elements doubled, and C_5 splits into C_5 (rotation by $+2\pi/3$) and C_5 (rotation by $-2\pi/3$) with 8 elements in each.

In the double cubic group, there are altogether 8 classes, and hence 8 irreducible representations, the dimensions of which are given by

$$48 = 1^2 + 1^2 + 2^2 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2.$$

In this manner, the character tables for the double cubic and double tetragonal symmetry groups can be worked out. In Bethe's article (9), double cubic groups and double tetragonal groups are shown on pages 155 and 152 respectively. Other symmetry groups are discussed in the following references: the trigonal double group in References 10, 11, and 12; and the rhomic double group in Reference 9.

7-SELECTION RULES

It can be shown that the probability per second that a magnetic dipole makes a transition from a state 1 to a state 2 under the influences of an r-f field whose magnetic vector lies in the direction of x-axis (steady magnetic field in z-direction) is given by

$$P = \frac{2\pi}{\hbar^2} \left| \langle 2 | g \mu_B J_x | 1 \rangle \right|^2 \rho(\nu_{21})$$

where $g_B J_x$ is the operator for the x-component of the magnetic moment $\vec{\mu}$ of an atom.

For the magnetic dipole transitions to be allowed, the matrix element of the magnetic dipole moment connecting the two states must not vanish. According to group theory (12), the matrix element between states characterized by representations Γ_i and Γ_j of an operator whose representation is Γ_m does not vanish if the products $\Gamma_i \Gamma_j \Gamma_m$ contains the identity representation Γ_1.

The selection rules are tabulated in Reference 12. Their derivations for the case of cubic symmetry are given in Appendix 4.

CRYSTALLINE STARK EFFECTS

SECTION IV

General discussions developed in earlier sections will now be applied to Cu^{++} ions in crystals.

The structure of the $CuSO_4 \cdot 5H_2O$ crystal has already been discussed earlier in Section II. The water molecules and the polarized

oxygen molecules give rise to an electric potential of cubic symmetry and a weak potential of tetragonal symmetry about the ion. We shall first show, from the group theoretical point of view, how the ground state of a free Cu^{++} ion splits under these electric fields, and next we shall calculate the extent of splitting by means of the perturbation calculations.

1-GROUP THEORETICAL CONSIDERATIONS

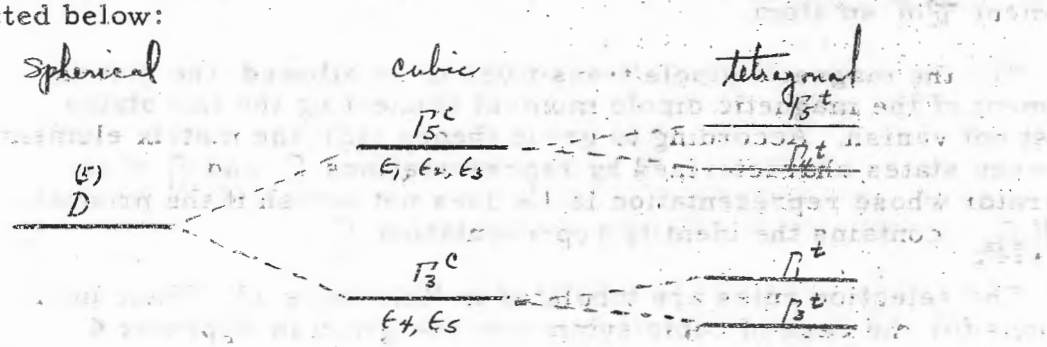
According to Hund's rules the ground state of Cu^{++} is $^2D_{5/2}$ (see Appendix 1), which, corresponding to $\ell = 2$, is 5-fold degenerate. Under the electric field of cubic symmetry the original 5-dimensional representation of the spherical group reduces to the irredicible representation Γ_3 and Γ_5 of the cubic group (see Bethe (9), p. 143, Table 2), the dimensions of which are 2 and 3 respectively.

Under the action of a small field of tetragonal symmetry $\Gamma_3^{c(2)}$ and $\Gamma_5^{c(3)}$ will undergo further splitting given by

$$\Gamma_5^{c(3)} = \Gamma_5^{t(2)} + \Gamma_4^{t(1)}$$
$$\Gamma_3^{c(2)} = \Gamma_1^{t(1)} + \Gamma_3^{t(1)},$$

This is verified in Appendix 4.

The splittings produced by fields of decreasing symmetry are as depicted below:



From group theoretical considerations alone it is not possible to determine the numerical values of the splitting and the arrangement of the energy levels. In order to determine these one must carry out the degenerate perturbation calculations.

2-SPLITTING OF THE GROUND LEVEL OF THE Cu^{++} ION UNDER THE ELECTRIC FIELD OF CUBIC SYMMETRY

Let orbital functions for the D state be represented by

$$\psi_2, \psi_1, \psi_0, \psi_{-1}, \psi_{-2}.$$

In order to obtain matrix elements of the cubic field we resort to the following formulas (13):

$$\langle L,M|V_{cubic}|L,M\rangle = K+pM^2\left\{7M^2+5-6L(L+1)\right\}$$

$$\langle L,M|V_{cubic}|L,M\pm4\rangle = \frac{p}{2}\left[\frac{(L\mp M)!\,(L\pm M+4)!}{(L\pm M)!\,(L\mp M-4)!}\right]^{1/2}.$$

All other matrix elements for which $\Delta M \neq 0$ or $\Delta M \neq \pm 4$ vanish. Here L is the orbital angular momentum quantum number, and M is the magnetic quantum number. The constants K and p are related to D_c in Equation (2.2)

$$\langle \pm 2|V_{cubic}|\pm 2\rangle = -K+12p$$

$$\langle \pm 1|\quad\quad|\pm 1\rangle = -K+24p$$

$$\langle 0|\quad\quad|0\rangle = -K$$

$$\langle 2|\quad\quad|-2\rangle = -12p.$$

Note that the signs of their matrix elements are opposite to those in the general formulas. This is because of the fact that the combined effect of 9 electrons in the third shell is equivalent to one positive electron.

Secular Determinant

$$\begin{array}{c|ccccc|c} & 2 & 1 & 0 & -1 & -2 & \\ 2 & -K+12p-E & 0 & 0 & 0 & -12p & \\ 1 & 0 & -K+24p-E & 0 & 0 & 0 & \\ 0 & 0 & 0 & -K-E & 0 & 0 & =0 \\ -1 & 0 & 0 & 0 & -K+24p-E & 0 & \\ -2 & -12p & 0 & 0 & 0 & -K+12p-E & \end{array}$$

We let $K+E=\epsilon$ and arrange the determinant such that rows and columns for $M \neq \pm 2$ form a 2 x 2 block. The resulting eigenvalues are

$$\epsilon_1 = \epsilon_2 = \epsilon_3 = 24p, \quad \epsilon_4 = \epsilon_5 = 0.$$

These give rise to the splitting of the original D-level under the cubic electric field as indicated in Subsection 1. From these eigenvalues the stabilized wave functions can be obtained in the following manner:

$\epsilon_1 = -24p$; $\quad c_{12}12p + c_{12}12p = 0$ $\quad c_{12} = -c_{1-2} = \frac{1}{\sqrt{2}}$ $\quad {}_0\psi^1 = \frac{1}{\sqrt{2}}(\varphi_2 - \varphi_{-2})$

$\epsilon_2 = -24p$; $\quad c_{21} = 1$ $\quad {}_0\psi^2 = \varphi_1$

$\epsilon_3 = -24p$; $\quad c_{3-1} = 1$ $\quad {}_0\psi^3 = \varphi_{-1}$

$\epsilon_4 = 0$; $\quad c_{42}(-12p) + c_{4-2}12p = 0$ $\quad c_{42} = c_{4-2} = \frac{1}{\sqrt{2}}$ $\quad {}_0\psi^4 = \frac{1}{\sqrt{2}}(\varphi_2 + \varphi_{-2})$

$\epsilon_5 = 0$ $\quad c_{50} = 1$ $\quad {}_0\psi^5 = \varphi_0$.

According to group theory these stabilized functions are the representatives of the two irreducible representations of the cubic group Γ_3 and Γ_5.

$$\overset{(3)}{\Gamma_5}{}^c \begin{cases} {}_0\psi^1 = \frac{1}{\sqrt{2}}(\varphi_2 - \varphi_{-2}) \\ {}_0\psi^2 = \varphi_1 \\ {}_0\psi^3 = \varphi_{-1} \end{cases} \qquad \overset{(2)}{\Gamma_3}{}^c \begin{cases} {}_0\psi^4 = \frac{1}{\sqrt{2}}(\varphi_2 + \varphi_{-2}) \\ {}_0\psi^5 = \varphi_0 \end{cases} \tag{4.1}$$

To determine the symmetry properties consider for example the first set of three functions. This set must be representatives of Γ_4 or Γ_5. In order to show that this set is Γ_5, let us subject the functions to rotations of class C_3; that is

$${}_0\psi^1(\phi + \tfrac{\pi}{2}) = -{}_0\psi^1(\phi)$$
$${}_0\psi^2(\phi + \tfrac{\pi}{2}) = i\,{}_0\psi^2(\phi)$$
$${}_0\psi^3(\phi + \tfrac{\pi}{2}) = -i\,{}_0\psi^3(\phi).$$

Hence,

$$\begin{pmatrix} \psi^1(\phi+\frac{\pi}{2}) \\ \psi^2(\phi+\frac{\pi}{2}) \\ {}_0\psi^3(\phi+\frac{\pi}{2}) \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 0 & i & 0 \\ 0 & 0 & -i \end{pmatrix} \begin{pmatrix} {}_0\psi^1(\phi) \\ {}_0\psi^2(\phi) \\ {}_0\psi^3(\phi) \end{pmatrix}.$$

Therefore, Character $(C_3) = -1$.

This shows that the three functions are the representatives of Γ_5^C.

3-FURTHER SPLITTING OF THE LEVELS UNDER A WEAK FIELD OF TETRAGONAL SYMMETRY

Assuming that the tetragonal field is weaker than the cubic field and using the wave functions obtained above, we now proceed to diagonalize the tetragonal field.

The perturbing Hamiltonian due to the tetragonal symmetry electric field is given by Equation (2.1). The nonvanishing matrix elements of this term are

$$\langle L,M|V_{tet}|L,M\rangle = K_1 + \frac{P_1}{2}\left[3M^2 - L(L+1)\right].$$

Hence,

$$\langle {}_0\psi^1|V_{tet}|{}_0\psi^1\rangle = \tfrac{1}{2}\langle 2|V_{tet}|2\rangle + \tfrac{1}{2}\langle -2|V_{tet}|-2\rangle$$
$$= -K_1 - 3P_1$$

$$\langle {}_0\psi^2| \quad |{}_0\psi^2\rangle = -K_1 + \tfrac{3}{2}P_1$$

$$\langle {}_0\psi^3| \quad |{}_0\psi^3\rangle = -K_1 - 3P_1$$

$$\langle {}_0\psi^5| \quad |{}_0\psi^5\rangle = -K_1 + 3P_1.$$

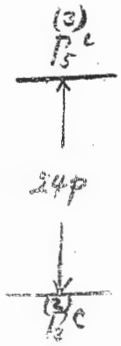
Secular Determinant

	$_0\psi^1$	$_0\psi^2$	$_0\psi^3$	$_0\psi^4$	$_0\psi^5$
$_0\psi^1$	$24p-3\rho_1-\epsilon$				
$_0\psi^2$		$24p+\frac{3}{2}\rho_1-\epsilon$			
$_0\psi^3$			$24p+\frac{3}{2}\rho_1-\epsilon$		
$_0\psi^4$				$-3\rho_1-\epsilon$	
$_0\psi^5$					$3\rho_1-\epsilon$

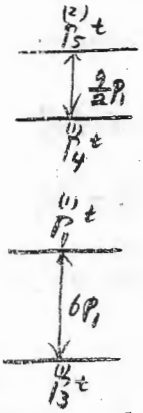
$= 0$

Since this determinant is diagonal, the eigenvalues can be obtained by inspection, and further stabilization of the wave functions is not necessary. Upon investigating the symmetry properties of the wave functions (Appendix 4), it can be shown that

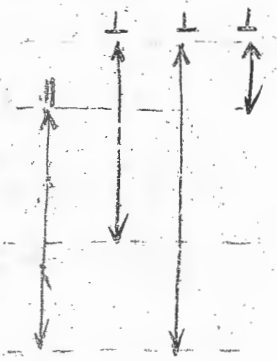
$$
\begin{aligned}
\Gamma_5^t: &\quad {}_0\psi^2 = \varphi_1 \\
&\quad {}_0\psi^3 = \varphi_{-1} \\
\Gamma_4^t: &\quad {}_0\psi^1 = \tfrac{1}{\sqrt{2}}(\varphi_2 - \varphi_{-2}) \\
\Gamma_1^t: &\quad {}_0\psi^5 = \varphi_0 \\
\Gamma_3^t: &\quad {}_0\psi^4 = \tfrac{1}{\sqrt{2}}(\varphi_2 + \varphi_{-2})
\end{aligned}
\qquad (4.2)
$$



Cubic field



Tetragonal field



Allowed magnetic dipole transitions

For a more detailed term structure for Cu^{++} in $CuSO_4 \cdot 6H_2O$ crystal the readers are referred to a paper by Polder (14). The discrepancy between the splittings obtained here and Polder's result must be due to the fact that he used the following crystalline potential

$$A(x^2+y^2-2z^2) + D(x^4+y^4+z^4) + Q(z^4+6x^2y^2)$$

where the Q ($z^4 + 6\,x^2y^2$) term was not considered in our calculation. The constants A, D, and Q are given in terms of the dipole moments and the distances between the dipoles and the ion.

$$A = -3\left(\frac{\mu_a}{a^4} - \frac{\mu_l}{b^4}\right), \quad D = -\frac{25}{4}\left(4\frac{\mu_a}{a^6} + 3\frac{\mu_l}{b^6}\right)$$

$$Q = \frac{25}{4}\left(\frac{\mu_a}{a^6} - \frac{\mu_l}{b^6}\right)$$

$CuSO_4 \cdot 5H_2O$: $\mu_a(H_2O) = 4\times10^{-18}$ c.g.s.

$\mu_l(O_2) = 3.3\times10^{-18}$ c.g.s.

X-ray data : $a = 2.0\,\text{Å}$, $b = 2.3\,\text{Å}$.

4-TRANSITIONS AMONG THE STARK LEVELS

a-Electric Dipole Transitions

The electric dipole transitions are allowed if the matrix element of the electric dipole moment is nonvanishing. However, the wave functions for the Stark levels arising from the same original level have the same parity, i.e., $(-1)^l$, and hence are simultaneously even or odd. Thus, the matrix elements vanish and the transitions are forbidden.

b-Magnetic Dipole Transitions

The Hamiltonian which gives rise to the magnetic dipole transitions is given by

$$\mathcal{H} = g\mu_B\left((\vec{L} + 2\vec{S}), \vec{H}_{osc.}\right)$$

where μ_B is the Bohr magneton of the electron, $\vec{L}$ the orbital angular momentum operator, $\vec{S}$ the spin operator, and $\vec{H}_{osc}$ the oscillating magnetic field vector of the r-f field.

