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Electron Spin Resonance of $Zn(ClO_4)_2 \cdot 6H_2O:Mn^{2+}$ in a Parallel and Perpendicular Configuration

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ESR measurements of $Zn(ClO_4)_2 \cdot 6H_2O:Mn^{++}$ are presented for experimental arrangements in which the static magnetic field is parallel as well as perpendicular to the microwave magnetic field. A comparison of the spectra for these two configurations yields a simple, direct determination of the relative signs of the parameters D and A, and D and B. Relative transition probabilities for the parallel-field case are calculated and found to have a particularly simple form. The values in gauss of the parameters in the spin Hamiltonian are $D=\pm 127 \pm 1$, $a=\pm 9.5 \pm 1$, $A=\mp 95.8 \pm 0.3$, $B=\mp 96.1 \pm 0.3$, and $E=0$; g is found equal to 1.999 ± 0.001.

I. INTRODUCTION

THE paramagnetic resonance of the divalent manganese ion in crystalline fields of axial but nearly cubic symmetry has been extensively studied. Abragam and Pryce[1] proposed that the dominant terms in the spin Hamiltonian are

$$\mathcal{H} = g\beta \mathbf{H} \cdot \mathbf{S} + D[S^2 - \tfrac{1}{3}S(S+1)] + E(S_x^2 - S_y^2) + AS_zI_z + B(S_xI_x + S_yI_y), \quad (1)$$

where $S=\frac{5}{2}$ and $I=\frac{5}{2}$ are the total electronic and nuclear spins, respectively, and z refers to the symmetry axis of the crystalline field. E is zero when the axial symmetry is complete. The validity of this theory for Mn^{++} in zinc fluosilicate and zinc ammonium sulphate was established by Bleaney and Ingram,[2] who give the angular dependence of the $\Delta M = 1$ and $\Delta m = 0$ transitions.

In recent years there has been considerable interest in the forbidden transitions $\Delta M = \pm 1$, $\Delta m = \pm 1$.[3] Bleaney and Rubins[4] ascribed the unexpectedly large strength of these transitions to cross terms in the Hamiltonian. Their ideas were extended by other authors.[5] Smith *et al.*[3] note that the selection rules forbidding these transitions can also be broken by a component of the static magnetic field $\mathbf{H}$ parallel to the microwave field $\mathbf{H}_1$.

In this paper we describe the ESR spectra of Mn^{++} in $Zn(ClO_4)_2 \cdot 6H_2O$, including the spectra for the configuration with $\mathbf{H}_1$ and $\mathbf{H}$ parallel (parallel-field case). Section III C contains a derivation of the relative transition probabilities for this case.

II. THEORETICAL

A. Crystal Structure

Wyckoff[6] gives the crystal structure of magnesium perchlorate. Since the cell dimensions for zinc perchlorate and magnesium perchlorate are the same to within 2%, it is reasonable to assume that the structures are essentially the same. The crystal structure is described as orthorhombic pseudohexagonal with two metal ions per unit orthorhombic cell. ESR spectra are determined by the configuration about the metal ions. Surrounding each such ion there are six water molecules arranged at the face centers of a cube, one of whose body diagonals is along the crystallographic c axis. There is a slight extension of the cube along this axis giving the configuration trigonal symmetry. The configuration about the second ion in the unit cell is obtained from the first by a 60° rotation about the c axis. Hence if the trigonal symmetry is exact, the spectra of the two ions will coincide.

B. Theoretical Spectra

Several authors have considered the solution of the Hamiltonian (1) by perturbation theory.[5,7] The direction of the magnetic field is taken to be the z axis and the axis of quantization for the electronic spin (quantum numbers S and M). We take the crystallographic c axis to be obtained from the z axis by a rotation about the x axis through an angle θ. The axis of quantization for the nuclear spin (quantum numbers I and m) is taken to lie in the plane of the z and c axes and at an angle ψ to the former given by $\cos\psi = (A/K)\cos\theta$, where $K^2 = A^2\cos^2\theta + B^2\sin^2\theta$. With these transformations the Hamiltonian becomes $\mathcal{H} = \mathcal{H}_{\mathrm{fs}} + \mathcal{H}_{\mathrm{hfs}}$, where

$$\mathcal{H}_{\mathrm{fs}} = g\beta H S_z + D\{\tfrac{1}{2}(3\cos^2\theta - 1)S_z^2 + [i(\tfrac{1}{2} - S_z)S_+ + i(\tfrac{1}{2} + S_z)S_-] \times \cos\theta \sin\theta - \tfrac{1}{4}\sin^2\theta(S_+^2 - S_-^2)\} \quad (2)$$

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[1] A. Abragam and M. H. L. Pryce, Proc. Roy. Soc. (London) **A205**, 135 (1951).

