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SOME THEORETICAL PROBLEMS CONCERNING PARAMAGNETIC SUBSTANCES AT LOW TEMPERATURE

J. M. Jauch

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SOME THEORETICAL PROBLEMS CONCERNING PARAMAGNETIC SUBSTANCES AT LOW TEMPERATURE

J. M. Jauch

The content of this report is rather incomplete. No attempt is made to discuss the problems systematically. Instead various aspects are taken up and it is attempted to discuss them in such a form that the general principles involved are brought to light. These general principles are then easily applied to related problems and thus furnish the basis for the understanding of many low temperature phenomena in the paramagnetic salts. The problems selected are problems which arose out of discussions with the low temperature research group, in particular, with Dr. Louis Roberts.

1) The Kramers degeneracy

In 1930 Kramers[1] proved a general theorem which is of great importance in the discussions of magnetic properties of paramagnets at low temperature. Wigner[2] has brought Kramers' theorem on a more general basis and has shown in particular that Kramers' transformation of spin conjugation is nothing else than the transformation associated with time inversion. Since both these papers are not easily accessible we shall give a simple derivation of Kramers' result.

Kramers' theorem states that if a system of electrons is brought into an arbitrary electric field then there remains always a two fold degeneracy if the number of electrons is odd.

We consider a system of n electrons. The stationary states ψ and their eigenvalues E are obtained from the Schrodinger equation

$$\mathcal{H}\psi = E\psi \tag{1.1}$$

The Hamiltonian operator $\mathcal{H}$ may depend on the spin and orbital angular momentum of the individual electrons in addition to the usual dependence on the momenta. It also may contain an arbitrary potential energy. One easily verifies that in the non-relativistic theory the operator $\mathcal{H}$ contains the spin operators $\underline{\sigma}^{(r)}$ for the $r^{\underline{th}}$ electron either in an even power multiplied with an even power of the momenta $P^{(s)}$ of the $s^{\underline{th}}$ electron or it contains them both in an odd power. Remembering that P in the Schrödinger representation is purely imaginary, we find with the standard representation of the spin matrices

$$\sigma_1 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \qquad \sigma_2 = \begin{pmatrix} 0 & -i \\ i & 0 \end{pmatrix} \qquad \sigma_3 = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix}$$

for the complex conjugate $\mathcal{H}^*$ of the Hamiltonian (not Hermitian conjugate !)

$$\mathcal{H}^*(\sigma_1^{(r)}\ \sigma_2^{(r)}\ \sigma_3^{(r)}) \equiv \mathcal{H}(-\sigma_1^{(r)}, \sigma_2^{(r)}, -\sigma_3^{(r)}) \tag{1.2}$$

$\mathcal{H}^*$ can be restored to its original form if we can find an operator $\sum$ which anti-commutes with σ_1 σ_3 but commutes with σ_2.

$$\left.\begin{aligned} \sigma_1^{(r)} \sum &\equiv - \sum \sigma_1^{(r)} \\ \sigma_2^{(r)} \sum &\equiv \sum \sigma_2^{(r)} \\ \sigma_3^{(r)} \sum &\equiv - \sum \sigma_3^{(r)} \end{aligned}\right\} \quad \text{for all } r \equiv 1, \ldots n \tag{1.3}$$

This operator is uniquely determined by

$$\sum = \prod_{r=1}^{n} \sigma_2^{(r)} \tag{1.4}$$

It has the further properties

$$\sum^{2} = 1 \tag{1.5}$$

$$\sum^{+} = \sum \qquad \text{(Hermitian conjugate)} \tag{1.6}$$

$$\sum^{*} = (-1)^{n} \sum \qquad \text{(complex conjugate)} \tag{1.7}$$

From (1.5) and (1.6) it follows that $\sum$ is also unitary. It follows from (1.2) and (1.3) that if ψ is a solution of (1.1) with eigenvalue E, then $\bar{\psi} = \sum \psi^{*}$ is also a solution with the same eigenvalue. For taking the complex conjugate of (1.1) gives

$$\mathcal{H}^{*} \psi^{*} = E \psi^{*} = \mathcal{H}^{*} \sum \psi = E \sum \bar{\psi}$$

and since $\sum \mathcal{H}^{*} \sum = \mathcal{H}$

$$\mathcal{H} \bar{\psi} = E \bar{\psi} \qquad \text{q.e.d.}$$

We show next that the state $\bar{\psi}$ is orthogonal to ψ if n is odd. This is then equivalent to Kramers' theorem. Now

$$(\bar{\psi}, \psi) = (\sum \psi^{*}, \psi) = (\psi^{*}, \sum \psi) = (\sum^{*} \psi^{*}, \psi) = (-1)^{n} (\bar{\psi}, \psi)$$

thus for n odd

$$(\bar{\psi}, \psi) = 0 \qquad \text{q.e.d.}$$

As a generalization we find: The degree of degeneracy is always even if the number of electrons is odd. The converse is not true.

2) <u>The quenching of orbital motion</u>

In paramagnetic salts one observes quite frequently that the magnetic moment which enters into the formula for the susceptibility is much better represented by the value obtained from the spin only of the ion. The mechanism is known as quenching. However, in most cases the g-factor obtained from the experiments differs appreciably from the value 2 of an ordinary spin. Moreover the salts may be magnetically anisotropic, that is, g may be a symmetric tensor. The mechanism of quenching has often been discussed in the literature, but discussion were either restricted to specific examples[3] or are of such general qualitative nature[4] that no detailed quantitative use can be made of it. Recently Pryce has given a formula which allows one to calculate the effect of quenching in a convenient way. We shall derive Pryce's formula in a different way.

The Hamitonian of an ion in a crystal and in an external magnetic field may be written as

$$\mathcal{H} = V - \beta(\underline{L} + 2\underline{S}) \cdot \underline{H} + \lambda\, \underline{L} \cdot \underline{S} \qquad (2.1)$$

The first term is the potential of the crystalline electric field, the second the energy due to the magnetic field and the last is the spin orbit interaction. Exchange and magnetic dipole interaction as well as nuclear interactions are disregarded. They are of no importance for this problem. β is the Bohr magneton. The term in V alone will remove partly the 2L + 1 fold orbital degeneracy and introduce a splitting which is in general large compared to any of the other terms. We thus treat the Hamiltonian

$$\mathcal{H}' = \beta(\underline{L} + 2\underline{S}) \cdot \underline{H} + \lambda\, \underline{L} \cdot \underline{S} \qquad (2.2)$$

as a small perturbation compared to V.