Let us disregard the spin of the Cu^{++} ion for the moment (D state). Since the orbital magnetic moment $\mu_B L$ is an axial vector, according to the selection rules worked out by Kittel and Luttinger (12), we find that the following magnetic dipole transitions are allowed between the tetragonal field Stark levels (see Subsection 3):

$\vec{H}_{osc} \parallel$ z-axis $\qquad \Gamma_3^t \rightarrow \Gamma_4^t$

$\vec{H}_{osc} \perp$ z-axis $\qquad \Gamma_1^t \leftrightarrow \Gamma_5^t, \quad \Gamma_3^t \leftrightarrow \Gamma_5^t, \quad \Gamma_4^t \leftrightarrow \Gamma_5^t.$

Since the energy separations are of the order of 10,000 cm^{-1}, these transitions occur in visible and infrared regions and are responsible for the color of paramagnetic crystals.

5. INTRODUCTION OF SPIN

Next we diagonalize the electron spin-orbit term

$$\lambda(\vec{L}\cdot\vec{S}).$$

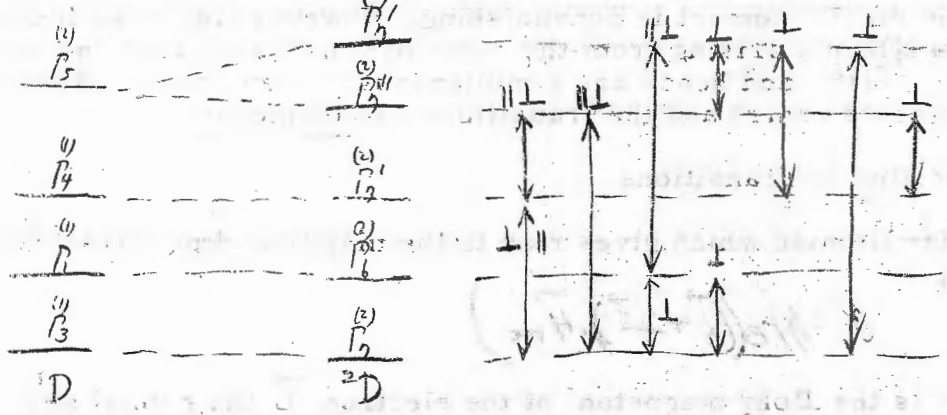
The wave function which takes electron spin into account is obtained by multiplying the electron spin wave function into the orbital wave function. For example, the wave function for Γ_3^2 becomes

$$\frac{\varphi_2+\varphi_{-2}}{\sqrt{2}}\alpha, \qquad \frac{\varphi_2+\varphi_{-2}}{\sqrt{2}}\beta$$

where α and β are the Pauli electron spin function having the eigenvalues + 1/2 and - 1/2 respectively.

Consider now the symmetry properties of the new wave functions. According to Bethe (9), p. 153, the functions corresponding to the 1/2 spin angular momentum in the tetragonal double group belong to the irreducible representation Γ_6. Using the double tetragonal group we find

$$\Gamma_3\Gamma_6=\Gamma_7^{(2)}, \quad \Gamma_1\Gamma_6=\Gamma_6^{(2)}, \quad \Gamma_4\Gamma_6=\Gamma_7^{(2)\prime}, \quad \Gamma_5\Gamma_6=\Gamma_6^{(2)\prime}+\Gamma_7^{(2)\prime\prime}$$



Tetragonal Field

We note that the electric field removes all but the spin degeneracy as predicted by Kramer's spin degeneracy theorem. According to the selection rules given by Kittel and Luttinger (12), the following transitions are allowed among these levels:

$\vec{H}$ // z axis : $\Gamma_6 \leftrightarrow \Gamma_6$, $\Gamma_7 \leftrightarrow \Gamma_7$

$\vec{H}$ ⊥ z axis : $\Gamma_{6,7} \leftrightarrow \Gamma_6$, $\Gamma_7 \leftrightarrow \Gamma_7$.

These are indicated on the diagram of the tetragonal field.

6-SPIN-ORBIT COUPLING

According to Kramer's rule the spin degeneracy can be removed only by an externally applied magnetic field. Since each one of these levels contains only the spin degeneracy, the spin-orbit coupling term $\lambda(\vec{L}\cdot\vec{S})$ cannot remove the degeneracy involved.

This statement can be verified as follows:

$$\langle \tfrac{1}{2}|\lambda(\vec{L}\cdot\vec{S})|\tfrac{1}{2}\rangle = \lambda \int \frac{\varphi_2^* + \varphi_{-2}^*}{\sqrt{2}} \alpha^* (\vec{L}\cdot\vec{S}) \frac{\varphi_2 + \varphi_{-2}}{\sqrt{2}} \alpha \, d^3x$$

$$(L\cdot S) = \tfrac{1}{2}(L_x + iL_y)(S_x - iS_y) + \tfrac{1}{2}(L_x - iL_y)(S_x + iS_y) + L_z S_z \quad (4.3)$$

$$L_z \varphi_m = m\varphi_m, \quad (L_x \pm iL_y)\varphi_m = \sqrt{L(L+1) - m(m\pm 1)}\ \varphi_{m\pm 1} \quad (4.4)$$

$$\left.\begin{aligned} &S_z\alpha = \tfrac{1}{2}\alpha, \quad S_z\beta = \tfrac{1}{2}\alpha \\ &(S_x - iS_y)\alpha = \beta, \quad (S_x + iS_y)\beta = \alpha \\ &(S_x + iS_y)\alpha = (S_x - iS_y)\beta = 0. \end{aligned}\right\} \quad (4.5)$$

Hence,

$$\langle \tfrac{1}{2}|\lambda(L\cdot S)|\tfrac{1}{2}\rangle = \frac{\lambda}{2}\left[\int (\varphi_2^* L_z \varphi_2 + \varphi_{-2}^* L_z \varphi_{+2} + \varphi_2^* L_z \varphi_{-2} + \varphi_{-2}^* L_z \varphi_{-2}) d^3x\right] \cdot \sum \alpha^* S_z \alpha = 0.$$

Similarly, one can easily show

$$\langle \tfrac{1}{2}|\lambda(L\cdot S)|-\tfrac{1}{2}\rangle = \langle -\tfrac{1}{2}|\lambda(L\cdot S)|\tfrac{1}{2}\rangle = \langle -\tfrac{1}{2}|\lambda(L\cdot S)|-\tfrac{1}{2}\rangle = 0.$$

Hence, the ground state will neither split nor shift under the influence of the spin-orbit coupling in the first-order calculation. The wave functions, however, are affected to this order of approximation. The first-order wave functions are given by

$$\psi^\alpha = {}_0\psi^\alpha + \sum_\beta{}' \frac{\langle\alpha|\lambda(L\cdot S)|\beta\rangle}{{}_0E^\alpha - {}_0E^\beta} {}_0\psi^\beta$$

where ${}_0\psi^\alpha$ are the wave functions given in Equation (4.2) and ${}_0E^\alpha$ are the corresponding eigenvalues. The ${}_0\psi^\beta$ that will contribute to this correction are just those having the same symmetry property as that of the ground state. The ground state is Γ_1. Those contributing to the correction will be Γ_3' and Γ_3''. The reason for this is that $\lambda(L\cdot S)$ is a scalar quantity and hence belongs to Γ_1. Therefore, for the matrix element $\langle\alpha|\lambda(L\cdot S)|\beta\rangle$ to be

nonvanishing, $\Gamma_\alpha \Gamma_i \Gamma_\beta = \Gamma_\alpha \Gamma_\beta$ must contain Γ_i. Resorting to Bethe (9) (Table 7 on p. 152) we can easily prove that $\Gamma_6 \Gamma_6$ contains Γ_1, but $\Gamma_6 \Gamma_7$ does not contain Γ_1. Thus the states in ^2D which are significant for our purpose are Γ_3, Γ_3' and Γ_3''.

$$\Gamma_3: \quad {}_0\psi(\Gamma_3; \alpha,\beta) = \frac{\varphi_2 + \varphi_{-2}}{\sqrt{2}}\alpha, \quad \frac{\varphi_2 + \varphi_{-2}}{\sqrt{2}}\beta$$

$$\Gamma_3': \quad {}_0\psi(\Gamma_3'; \alpha,\beta) = \frac{\varphi_2 - \varphi_{-2}}{\sqrt{2}}\alpha, \quad \frac{\varphi_2 - \varphi_{-2}}{\sqrt{2}}\beta$$

$$\Gamma_3'': \quad {}_0\psi(\Gamma_3''; \alpha,\beta) = \frac{\varphi_1}{\sqrt{2}}\alpha, \quad \frac{\varphi_{-1}}{\sqrt{2}}\beta$$

Since the tetragonal field is weaker than the cubic field, the changes introduced by the tetragonal field must be small in comparison to the spacing of the cubic levels. Therefore, we may safely use the latter energy levels.

Thus the wave functions for the positive and negative spin states of the ground state Γ_3' are:

$$f_+ = {}_0\psi(\Gamma_3'\alpha) + \frac{1}{E_3 - E_4}\Big[\langle\Gamma_3'\alpha|\lambda(L\cdot S)|\Gamma_3'\alpha\rangle\, {}_0\psi(\Gamma_3'\alpha) + \langle\Gamma_3\alpha|\lambda(L\cdot S)|\Gamma_3'\beta\rangle\, {}_0\psi(\Gamma_3'\beta)\Big]$$
$$+ \frac{1}{E_3 - E_5}\Big[\langle\Gamma_3'\alpha|\lambda(L\cdot S)|\Gamma_3''\alpha\rangle\, {}_0\psi(\Gamma_3''\alpha) + \langle\Gamma_3'\alpha|\lambda(L\cdot S)|\Gamma_3''\beta\rangle\, {}_0\psi(\Gamma_3''\beta)\Big]$$

$$f_- = {}_0\psi(\Gamma_3'\beta) + \frac{1}{E_3 - E_4}\Big[\langle\Gamma_3\beta|\lambda(L\cdot S)|\Gamma_3'\alpha\rangle\, {}_0\psi(\Gamma_3'\alpha) + \langle\Gamma_3\beta|\lambda(L\cdot S)|\Gamma_3'\beta\rangle\, {}_0\psi(\Gamma_3'\beta)\Big]$$
$$+ \frac{1}{E_3 - E_5}\Big[\langle\Gamma_3\beta|\lambda(L\cdot S)|\Gamma_3''\alpha\rangle\, {}_0\psi(\Gamma_3''\alpha) + \langle\Gamma_3\beta|\lambda(L\cdot S)|\Gamma_3''\beta\rangle\, {}_0\psi(\Gamma_3''\beta)\Big].$$

The matrix elements involved are calculated by making use of the Equations (4.3), (4.4), and (4.5)

$$f_+ = \frac{\varphi_2 + \varphi_{-2}}{\sqrt{2}}\alpha + \frac{\lambda}{E_3 - E_4}\frac{\varphi_2 - \varphi_{-2}}{\sqrt{2}}\alpha + \frac{\lambda}{E_3 - E_5}\frac{\varphi_{-1}}{\sqrt{2}}\beta$$

$$f_- = \frac{\varphi_2 + \varphi_{-2}}{\sqrt{2}}\beta - \frac{\lambda}{E_3 - E_4}\frac{\varphi_2 - \varphi_{-2}}{\sqrt{2}}\beta + \frac{\lambda}{E_3 - E_5}\frac{\varphi_{+1}}{\sqrt{2}}\alpha \qquad (4.6)$$

Since $L_z S_z \quad \frac{\psi_2 + \psi_{-2}}{\sqrt{2}}\alpha = \frac{\psi_2 + \psi_{-2}}{\sqrt{2}}\alpha$

$$\frac{1}{2}(L_x + iL_y)(S_x - iS_y)\frac{\psi_2 + \psi_{-2}}{\sqrt{2}}\alpha = \frac{\psi_{-1}}{\sqrt{2}}\beta$$

$$\frac{1}{2}(L_x - iL_y)(S_x + iS_y)\frac{\psi_2 + \psi_{-2}}{\sqrt{2}}\beta = \frac{\psi_{+1}}{\sqrt{2}}\alpha,$$

the wave function (Equation 4.6) can be written in the form

$$f_+ = \left[1 - \frac{\lambda}{E_4 - E_3} L_z S_z - \frac{\lambda}{E_5 - E_3}\frac{1}{2}(L_x + iL_y)(S_x + iS_y)\right]\frac{\psi_2 + \psi_{-2}}{\sqrt{2}}\alpha$$

$$f_- = \left[1 - \frac{\lambda}{E_4 - E_3} L_z S_z - \frac{\lambda}{E_5 - E_3}\frac{1}{2}(L_x - iL_y)(S_x + iS_y)\right]\frac{\psi_2 + \psi_{-2}}{\sqrt{2}}\beta$$

or $$f_+ = O\,\frac{\psi_2 + \psi_{-2}}{\sqrt{2}}\alpha, \qquad f_- = \bar{O}\,\frac{\psi_2 + \psi_{-2}}{\sqrt{2}}\beta \tag{4.7}$$

where $\bar{O}$ is the Hermitian conjugate of the operator O.

ZEEMAN EFFECT IN Cu^{++} IONS IN CRYSTALS

SECTION V

Let us now consider the Zeeman term in the Hamiltonian—namely,

$$g_s \mu_B \left((\vec{L} + 2\vec{S}), \vec{H}\right).$$

This term is of interest to us because the splitting produced by a magnetic field of the order of a few thousand gauss is comparable to the energy associated with electromagnetic waves of microwave frequencies, i.e., resonance absorption occurs at these frequencies. Moreover, only the transitions among the magnetic levels of the lowest electron state give rise to appreciable absorption; other higher states are not sufficiently populated to produce observable effects. This follows from the fact that according to the Boltzmann distribution function the ratio of the populations N_i and N_j of states i and j is given by

$$N_i / N_j = e^{-(E_i - E_j)/kT}$$

where E_i and E_j are the energies of the states i and j respectively. Here $E_i - E_j$ is of the order of 10,000 cm^{-1}, whereas KT at room temperatures is of the order of 200 cm^{-1}. Thus the population of the higher state is negligible in comparison with that of the lowest electron state.