[2] B. Bleaney and J. E. Ingram, Proc. Roy. Soc. (London) **A205**, 336 (1951).

[3] S. R. P. Smith, P. V. Auzins, and J. E. Wertz, Phys. Rev. **166**, 122 (1968), and references therein.

[4] B. Bleaney and R. S. Rubins, Proc. Phys. Soc. (London) **77**, 103 (1961); **78**, 778(E) (1961).

[5] H. W. deWijn and R. F. van Balderen, J. Chem. Phys. **46**, 1381 (1966), and references therein.

[6] R. W. G. Wyckoff, *Crystal Structures* (Interscience Publishers, Inc., New York, 1965), 2nd ed., Vol. 3, p. 814.

[7] B. Bleaney, Phil. Mag. **42**, 441 (1951).

and

$$\mathcal{H}_{\mathrm{hfs}}=KS_zI_z+(A^2-B^2)(2IK)^{-1}(S_+-S_-)\sin\theta\cos\theta$$
$$-(4K)^{-1}AB(S_+-S_-)(I_+-I_-)$$
$$+\tfrac{1}{4}B(S_++S_-)(I_++I_-).\quad(3\mathrm{a})$$

When $A=B$, (3a) becomes

$$\mathcal{H}_{\mathrm{hfs}}=AS_zI_z+\tfrac{1}{2}A(S_+I_-+S_-I_+).\quad(3\mathrm{b})$$

In this form, using $g\beta HS_z$ as the zero-order Hamiltonian, the magnetic field at which transitions occur may be determined by perturbation theory.[8] For the $\Delta M=\pm1$ transitions in manganese the ESR fine-structure spectrum is described by Bleaney and Ingram[2] as

$$H_{\mathrm{fs}}(\pm\tfrac{5}{2}\leftrightarrow\pm\tfrac{3}{2})=H_0\mp2D(3\cos^2\theta-1)$$
$$-32D^2H_0^{-1}\cos^2\theta\sin^2\theta+D^2H_0^{-1}\sin^4\theta\mp2pa,$$
$$H_{\mathrm{fs}}(\pm\tfrac{3}{2}\leftrightarrow\pm\tfrac{1}{2})=H_0\mp D(3\cos^2\theta-1)$$
$$+4D^2H_0^{-1}\cos^2\theta\sin^2\theta-5D^4(4H_0)^{-1}\sin^4\theta\pm\tfrac{5}{2}pa,$$
$$H_{\mathrm{fs}}(\tfrac{1}{2}\leftrightarrow-\tfrac{1}{2})=H_0+16D^2H_0^{-1}\cos^2\theta\sin^2\theta-2D^2H_0^{-1}\sin^4\theta.$$
$$(4)$$

Here the terms in pa describe the small effect of the cubic field with $p=(1-5\phi)$ and $\phi=(l^2m^2+m^2n^2+n^2l^2)$, l, m, and n being the direction cosines of $\mathbf{H}$ relative to the cubic axes. D is now measured in gauss rather than energy units, and $g\beta H_0=h\nu$ with ν the microwave frequency.

Along with the transitions $\Delta M=\pm1$ we will be concerned with the hyperfine transitions $\Delta m=0$, ∓1. To suppress the angular dependence we consider only $\theta=0°$ and $\theta=90°$. To the fine-structure terms we then add for $\theta=0°$ the terms

$$H_{\mathrm{hfs}}(m\leftrightarrow m)=-Am-A^2(2H_0)^{-1}$$
$$\times[(35/4)-m^2+m(2M-1)],\quad(5)$$
$$H_{\mathrm{hfs}}(m\leftrightarrow m+1)=-A(m-M+1)$$
$$-A^2H_0^{-1}[(35/4)+Mm-\tfrac{1}{2}(M-m-1)(M-m-2)].$$
$$(6)$$

For $\theta=90°$ A should be replaced by B in the first term of each expression. In calculating the correction term we have assumed $B=A$.