Denote with n the quantum number for the orbital states in the potential V and E_n their energy. In case the ground state is degenerate, we denote their quantum numbers with n_o, thus $E_{n_o} = 0$. The spin states which under the action of V alone are still degenerate, we denote with s. The operator $\mathcal{H}'$ is then a matrix with respect to these quantum numbers which we denote with $(n\ s\,|\,\mathcal{H}'\,|\,n'\ s')$. In general it will contain off-diagonal elements in n which we can remove in first order in β and λ by a canonical transformation

$$\overline{\mathcal{H}} = S^{-1}\mathcal{H}\ S \tag{2.3}$$

Define a Hermitian operator $\sum$ by $e^{i\sum} = S$, then (2.3) becomes

$$\overline{\mathcal{H}} = \mathcal{H} + i\left[\mathcal{H}, \sum\right] + \frac{i^2}{2!}\left[(\mathcal{H}, \sum), \sum\right] + \cdots \tag{2.4}$$

We shall now choose $\sum$ in such a way, that the first order matrix elements of $\mathcal{H}'$ in λ or β which connect different levels E_n cancel. This leads to

$$(n\ s\,|\,\sum\,|\,n'\ s') = \left\{\begin{array}{ll} i\ \dfrac{(n\ s\,|\,\mathcal{H}'\,|\,n'\ s')}{E_n - E_{n'}} & \text{for } E_n \neq E_{n'} \\ 0 & \text{otherwise} \end{array}\right\} \tag{2.5}$$

Inserting this in the third term in (2.4) we obtain

$$(n_o\ s\,|\,\overline{\mathcal{H}}\,|\,n_o'\ s') = (n_o\ s\,|\,\mathcal{H}'\,|\,n_o'\ s') + \sum_{m,t} \frac{(n_o\ s\,|\,\mathcal{H}'\,|\,m\ t)(m\ t\,|\,\mathcal{H}'\,|\,n_o'\ s')}{E_{n_o} - E_m} \tag{2.6}$$

for the transformed Hamiltonian. This operator contains now only matrix elements which refer to states of the same unperturbed energy $E_{n_o} = E_{n_o'} = 0$.

With the special Hamiltonian (2.2) we obtain by defining the quantities

$$(n_o | \Lambda_{ij} | n_o') = \sum_m \frac{(n_o | L_i | m)(m | L_j | n_o')}{E_{n_o} - E_m} \tag{2.7}$$

$$(n_o\, s | \bar{\mathcal{H}} | n_o'\, s') = -\beta (n_o | L_i | n_o') H_i \delta_{ss'} + \lambda (n_o | \underline{L} | n_o') \cdot (s | \underline{S} | s')$$

$$- 2\beta \underline{H}(s | \underline{S} | s') \delta_{n_o n_o'} + (n_o | \Lambda_{ij} | n_o')(S | (\lambda S_i - \beta H_i)(\lambda S_j - \beta H_j) | s') \tag{2.8}$$

This formula simplifies considerably for the case that the lowest level is single in the orbital quantum number n_o. In this case (see below)

$$(n_o | L_i | n_o) = 0 \tag{2.9}$$

and we may write for $\bar{\mathcal{H}}$ in operator form:

$$\bar{\mathcal{H}} = -2\beta \underline{H} \cdot \underline{S} + \lambda^2 \Lambda_{ij} S_i S_j + \beta^2 \Lambda_{ij} H_i H_j - 2\beta\lambda \sum \Lambda_{ij} S_i H_j \tag{2.10}$$

The first and last term together may be written

$$-\beta g_{ik} H_i S_k \quad \text{with} \quad g_{ik} = 2(\delta_{ik} + \lambda \Lambda_{ij}) \tag{2.11}$$

and describes the anisotropic magnetic g-factor. The second term is a "pseudo quadrupole" term and gives rise to a second order Stark splitting of the spin levels. The third term is quadratic in the magnetic field and gives a temperature independent term for the susceptibility. Since Λ_{ij} is a negative definite symmetric tensor it may always be diagonalized in a suitable coordinate system and takes then the form

$$\Lambda_{ij} = \Lambda_i \delta_{ij} \qquad \text{with } \Lambda_i < 0 \,. \tag{2.12}$$

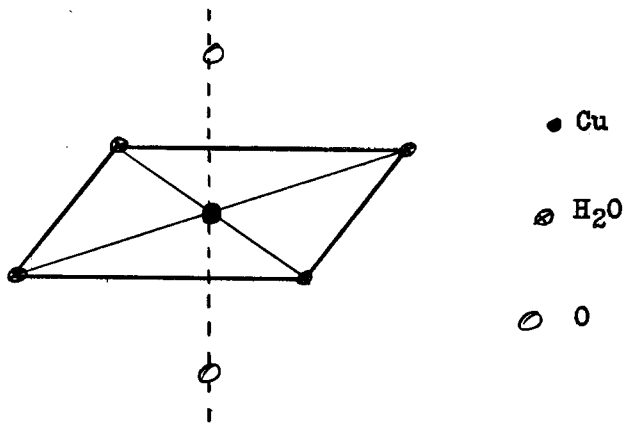
The Λ_i are of the order of magnitude $\frac{1}{E}$ where E is the separation of the nearest level. The equation (2.10) for $\overline{\mathcal{H}}$ establishes a connection between the Stark splitting of the spin levels, the temperature independent part of the susceptibility and the anisotropy and magnitude of the g-factor. It is also seen that $g \lesssim 2$ for $\lambda \gtrsim 0$ which corresponds to normal or inverted multiplets for the free ions. There remains to prove (2.9) for a single orbital level. This is so because $L_i^* = - L_i$. The solution of the Schrodinger equation may be assumed real since the Hamiltonian for the unperturbed problem contains only the first term in (2.1) in addition to the kinetic energy and is, therefore, real. Thus if ψ is a solution ψ^* is one too and if the level is single they differ only by a factor of magnitude 1. Thus we may normalize ψ so that $\psi^* = \psi$. Then we have with $\psi = \psi_{n_o}$

$$(n_o | L_i | n_o) = (\psi, L_i \psi) = (\psi, L_i \psi)^* = - (\psi^*, L_i \psi^*) = - (\psi, L_i \psi) = 0$$

q.e.d.

3) <u>Curie constants of $Cu\,SO_4 \cdot 5\,H_2O$</u>

The free Cu^{++}-ion is a $^2D_{5/2}$ with a spin orbit constant $\lambda = - 852\ cm^{-1}$, corresponding to an inverted doublet of separation 2330 cm^{-1}. In the $Cu\,SO_4 \cdot 5\,H_2O$ crystal the ion is surrounded by four water molecules in a plane and two oxygen ions on the axis perpendicular to this plane. The symmetry of the electric field due to

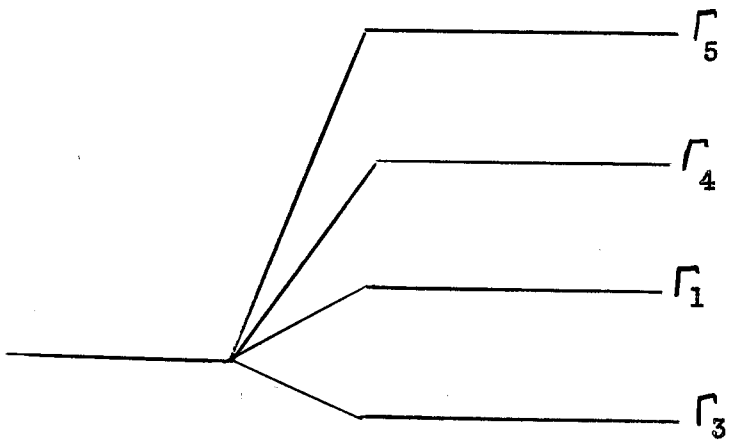


the electric dipoles of the water and oxygen is thus tetragonal and we shall henceforth refer to the axis through the oxygen as the tetragonal axis. The crystal structure is triclinic with the following lattice constants and angles[6]:

$$a = 6.12\ \text{Å} \qquad \alpha = 82^\circ\ 16'$$
$$b = 10.7\ \text{Å} \qquad \beta = 107^\circ\ 26' \qquad (3.1)$$
$$c = 5.97\ \text{Å} \qquad \gamma = 102^\circ\ 40'$$

There are two Cu-ions in each unit all at the sites (0, 0, 0) and ($\frac{1}{2}$, $\frac{1}{2}$, 0). They are inequivalent, their tetragonal axes making an angle $\theta = 82^\circ\ 14'$ with each other. Their separation is 5.542 Å and they are nearest neighbors.