We shall now proceed to diagonalize the energy operator $g_s \mu_B ((\vec{L}+2\vec{S})\cdot\vec{H})$ by using the wave functions given in Equation (4.7)

$$\langle t_\pm | ((\vec{L}+2\vec{S})\cdot\vec{H}) | t_\pm \rangle = \oint \overline{O\,\frac{\psi_2+\psi_{-2}}{\sqrt{2}}\binom{\alpha}{\beta}}\,((\vec{L}+2\vec{S})\cdot\vec{H})\,O\,\frac{\psi_2+\psi_{-2}}{\sqrt{2}}\binom{\alpha}{\beta}\,d\tau$$

$$= \oint \overline{\frac{\psi_2+\psi_{-2}}{\sqrt{2}}\binom{\alpha}{\beta}}\;\overline{O}((\vec{L}+2\vec{S})\cdot\vec{H})\,\frac{\psi_2+\psi_{-2}}{\sqrt{2}}\binom{\alpha}{\beta}\,d\tau$$

$$((\vec{L}+2\vec{S})\cdot\vec{H}) = (L_z+2S_z)H_z + (\tfrac{1}{2}L_+ + S_+)H_- + (\tfrac{1}{2}L_- + S_-)H_+$$

$$L_\pm = L_x \pm i L_y,\quad S_\pm = S_x \pm i S_y,\quad H_\pm = H_x \pm i H_y.$$

We expand the operator $\overline{O}((L + 2S) \cdot H)\, O$ and disregard quadratic terms in λ and terms whose matrix elements vanish.

$$\overline{O}\,(L_z+2S_z)H_z\,O = 2S_z H_z - \frac{2\lambda}{E_4-E_3}L_z^2 S_z H_z$$

$$\overline{O}\,(\tfrac{1}{2}L_+ + S_+)H_-\,O = H_- S_+ - \frac{\lambda}{E_5-E_3}H_-\tfrac{1}{4}(L^2-L_z^2)S_+$$

$$\overline{O}\,(\tfrac{1}{2}L_- + S_-)H_+\,O = H_+ S_- - \frac{\lambda}{E_5-E_3}H_+\tfrac{1}{4}(L^2-L_z^2)S_-$$

Here the following operator equations were used

$$S_z S_\pm = S_\pm (S_z \pm 1)$$

$$L_\mp L_\pm = L^2 - L_z^2 \mp L_z.$$

The matrix elements are now calculated by making use of the formulas (4.4) and (4.5).

$$\langle t_\pm | \mu_B ((\vec{L}+2\vec{S})\cdot\vec{H}) | t_\pm \rangle = 2H_z\mu_B \int \overline{\frac{\psi_2+\psi_{-2}}{\sqrt{2}}}\left(1-\frac{\lambda}{E_4-E_3}L_z^2\right)\frac{\psi_2+\psi_{-2}}{\sqrt{2}}\,d\tau \cdot \sum \binom{\alpha}{\beta} S_z \binom{\alpha}{\beta}$$

$$= \pm H_z \mu_B \left(1-\frac{4\lambda}{E_4-E_3}\right)$$

$$\langle t_\pm | \quad | t_\mp \rangle = H_\mp \mu_B \left(1-\frac{\lambda}{E_5-E_3}\right)$$

Let $$g_{\parallel} = 2\left[1 - \frac{4\lambda}{E_4 - E_3}\right]$$

$$g_{\perp} = 2\left[1 - \frac{\lambda}{E_5 - E_3}\right]. \qquad (5.1)$$

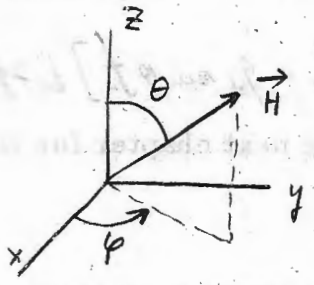
The secular determinant now becomes

$$\begin{vmatrix} \frac{1}{2}\mu_B g_{\parallel} H_z - E & \frac{1}{2}\mu_B g_{\perp} H_- \\ \frac{1}{2}\mu_B g_{\perp} H_+ & -\frac{1}{2}\mu_B g_{\parallel} H_z - E \end{vmatrix} = 0.$$

Hence, $$E_{1,2} = \pm \frac{1}{2} g \mu_B H, \qquad (5.2)$$

where $$g = \sqrt{g_{\parallel}^2 \cos^2\theta + g_{\perp}^2 \sin^2\theta}$$

and θ is the angle that the magnetic field makes with the tetragonal field axis. The values of g for magnetic field parallel and perpendicular to the tetragonal field are $g_{\parallel}$ and $g_{\perp}$ respectively. This is the reason for the above notation.



Experimentally, $g_{\parallel} = 2.4$ and $g_{\perp} = 2.06$. Let us now proceed to stabilize the wave functions.

$$C_{11}\left(\tfrac{1}{2}\mu_B g_{\parallel} H_z - E_1\right) + C_{12}\tfrac{1}{2}\mu_B g_{\perp} H_- = 0$$

$$C_{21}\tfrac{1}{2}\mu_B g_{\perp} H_+ - C_{22}\left(\tfrac{1}{2}\mu_B g_{\parallel} H_z - E_2\right) = 0.$$

Let $$C_{11} = \tfrac{1}{2}\mu_B g_{\perp} H_- \gamma$$

$$C_{12} = -\left(\tfrac{1}{2}\mu_B g_{\parallel} H_z - \tfrac{1}{2}\mu_B g H\right)\gamma.$$

Since $C_{+\frac{1}{2}}^2 + C_{-\frac{1}{2}}^2 = 1$

$$\gamma = 2/H\beta g.$$

$$\therefore \quad C_{+\frac{1}{2}} = \frac{g_\perp \sin\theta\, e^{i\varphi}}{\sqrt{2g(g - g_\parallel \cos\theta}}, \qquad C_{-\frac{1}{2}} = \frac{g - g_\parallel \cos\theta}{\sqrt{2g(g - g_\parallel \cos\theta)}} \tag{5.3}$$

Proceeding similarly,

$$C_{+\frac{1}{2}} \frac{(g - g_\parallel \cos\theta) e^{-i\varphi}}{\sqrt{2g(g - g_\parallel \cos\theta)}} \quad \text{and} \quad C_{-\frac{1}{2}} = -\frac{g_\perp \sin\theta}{\sqrt{2g(g - g_\parallel \cos\theta)}} \tag{5.4}$$

Hence, the stabilized functions $f_{+\frac{1}{2}}$ and $f_{-\frac{1}{2}}$ become

$$f_{+\frac{1}{2}} = [g_\perp \sin\theta\, e^{i\varphi} f_+ + (g - g_\parallel \cos\theta) f_-][2g(g - g_\parallel \cos\theta)]^{-\frac{1}{2}}$$

$$f_{-\frac{1}{2}} = [(g - g_\parallel \cos\theta) e^{-i\varphi} f_+ - g_\perp \sin\theta\, f_-][2g(g - g_\parallel \cos\theta)]^{-\frac{1}{2}}.$$

These functions are needed in the next chapter for the calculation of the hyperfine structure.

NUCLEAR EFFECTS – HYPERFINE STRUCTURE IN SOLIDS

SECTION VI

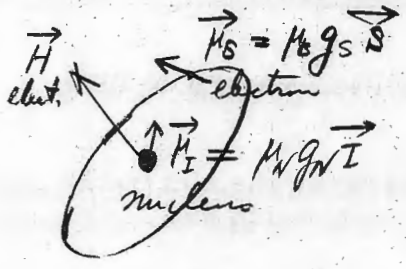
Penrose(2) was the first to discover that the Cu^{++} ion absorption curve consists of four components when the sample was sufficiently magnetically dilute. This structure is known to be due to the effects of interaction of the electrons with the copper nucleus. The theory of this effect is now discussed in the following Subsections.

1-HAMILTONIAN

Let us summarize the nuclear interaction terms in the Hamiltonian

Electric	Magnetic
$(W_Q)_{electric} \sim 10^{-4}\,cm^{-1}$	$\mu_B((\vec{L}+2\vec{S})\cdot\vec{H}) \sim 10^{-1}\,cm^{-1}$ $(H \sim 10^3\,gauss)$
$(W_Q)_{crystal} \sim 10^{-4}\,cm^{-1}$	$(\vec{L},\vec{I})$ $\frac{3(\vec{I},\vec{r})(\vec{S},\vec{r})}{r^2} - (\vec{I},\vec{S})$ $(\vec{I},\vec{S})$, $(\vec{I},\vec{H})$ $\Big\}\sim 10^{-3}\,cm^{-1}$

2-ORIGIN OF THE MAGNETIC INTERACTION TERMS



a. Terms Arising from the Interactions with the External Constant Magnetic Field H

(1) Electronic $\mu_B((\vec{L}+2\vec{S})\cdot\vec{H})$

(2) Nuclear $(\vec{\mu}_I\cdot\vec{H})$

$\vec{\mu}_I = \mu_N g_N \vec{I}$ (nuclear magnetic moment)

$\mu_N = \frac{e\hbar}{2Mc}$ (nuclear magneton)

g_N = nuclear g-factor

$\vec{I}$ = nuclear spin

b. Terms Arising from the Electronic Orbital Motion

The interaction of the electron orbital motion with the nuclear magnetic moment gives rise to the term $a_L(\vec{L}\cdot\vec{I})$, where $a_L = \mu_B \mu_N g_S g_L / r^3$ in which r is the radial distance from the nucleus to the electron.

c. Electronic Spin -- Nuclear Spin Interaction

These interactions give

$$a_L \left\{ \frac{3(\vec{I},\vec{r})(\vec{S},\vec{r})}{r^2} - (\vec{I}\cdot\vec{S}) \right\}.$$

d. Further Proposal of Abragam and Pryce (15)

It was proposed that the electron ground state consists of a small amount of admixture arising from an unpaired s-electron. For such an electron the magnetic interaction with the nucleus is given by

$$a_3(\vec{I}\cdot\vec{S}).$$

The coefficient a_3 depends, among other things, upon the value of the s-electron wave function at the nucleus.

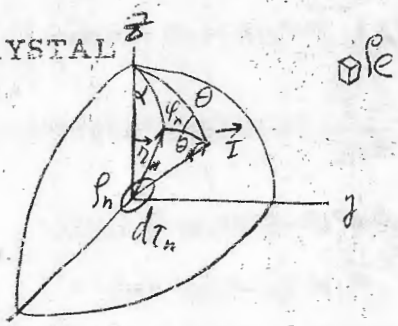
3. ORIGIN OF THE ELECTRIC INTERACTION TERMS

$W_{crystal}$ - interaction between the electronic structure of the magnetically active ion and the electrostatic field of the lattice

$(W_Q)_{crystal}$ - interaction between the electric charge distribution over the nucleus (nuclear electric quadrupole moment) and the electrostatic field of the lattice

$(W_Q)_{electric}$ - interaction between the electronic structure of the ion and the electric charge distribution over the nucleus.

4. EFFECTS OF $(W_Q)_{CRYSTAL}$



The crystalline electric field of tegragonal symmetry was given in Equation (2.1).

$$(W_Q)_{crystal} = \frac{1}{4}\left(\frac{\partial^2 V}{\partial z^2}\right)_0 \int (3z_N^2 - r_N^2)\rho_N d\tau_N$$

$$= \frac{1}{2}\left(\frac{\partial^2 V}{\partial z^2}\right)_0 \int r_N^2 P_2^0(\cos\alpha)\rho_N d\tau_N$$

According to the addition theorem of the spherical harmonics,

$$\cos Q = \cos\theta \cos\theta_N + \sin\theta \sin\theta_N \cos\varphi_N$$

$$P_2^0(\cos Q) = \sum_{m=0}^{2} (2-\delta_{m0}) \frac{(2-m)!}{(2+m)!} P_2^m(\cos\theta) P_2^m(\cos\theta_N) \cos m\varphi_N .$$

Hence, $(W_Q)_{\text{crystal}}$ =

$$\frac{1}{2}\left(\frac{\partial^2 V}{\partial z^2}\right)_0 \int_0^{\infty} \int_0^{\pi} r_N^4 dr_N \sin\theta_N d\theta_N \times$$

$$\times \sum_{m=0}^{2} (2-\delta_{m0}) \frac{(2-m)!}{(2+m)!} \int_0^{2\pi} P_2^m(\cos\theta) P_2^m(\cos\theta_N) \cos m\varphi_N \rho_N d\varphi_N .$$

Assuming that ρ_N is symmetric about the nuclear spin vector, or ρ_N is independent of φ_N, and making use of the formula

$$\int_0^{2\pi} \cos m\varphi_N d\varphi_N = 2\pi\delta_{m0}$$

$$(W_Q)_{\text{crystal}} = \frac{1}{2}\left(\frac{\partial^2 V}{\partial z^2}\right)_0 P_2^0(\cos\theta) \iiint r_N^2 P_2^0(\cos\theta_N) \rho_N r_N^2 dr_N \sin\theta_N d\theta_N d\varphi_N$$

$$= \frac{1}{8}\left(\frac{\partial^2 V}{\partial z^2}\right)_0 (3\cos^2\theta - 1) \int r_N^2 (3\cos^2\theta_N - 1) \rho_N d\tau_N .$$

The nuclear electric quadrupole moment is defined as follows:

$$eQ = \int r_N^2 (3\cos^2\theta_N - 1) \rho_N d\tau_N$$

Hence, $(W_Q)_{\text{crystal}}$ = $\frac{1}{8}\left(\frac{\partial^2 V}{\partial z^2}\right)_0 eQ (3\cos^2\theta - 1)$.

To obtain the quantum-mechanical operator, consider

$$(W_Q)_{\text{crystal}} = \frac{1}{4}\left(\frac{\partial^2 V}{\partial z^2}\right)_0 \int \rho_N r_N^2 (3\cos^2\alpha - 1) d\tau_N ,$$

where that angle α is the angle which the vector r_N makes with the z-axis fixed in space--not necessarily coinciding with the direction of I. It turns out that the integral is proportional to

$$3I_z^2 - I(I+1).$$

Hence,

$$\int r_N^2 (3\cos^2\alpha - 1) \rho_N d\tau_N = C\left[3I_z^2 - I(I+1)\right].$$

Since this holds for any direction of $\vec{I}$ with respect to z, take a particular case where $\vec{I}$ coincides with z. Then,

$$eQ = C\,I(2I-1), \quad \text{or} \quad C = eQ/I(2I-1).$$

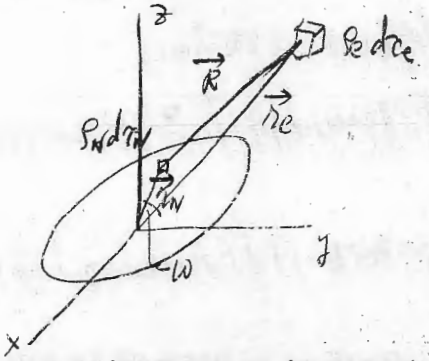
Thus

$$(W_Q)_{\text{crystal}} = \frac{1}{4}\left(\frac{\partial^2 V}{\partial z^2}\right)_0 \frac{eQ}{I(2I-1)}\left(3I_z^2 - I(I+1)\right). \qquad (6.1)$$

For large values of I, this approaches the classical expression given previously.

5-EFFECTS OF $(W_Q)_{\text{ELECTRIC}}$

This term arises from the electrostatic interaction of the nuclear and electron charge distributions.