The first term of (6) has a useful property. For $M=S$ we have that $m-M+1=(m+1)-S\leq0$, provided that $I\leq S$. Thus the hyperfine lines either all lie at greater field than $H_{\mathrm{fs}}(S\leftrightarrow S-1)$ or all lie at smaller field, depending on the relative signs of D and A. For $\theta=0°$ the parallel-field case spectrum will have a larger overall splitting (in gauss) than the perpendicular-field case spectrum if D and A have opposite signs. If D and A have the same sign the reverse will hold. For $\theta=90°$ the parallel case will have a smaller over-all splitting than the perpendicular case if D and B have opposite signs. and the reverse will be true if D and B have the same sign. Thus a simple comparison of the two spectra (parallel and perpendicular) at each angle ($\theta=0°$ and $\theta=90°$) determines the relative signs of D and A and of D and B. Previously it was necessary to consider second-order effects in the spectra to obtain these relative spins.[2,9]

C. Transition Probabilities

We now calculate the transition probabilities for the parallel-field case. If we denote the perturbed wave functions by $|\alpha\rangle$, then we have, including terms up to order $(g\beta H)^{-1}$ (Ref. 8),

$$|\alpha\rangle=|Mm\rangle+\sum_{M'}^{M'\neq M}\sum_{m'}\frac{\langle M'm|\mathcal{H}_1|Mm\rangle}{g\beta H(M-M')}|M'm'\rangle+\sum_{m'}^{m'\neq m}\sum_{M''}^{M''\neq M}\sum_{m''}\frac{\langle Mm'|\mathcal{H}_1|M''m''\rangle\langle M''m''|\mathcal{H}_1|Mm\rangle}{g\beta H(M-M'')A(m-m')}|Mm'\rangle,\quad(7)$$

where $\mathcal{H}_1=\mathcal{H}-g\beta HS_z$. For this calculation we assume $A=B$. In the perpendicular-field case the last term admixes off diagonal terms in the Hamiltonian and contributes to the relatively large strength of forbidden transitions. For the parallel-field case the matrix element $\langle\alpha|\mu_z|\bar{\alpha}\rangle$, where $\mu_z=g\beta S_z$, replaces the usual $\langle\alpha|\mu_x|\bar{\alpha}\rangle$ in the transition-probability calculation. This makes for a significant simplification; the result when carried to order H^{-1} is

$$\langle\alpha|\mu_z|\bar{\alpha}\rangle=-H^{-1}\langle Mm|\mathcal{H}_1|\bar{M}\bar{m}\rangle|_{\bar{M}\neq M}.$$

The relative transition probabilities for the transitions $\alpha\leftrightarrow\bar{\alpha}$ are given by the modulus squared of this matrix element. Using the Hamiltonian given in (2) and (3b) one finds the relative intensities of the various transitions as

$$\Delta M=1,\qquad\Delta m=0;$$
$$|\langle\alpha|\mu_z|\bar{\alpha}\rangle|^2=(D\cos\theta\sin\theta)^2(2H)^{-2}(2M-1)^2$$
$$\times[S(S+1)-M(M-1)],\quad(8)$$
$$\Delta M=\pm1,\qquad\Delta m=\mp1;$$
$$|\langle\alpha|u_z|\bar{\alpha}\rangle|^2=A^2(2H)^{-2}[S(S+1)-M(M-1)]$$
$$\times[I(I+1)-m(m+1)],\quad(9)$$
$$\Delta M=2,\qquad\Delta m=0;$$
$$|\langle\alpha|\mu_z|\bar{\alpha}\rangle|^2=(D\sin^2\theta)^2(4H)^{-2}[S(S+1)$$
$$-(M-1)(M-2)][S(S+1)-M(M-1)].\quad(10)$$

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[8] E. U. Condon and G. H. Shortley, *The Theory of Atomic Spectra* (Cambridge University Press, Cambridge, England, 1951), p. 34.

[9] W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960), p. 71.

To the order of perturbation theory used these are the only transitions that can be observed in the parallel-field case for the Hamiltonian (1) assuming $A=B$. Anisotropy in the hyperfine splitting, cubic-field terms in the Hamiltonian, and interactions between neighboring ions could give additional transitions.