The splitting of the orbital levels due to the electric field of tetragonal symmetry was calculated by Polder[7]. The zeroth order wave functions are determined from group theory entirely.



They split into five levels with their wave functions given by:

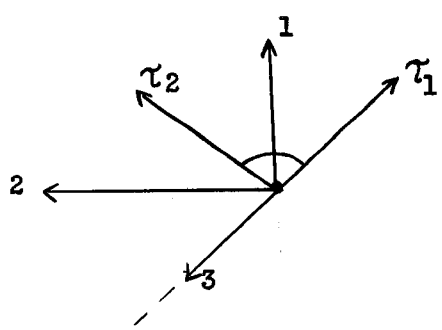
$$\left.\begin{aligned}
&\Gamma_3 : \frac{1}{\sqrt{2}}(\varphi_2 + \varphi_{-2}) \\
&\Gamma_1 : \varphi_0 \\
&\Gamma_4 : \frac{i}{\sqrt{2}}(\varphi_2 - \varphi_{-2}) \\
&\Gamma_5 : \begin{cases} \varphi_1 \\ \varphi_{-1} \end{cases} \text{degenerate}
\end{aligned}\right\} \qquad (3.2)$$

We denote the energy differences to the ground state with A, B, C. They are of order 10^4 cm^{-1}. The tensor Λ_{ik} is diagonal in a coordinate system which coincides with the octahedron and has then the values

$$\Lambda_{ik} = - \begin{pmatrix} \frac{4}{A} & 0 & 0 \\ 0 & \frac{1}{B} & 0 \\ 0 & 0 & \frac{1}{B} \end{pmatrix} \qquad (3.3)$$

An experimental determination of the susceptibility cannot be directly compared with the values derived from one type of ion. Instead the effect of both types of ions must be considered simultaneously. It is then more advantageous to introduce a coordinate system which is symmetrical with respect to the directions of the two ions. Let $\underline{\tau}_1$, $\underline{\tau}_2$ stand for the unit vectors in the directions of the tetragonal axes. The unit vector in the basic coordinate system are denoted with $\underline{\beta}_1$, $\underline{\beta}_2$, $\underline{\beta}_3$ and are given by

$$\left.\begin{aligned} \underline{\beta}_1 &= \frac{1}{2\cos\theta/2}(\underline{\tau}_2 + \underline{\tau}_1) \\ \underline{\beta}_2 &= \frac{1}{2\sin\theta/2}(\underline{\tau}_2 - \underline{\tau}_1) \\ \underline{\beta}_3 & \quad \frac{1}{\sin\theta/2}\,\underline{\tau}_1 \times \underline{\tau}_2 \end{aligned}\right\} \qquad (3.4)$$



In the coordinate system of one of the ions the g-tensor has the form

$$\overset{\circ}{g}_{ik} = g_i\,\delta_{ik} \qquad g_1 = 2\left(1 - \frac{4\lambda}{A}\right) \qquad (3.5)$$

$$g_2 = g_3 = 2\left(1 - \frac{\lambda}{B}\right)$$

by (2.11) and (3.3). In the basic coordinate system it is transformed according to the laws of tensor transformation into a non-diagonal tensor given by

$$
\begin{aligned}
g_{11} &= g_1 \cos^2 \theta/2 + g_2 \sin^2 \theta/2 \\
g_{22} &= g_1 \sin^2 \theta/2 + g_2 \cos^2 \theta/2 \\
g_{12} &= g_{21} = \pm (g_2 - g_1) \cos \theta/2 \sin \theta/2 \\
g_{33} &= g_2
\end{aligned}
\tag{3.6}
$$

all others zero. The two signs in g_{12} correspond to the two types of ions. A similar expression results for Λ_{ik}.

The relevant terms in the Hamiltonian (2.10) may now be written

$$\mathcal{H} = \mathcal{H}_o = -\beta \sum_r g_{ik}^{(r)} S_i^{(r)} H_k + \beta^2 \sum_r \Lambda_{ik}^{(r)} H_i H_k \tag{3.7}$$

The second term in (2.10) is simply an additive constant for a spin $S = \frac{1}{2}$ and may, therefore, be omitted. The second term in (3.7) gives rise to the temperature independent term in the susceptibility which was calculated by Polder[7]. Since it commutes with the first term its effect may be calculated separately and need not be given here.

The magnetic property of the material can be calculated from the standard expressions

$$\chi_{ik} = \lim_{\underline{H} \to 0} kT \frac{\partial^2}{\partial H_i \, \partial H_k} \ln Z \tag{3.8}$$

$$Z = \mathrm{tr}\, e^{-\mathcal{H}/kT} \tag{3.9}$$

For weak fields ($\beta H << kT$) one may evaluate (3.9) for the partition function Z by developing the exponential

$$Z = \mathrm{tr}\left\{1 - \frac{\mathcal{H}}{kT} + \frac{1}{2!}\left(\frac{\mathcal{H}}{kT}\right)^2 + - \quad \cdots \right\} \tag{3.10}$$

Since $\mathrm{tr}\,\mathcal{H} = 0$

$$\mathrm{tr}\,\mathcal{H}^2 = (2S+1)^N \frac{1}{3} S(S+1)\beta^2 \sum_{r,i} g_{ik}^{(r)} g_{ie}^{(r)} H_k H_e \tag{3.11}$$

$$\ln Z = \mathrm{const} + \frac{1}{2!(2S+1)^N}\,\mathrm{tr}\left(\frac{\mathcal{H}}{kT}\right)^2 + \cdots \tag{3.12}$$

Furthermore

$$\sum_{r,i} g_{ik}^{(r)} g_{ie}^{(r)} = N \gamma_k^2 \delta_{ke} \tag{3.13}$$

$$\left.\begin{aligned} \gamma_1^2 &= g_1^2 \cos^2 \theta/2 + g_2^2 \sin^2 \theta/2 \\ \gamma_2^2 &= g_1^2 \sin^2 \theta/2 + g_2^2 \cos^2 \theta/2 \\ \gamma_3^2 &= g_3^2 \end{aligned}\right\} \tag{3.14}$$