This electrostatic interaction energy is seen to be

$$W = \int_{\text{elect. conf.}} \cdots\cdots \int_{\text{nucleus}} \rho_e\, d\tau_e\, \rho_N\, d\tau_N / R$$

where

$$R = \sqrt{r_N^2 + r_e^2 - 2 r_N r_e \cos\omega}$$

Since $r_N < r_e$, we can expand $\frac{1}{R}$ as follows:

$$\frac{1}{R} = \frac{1}{r_e} \sum_{\ell=0}^{\infty} \left(\frac{r_N}{r_e}\right)^{\ell} P_\ell(\cos\omega).$$

Then,

$$W = -\frac{Ze^2}{r} + (W_Q)_{\text{crystal}},$$

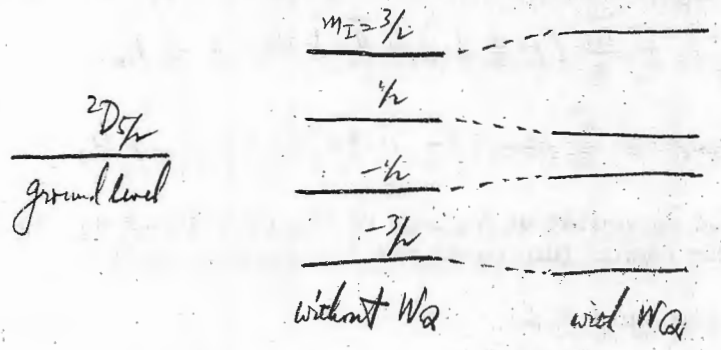
where

$$(W_Q)_{\text{crystal}} = \iint \rho_e\, d\tau_e\, \rho_N\, d\tau_N\, r^2\, P_2(\cos\omega)/r_e^3.$$

By repeating arguments similar to those given earlier, it can be shown that

$$(W_Q)_{\text{electric}} = \frac{e^2Q}{2I(I+1)} \left\langle \frac{3(\vec{I}\cdot\vec{r}_e)^2}{r_0^5} - \frac{I(I+1)}{r_e^3} \right\rangle_{av.} \tag{6.2}$$

The combined effects of $(W_Q)_{\text{elect.}}$ and $(W_Q)_{\text{cryst.}}$ are to make the hyperfine splitting of each electronic Zeeman level unequal. For instance, for Cu^{++} ($I = 3/2$) we may have the following situation:



6. DIAGONALIZATION OF THE NUCLEAR MAGNETIC INTERACTION TERMS

We shall now diagonalize the nuclear magnetic interaction terms in Subsection 1. The electronic functions for the ground states separated by the external magnetic field are given by f_+ and f_- in Equation (5.4). For our purpose we shall write them in the following form

$$f_\pm = \varphi_+(v\alpha \pm w\beta) - \frac{\lambda_1}{2} L_z \varphi_+(v\alpha \mp w\beta) - \frac{\lambda_2}{2}(v L_+ \varphi_+ \beta \pm w L_- \varphi_+ \alpha)$$

where

$$\varphi_+ = \frac{1}{\sqrt{2}}(\varphi_2 + \varphi_{-2}), \quad \lambda_1 = \frac{\lambda}{E_4 - E_3}, \quad \lambda_2 = \frac{\lambda}{E_5 - E_3} \tag{6.3}$$

(6.4)

and

$$v = C_{11}, \quad w = C_{12}.$$

Introducing the nuclear spin wave function $\chi(I, m_I)$, the total wave functions now become

$$\psi_{+,I,m_I} = f_+ \chi(I, m_I), \quad \psi_{-,I,m_I} = f_- \chi(I, m_I). \tag{6.5}$$

The nuclear magnetic interaction energy operators may be written as follows

$$\mathcal{H}_N = a_1(\vec{I}\cdot\vec{I}) + a_2\left\{\frac{3(\vec{I}\cdot\vec{r})(\vec{S}\cdot\vec{r})}{r^2} - (\vec{I}\cdot\vec{S})\right\} + a_3(\vec{I}\cdot\vec{S}) + \gamma(\vec{I}\cdot\vec{H}) \tag{6.6}$$

where a_1, a_2, and a_3 are unspecified functions of r only, $\gamma = \mu_N g_N$ (6.7) and H is the external constant magnetic field. The matrix elements of these operators with respect to the electronic and nuclear state functions Equation (6.5) turn out to be (the derivation is given in Appendix 5).

$$\int \psi^*_{\pm, I, m_I} \mathcal{H}_N \psi_{\pm, I, m_I} \, d\tau$$

$$= \alpha_\pm^* \langle m_I | I_+ | m_I' \rangle + \alpha_\pm \langle m_I | I_- | m_I' \rangle + \beta_\pm \langle m_I | I_z | m_I' \rangle \qquad (6.8)$$

where

$$\alpha_\pm = \pm \left\{ -\bar{a}_1 \lambda_2 + \frac{\bar{a}_2}{\eta}(1 + \tfrac{3}{2}\lambda_2) + \frac{\bar{a}_3}{2} \right\} vw + \frac{\gamma}{2} H_+$$

$$\beta_\pm = \pm \left\{ -\bar{a}_1 4\lambda_1 - \frac{\bar{a}_2}{\eta}(2 + 3\lambda_2) + \frac{\bar{a}_3}{2} \right\} (v^2 - w^2) + \gamma H_z \; ; \qquad (6.9)$$

and $\bar{a}_1$, $\bar{a}_2$, and $\bar{a}_3$ are the expectation values of the operators a_1, a_2, and a_3 with respect to the radial functions for the ground state.

Since a Cu nucleus has spin 3/2,

$$\langle m_I | I_+ | m_I' \rangle = \sqrt{15/4 - m_I'(m_I'+1)} \; \delta(m_I, m_I'+1)$$

$$\langle m_I | I_- | m_I' \rangle = \sqrt{15/4 - m_I'(m_I'-1)} \; \delta(m_I, m_I'-1)$$

$$\langle m_I | I_z | m_I' \rangle = m_I' \, \delta(m_I, m_I').$$

Thus, the secular determinant for the upper electronic level designated by a + sign is as indicated in Table 4.

TABLE 4

Determinant for Upper Electronic Level Designated by a + Sign

	$3/2$	$1/2$	$-1/2$	$-3/2$
$3/2$	$3/2\beta_+ - E_+$	$\sqrt{3}\alpha_+^*$	0	0
$1/2$	$\sqrt{3}\alpha_+$	$\frac{1}{2}\beta_+ - E_+$	$2\alpha_+^*$	0
$-1/2$	0	$2\alpha_+$	$-\frac{1}{2}\beta_+ - E_+$	$\sqrt{3}\alpha_+^*$
$-3/2$	0	0	$\sqrt{3}\alpha_+$	$-\frac{3}{2}\beta_+ - E_+$

$= 0$

Solving this secular determinant, we obtain the eigenvalues

$$E_+(m_I) = m_I \sqrt{\beta_+^2 + 4\alpha_+^* \alpha_+} \; . \qquad (6.10)$$

Introducing v, w, λ_1 and λ_2 in Equation (6.4),

$$vw = g_\perp/2g \cdot \sin\theta, \qquad v^2 - w^2 = g_\parallel/g \cdot \cos\theta$$

$$\lambda_1 = \frac{1}{8}(2 - g_\parallel), \text{ and } \lambda_2 = \frac{1}{2}(2 - g_\perp). \tag{6.11}$$

Further, we let Hy = o; for which case $\alpha^* = \alpha$. Then, from Equation (6.9), we obtain

$$\alpha_+ = \frac{1}{2}\left\{\bar{a}_1(g_\perp - 2) - \bar{a}_2\frac{3}{14}(g_\perp - 2) + \bar{a}_2\frac{2}{7} + \bar{a}_3\right\}\frac{g_\perp}{2g}\sin\theta$$

$$+ \frac{\gamma H}{2}\sin\theta \tag{6.12}$$

$$\beta_+ = \left\{\bar{a}_1(g_\parallel - 2) + \bar{a}_2\frac{3}{7}(g_\perp - 2) - \bar{a}_2\frac{4}{7} + \bar{a}_3\right\}\frac{g_\parallel}{2g}\cos\theta$$

$$+ \gamma H \cos\theta.$$

When

$\vec{H} \parallel$ z axis, $\sin\theta = 0$ and $\cos\theta = 1$,

$$_\parallel E_\perp(m_I) = m_I\left[\left\{\bar{a}_1(g_\parallel - 2) + \bar{a}_2\frac{3}{7}(g_\perp - 2) - \bar{a}_2\frac{4}{7} + \bar{a}_3\right\}\frac{g_\parallel}{2g} + \gamma H\right].$$

Recognizing that $m_I \gamma H$ represents the electronic energy level due to the spin state m_I of the Cu nucleus,

$$\Delta\nu_\parallel = \bar{a}_1(g_\parallel - 2) + \bar{a}_2\frac{3}{7}(g_\perp - 2) - \bar{a}_2\frac{4}{7} + \bar{a}_3 \tag{6.13}$$

must represent the hyperfine component separation in a parallel magnetic field.

Similarly, when $\vec{H} \perp$ z axis,

$$_\perp E_+(m_I) = m_I\left[\left\{\bar{a}_1(g_\perp - 2) - \bar{a}_2\frac{3}{14}(g_\perp - 2) + \bar{a}_2\frac{2}{7} + \bar{a}_3\right\}\frac{g_\perp}{2g} + \gamma H\right]$$

$$= m_I \Delta\nu_\perp$$

where

$$\Delta\nu_\perp = \bar{a}_1(g_\perp - 2) - \bar{a}_2\frac{3}{14}(g_\perp - 2) + \bar{a}_2\frac{2}{7} + \bar{a}_3 \tag{6.14}$$

must represent the hyperfine component separation in a perpendicular magnetic field.

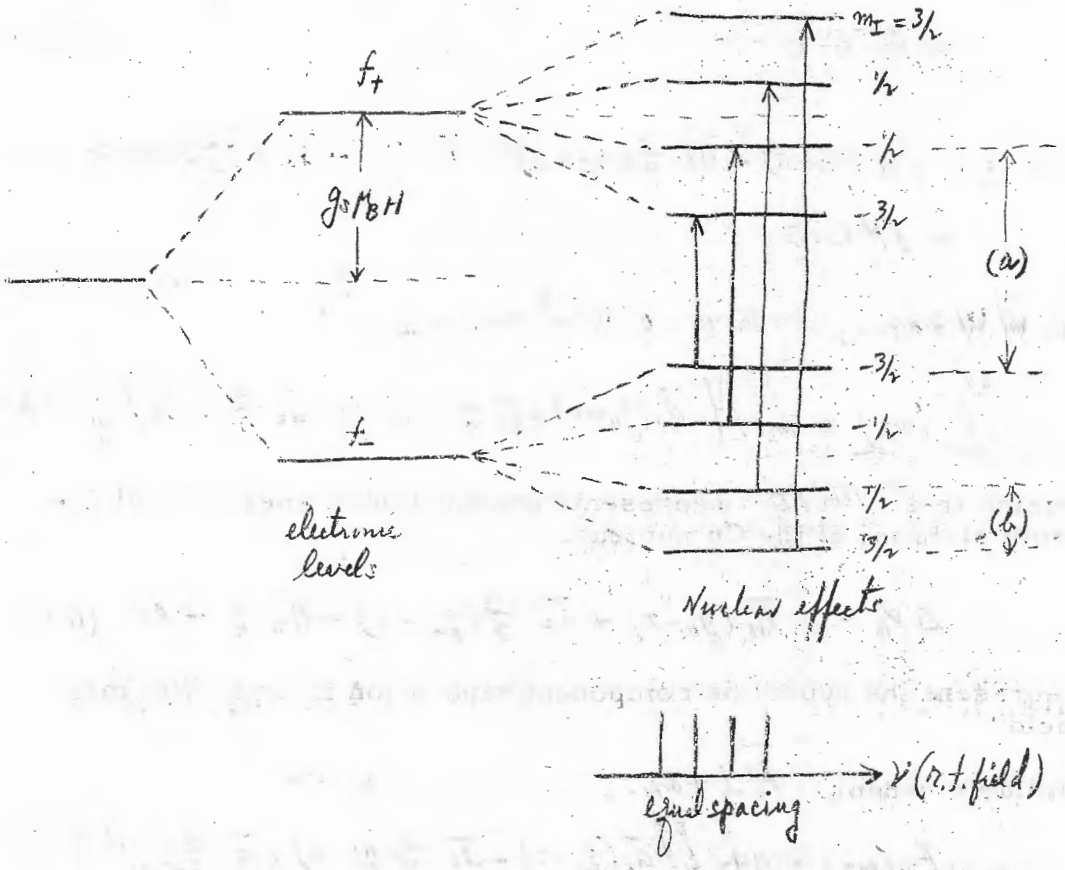
Equations (6.13) and (6.14) derived here agree with the similar expressions obtained by Abragam and Pryce (15) and Carr and Kukuchi (16).

Introducing the electronic energy levels without nuclear effects Equation (5.2) and substituting Equations (6.12), (6.13) and (6.14) into (6.10) we obtain for the upper energy level

$$E_+(m_I) = g\mu_B H + \left[\left(\frac{\Delta\nu_{\parallel} g_{\parallel}}{2g} + \gamma H\right)^2 \cos^2\theta + \left(\frac{\Delta\nu_{\perp} g_{\perp}}{2g} + \gamma H\right)^2 \sin^2\theta\right]^{1/2} m_I . \tag{6.15}$$

Similarly for the lower energy level,

$$E_-(m_I) = -g\mu_B H - \left[\left(\frac{\Delta\nu_{\parallel} g_{\parallel}}{2g} - \gamma H\right)^2 \cos\theta + \left(\frac{\Delta\nu_{\perp} g_{\perp}}{2g} - \gamma H\right)^2 \sin^2\theta\right]^{1/2} m_I .$$



Transitions indicated in the diagram are the allowed ones from the selection rules derived in the next section. Without the effects of the nuclear electric quadrupole moment, the spacings between the hyperfine levels are all the same, and consequently the absorption frequencies occur with equal spacing.