III. EXPERIMENTAL

A. Sample Preparation

Single crystals in zinc perchlorate may be grown by slow evaporation from aqueous solution. The crystals grow in long needles with a hexagonal cross section. Our procedure was to prepare a nearly saturated solution of the zinc and manganese salts, mixed in the appropriate proportions, and to allow this solution to evaporate in a Pyrex dish at room temperature. The dish was covered with Saran wrap which had several holes cut into it of approximately 0.1 cm^2 area. After crystallization began the dish was covered with Saran wrap with only a small tear in it, thus severely limiting the evaporation rate. With this technique the long needles grew in breadth, and it was possible to grow single crystals with a cross section of approximately 0.05 cm^2. That the needle axis is the crystallographic c axis was confirmed by observing the ESR spectra, with **H** in the plane perpendicular to this axis, as a function of rotation in the plane. There was no appreciable variation in the spectra, indicating also that E is negligible in (1).

B. Fine Structure

The fine structure of zinc perchlorate with 0.1% by weight of manganese perchlorate was studied at room temperature in the usual configuration, rf field perpendicular to the dc field. A standard superhetrodyne spectrometer operating at 9.7 GHz was used for all measurements. In Fig. 1 the position of the midpoint of the central hyperfine lines for each $\Delta M=1$ transition is plotted along with the theoretical curves (4). The curves are normalized at $\theta=0°$ and the value of the parameters are $D=127\pm1$ G and $a=9.5\pm1.0$ G. A and B are obtained from the average hyperfine splitting at $\theta=0°$ and $\theta=90°$, respectively, and are $A=-95.8\pm 0.3$ G and $B=96.1\pm0.3$ G. The value of g is obtained from a diphenylpicrylhydrazyl (DPPH) marker as $g=1.999\pm0.001$. The signs of the parameters are relative.

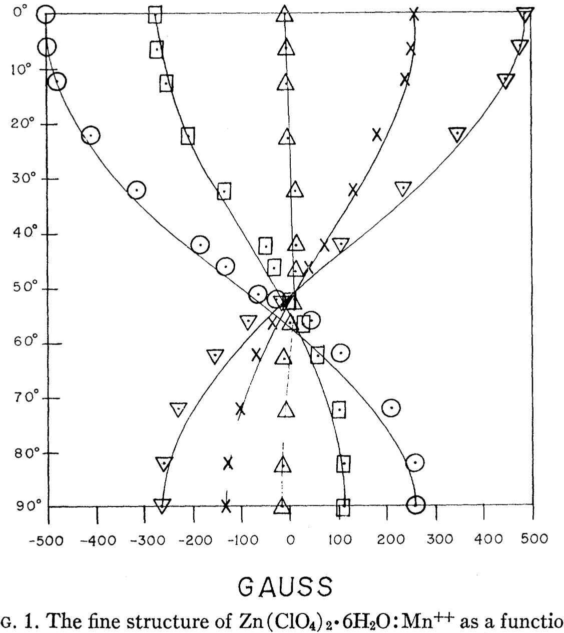

FIG. 1. The fine structure of $Zn(ClO_4)_2 \cdot 6H_2O:Mn^{++}$ as a function of θ. The magnetic field is measured relative to $H_0=(g\beta)^{-1}h\nu$.

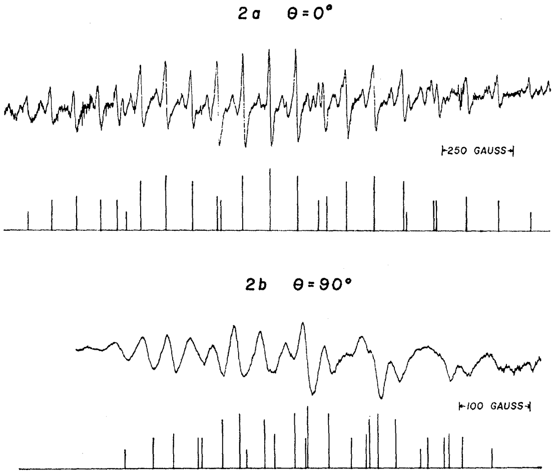

FIG. 2. Two spectra of $Zn(ClO_4)_2 \cdot 6H_2O:Mn^{++}$ obtained in the parallel-field configuration compared with the theoretical predictions of Eqs. (4), (6), and (9). The upper figure (a) is for $\theta=0°$, the lower (b) for $\theta=90°$.