Inserting (3.14), (3.13), (3.12), (3.11) in (3.8) one obtains finally

$$\chi_{ik} = \chi_i \delta_{ik} \tag{3.15}$$

$$\chi_i = \frac{N\beta^2}{kT} \frac{1}{3} S(S+1)\gamma_i^2 = \frac{C_i}{T} \tag{3.16}$$

The Curie constants C_i for single crystals were measured by Krishnan and Mookberji[8] and were found to be

$$C_1 \simeq C_2 = .48 \quad \text{degree/mol}$$
$$C_3 = .40 \quad \text{degree/mol} \tag{3.17}$$

The best agreement with experiment is obtained for $A = 15214\ cm^{-1}$ $B = 25818\ cm^{-1}$

$$\gamma_1 = 2.29 \qquad C_1 = .493 \quad \text{degree/mol}$$
$$\gamma_2 = 2.24 \qquad C_2 = .471 \quad \text{degree/mol} \tag{3.18}$$
$$\gamma_3 = 2.07 \qquad C_3 = .401 \quad \text{degree/mol}$$

A slight discrepancy seems real, since the experimental values of the Curie constants show no variation in the 1 - 2 plane of the basic coordinate system. A further corroboration of this is found in the magnetic resonance absorption measurements to be discussed later. The explanation of this must be sought in the fact that we assumed without justification that the tetragonal axes of the electric field are identical with the axes of the octahedron of water and oxygen. This is true, if only nearest neighbors are considered. However already the inclusion of the next nearest neighbors with electric dipoles shows that the effect of these is not entirely negligible and is indeed of the right order of magnitude and the right sign. That is they are so located as to produce a tendency for increasing the angle θ.

4) Super exchange in $Cu\ SO_4 \cdot 5\ H_2O$

Already Polder[7] has found the theory not adequate for describing the fact that the powder susceptibility follows a Weiss law

$$\chi = \frac{C}{T + \theta}$$

with a Weiss constant $\theta = 0.7^{\circ}$ K[9]. Krishnan and Mookberji[8] also found a Weiss law at higher temperatures ($T > 90^{\circ}$) with Weiss constants which depend on the orientation of the single crystals and even change signs. Unfortunately, errors are not given by these last mentioned authors. A rough estimate of the errors on the basis of the scattering of the values reveals, however, that no conclusion can be drawn as to the value of θ. The above mentioned value obtained for powder at much lower temperature appears to be certain.

It is clear that the simple electronic levels can never give such a law for the susceptibility since the doubly degenerate level of the ground state can never split by any electric field whatever (Kramers' theorem). The explanation of this effect must be found in an interaction of the magnetic ions. Among the various interactions which are known to be operative, the following ones are possible.

a) Ordinary exchange interaction: This effect is almost certainly too small. The next nearest neighbors are 5.542 Å away and a rough estimate with hydrogen-like wave functions shows the exchange integral to be too small by a factor 100. In addition the ions are completely surrounded by water and oxygen and it is very difficult to conceive of any direct exchange under these circumstances.

b) The magnetic dipole interaction: The expression for this interaction is very well known. Following the method of Van Vleck[10] one can calculate its contribution to the susceptibility with the result

$$\chi_{ke} = - \frac{4\beta^4 \left[\frac{1}{3} S(S+1)\right]^2}{k^3 T^2} \sum_{\substack{r,r' \\ i,j}} g_{ik}^{(r)} g_{je}^{(r')} \left\{ \frac{1}{R^3} \delta_{ik} - \frac{3}{R^5} X_i X_j \right\} \tag{4.1}$$

where X_i is the ith component of the radius vector between the ions r, r' and R is the distance of these ions. There are two points in which this case is different from the previously discussed ones. In the first place we have a triclinic lattice. For such a lattice it is no longer true that the contribution of the ions within a sphere to the expression (4.1) vanish as it is known to be the case for cubic lattices. As a consequence the magnetic dipole interaction for a spherically molded specimen which is just zero for cubic lattices does no longer vanish. The second difference from previous treatments is due to the fact that there are two different kinds of ions. Although these effects are not expected to be large, a numerical evaluation of (4.1) was carried out with sufficient number of nearest neighbors (about 30) to see the convergence of this expression. The correction to the susceptibility at 1° K is only a few percent and is, therefore, negligible.

c) Nuclear interactions: Nuclear interactions certainly play a role in the magnetic properties of ions. The recent discovery of the hyperfine structure in magnetic resonance absorption is a convincing proof of this[11-15]. However, nuclear interactions cannot be considered as the cause for the departure from the Curie law for two compelling reasons: They are much too small and the correction to the isotropic susceptibility (powder value) is rigorously zero.

d) The effect of superexchange: There are many substances known where the exchange interaction is very large although the magnetic ions are separated by non-magnetic ions. There are notably the antiferromagnetic oxides, sulfides, selenides and tellurides of the transition metals. The result of neutron diffraction on such crystals also show a marked correlation of the spins at

adjacent sites for the ions[16].

On the theoretical side it was pointed out by Kramers[17] that magnetic ions could interact via the excited states of intermediate non-magnetic ions. This superexchange is expected to be of an order of magnitude which seems to fit very well the experimental data on the above mentioned crystals[18]. Since all the other possibilities are eliminated it must be concluded that superexchange is also operative in the $CuSO_4 - 5H_2O$ crystals. A similar conclusion was reached by Opechowski[19] for the case of the Tutton salt $K_2Cu(SO_4)_2 \cdot 6H_2O$ where a somewhat smaller Weiss constant of $\theta \cong 0.052^\circ$ K was observed by DeKlerk[20]. Unfortunately, the actual exchange interaction is very difficult to evaluate. The superexchange will in general lead to an interaction which may be of the form

$$\sum_{\substack{rr' \\ ik}} \gamma_{ik}^{rr'} S_i^{(r)} S_k^{(r')}$$

and thus introduces a large number of parameters. So long as only orders of magnitude are discussed we may assume it to be of the form

$$\mathcal{H}_{ex} = \sum \gamma^{rr'} \underline{S}^{(r)} \cdot \underline{S}^{(r')} \tag{4.2}$$

and we shall later assume further that only nearest neighbors interact. The assumption of an isotropic exchange (4.2) is not a serious restriction for the calculation of the Weiss constant. However, the assumption of isotropy will affect any statement which will depend on the fact that the total spin $S = \sum_r S^{(r)}$ commutes with (4.2) while it does not for an anistoropic exchange. This has a decided effect on the theory of exchange-narrowing of magnetic resonance lines to be discussed below.

Further experimental evidence for the existence of the superexchange are the specific heat measurements. J. Ashmead[21] found that the specific heat of $Cu\,SO_4 \cdot 5\,H_2O$ has a maximum at about 1° K, and Duychaerts[22] finds that the tail at high temperature follows the law $C = A/T^2$ with $A \simeq 1.5$ degree cal/mol.