7-SELECTION RULES FOR THE ALLOWED ELECTRONIC AND NUCLEAR TRANSITIONS

When the crystal is subjected to an r-f field in addition to the constant magnetic field, the total Hamiltonian may be written in the following way:

$$\mathcal{H} = \mathcal{H}_1 \text{(time independent)} + \mathcal{H}_2 \text{(time dependent)},$$

where $$\mathcal{H}_2 = \mu_B\left((\vec{L}+2\vec{S})\cdot\vec{H}_{osc}(t)\right) + \gamma(\vec{I}\cdot\vec{H}_{osc}(t)).$$

Let us take the matrix element of $\mathcal{H}_2$ connecting states characterized by (m_S, m_I) and (m_S', m_I').

$$\langle m_S', m_I'|\mathcal{H}_2|m_S, m_I\rangle = 2\mu_B\langle m_S'|(\vec{S}\cdot\vec{H}_{osc})|m_S\rangle + \mu_N g_N\langle m_I'|(\vec{I}\cdot\vec{H}_{osc})|m_I\rangle \quad (6.16)$$

$$= 2\mu_B\langle m_S'|\tfrac{1}{2}S_+H_- + \tfrac{1}{2}S_-H_+ + S_zH_z|m_S\rangle\langle m_I'|m_I\rangle$$

$$+ \mu_N g_N\langle m_I'|\tfrac{1}{2}I_+H_- + \tfrac{1}{2}I_-H_+ + I_zH_z|m_I\rangle\langle m_S'|m_S\rangle. \quad (6.17)$$

Here, H_{osc} is the amplitude of the oscillating magnetic field.

a. First Matrix Elements

These elements will be nonvanishing if

$$\Delta m_I = 0 \quad \text{and} \quad \Delta m_S = 0 \quad \text{for } H_{osc} \parallel z\text{-axis}$$

$$\Delta m_S = \pm 1 \quad \text{for } H_{osc} \perp z\text{-axis}.$$

The upper case is a possibility if the first excited electronic levels lie sufficiently close to the ground levels so that r-f field can cause transitions energetically. For the case of Cu^{++} where the first excited levels lie above the ground levels by as much as 10,000 cm^{-1} the lower case applies.

$$\Delta m_I = 0, \quad \Delta m_S = \pm 1 \quad \text{for } H_{osc} \perp z\text{-axis}.$$

Note that the transition probabilities for the case (a) are proportional to μ_B^2. Case (a) applies in general to the electronic paramagnetic absorption.

b. Second Matrix Elements in Equation (6.17)

These elements are nonvanishing if

$$\Delta m_S = 0 \quad \text{and} \quad \Delta m_I = 0 \quad \text{for } H_{osc} \parallel z\text{-axis}$$

$$\Delta m_I = \pm 1 \quad \text{for } H_{osc} \perp z\text{-axis}.$$

The transition probabilities are proportional to μ_n^2. The lower case would be the nuclear resonance in paramagnetic ions which has so far not been observed. Since $\mu_B/\mu_N \sim 10^3$, the electronic transition probabilities are large in comparison to those of the nuclear transitions.

Weak Magnetic Fields

In the preceding analysis, it is assumed that there is no appreciable mixing of the electron magnetic levels, i.e., strong magnetic field case. For weak fields, the selection rules will be much more involved.

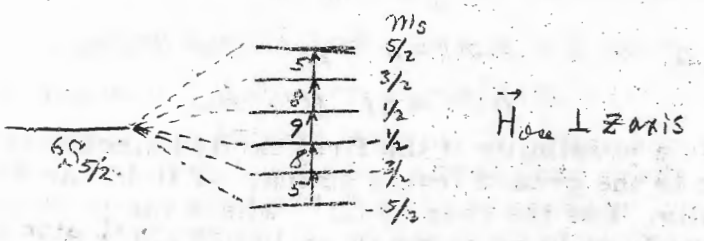
8. HYPERFINE STRUCTURE IN Mn^{++} CRYSTAL

According to the Hund's rules the ground state of Mn^{++} is $^6S_{5/2}$. If the ground state is strictly an S state, the total orbital angular momentum of the incomplete third shell is zero, and consequently the first two terms of the nuclear interaction Hamiltonian (6.6) would vanish since they are proportional to L (see Appendix 6). The total magnetic interaction Hamiltonian then would be

$$H_{mag} = \mu_B g(\vec{S}\cdot\vec{H}) + a(\vec{I}\cdot\vec{S}) + \mu_N g_N(\vec{I}\cdot\vec{H}).$$

Zeeman Effect

Due to the first term, when the external constant magnetic H field is in the direction of the z-axis, the $^6S_{5/2}$ state splits into six magnetic levels according to S = 5/2.



Transition Probabilities

According to the statement in a of Subsection 7 the allowed absorption transitions occur under the selection rules

$$\Delta m_I = 0, \quad \Delta m_S = 1.$$

These are indicated in the diagram.

c. Relative Intensities for the Five Transitions

$$\langle m_s+1 | 2\mu_B (\vec{S}\cdot\vec{H}_{osc}) | m_s \rangle = \mu_B \sqrt{S(S+1) - m_s(m_s+1)}\, H_-.$$

For Hy = 0 and S = 5/2,

$$|\langle m_s+1 | 2\mu_B (\vec{S}\cdot\vec{H}_{osc}) | m_s \rangle|^2 = \mu_B^2 H_x^2 (5, 8, 9, 8, 5).$$

In this manner we obtain the relative intensities of the transitions as indicated in the diagram. Note, however, that these transitions give rise to only one line because the energy levels are equally spaced.

d. Influence of the Crystal Electric Fields Upon the Zeeman Levels

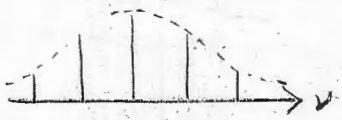
The crystalline Stark effects upon the ground state of Mn^{++} have been discussed by Kittel and Luttinger (12) and Bleaney and Ingram (17).

(1) $V_{crystal} = 0$

Under this condition the Zeeman levels will be equally spaced, and consequently the paramagnetic absorption spectrum consists of one line.

(2) $V_{crystal} \neq 0$

Now the Zeeman levels will be unequally spaced, possibly giving rise to five lines.



Further, if $2\mu_B (\vec{S}\cdot\vec{H}) > V_{crystal}$, one may expect that there will be either gradual increase or gradual decrease in the Zeeman level separations, giving rise to a type of absorption curve indicated above.

If $2\mu_B (\vec{S}\cdot\vec{H}) < V_{crystal}$, one may expect no such symmetry in the separations of the levels, resulting in an asymmetry in the absorption curve as exemplified below.

e. Nuclear Levels

$$\langle m_s', m_I' | a_3(\vec{I}\cdot\vec{S}) + \gamma(\vec{I}\cdot\vec{H}) | m_s, m_I \rangle$$

$$= \bar{a}_3 \Big\{ \tfrac{1}{2}\sqrt{I(I+1) - m_I(m_I+1)}\, \delta(m_I', m_I+1) \sqrt{S(S+1) - m_s(m_s-1)}\, \delta(m_s', m_s-1)$$

$$+ \tfrac{1}{2}\sqrt{I(I+1) - m_I(m_I-1)}\, \delta(m_I', m_I-1) \sqrt{S(S+1) - m_s(m_s+1)}\, \delta(m_s', m_s+1)$$

$$+ m_I m_s\, \delta(m_I', m_I)\, \delta(m_s', m_s) \Big\} + \mu_N g_N\, \delta(m_s', m_s) \langle m_I' | (\vec{I}\cdot\vec{H}) | m_I \rangle.$$

Disregarding $(\vec{I} \cdot \vec{H})$ term as small in comparison to the $a_3(\vec{I} \cdot \vec{S})$ term we obtain a diagonal secular determinant for each value of m_s. The eigenvalues for $m_s = -5/2$ and $-3/2$ are given below. The spin of Mn nucleus is 5/2.

$$m_s = -5/2; \quad E(m_I) = \bar{a}_3 \left(\frac{25}{4}, \frac{15}{4}, \frac{5}{4}, -\frac{5}{4}, -\frac{15}{4}, -\frac{25}{4}\right)$$

$$m_s = -3/2; \quad E(m_I) = \bar{a}_3 \left(\frac{15}{4}, \frac{9}{4}, \frac{3}{4}, -\frac{3}{4}, -\frac{9}{4}, -\frac{15}{4}\right)$$

7. Transitions Induced by an R-F Field

The selection rules stated in a of Subsection 7 applied for principal absorptive transitions are

$$\Delta m_I = 0, \quad \Delta m_S = 1 \quad \text{for} \quad H_{rf} \perp z\text{-axis}$$

There are thirty allowed transitions according to these rules. The transitions among the nuclear levels belonging to the same electronic level or the different nuclear levels belonging to different electronic levels are either exceedingly weak or forbidden.

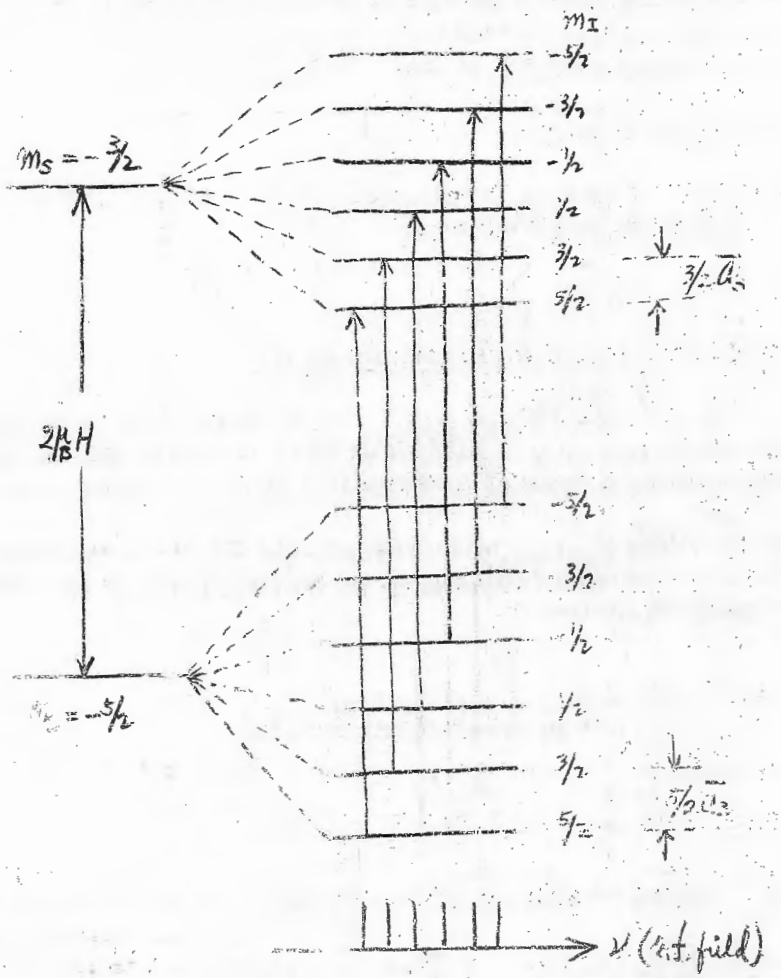
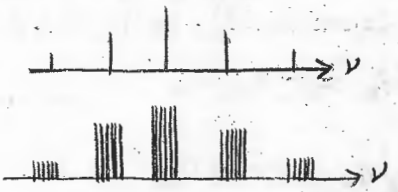


Figure 3 - Allowed transitions between nuclear levels of Mn^{++}

Since the matrix elements for these transitions are all the same in magnitude, the intensities of the absorption lines are again the same (see Equation 6.17). Note that m_s goes from -5/2 to 5/2 as one goes up in the electronic levels; whereas m_I goes from 5/2 to - 5/2 as one goes up in the nuclear levels. This is simply due to the fact that the electronic magnetic moment is in the direction opposite to the spin angular momentum; whereas the nuclear magnetic momentum is in the same direction as the nuclear spin angular momentum.

g. Influence of the Crystal Electric Field Upon the Hyperfine Levels (Qualitative)

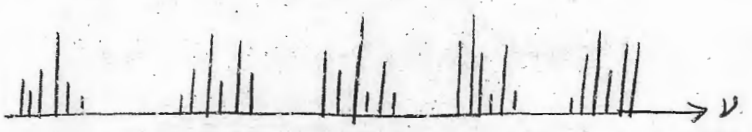
The diagram (Figure 3) would be the case if the influence $V_{crystal}$ upon the hyperfine levels is not considered. For $2\mu_B (\vec{S} \cdot \vec{H}) > V_{crystal}$ nuclear interaction terms,



with no nuclear effects;

with nuclear effects.

However, actually it is found that the crystalline Stark splitting is smaller than the hyperfine splitting (3), giving rise to an asymmetric distribution of absorption frequencies.



If all the hyperfine absorption curves are symmetric, then one may conclude that the $V_{crystal}$ is weak and consequently the fine structure (electronic) absorption curve is symmetric. It appears that the asymmetry in the individual hyperfine absorption curves may be ascribed to asymmetric fine-structure absorption curve, for which case $V_{crystal}$ must be strong (see d of Subsection 6).

h. Population Distribution Among the Fine Structure Levels

This distribution is given by $N_i = \alpha e^{-E_i/kT}$

where $E_i \sim \mu_B H \sim 10^{-16}$ ergs, and $kT \sim 10^{-14}$ ergs at $T \sim 300\,^{\circ}K$.

Hence, $kT \gg E_i$, the variations in the populations would be very small.

At $T \sim 1\,^{\circ}K$, $kT \sim \mu_B H \sim 10^{-16}$ ergs. Thus, at these temperatures the populations of the upper levels may be suppressed in comparison to those of the lower levels, resulting in changes in the intensity of the individual absorption line as one lowers the temperature. England and Schneider lowered the temperature to 4.5K, but no changes in the intensities were observed.

However, there may still be changes in the general structure of the absorption curve due to slight variations in the crystal potential and the effective gyromagnetic ratio g.

9-DETERMINATION OF THE PARAMETERS $\bar{a}_1$, $\bar{a}_2$, and $\bar{a}_3$ FOR HYPERFINE STRUCTURE IN Cu^{++} AND Mn^{++}

The experimental methods employed to determine these parameters are (a) paramagnetic absorption and (b) optical spectroscopy.

a. Paramagnetic Absorption

(1) Determination of the parameters in the case of Cu^{++}

Theoretically, without the term $\bar{a}_3$, from (6.13) and (6.14) we obtain

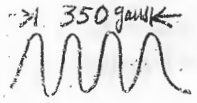
$$\Delta\nu_{\parallel} = \left\{ g_{\parallel} - 2 + \frac{3}{7}(g_{\perp} - 2) - \frac{4}{7} \right\} a_L = -0.13\, a_L$$

$$\Delta\nu_{\perp} = \left\{ g_{\perp} - 2 - \frac{3}{14}(g_{\perp} - 2) + \frac{2}{7} \right\} a_L = 0.36\, a_L$$

where $\bar{a}_1 = \bar{a}_2 = a_L$ (see b and c of Subsection 2, Section 6). $g_{\parallel} = 2.45$, and $g_{\perp} = 2.09$ were used by Abragam and Pryce (18).

Thus, $\left| \Delta\nu_{\parallel} / \Delta\nu_{\perp} \right| \approx 1/3$.

Experimentally it turns out, according to Ingram (19),



$$\Delta\nu_{\parallel} = \frac{350}{3} \quad \text{gauss}$$

$$\Delta\nu_{\perp} = \frac{50}{3} \quad \text{gauss}$$

Hence, $\left| \Delta\nu_{\parallel} / \Delta\nu_{\perp} \right|_{exp.} \approx 7$.