Finally the magnetic resonance measurements[23-25] on $Cu\,SO_4 \cdot 5\,H_2O$ show a line width which is much smaller than the width expected on the basis of magnetic dipole interaction. The explanation of this phenomenon has been given by Van Vleck and Gorter[26] as due to an exchange interaction. Also the Bagguley and Griffith observed a very interesting phenomenon. If the constant field was along $\underline{\tau}_1$ the resonance should occur at two points corresponding to the two g-factor in a direction parallel and perpendicular to the tetragonal axis. However, only at $\lambda = 0.85$ cm are the two lines separated. At $\lambda = 3.04$ they are merged into one single line half-way between the two expected positions. This is just what would be expected if the two types of ions have an appreciable exchange[27]. A very rough estimate was made by Bagguley and Griffith on the assumption that the lines begin to separate if the precessional frequency is equal to the exchange frequency which occurs at 1.73 cm. They find thus a value of 0.15 cm^{-1} for the exchange interaction constant.

The effect of an exchange term of the form (4.2) can be calculated by extending the series development (3.10) one more term. We find then for the partition function (omitting irrelevant terms)

$$\ln Z = \frac{1}{(2S+1)^N} \left\{ \frac{1}{2!} \operatorname{tr} \left(\frac{\mathcal{H}}{kT}\right)^2 - \frac{1}{3!} \operatorname{tr} \left(\frac{\mathcal{H}}{kT}\right)^3 \right\} \tag{4.3}$$

The value of the first term is given in (3.11), (3.13). The exchange term (4.2) contributes the second term in (4.3) the amount

$$\mathrm{tr}\,\mathcal{H}^3 = 2.3\beta^2\,\mathrm{tr}\sum_{\substack{rr'\\ ikhje}} g_{ik}^{(r)}\,S_i^{(r)}\,H_k\,\gamma_{rr'}\,S_h^{(r)}\,S_h^{(r')}\,g_{je}^{(r')}\,S_j^{(r')}\,H_e$$

$$= 2.3\beta^2\,(2S+1)^N\left[\frac{1}{3}\,S(S+1)\right]^2 \sum_{\substack{r,r'\\ i}} \gamma_{rr'}\,g_{ik}^{(r)}\,g_{ie}^{(r')}\,H_k\,H_e \tag{4.4}$$

If we assume that the exchange is effective only between ions of different kind then the summation over r and r' can be carried out. Neglecting surface effects, we may write

$$\sum_{\substack{r,r'\\ i}} \gamma_{rr'}\,g_{ik}^{(r)}\,g_{ie}^{(r')} = \frac{N}{2}\,\gamma\sum_i\,(g_{ik}^{+}\,g_{ie}^{-} + g_{ik}^{-}\,g_{ie}^{+}) \tag{4.5}$$

Here the $\pm$ signs refer to the two tensors coming from the two different ions (see equ. (3.6)) and

$$\gamma = \sum_{r'} \gamma_{rr'} \quad \text{(independent of r)}$$

With the values (3.6) for $g_{ik}^{\pm}$ we find for the sum in (4.5)

$$\frac{1}{2}\sum_i\,(g_{ik}^{+}\,g_{ie}^{-} + g_{ik}^{-}\,g_{ie}^{+}) = h_k^2\,\delta_{ke} \tag{4.6}$$

$$\left.\begin{aligned} h_1^2 &= g_{11}^2 - g^2 \\ h_2^2 &= g_{22}^2 - g_{12}^2 \\ h_3^2 &= g_2^2 \end{aligned}\right\} \tag{4.7}$$

Writing for the principle susceptibility $\chi_i + \chi_i'$ where χ_i is calculated in (3.16) we have for χ_i'

$$\chi_i' = - \left[\frac{1}{3} S(S+1)\right]^2 2 \frac{N\beta^2\gamma}{(kT)^2} h_i^2 \tag{4.8}$$

This defines the Weiss constant

$$- \frac{\theta_i}{T} \chi_i = \chi_i'$$

or

$$\theta_i = - T \frac{\chi_i'}{\chi_i} = \frac{S(S+1)}{3} 2 \frac{\gamma}{k} \left(\frac{h_i}{\gamma_i}\right)^2$$

or with $S = \frac{1}{2}$

$$k\,\theta_i = \frac{1}{2} \gamma \left(\frac{h_i}{\gamma_i}\right)^2 \tag{4.9}$$

The powder value of θ is found to be

$$k\,\theta = \frac{k}{C_1 + C_2 + C_3} (C_1\,\theta_1 + C_2\,\theta_2 + C_3\,\theta_3) \tag{4.10}$$

$$k\,\theta = \gamma/2 \; \frac{h_1^2 + h_2^2 + h_3^2}{\gamma_1^2 + \gamma_2^2 + \gamma_3^2} \sim \frac{\gamma}{2} \tag{4.11}$$

The following values for γ_i and h_i were found previously

$$\gamma_1^2 = 5.26 \qquad h_1^2 = 5.16$$

$$\gamma_2^2 = 5.01 \qquad h_2^2 = 4.93 \tag{4.12}$$

$$\gamma_3^2 = 4.29 \qquad h_3^2 = 4.29$$

This gives for γ

$$\gamma = 2\ k\ 0 = 2 \times 0.7 \times .695\ cm^{-1}$$

$$\gamma = 0.98\ cm^{-1} \tag{4.13}$$

and for θ_i

$$\theta_1 = .69^\circ$$

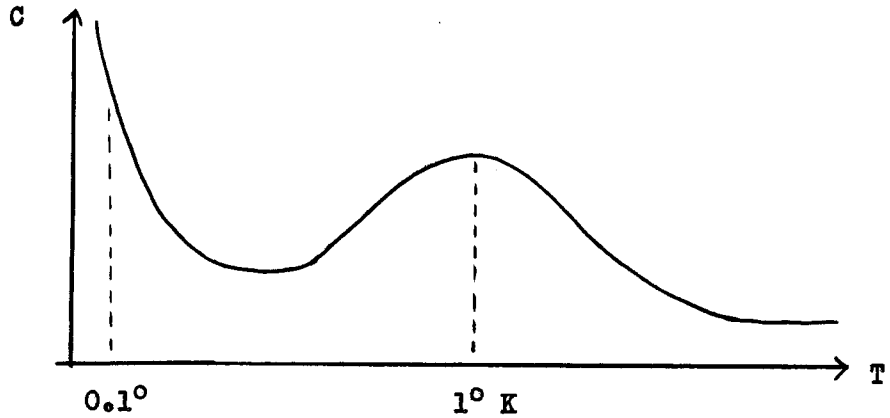
$$\theta_2 = .67^\circ \tag{4.14}$$

$$\theta_3 = .71^\circ$$

Thus a very slight asymmetry should be present even for an isotropic exchange. For anisotropic exchange the asymmetry would be correspondingly larger. An accurate determination of θ_i at low temperature has not been published. It would furnish an excellent way of finding out the type of interaction for the superexchange in this particular case.