Abragam and Pryce set $\bar{a}_3 = -K\bar{a}_2$ in their theoretical investigations and assumed $K = 0.25$ in order to agree with experimental results.

$$a_L = 0.032\ cm^{-1}.$$

The term $a_3(\vec{I} \cdot \vec{S})$ in the nuclear interaction Hamiltonian was first phenomenologically introduced by Abragam and Pryce for the purpose of improving the agreement between theory and the experiment. The underlying idea is that the terms involving a_1 and a_2 in the Hamiltonian are

angular dependent, reflecting the effects of the crystalline electric fields, and are essentially responsible for the anisotropy in the hyperfine splitting. Contrary to this, the term $a_3(\vec{I} \cdot \vec{S})$ is independent of the angle from the axis of quantization, and hence would modify $\Delta\nu_{\parallel}$ and $\Delta\nu_{\perp}$ in a manner essentially different from the a_1 and a_2 terms.

One recalls the fact that this term exists for S-state in the Fermi theory (20) of hyperfine structure for H-atom based on the Dirac's relativistic quantum mechanical equation of motions for the electron.

(2) Determination of the parameters in the case of Mn^{++}

Let us now see what this term implies in the Mn^{++} case.

$$a_3 \approx \mu_I |\psi(0)|^2$$

Assuming that the amount of admixture of the state in which impaired s-electrons occur in the free ion ground state is the same for both Cu^{++} and Mn^{++} ions, one may consider $|\psi(0)|^2$ for these two ions are equal in magnitude. Then

$$\frac{a_3(Cu^{++})}{a_3(Mn^{++})} \approx \frac{\mu_I(Cu^{63,65})}{\mu_I(Mn^{55})}.$$

Hence,

$$a_3(Mn^{++}) \approx \frac{\mu_I(Mn^{55})}{\mu_I(Cu^{63,65})} a_3(Cu^{++}).$$

The latest values on the nuclear magnetic moments (21) are

$\mu_I(Cu^{63})$ = 2.2215 Bohr magneton

$\mu_I(Cu^{65})$ = 2.3796 Bohr magneton

$\mu_I(Mn^{55})$ = 3.0 Bohr magneton

Dividing $\bar{a}_3$ (Cu^{++}) = 0.032 by 4 (I = 3/2) we obtain $\bar{a}_3$ (Mn^{++}) for each state of the nuclear spin in the following manner:

$$\overline{a_3}(Mn^{++}) \approx 0.0104 \text{ cm}^{-1}.$$

The magnetic field which corresponds to this energy is given by

$$H \approx \frac{hc}{g\mu_B} 0.0104 \approx 100 \text{ gauss}$$

Thus, the hyperfine separations should be approximately 100 gauss. Actually they are 65-75 gauss in England and Schneider's experiment (3) and 89 gauss according to E. Spencer's work at this Laboratory.

b. Optical Spectroscopy

When Cu^{++} is inbedded in a crystal, the $V_{crystal}$ having no spherical symmetry mixes the quantum states characterized by the orbital quantum number ℓ. Under such circumstances quantum states cannot be labeled by the total angular momentum quantum number j.

However, for Cu^{++} in the gaseous state, when the potential is spherically symmetric, the states can be characterized by quantum numbers ℓ, s, and j. With respect to such a quantum-mechanical representation it is possible to write each term in the nuclear magnetic interaction Hamiltonian (6.6) in terms of the operator $(\vec{J} \cdot \vec{I})$.

$$\mathcal{H}_N = a_1(\vec{L}\cdot\vec{I}) + a_2\left\{\frac{3(I\cdot r)(s\cdot r)}{r^2} - (I\cdot s)\right\} + a_3(I\cdot s) = a_J(\vec{J}\cdot\vec{I})$$

$$\text{For } S = 1/2,\ J = L \pm 1/2, \quad a_J = \frac{L(L+1)}{J(J+1)}\,a_1 \quad \text{for } a_3 = 0,\ \bar{a}_1 = \bar{a}_2.$$

The last formula is found in Reference (22). a_J as measured in spectroscopic analysis will now be compared with a_J as obtained from the paramagnetic absorption experiment.

Ritschl (23) obtained the following values from spectroscopic analysis:

$$a_{J=5/2} = 0.022\ \text{cm}^{-1}$$

$$a_{J=3/2} = 0.060\ \text{cm}^{-1}.$$

Hence,

$$a_L = \frac{5/2\ 7/2}{2.3}\ 0.022\ \text{cm}^{-1} = 0.032\ \text{cm}^{-1}$$

$$a_L = \frac{3/2\ 5/2}{2.3}\ 0.060\ \text{cm}^{-1} = 0.037\ \text{cm}^{-1}.$$

In these calculations for the spectroscopic observations $\bar{a}_2$ is disregarded in comparison with a_L. These values can be compared with $a_L = 0.032$, a result deduced from the paramagnetic absorption experiments. Agreement is good provided the $\bar{a}_3$ term is included.

MAGNETIC SUSCEPTIBILITY AND NUCLEAR SPECIFIC HEAT

SECTION VII

We have pointed out that paramagnetic absorption measurements on the one hand and optical hyperfine structure measurements on the other give discordant results, unless we postulate a small admixture of state arising

from impaired s-electrons. Let us now examine the results obtained from nuclear specific heat measurements.

1-EXPERIMENT

A very beautiful experiment was carried out by Benzie and Cook (24) to measure the contribution of the electron-nuclear interaction to the specific heat. This was done by measuring the specific heat of four different salts of Cu^{++} at varying concentrations. When the specific heat was plotted against the concentrate of Cu^{++} ion, the points fell on four lines. These curves were then extrapolated to zero concentration. This residual specific heat was then taken to be the specific heat arising from the electron-nuclear interaction. The value obtained was

$$CT^2/k = 1.1 \times 10^{-4}$$

where C is the contribution to the specific heat per atom and k is Boltzmann's constant. From a theoretical point of view, there must be a relation of the form

$$CT^2/k = f(a)$$

where a is the electron-nuclear coupling constant. We shall now determine the form of f(a) in order to compare the theoretical and experimental values of the nuclear specific heat.

2-STATISTICAL THERMODYNAMICS

The magnetic moment and the specific heat of a paramagnetic substance are related to the partition function through the following relation:

$$M = -\left(\frac{\partial E}{\partial H}\right)_T = kT\left(\frac{\partial \ln Z}{\partial H}\right)_T$$

$$C_H = T\left[\frac{\partial^2}{\partial T^2}(kT \ln Z)\right]_H \qquad (7.1)$$

where F is the free energy, Z the partition function, and H the external static magnetic field. The partition function is defined as follows:

$$Z = \sum_{\text{all}} e^{-E_j/kT} = \sum_{\text{distinct}} g_j e^{-E_j/kT}$$

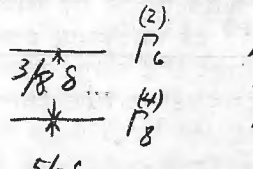
where g_j is the statistical weight, or the degree of degeneracy of the energy level E_j.

For example, consider the partition function of the Gd^{+++} ion in zero field. According to Hund's rule, the ground state is $^8S_{7/2}$, which splits in a cubic field into the levels

$$^8S_{7/2} = \Gamma_6^{(2)} + \Gamma_7^{(2)} + \Gamma_8^{(4)}.$$

There are two possible arrangements of these levels.

(a)



$E_6 = \delta$

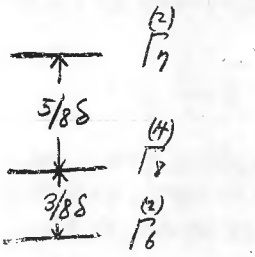
$E_8 = 5/8\,\delta$

$E_7 = 0$

For this case

$$Z = 2 + 4e^{-5\delta/8kT} + 2e^{-\delta/kT}.$$

(b)



$E_7 = \delta$

$E_8 = 3/8\,\delta$

$E_6 = 0$

Then, the partition function would be

$$Z = 2 + 4e^{-3\delta/kT} + 2e^{-\delta/kT}.$$

We shall now derive the expression for M and C_H quoted in (7.1). According to statistical mechanics the entropy S is related to the thermodynamical probability W through the relation (see for instance Slater, Chemical Physics)

$$S = k \ln W$$

where k is again the Boltzmann's constant. Further

$$W = \frac{N!}{N_1!\, N_2! \ldots}$$

where N is the total number of particles, and N_i the number of particles in the i_{th} cell. Introducing

$$f_i \equiv \frac{N_i}{N}$$

and using the Sterling approximation, we obtain

$$S = -k \sum_i f_i \ln f_i .$$

The thermodynamic potential at constant volume is given by

$$F \equiv U - TS = - kT \ln Z.$$

Here U is the internal energy of the system.

From the First and Second Laws of Thermodynamics, we have

$$\delta Q = dU + M dH, \quad \delta S = \delta Q / T$$

or

$$T dS = dU + M dH;$$

therefore

$$dF = -M dH - S dT;$$

consequently

$$M = -\left(\frac{\partial F}{\partial H}\right)_T .$$

From Equation (7.1) we then obtain

$$M = kT \left(\frac{\partial \ln Z}{\partial H}\right)_T , \quad S = -\left(\frac{\partial F}{\partial T}\right)_H = \left[\frac{\partial}{\partial T}(kT \ln Z)\right]_H .$$

The expression for the specific heat is derived as follows:

$$C_H = T\left(\frac{\partial S}{\partial T}\right)_H = T\left[\frac{\partial^2}{\partial T^2}(kT \ln Z)\right]_H .$$

3-SCHOTTKY HEAT

Anomaly in the specific heat (called Schottky heat) occurs whenever kT becomes comparable with the separation between two distinct energy levels of the material. We shall exemplify this phenomenon in the case of two distinct energy levels under the assumption that each energy level is nondegenerate.

E_2 $\quad g_2 = 1$

ΔE

E_1 $\quad g_1 = 1$

$$Z = e^{-E_1/kT}\left(1 + e^{-\Delta E/kT}\right)$$

$$\ln Z = -\frac{E_1}{kT} + \ln\left(1 + e^{-\Delta E/kT}\right)$$

Then

$$C_H = \frac{1}{kT^2}\,\frac{(\Delta E)^2 e^{-\frac{\Delta E}{kT}}}{\left(1 + e^{-\Delta E/kT}\right)^2}$$

Let $x \equiv \Delta E/kT$ and plot C_H versus x for small and large values of x.

$$C_H(x) = \frac{k x^2 e^{-x}}{(1 + e^{-x})^2}$$

As $x \to 0$, $C_H(x) \sim x^2$. As $x \to \infty$, $C_H(x) \sim e^{-x}$.

The value of x for which C_H is maximum is given by

$$\frac{d\,C_H(x)}{dx} = 0 \quad \text{or} \quad \frac{x-2}{x+2} = e^{-x}$$

thus,

$$x_{max} = \Delta E/kT = 2.4.$$

Hence, the maximum value in the specific heat occurs in the vicinity of $kT = \Delta E$.

4. NUCLEAR SPECIFIC HEAT OF Cu^{++}

We need to start from

$$Z = \sum_j e^{-E_j/kT}$$

where E_j are the energy levels of the Cu^{++} ion. Then we obtain

$$C_H = T\left[\frac{\partial^2}{\partial T^2}(kT\ln Z)\right]_H = \frac{1}{kT^2}\,\frac{\sum_{ij}(E_i^2 - E_iE_j)\,e^{-\frac{E_i+E_j}{kT}}}{\left(\sum_i e^{-E_i/kT}\right)^2}.$$

The energy level splitting E_i are of the order of

$$\mu_N \mu_B / r^3 \sim 10^{-19}\ \text{ergs}.$$

Even near $1^{\circ}K$, where experimental measurements were made,

$$kT \approx 10^{-16}\ \text{ergs};$$

thus

$$E_i \ll kT.$$

Then we may make a power expansion of the exponential.

$$C_H = \frac{1}{kT^2}\,\frac{\sum_{ij}(E_i^2 - E_iE_j)}{(\Sigma 1)^2}$$

$$= \frac{1}{kT^2}\,\frac{N\sum_i E_i^2 - \sum_{ij} E_iE_j}{N^2}$$

Here N designates the number of hyperfine energy levels.

The results obtained in Section VI, Subsection 7, for Cu^{++} may be combined and (6.6) may be written in the following matrix operator form:

$$\mathcal{H}_{nuc.} = (\Delta\nu_{\parallel})\, I_z S_z + (\Delta\nu_{\perp})(I_x S_x + I_y S_y).$$

Since the diagonal sums of the eigenvalues of individual operators are all zero,

$$\sum_i E_i = \sum_{m_I, m_S} \langle m_S, m_I | \mathcal{H}_{nuc} | m_S, m_I \rangle = 0$$

$$\sum_i E_i^2 = \sum_{m_I, m_S} \langle m_S, m_I | \mathcal{H}_{nuc}^2 | m_S, m_I \rangle$$

$$= \sum_{m_I, m_S} \langle m_S, m_I | (\Delta\nu_{\parallel})^2 I_z^2 S_z^2 + (\Delta\nu_{\perp})^2 (I_x S_x + I_y S_y)^2$$

$$+ (\Delta\nu_{\parallel})(\Delta\nu_{\perp})\left\{ I_z S_z (I_x S_x + I_y S_y) + (I_x S_x + I_y S_y) I_z S_z \right\} | m_S, m_I \rangle$$

$$= \sum_{m_S, m_I} \langle m_S, m_I | (\Delta\nu_{\parallel})^2 I_z^2 S_z^2 + (\Delta\nu_{\perp})^2 (I_x^2 S_x^2 + I_y^2 S_y^2) | m_S, m_I \rangle.$$

Since

$$\sum_{m_S} \langle m_S | S_x^2 | m_S \rangle = \sum_{m_S} \langle m_S | S_y^2 | m_S \rangle = \sum_{m_S} \langle m_S | S_z^2 | m_S \rangle = \frac{1}{3} S(S+1)(2S+1)$$

and

$$\sum_{m_I} \langle m_I | I_x^2 | m_I \rangle = \sum_{m_I} \langle m_I | I_y^2 | m_I \rangle = \sum_{m_I} \langle m_I | I_z^2 | m_I \rangle = \frac{1}{3} I(I+1)(2I+1)$$

and

$$N = (2I+1)(2S+1),$$

$$C_H = \frac{1}{kT^2}\left[(\Delta\nu_{\parallel})^2 + 2(\Delta\nu_{\perp})^2\right]\frac{1}{9} I(I+1) S(S+1).$$

This result was obtained by Bleaney (25) and Brinkman and Kikuchi (26).

According to Ingram, hyperfine structure component separations for parallel and perpendicular fields are

$$\Delta H_{\parallel} = \frac{350}{3} \text{ gauss}$$

$$\Delta H_{\perp} = \frac{50}{3} \text{ gauss}$$

The quantities $\Delta\nu_{\parallel}$ and $\Delta\nu_{\perp}$, expressed in energy units, are related to the above quantities as follows:

$$\Delta\nu_{\parallel} = g_{\parallel} \mu_B \Delta H_{\parallel}$$

$$\Delta\nu_{\perp} = g_{\perp} \mu_B \Delta H_{\perp}.$$

Then $\Delta\nu_{\perp}$ may be neglected in comparison to $\Delta\nu_{\parallel}$; therefore

$$\frac{C_T}{T^2} = \frac{g_{\parallel}^2 \mu_B^2}{k^2} (\Delta H_{\parallel})^2 \frac{1}{9} \left(\frac{3}{2}\right)\left(\frac{5}{2}\right)\left(\frac{1}{2}\right)\left(\frac{3}{2}\right)$$

$$= \frac{5}{16} \frac{g_{\parallel}^2 \mu_B^2}{k^2} (\Delta H_{\parallel})^2$$

Using

$g_{\parallel}$ = 2.4

μ_B = .928 x 10^{-20} erg/gauss

k = 1.38 x 10^{-16} erg/°K

we then get

$$\frac{C_T}{k} = 1.1 \times 10^{-4}$$

which is in excellent agreement with experiment.

ACKNOWLEDGMENTS

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APPENDIX 1
SPECTROSCOPIC RULES

a. Spectroscopic Terminology for a State of an Atom

In Russel-Saunder's approximation each atomic state or term is designated by

$$^{2S+1}L_J$$

where L, S, and J are respectively the orbital spin, and total angular momentum quantum numbers.

Spectroscopic terms S, P, D, ... refer to different values of L, i.e.,

L	= 0	1	2	3	4	5
Spect. term	= S	P	D	F	G	H

$J = L \pm S$

$2S + 1$ = multiplicity of the term

Examples: $Cu^{++}(^2D_{5/2})$, $Mn^{++}(^6S_{5/2})$, $Ti(^3F_2)$

$Nd^{++}(^4I_{9/2})$, $Cr^{++}(^5D_0)$, $Ti^{+++}(^2D_{5/2})$, etc.

b. Hund's Rule for the Determination of the Ground State of an Atom

Hund's rules states: Out of all the terms arising from a given configuration (1) the term with the highest multiplicity, i.e., highest S value, in general, lies deepest; and (2) of these, the term with the highest L value lies deepest.

Example 1.

$\underline{Cr^{++}}$: Electronic configuration: $1S^2\ 2S^2\ 2p^6\ 35^2\ 3p^6\ 3d^4$.

The states of an atom which are possible for the incomplete $3d^4$ shell are (27,28)

$^1(SDG)$ $^3(PF)$ $^1(SDFGI)$ $^3(PDFGH)$ $^5(D)$

Hund's rule (1) gives 5D for the ground state; hence, L = 2 and S = 2.

$$J = L \pm S = 2 \pm 2.$$

Rule to determine the value for J: If the incomplete shell is more than half-filled, take the larger value for J; if it is less than half-filled, take the smaller value for J.

Hence,

$$Cr^{++} (^5D_0).$$

Example 2.

$\underline{Cu^{++}}$: $3d^9$ - incomplete shell, the only possible state is 2D

$$L = 2, S = 1/2, J = 2 \pm 1/2.$$

Since the incomplete 3d shell is more than half-filled, we take the larger value for J, i.e., J = 5/2.

Hence,

$$Cu^{++} (^2D_{5/2}).$$

In the cases of Ti^{++++} and V^{+++} there is an electron outside of the complete inner shells moving along an orbit with an angular momentum $\vec{L}$. Since the electron is negatively charged, the orbital magnetic moment $\vec{\mu}_L$ lies in the direction opposite to $\vec{L}$ and gives rise to a magnetic field at the position of the electron parallel to $\vec{L}$. Since the spin magnetic moment $\vec{\mu}_S$ is directed opposite to the spin angular momentum $\vec{S}$, the orbital magnetic field tends to line $\vec{\mu}_S$ in the direction of $\vec{L}$, or $\vec{S}$ in the direction opposite to $\vec{L}$.

$$J = L - 1/2 = 2 - 1/2 = 3/2.$$

One may extend this reasoning to cases in which the incomplete shells are less than half-filled.

In the case of Cu^{++} the 3d shell lacks one electron, which may be regarded as the superposition of the complete 3d shell (10 electrons) and one positively charged electron which revolves about a given angular momentum $\vec{L}$. Dynamically this situation is equivalent to one which the positively charged electron is revolving about $\vec{L}$ in the direction opposite to that of the 3d electrons.

Because of the positive charge, the orbital magnetic moment $\vec{\mu}_L$ is again in opposite direction to $\vec{L}$, tending to line $\vec{\mu}_S$ parallel to $\vec{L}$. However, $\vec{\mu}_S$ is now in the same direction as $\vec{S}$.

Thus,

$$J = L + 1/2 = 2 + 1/2 = 5/2.$$

This reasoning may be extended to cases in which the incomplete shells are more than half-filled.

APPENDIX 2
ELEMENTS, CLASSES, AND CLASS PRODUCTS OF CUBIC GROUPS

(A few of the results quoted in Section III will be proved in this Appendix)

a. Group Elements

The 24 elements of the cubic group can be generated by the two rotations A and B, where

A - - - rotation by $\pi/2$ about x-axis.

B - - - rotation by $\pi/2$ about y-axis.

These generates of the group satisfy the relation

$$A^4 = B^4 = (AB^2)^2 = (A^2B)^2 = (AB)^3 = E$$

where E is the identity element.

The elements belonging to different classes are:

$$E = E.$$

$$C_2 = A^2 + B^2 + A^2B^2.$$

$$C_3 = A + A^{-1} + B + B^{-1} + B^{-1}A^{-1} + BA^{-1}B^{-1}.$$

$$C_4 = AB^2 + A^{-1}B^2 + A^2B + A^2B^{-1} + ABA + AB^{-1}A.$$

$$C_5 = AB + A^{-1}B + BA^{-1} + BA + B^{-1}A + AB^{-1} + B^{-1}A^{-1} + A^{-1}B^{-1}.$$

The elements belonging to any particular class can be obtained algebraically from the definition of class—namely,

$$C = X^{-1}CX$$

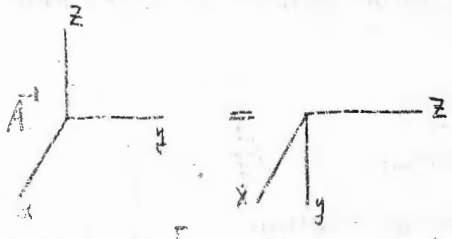
where X is any element of the group. However, for ease of visualization, we shall present a geometric proof.

b. Elements of Class C_3

1st element of C_3 [rotation by $\pi/2$ (x-axis)]

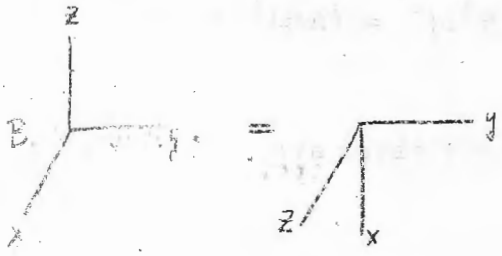
$(C_3)_1 = A$

2nd element [rotation by $-\pi/2$ (x-axis)]



$(C_3)_2 = A^{-1}$

3rd element [rotation by $\pi/2$ (y-axis)]



$(C_3)_3 = B$

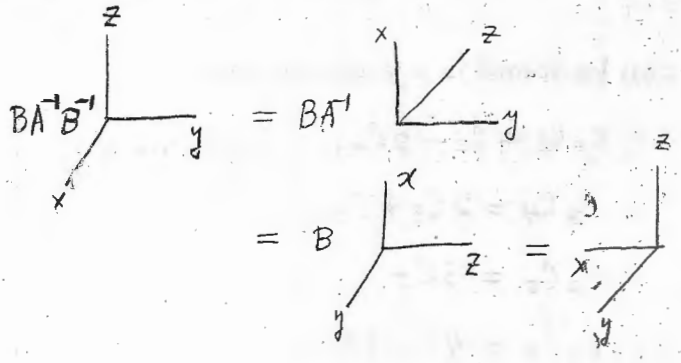
4th element [rotation by $-\pi/2$ (y-axis)]

$(C_3)_4 = B^{-1}$

5th element [rotation by $\pi/2$ (z-axis)]

$(C_3)_5 = B^{-1}A^{-1}B.$

6th element [rotation by $-\pi/2$ (z-axis)]



$$(C_3)_6 = BA^{-1}B^{-1}.$$

Hence,

$$C_3 = A + A^{-1} + B + B^{-1} + B^{-1}A^{-1}B + BA^{-1}B^{-1}.$$

The elements of other classes can be obtained in a similar manner.

c. Class Products

If a class, C_i, is represented formally by

$$C_i = A_1^{(i)} + A_2^{(i)} + \cdots\cdots + A_{h_i}^{(i)} = \sum_{\ell=1}^{h_i} A_{h_i}^{(i)}$$

where $A^{(i)}_{h_i}$ are the group elements contained in class C_i, then the class product is defined as

$$C_i C_K = \sum_{\ell=1}^{h_i} A_\ell^{(i)} \sum_{m=1}^{h_K} A_m^{(k)}.$$

Further, since the product of two elements of a group is another element of the group, we can write the above in the form

$$C_i C_K = \sum_\ell c_{iK\ell} C_\ell.$$

For example, consider $(C_2)^2$.

$$(C_2)^2 = (A^2 + B^2 + A^2B^2)^2 = A^4 + A^2B^2 + A^4B^2 + B^2A^2 + B^4 + B^2A^2B^2 + A^2B^2A^2 + A^2B^4 + A^2B^2A^2B^2$$

$$= E + A^2B^2 + B^2 + B^2A^2 + E + A^2 + B^2 + A^2 + E$$

$$= 3E + 2C_2,$$

Thus $C_{221} = 3$ and $C_{222} = 2$.

The following class products can be found in a similar way:

$$C_2^2 = 3E + 2C_2 \qquad C_2 C_3 = C_3 + 2C_4$$

$$C_3^2 = 6E + 2C_2 + 3C_5 \qquad C_2 C_4 = 2C_3 + C_4$$

$$C_4^2 = 6E + 2C_2 + 3C_5 \qquad C_2 C_5 = 3C_5$$

$$C_5^2 = 8E + 8C_2 + 4C_5 \qquad C_3 C_4 = 4C_2 + 3C_5$$

$$C_3 C_5 = C_4 C_5 = 4C_3 + 4C_4.$$

APPENDIX 3
CONSTRUCTION OF THE CHARACTER TABLE

For this purpose, several theorems are needed. These will be stated without proof (29,30).

Theorem I. The number of nonequivalent irreducible representations of group G is equal to the number of classes of elements in G.

Applied to the cubic group which has five classes, there are five irreducible representations.

Our problem now is to fill in the following table:

Classes

	$C_1 = E$	C_2	C_3	C_4	C_5
Γ_1	$\chi_1^{(1)}$	$\chi_2^{(1)}$	$\chi_3^{(1)}$	$\chi_4^{(1)}$	$\chi_5^{(1)}$
Γ_2	$\chi_1^{(2)}$	$\chi_2^{(2)}$	$\chi_3^{(2)}$	$\chi_4^{(2)}$	$\chi_5^{(2)}$
Γ_3	$\chi_1^{(3)}$	$\chi_2^{(3)}$	$\chi_3^{(3)}$	$\chi_4^{(3)}$	$\chi_5^{(3)}$
Γ_4	$\chi_1^{(4)}$	$\chi_2^{(4)}$	$\chi_3^{(4)}$	$\chi_4^{(4)}$	$\chi_5^{(4)}$
Γ_5	$\chi_1^{(5)}$	$\chi_2^{(5)}$	$\chi_3^{(5)}$	$\chi_4^{(5)}$	$\chi_5^{(5)}$

Irreducible representations

The characters in column C_1 are obtained by the use of the following theorem:

Theorem II. The dimensions of the irreducible representations satisfy

$$\sum_{\ell=1}^{n} [\chi_1^{(\ell)}]^2 = g$$

where g is the number of elements in G.

For the cubic group, the above theorem gives

$$[\chi_1^{(1)}]^2 + [\chi_1^{(2)}]^2 + [\chi_1^{(3)}]^2 + [\chi_1^{(4)}]^2 + [\chi_1^{(5)}]^2 = 24$$

which has the solution

$$1^2 + 1^2 + 2^2 + 3^2 + 3^2 = 24.$$

These are the numbers that will appear in the column under E.

To fill in the rest of the table a few more theorems are needed.

Theorem III. The characters of different representations satisfy

$$\sum_{i=1}^{n} h_i \chi_i^{(u)} \chi_i^{(v)} = \delta_{uv} g$$

where h_i is the number of elements in class i. The summation is over all classes.

Theorem IV. The characters appearing in different columns, i and k, satisfy

$$\sum_{\nu=1}^{n} \chi_i^{(\nu)} \chi_k^{(\nu)} = \delta_{ik} \frac{g}{h_i}$$

where the summation is now over all representations.

Theorem V. The characters for any one representation satisfy

$$h_i h_k \chi_i \chi_k = \chi_i \sum_{\ell=1}^{n} c_{ik\ell} h_\ell \chi_\ell.$$

Let us designate the two one-dimensional representations by Γ_1 and Γ_2. Let us first determine the characters for Γ_1. To do this apply Theorem III. We then get

$$\chi_1^2 + 3\chi_2^2 + 6\chi_3^2 + 6\chi_4^2 + 8\chi_5^2 = 24 \qquad (1)$$

Since the sums of coefficients of the X's is just 24, and since the characters are roots of unity, we conclude that the X's must be either +1 or -1. Let us pick all the X's to be +1. This we shall call Γ_1, or the identity representation.

To determine the X's for Γ_2, we apply Theorem III once more. Then

$$1^2 + 3\chi_2^2 + 6\chi_3^2 + 6\chi_4^2 + 8\chi_5^2 = 0. \qquad (2)$$

Furthermore, from the class product

$$C_2^2 = 3E + 2C_2$$

we obtain $C_{221} = 3$ and $C_{222} = 2$. Then from Theorem V, we get

$$3^2 \chi_2^{(2)} \chi_1^{(2)} = \chi_1^{(2)} \left[C_{221} h_1 \chi_1^{(2)} + C_{222} h_2 \chi_2^{(2)} \right]$$

$$= 1 \left[3 \cdot 1 \cdot 1 + 2 \cdot 3 \chi_2^{(2)} \right]$$

$$\therefore \left[\chi_2^{(2)} - 1 \right] \left[\chi_2^{(2)} + 1/3 \right] = 0$$

$$\chi_2^{(2)} = 1.$$

It is possible to show that

$$\chi_3^{(2)} = \chi_4^{(2)}$$

by using

$$C_2 C_4 = 2C_3 + C_4$$

and Theorem V. Then Equation (2) becomes

$$1^2 + 3 \cdot 1^2 + 12\chi_3^{(2)} + 8\chi_5^{(2)} = 0$$

or

$$12\chi_3^{(2)} + 8\chi_5^{(2)} = -4$$

Since the X's are either +1 or -1, the obvious solutions are

$$\chi_3^{(2)} = \chi_4^{(2)} = -1, \quad \chi_5^{(2)} = 1.$$

We can proceed similarly to find the characters for Γ_3, Γ_4 and Γ_5

APPENDIX 4
IRREDUCIBLE REPRESENTATIONS OF ^2D WAVE FUNCTIONS UNDER THE TETRAGONAL FIELD

We shall verify the irreducible representations attached to the Cu^{++} wave functions under the tetragonal field (4.2).