5) <u>The specific heat of $Cu\ SO_4 \cdot 5\ H_2O$</u>

The specific heat was found to have a maximum at 1° K. It increases again sharply at about 0.1° K [21]. This last increase is due to the magnetic



Specific heat of $Cu\,SO_4 \cdot 5\,H_2O$

dipole interaction and confirms the estimate of the effect of this interaction. The maximum at 1° K must be due to the same cause which gives rise to the Weiss constant at the same time confirming that this effect is not due to the magnetic interaction. The contribution of the exchange interaction to the specific heat is in principle calculated from the formulae

$$Z = \mathrm{tr}\, e^{-\sum \gamma_{rr'}\, \underline{S}^{(r)} \cdot \underline{S}^{(r')} / kT} \tag{5.1}$$

and

$$E = kT^2 \frac{\partial}{\partial T} \ln Z \qquad\qquad C = \frac{\partial E}{\partial T} \tag{5.2}$$

$$Z = \mathrm{tr}\left\{1 + \frac{2}{2!} \sum_{rr'} \frac{\gamma_{rr'}\gamma_{r'r}}{(kT)^2}\, \mathrm{tr}\,(\underline{S}^{(r)} \cdot \underline{S}^{(r')})(\underline{S}^{(r')} \cdot \underline{S}^{(r)}) + \cdots\right\}$$

$$= N(2S+1)\left\{1 + 2\,\frac{1}{2}\left[\frac{S(S+1)}{3}\right]^2 3\,\frac{1}{(kT)^2} \sum_{rr'} \gamma^2_{rr'} + \cdots\right\}$$

$$\ln Z = \text{const.} + \frac{3}{16}\,\frac{N}{(kT)^2} \sum_{r'} \gamma^2_{rr'} \tag{5.3}$$

This gives for $\gamma << kT$

$$C = \frac{A}{T^2} \quad \text{with } A = \frac{3}{8} \frac{N}{k} \sum_{r'} \gamma^2_{rr'} \tag{5.4}$$

With the assumption that only one nearest neighbor is interacting (thereby under estimating A) we find with $\gamma \sim 1\ cm^{-1}$

$$A = \frac{3}{8} \left(\frac{1}{0.64}\right)^2 R \tag{5.5}$$

$$A = 0.78 \times R \sim 1.5 \text{ cal degree/mol} \tag{5.6}$$

This value agrees excellently with Duychaert's[22] value A = 1.5 cal degree/mol. Thus confirming one conjecture that the specific heat anomaly and the Weiss constant are due to one and the same interaction. We also find that the interaction is probably appreciable for only two nearest neighbors since the inclusion of more terms in (5.4) would increase A beyond its experimental value.

6) Nuclear interactions of paramagnetic ions

The main reason why nuclear physicists are interested in paramagnets is because the paramagnetic ions interact with the nuclei and through this interaction give rise to a number of interesting effects. There are two main lines of research which are made possible through the nuclear interactions.

The first is the possibility of nuclear alignment through their interaction with the magnetic ions, which was pointed out by M. E. Rose[35] and Gorter[34]. The effective magnetic field of the ions at the position of the nuclei is of the order $10^5 - 10^6$ gauss. A direct alignment would require very strong fields and temperatures

of the order 10^{-3} °K. Due to these strong internal magnetic fields it is sufficient to saturate the ions themselves, their coupling with the nuclei producing almost complete alignment of the latter. The saturation of the ions can be achieved at convenient field strengths of the order $\sim 10^4$ gauss while the temperature need only be about as low as 1° K. The theory of this effect has been worked out by Rose for the case of almost complete saturation of the ions. A more rigorous theory which would be desirable gives rise to great mathematical difficulties. So far it was not possible to improve this theory by a more rigorous treatment.

The second type of research is to measure the magnetic and electric quadrupole moment of nuclei through their interaction with the paramagnetic ions. The most useful tool for this purpose is the magnetic resonance absorption. For the observation of nuclear interaction it is necessary to use diluted substances so as to minimize the magnetic interaction. The hyperfine structure of magnetic resonance absorption was discovered by Penrose[28] and was further investigated by Bleaney and Ingram[29-30] and Ingram[31].

There are two types of nuclear interaction which come into play in these experiments.

a) <u>The magnetic dipole interaction</u> which is described by a Hamiltonian

$$\mathcal{H}_m = a(J \cdot I) \tag{6.1}$$

The interaction constant a is of order

$$a \sim \frac{\beta^2}{hc} \frac{m}{M} \left\langle \frac{1}{r^3} \right\rangle_{av} \sim \frac{1}{hc} \left(\frac{e\hbar}{2mc}\right)^2 \frac{m}{M} \left\langle \frac{1}{r^3} \right\rangle_{av} \sim 10^{-3} \text{ cm}^{-1} \tag{6.2}$$

b) <u>The quadrupole interaction.</u> There are two effects due to the electric quadrupole of the nucleus. One is due to the interaction of the quadrupole with the crystalline electric field. This term has in a tetragonal field the form

$$\mathcal{H}_q = \frac{Z\,e\,q\,Q}{I(2I-1)}\left\{3\,I_3^2 - I(I+1)\right\} \qquad (6.3)$$

where Q is the nuclear quadrupole moment and is of order 10^{-24} cm^2 and

$q = -\frac{1}{4}\left(\frac{\partial^2 V}{\partial Z^2}\right)_0$. (Z is the tetragonal axis.) The q-values are of the order

$$\frac{eq}{hc} \sim 10^{19}\ \text{cm}^{-3}$$

and this effect is then of order $10^{-3} - 10^{-4}$ cm^{-1} for $Q \sim 10^{-24}$ cm^2.

The second effect is due to the interaction of the quadrupole moment with the electric field produced by the electrons of the magnetic ions. This effect is described by a term of the form[32]

$$\mathcal{H}_q' = \frac{e^2\,q'\,Q}{2S(2S-1)\,I(2I-1)}\left\{\frac{3}{4}(I\cdot S)\left[(I\cdot S)+1\right] - I(I+1)\,S(S+1)\right\} \qquad (6.4)$$

where $q' = \left\langle \frac{3\cos^2\theta - 1}{r^3} \right\rangle_{av}$

and represents apart from a factor e the average value of $\frac{\partial^2 V}{\partial Z^2}$ at the position of the nucleus. It is interesting to note that the nuclear quadrupole moment gives rise to these two different interactions. This furnishes us in principle with

enough information which enables us to calculate the nuclear quadrupole moment from the observed hyperfine spectrum. The usual difficulty of calculating q' can be avoided by obtaining Q directly from the term (6.3). The q-value which enters in (6.3) is known from the observed splitting due to the electric field and can be determined by a measurement of the g-factors.

At the present time, however, the theory of the hyperfine structure is not sufficiently certain as to allow such conclusions[33]. More theoretical work is necessary before the method outlined here may be used to determine quadrupole moments directly.

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APPENDIX

ON THE HYPERFINE STRUCTURE IN THE SOLID STATE

The hyperfine structure in the magnetic resonance absorption was observed for the first time by R. P. Penrose[28] in a copper tutton salt with 95% of copper replaced by magnesium. Four lines corresponding to the nuclear spin 3/2 of the copper were observed with an maximum overall separation of 93 gauss at a wave length of 3.2 cm. The maximum was in the direction of the K_1 axis, that is the axis of maximum g-value. The mimimum was along the K_2 axis where g is mimimum also. According to Bleaney the ratio of the splitting is of order six.