Let the wave functions ${}_0\psi^1$ and ${}_0\psi^4$ be operated on by symmetry operations C_3 and C_4 of the tetragonal group (see H. Bethe (9), p. 147).

$$C_3\,{}_0\psi^1 = \frac{1}{\sqrt{2}}\left(C_3\varphi_2 - C_3\varphi_{-2}\right) = \frac{1}{\sqrt{2}}\left(\varphi_2 e^{i\pi} - \varphi_{-2}e^{-i\pi}\right) = -{}_0\psi^1$$

Since

$$\begin{aligned} C_4\,P_\ell^m(\cos\theta)\,e^{im\phi} &= P_\ell^m(\cos(\pi-\theta))\,e^{im(\pi-\phi)} \\ &= P_\ell^m(-\cos\theta)\,e^{-im\phi}e^{im\pi} \\ &= P_\ell^m(\cos\theta)\,e^{-im\phi}(-1)^{\ell+m}e^{im\pi}, \end{aligned}$$

$$C_4\,{}_0\psi^1 = \frac{1}{\sqrt{2}}\left(C_4\varphi_2 - C_4\varphi_{-2}\right) = \frac{1}{\sqrt{2}}\left\{(-1)^4 e^{i2\pi}\varphi_{-2} - e^{-i2\pi}\varphi_2\right\} = -{}_0\psi^1$$

Hence, from the character table of the tetragonal group (H. Bethe (9), Table 5),

$${}_0\psi^1 : \Gamma_4^t.$$

Similarly,

$$C_3\,{}_0\psi^4 = -{}_0\psi^1, \qquad C_4\,{}_0\psi^4 = {}_0\psi^4$$

hence

$${}_0\psi^4 : \Gamma_3^t.$$

Let us now consider ${}_0\psi^5$.

$$C_3\,{}_0\psi^5 = C_3\varphi_0 = \varphi_0, \qquad C_4\,{}_0\psi^5 = C_4\varphi_0 = (-1)^2\varphi_0 = \varphi_0.$$

Hence, from the character table it is easy to see that ${}_0\psi^2$ and ${}_0\psi^3$ belong to Γ_5^t.

APPENDIX 5
DERIVATION OF SELECTION RULES FOR MAGNETIC DIPOLE TRANSITIONS

In order to derive selection rules we must first determine the representations of a magnetic dipole moment in various symmetry groups.

The magnetic dipole is an axial vector, and hence it transforms like the coordinates under rotation and does not change its sign under reflection. The transformation matrix of the coordinate under rotation through Φ about z-axis is

$$\begin{pmatrix} \cos\Phi & -\sin\Phi & 0 \\ \sin\Phi & \cos\Phi & 0 \\ 0 & 0 & 1 \end{pmatrix}.$$

Hence, the character of the magnetic dipole moment under rotation symmetry would be given by

$$\chi(C_i) = 1 + 2\cos\Phi \qquad (A5.1)$$

1. Cubic Symmetry

Since $\Phi_1 = 0$, $\Phi_2 = \pi$, $\Phi_3 = \pi/2$, $\Phi_4 = \pi$, $\Phi_5 = 2\pi/3$,

$$\chi(E) = 3, \quad \chi(C_2) = -1, \quad \chi(C_3) = 1, \quad \chi(C_4) = -1, \quad \chi(C_5) = 0.$$

Hence, $\Gamma(\vec{\mu}) = \Gamma_4$. Hence,

2. Tetragonal Symmetry

From the classes of rotations of the tetragonal group given in section III we see that the angles to be used in (A5.1) are

$$\Phi_1 = 0, \quad \Phi_3 = \pi/2, \quad \Phi_2 = \Phi_4 = \Phi_5 = \pi$$

$$\chi(E) = 3, \quad \chi(C_3) = 1, \quad \chi(C_2) = \chi(C_4) = \chi(C_5) = -1$$

$$\therefore \Gamma(\vec{\mu}) = \Gamma_2 + \Gamma_5.$$

We can further identify Γ_2 with z- and Γ_5 with the x- and y-components of the magnetic moment operator. The proof that the representation of μ_z is Γ_2 is as follows. For rotations of classes E_1, C_2, and C_3, i.e., rotation about the z-axis, μ_z remain the same; whereas for rotation of class C_4 and C_5, μ_z changes its sign. Therefore

$$\chi(E) = \chi(C_2) = \chi(C_3) = 1, \chi(C_4) = \chi(C_5) = -1.$$

which are just the characters of the representation Γ_2. For trigonal symmetry

$$\Gamma_{(\vec{\mu})} = \Gamma_2 + \Gamma_3 = \Gamma_z + \Gamma_{(xy)}$$

and for rhombic symmetry

$$\Gamma_{(\vec{\mu})} = \Gamma_2 + \Gamma_3 + \Gamma_4 = \Gamma_{(x)} + \Gamma_{(y)} + \Gamma_{(z)}.$$

3. Allowed Transitions

We have pointed out that in order for a transition to be allowed the matrix element must not vanish. For this to be the case the product of the representations of the final and neutral states and of the magnetic moment operator must contain Γ_1. This also means that the product of the representations of the initial and final states must contain the representation of the magnetic moment operator. This can be proved in the following way. We need to determine the condition under which Γ_1 is contained in the product

$$\Gamma_i \Gamma_j \Gamma_m$$

where Γ_i and Γ_j are the representative of the initial and final state, and Γ_m is that of the magnetic moment operator. Using the theorem on page 170, Reference 29 we find

$$\Gamma_i \Gamma_j = \sum_w g_{ijw} \Gamma_w$$

and we obtain

$$\Gamma_i \Gamma_j \Gamma_m = \sum_w g_{ijw} \Gamma_w \Gamma_m = \sum_w g_{ijw} \sum_s g_{wms} \Gamma_s.$$

We are interested in the coefficient of Γ_1, i.e.,

$$\text{coefficient of } \Gamma_1 = \sum_w g_{ijw} g_{wm1}.$$

But

$$g_{wm1} = \delta_{wm}$$

$\therefore$ coefficient of $\Gamma_1 = g_{ijm}$. See page 173 of Reference 29.

Thus the number of times that Γ_1 is contained in the product $\Gamma_i \Gamma_j \Gamma_m$ is just equal to the number of times $\Gamma_i \Gamma_j$ contains Γ_m.

Let us now apply these remarks to the cubic group. From the character table we obtain

$$\Gamma_1 \Gamma_1 = \Gamma_1 \qquad \Gamma_3 \Gamma_4 = \Gamma_4 + \Gamma_5$$

$$\Gamma_2 \Gamma_3 = \Gamma_3 \qquad \Gamma_3 \Gamma_5 = \Gamma_4 + \Gamma_5$$

$$\Gamma_2 \Gamma_4 = \Gamma_5 \qquad \Gamma_4 \Gamma_5 = \Gamma_2 + \Gamma_3 + \Gamma_4 + \Gamma_5$$

$$\Gamma_2^2 = \Gamma_1 \qquad \Gamma_4^2 = \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$$

$$\Gamma_3^2 = \Gamma_1 + \Gamma_2 + \Gamma_3 \qquad \Gamma_5^2 = \Gamma_1 + \Gamma_3 + \Gamma_4 + \Gamma_5$$

Also by using the character table for the double group, there results

$$\Gamma_6^2 = \Gamma_1 + \Gamma_4 \qquad \Gamma_6\Gamma_7 = \Gamma_2 + \Gamma_5$$

$$\Gamma_7^2 = \Gamma_1 + \Gamma_4 \qquad \Gamma_6\Gamma_8 = \Gamma_3 + \Gamma_4 + \Gamma_5$$

$$\Gamma_8^2 = \Gamma_1 + \Gamma_2 + \Gamma_3 + 2\Gamma_4 + 2\Gamma_5 \qquad \Gamma_7\Gamma_8 = \Gamma_3 + \Gamma_4 + \Gamma_5.$$

We see then that the allowed transitions for the cubic group are

$\Gamma_1 \leftrightarrow \Gamma_4$ $\quad \Gamma_4 \leftrightarrow \Gamma_4$ $\quad \Gamma_6 \leftrightarrow \Gamma_6$ $\quad \Gamma_6 \leftrightarrow \Gamma_8$

$\Gamma_2 \leftrightarrow \Gamma_5$ $\quad \Gamma_5 \leftrightarrow \Gamma_5$ $\quad \Gamma_7 \leftrightarrow \Gamma_7$ $\quad \Gamma_7 \leftrightarrow \Gamma_8$

$\Gamma_3 \leftrightarrow \Gamma_4$ $\quad \Gamma_8 \leftrightarrow \Gamma_8$

$\Gamma_3 \leftrightarrow \Gamma_5$

$\Gamma_4 \leftrightarrow \Gamma_5$

APPENDIX 6
HYPERFINE STRUCTURE CALCULATIONS

$$\int f_+^* (a_1 (\vec{l}\cdot\vec{I}))\, f_+ = \frac{a_1}{2} I_- \int f_+^* L_+ f_+ + \frac{a_1}{2} I_+ \int f_+^* L_- f_+ + a_1 I_z \int f_+^* L_z f_+ .$$

Introducing f_+ from (4.7) and disregarding quadratic terms in λ's,

$$\int f_+^* L_+ f_+ = \frac{\lambda_2^2}{2} v \int \varphi_+^* L_- L_+ \varphi_+ \sum \alpha S_+(\nu\alpha + w\beta) - \frac{\lambda_2^2}{2} w \int \varphi_+^* L_+ L_- \varphi_+ \sum (\nu\alpha + w\beta) S_+\beta$$

$$= -2\lambda_2 \nu w$$

Here we made use of (4.2) and (4.3).

$$\int f_+^* L_- f_+ = -\frac{\lambda_2^2}{2} w \int \varphi_+^* L_+ L_- \varphi_+ \sum \beta S_-(\nu\alpha + w\beta) - \frac{\lambda_2^2}{2} v \int \varphi_+^* L_+ L_- \varphi_+ \sum (\nu\alpha + w\beta) S_-\alpha$$

$$= -2\lambda_2 \nu w$$

$$\int f_+^* L_z f_+ = -2\lambda_1 \int \varphi_+^* L_z^2 \varphi_+ \sum (\nu\alpha + w\beta) S_z (\nu\alpha + w\beta) = -\lambda_1 (\nu^2 - w^2)$$

Hence, $\int f_+^* (a_1(\vec{L}\cdot\vec{I}))f_+ = -\bar{a}_1\{\lambda_2 vw(I_+ + I_-) + \lambda_1 4(v^2-w^2)I_z\}$.

Similarly, $\int f_-^* (a_1(\vec{L}\cdot\vec{I}))f_- = \bar{a}_1\{\lambda_2 vw(I_+ + I_-) + \lambda_1 4(v^2-w^2)I_z\}$.

2.

$$\int f_+^* a_2\left(\frac{3(\vec{I}\cdot\vec{r})}{r^2} - (\vec{I}\cdot\vec{S})\right)f_+ = \frac{\bar{a}_2}{21}\int f_+^*\{2L^2(\vec{S}\cdot\vec{I}) - 3(\vec{I}\cdot\vec{L})(\vec{S}\cdot\vec{L}) - 3(\vec{S}\cdot\vec{L})(\vec{I}\cdot\vec{L})\}f_+$$

Here we made use of the Equation (65.39), p. 557 of Reference (31). Proceeding similarly it is easy to show

$$\int f_+^* 2L^2(S\cdot I)f_+ = 6vw(I_+ + I_-) + 6(v^2-w^2)I_z$$

$$(\vec{I}\cdot\vec{L})(\vec{S}\cdot\vec{L}) + (\vec{S}\cdot\vec{L})(\vec{I}\cdot\vec{L}) = \tfrac{1}{2}I_+S_+L_-^2 + \tfrac{1}{2}I_-S_-L_+^2 + \tfrac{1}{2}(I_+S_- + I_-S_+)(L^2-L_z^2) + \tfrac{1}{2}(I_zS_z + I_+S_z)(2L_z+1)L_- + \tfrac{1}{2}(I_zS_- + I_-S_z)(2L_z-1)L_+ + 2I_zS_zL_z^2$$

$$\int f_+^* I_+S_+L_-^2 f_+ = \int f_+^* I_-S_-L_+^2 f_+ = 0$$

$$\int f_+^* \tfrac{1}{2}(I_+S_- + I_-S_+)(L^2-L_z^2)f_+ = vw(I_+ + I_-)$$

$$\int f_+^* \tfrac{1}{2}(I_zS_+ + I_+S_z)(2L_z+1)L_-f_+ = \lambda_2(2v^2-w^2)I_z - \tfrac{3}{2}\lambda_2 vwI_+ - \frac{\lambda_2}{2}(v^2+w^2)I_z$$

$$\int f_+^* \tfrac{1}{2}(I_zS_- + I_-S_z)(2L_z-1)L_+f_+ = \lambda_2(-2w^2+v^2)I_z - \tfrac{3}{2}\lambda_2 vwI_- + \frac{\lambda_2}{2}(v^2+w^2)I_z$$

$$\int f_+^* 2I_zS_zL_z^2 f_+ = 4(v^2-w^2)I_z$$

Hence, $$\int f_+^* a_2\left\{\frac{3(\vec{I}\cdot\vec{r})(\vec{S}\cdot\vec{r})}{r^2} - (\vec{I}\cdot\vec{S})\right\}f_+$$

$$= \frac{\bar{a}_2}{7}\left\{\left(1+\tfrac{3}{2}\lambda_2\right)vw(I_+ + I_-) - (2+3\lambda_2)(v^2-w^2)I_z\right\}.$$

$$\int f_+^* a_2(\vec{I},\vec{S}) f_+ = \frac{a_2}{2}\{vw(I_+ + I_-) + (v^2 - w^2) I_z\}$$

$$\int f_+^* \gamma(I,H) f_+ = \frac{\gamma}{2} H_+ I_- + \frac{\gamma}{2} H_- I_+ + \gamma H_z I_z$$

Thus,

$$\int f_+^* \left[a_1(\vec{I},\vec{I}) + a_2\left\{\frac{3(\vec{I},\vec{n})(\vec{S},\vec{n})}{r^2} - (\vec{I},\vec{S})\right\} + a_3(\vec{I},\vec{S}) + \gamma(\vec{I},\vec{H})\right] f_+$$

$$= \alpha^* I_+ + \alpha I_- + \beta I_z$$

α and β are given in Equation (6.12) as α_+ and β_+.

* * *

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