The effect was also observed in the cobalt salts by Bleaney and Ingram[30] where it was found to be very large.

In another copper salt, the copper fluosilicate ($Cu\ Si\ F_6 \cdot 6\ H_2O$) a very small hyperfine structure was observed.

Finally, Bleaney stated on several occasions that Mn^{++}-ions also produce a hyperfine splitting corresponding to a nuclear spin 5/2. A detailed paper on this is not available yet.

The theory of these effects has not been very successful up to this time. The two most conspicious failures occur in the copper tutton salts and the case of the maganese.

In the first case Pryce and Abragam[33] obtained the result that the hyperfine splitting for the parallel and perpendicular case are proportional to

$$\left.\begin{aligned} \Delta E_{\parallel} &\sim -\frac{4}{7} + g_{\parallel} - 2 \\ \Delta E_{\perp} &\sim \frac{2}{7} + g_{\perp} - 2 \end{aligned}\right\} \qquad (1)$$

thus giving a ratio with $g_{\parallel} \sim 2.40 \quad g_{\perp} \sim 2.09$

$$\left| \frac{\Delta E_{\parallel}}{\Delta E_{\perp}} \right| \sim \frac{0.17}{0.39} \qquad (2)$$

This is a variation in the opposite sense from the experimental results.

Even more difficult to understand is the hyperfine structure in the Mn^{++} ion. The electronic configuration of this ion is $d^5\ {}^6S$ and theoretically no hyperfine splitting can result from such a state whether it arises from magnetic dipole or electric quadrupole interaction.

In a recent letter to the editor[36] Abragam proposed a solution which seems to us to be highly improbable to be the correct answer to this problem. According to Abragam the whole hyperfine structure in Mn^{++} and a strong correction to that in Cu^{++} should arise from the excitation of an electron into a 4s state. Since it is known that the S-functions have a very large hyperfine structure there results an appreciable perturbation in second order to the first order calculation. It is difficult to say whether this effect is large enough. An admixture of 4% of the excited state would require an overall separation of $\sim$ 2.5 cm^{-1} for this state to give the right order of magnitude in Mn^{++}.

We shall show that at least the difficulty with the copper disappears if the interaction with the magnetic dipole moment is correctly taken into account.

Care must be taken to calculate correctly the contribution to this interaction arising from the electronic configuration d^9. This configuration is not equivalent to a single d-electron in this case since for the spin-part of the interaction the d^9 configuration acts as for a one electron problem with positive charge (positive hole). This effect is very similar to the well-known inversion of the multiplets when going from the first half of the d-shell to the second half.

In order to discuss this effect more in detail we start out with the complete Hamiltonian of the Cu^{++} ion and the nucleus in the crystal and in an external magnetic field $\underline{H}$.

$$\left.\begin{aligned}\mathcal{H} = V_{cryst.} &- \beta\,\underline{L}\cdot\underline{H} - 2\beta(\underline{S}\cdot\underline{H}) + \lambda(\underline{L}\cdot\underline{S}) \\ &- \beta\, g_n \frac{m}{M}(\underline{I}\cdot\underline{H}) \\ &+ a\,(\underline{L}\cdot\underline{I}) + a\sum_{r=1}^{q} P_{ik}^{(r)}\, S_i\, I_k\end{aligned}\right\} \qquad (3)$$

Here the first term represents the crystalline electric field of tetragonal symmetry arising from the electric dipoles surrounding the ion. The second and third terms are the magnetic energy of the orbital and spin magnetic moments of the ion. The fourth term is the spin-orbit coupling term. The fifth is the magnetic energy of the nuclear dipole. The last two terms which concern us here mostly are the magnetic interaction of the ion with the nucleus. The interaction constant is

$$a = 2\beta^2\, g_n \frac{m}{M} \left\langle \frac{1}{r^3} \right\rangle_{av} \sim 10^{-2}\ \mathrm{cm}^{-1} \qquad (4)$$

where $\beta = \frac{e\hbar}{2\,mc}$ and g_n is the nuclear g-factor. The summation over r is over all the nine electrons in the d-shell and

$$P_{ik} = \frac{3}{r^2}\chi_i \chi_k - \delta_{ik} \tag{5}$$

where χ_i are the coordinates of one of the electrons. Since it is the last two terms which cause a hyperfine splitting in the magnetic resonance absorption we shall give a derivation of these terms starting from first principles.

We may consider the nucleus as the source of an internal magnetic field $\underline{H}'$ deriving from a vector potential $\underline{A}$:

$$\underline{H}' = \nabla \times \underline{A} \tag{6}$$

with

$$\underline{A} = \frac{1}{r^3}\underline{\mu} \times \underline{\chi} \;, \quad \underline{\mu} = \beta\, g_n\, \underline{I}\, \frac{m}{M} \tag{7}$$

The contribution of this internal field to the Hamiltonian is obtained in the usual way by replacing $\underline{P}$ in the Schrodinger equation by $\underline{P} + \frac{e}{c}\underline{A}$. The $+$ sign comes here because we choose $e > 0$ and the electronic charge is $-e$. The additional terms in the Hamiltonian arise from two sources. One from the kinetic energy

$$\frac{1}{2\,m}\sum_n \left(\underline{P}^{(n)} + \frac{e}{c}\underline{A}^{(n)}\right)^2 \sim \sum_n \frac{P^{(n)2}}{2m} + \frac{e}{mc}\sum_n \underline{A}^{(n)} \cdot \underline{P}^{(n)} + \ldots \tag{8}$$

Since $\nabla \cdot \underline{A} = 0$, except at the origin where the wave functions vanish, we have written

$$\underline{A} \cdot \underline{P} + \underline{P} \cdot \underline{A} = 2\,\underline{A} \cdot \underline{P} \tag{9}$$

(This is not allowed for s-functions and gives rise to the well known hyperfine splitting for s-states discussed by Fermi.)

The second term is due to the interaction of $\underline{H}'$ with the magnetic moment of the spin and is given by

$$- 2\beta \sum_{n=1}^{q} \underline{S}^{(n)} \cdot \nabla_n \times \left(\frac{1}{r_n^3} \underline{\mu} \times \underline{\chi}^{(n)}\right) = a \sum_{n=1}^{q} P_{ik}^{(n)} S_i I_k \tag{10}$$

The second term in (8) may be evaluated further to give

$$\frac{e}{mc} \sum_{n=1}^{q} \underline{A}^{(n)} \cdot \underline{P}^{(n)} = \frac{e}{mc} \sum_{n=1}^{q} \frac{1}{r_n^3} \left(\underline{\chi}^{(n)} \times \underline{P}^{(n)}\right) \cdot \underline{\mu}$$

$$= a\, \underline{L} \cdot \underline{I} \tag{11}$$

(10) and (11) constitute the last two terms of (3). We have replaced $\sum_{n=1}^{q} \frac{1}{r_n^3}$ by $\left\langle \frac{1}{r^3} \right\rangle_{av}$ which already introduces the integration over the radial parts of the wave functions and we have written $\sum_{n=1}^{q} L^{(n)} = L$ for the total orbital angular momentum. The actual value of a is not of importance here, the relative sign of the two last terms is crucial, however, and we shall pay special attention to this sign in the evaluation of the sum over n in (10). Before doing this we shall rewrite the Hamiltonian after carrying out the Van Vleck transformation discussed in the first section of this report to eliminate the off-diagonal terms in the Hamiltonian connecting different energy levels of the V_{cryst} operator. If we dispose of the unimportant terms in the Hamiltonian which we need not discuss here since they do not affect the hyperfine splitting (there are four such terms,

one quadratic in the magnetic field, one quadratic in the operators $\underline{S}$, one quadratic in the operators $\underline{I}$ and the magnetic interaction of the nuclear moment) we arrive at the following Hamiltonian

$$\bar{\mathcal{H}} = -\beta \sum_i g_i S_i H_i + 2 a \lambda \sum \Lambda_i S_i I_i$$

$$+ a \sum_{n=1}^{q} (n_o | P_{ik}^{(n)} | n_o) S_i I_k \tag{12}$$

Here the g_i are the diagonal elements of the anisotropic g-tensor (the coordinate system is already adapted to the tetragonal symmetry of the problem) given in Eq. (3.5) of the text and Λ_i are the quantities (3.3). The $(n_o | P_{ik} | n_o)$ is the diagonal matrix element of the tensor P_{ik} for the ground state. It can be evaluated with the following group theoretical reasoning

Since $P_{ik} = P_{ki}$ and $\sum_i P_{ii} = 0$ the tensor P_{ik} transforms under rotations according to the irreducible representation D_2. Its matrix elements in the LM representation will thus involve transitions $\Delta M = \pm 2$, $\Delta M = \pm 1$ and $\Delta M = 0$. The parts of P_{ik} which involve these elements can be obtained by constructing those linear combinations which under rotations transform like the spherical harmonics $Y_2^{\pm 2}$, $Y_2^{\pm 1}$ and Y_2^0 respectively. Since the ground state is $\frac{1}{\sqrt{2}} (\varphi_2 + \varphi_{-2})$ only the last term is involved and for this one finds

$$(n_o | P_{ik} | n_o) S_i I_k = \frac{1}{6} (n_o | P_{11} + P_{22} - 2 P_{33} | n_o)(S_1 I_1 + S_2 I_2 - 2 S_3 I_3)$$

$$= -\frac{1}{2} (n_o | P_{33} | n_o)(S_1 I_1 + S_2 I_2 - 2 S_3 I_3) \tag{13}$$

We now reintroduce the summation over all the electrons which was omitted in (13) for simplicity. Here we make use of the fact that the operators $\underline{S}^{(n)}$ considered in the space of the resultant spin $\underline{S} = \sum_{n=1}^{q} \underline{S}^{(n)}$ are all proportional to the resultant spin operator $\underline{S}$. In our case where the resultant spin is actually also 1/2 the proportionality factor is 1. Thus the Hamiltonian for the spin interaction reduces finally to

$$- \frac{a}{2} \sum_n (n_o | P_{33}^{(n)} | n_o)(S_1 I_1 + S_2 I_2 - 2 S_3 I_3) \tag{14}$$

In order to evaluate $\sum_n (n_o | P_{33}^{(n)} | n_o)$ we need the matrix element $(M | P_{33} | M')$ for anyone of the nine electrons in the ion. According to a well known group theoretical theorem the M-dependence of this operator is exactly the same as that of the operator L_3^2 and we find thus

$$\sum_n (M | P_{33}^{(n)} | M') = C(M | L_3^2 | M')$$

$$= C \, \delta_{MM'} \, M^2 \tag{15}$$

with the proportionality constant

$$C = \frac{1}{L^2} \sum_n \left\langle 3 \cos^2 \vartheta^{(n)} - 1 \right\rangle_{M = L} \tag{16}$$

We find therefore

$$(n_o | P_{33} | n_o) = \frac{1}{2} C \left\{ (2 | L_3^2 | 2) + (-2 | L_3^2 | -2) \right.$$

$$= 4 C \tag{17}$$

Thus the problem reduces itself to calculating C.

Up to this point our work is presumably identical with that of Pryce and Abragam. Indeed one obtains their result by calculating (16) under the assumption of one electron in a 3d state. For then we have by simple integration

$$C = \frac{1}{L^2} \left\langle 3 \cos^2 \vartheta - 1 \right\rangle_{M = L} = - \frac{1}{L^2} \frac{2L}{2L + 3} = - \frac{1}{7} \tag{18}$$

Introducing this in (17) and (12) we find the result (1) which disagrees with experiment. The correct evaluation of (16) leads to a C with opposite sign. Using Slater wave functions (antisymmetrized products) one finds instead for C

$$C = \sum_{m=-(\ell-1)}^{+\ell} \left\langle 3 \cos^2 \vartheta - 1 \right\rangle_m = - \sum_{m=-(\ell-1)}^{+\ell} \frac{3 m^2 - \ell(\ell+1)}{(2\ell - 1)\ell} \frac{2\ell}{2\ell + 3}$$

$$= + \frac{2\ell}{2\ell + 3}$$ which for $\ell = L = 2$ (d-electrons !) gives

$$C = + \frac{1}{7} \tag{19}$$

This gives instead of (1) the result

$$\Delta E_{\parallel} \sim + \frac{4}{7} + g_{\parallel} - 2$$

$$\Delta E_{\perp} \sim - \frac{2}{7} + g_{\perp} - 2 \tag{20}$$

and

$$\frac{\Delta E_{\parallel}}{\Delta E_{\perp}} = \frac{0.97}{0.19} \cong 5 \tag{21}$$

This value is in satisfactory agreement with experiment. Accuracy can not be expected to be better than about 10% in C since Slater wave functions are only approximations. There is no doubt, however, that the theory is essentially correct.

As to the Mn^{++} case the present theory is obviously not capable of explaining the existence of a hyperfine structure at all since $\left\langle 3\cos^2\vartheta - 1\right\rangle_{L,M=L} = 0$ for the $3d^5\ {}^6S$ state of the electrons in the ion. In this case the existence of the hyperfine structure, if real, can indeed only be explained by a mechanism of the sort suggested by Abragam in his recent letter.

Since we have shown that good agreement with theory exists in the case of the Cu^{++} ion it may at first glance seem surprising that the mechanism, if applicable to the case of Mn, should not also be operative in the case of Cu. The answer is that it probably does but there exist in the case of Cu two excited states which contribute with opposite sign to the correction of hyperfine structure as was noted correctly by Abragam. These two states are characterized by their electronic configurations: $3d^8\ 4S\ {}^2D$ and $3S\ 3d^9\ 4S\ {}^2D$ of which the first is energetically lower.

The lower energy of the first state is partly counteracted by the higher principal quantums number (4) which is responsible for the hyperfine structure in this case. In the case of Cu the contribution from these two states nearly cancels then and this is the reason why this mechanism does not contribute any appreciable amount in the case of Cu while it may very well do so in the case of Mn.