C. Parallel-Field Case Spectra

Figure 2 shows the spectra of Mn^{++} in zinc perchlorate for the case when the microwave and static magnetic fields are parallel. Figure 2(a) is for $\theta=0°$ and a 0.1 wt% manganese perchlorate sample, and Fig. 2(b) is for $\theta=90°$ and 1 wt% manganese. A less dilute sample was used at $\theta=90°$ because geometrical restrictions make it inconvenient to use large crystals at this orientation. Shown with the experimental spectra are the theoretical line positions and relative intensities as calculated from (4), (6), and (9). Extra lines in the spectra are due to the "allowed" transitions $\Delta M=1$ and $\Delta m=0$, which occur because of a small residual component of the static field perpendicular to the microwave field. A comparison with the perpendicular case spectra for $\theta=0°$ and $\theta=90°$ shows that for $\theta=0°$ the parallel-field spectrum encompasses a larger range than does the perpendicular-field spectrum and that for $\theta=90°$ the reverse is true. From the discussion of Sec. II B it is thus clear that both D and A and D and B have opposite signs. This is consistent with the fact that at $\theta=0°$ the hyperfine splitting increases from series to series with increasing field strength, whereas at $\theta=90°$ it decreases.[2]

From the spectrum for $\theta=0°$ in the parallel case a simple determination of g can be made. The method entails a comparison of the position of the DPPH marker with the line $M=\frac{1}{2}\leftrightarrow M=-\frac{1}{2}$, $m=-\frac{1}{2}\leftrightarrow m=\frac{1}{2}$, which occurs ar $H=H_0-(17/2)A^2H_3^{-1}$.

If H_x denotes the position of the marker and g_x its g value then a measurement of $H-H_x$ allows us to calculate g from the equation

$$(H_0-H_x)/H_0=(g_x-g)/g_x.$$

This procedure gives the same g value as in Sec. III B.

The half-field spectrum ($\Delta M=2$) at $\theta=90°$ has also been investigated and the results are consistent with (10).

IV. DISCUSSION

The ESR spectrum of dilute manganese perchlorate is similar to that of dilute manganese fluosilicate.[2] An essential difference occurs in the relative signs of the parameters D, A, B, and a; whereas Bleaney and Ingram find D, A, B negative, and a positive in the fluosilicate, we find only relative signs; either D and a positive, A and B negative, or D and a negative and A and B positive. The magnitudes of the cubic-field parameter a, the hyperfine constants A and B, and the magnetogyric ratio g are virtually the same in both salts; the magnitude of D, however, appears somewhat smaller in the perchlorate.

A study of the parallel-field case spectra is useful as a check on the values of the parameters, especially g, and as discussed above gives a determination of the sign of D relative to A and B that is independent of second-order effects in the spectra. In general, the study of forbidden transitions can be expected to give information as to the relative importance of the various interactions in the Hamiltonian of the system. The parallel-field case is expecially well adapted to these studies because of the simplicity of the expression for the transition probabilities.

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Mössbauer Effect in Europium Alloys

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The Mössbauer effect of the 21.7-keV γ line of Eu^{151} has been employed to study the isomer shifts and the magnetic fields in Eu–Yb and Eu–Ba alloys. From these measurements the conduction-electron contribution to the hyperfine field in Eu metal due to the ion's own $4f$ electrons and due to the neighboring ions has been deduced. In addition, an explanation for the apparent lack of conduction-electron contribution to the hyperfine field in metallic Gd is offered.

1. INTRODUCTION

In magnetically ordered metals the exchange interactions between the ions take place via the conduction-electrons (CE).[1] These CE have in all cases at least some s character and thus penetrate into the atom. They have a finite density at the nucleus and their polarization gives rise to a hyperfine interaction with the nuclear moment via the Fermi-contact interaction. It is thus apparent that nuclear resonance methods are very suited for the study of the properties of the CE. NMR experiments measure the hyperfine field at the nucleus in the ordered state and from the Knight shift, the magnitude of the interaction between the electronic spins and the CE can be deduced. Mössbauer-effect studies are equally suited for the investigation of CE properties, since they measure simultaneously the charge (proportional to the isomer shift) and the spin density (proportional to the hyperfine field) at the nucleus.

Considerable information about transition metal and alloy exchange interactions[1] has been obtained by these studies. The experiments of Wertheim *et al.*,[2] Stearns and Wilson,[3] and Stearns[4] showed that an iron ion exhibits different fields when some of its neighbors are replaced by other ions. The interpretation of the experimental results is still uncertain. Whereas Wertheim *et al.*[1] consider the direct exchange between the ions to be the most important feature, Stearns[3,4] attributed these effects to the conduction electrons. By a careful analysis of the line shape of

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[1] For a survey in this field, see R. E. Watson, *Conduction Electron Charge and Spin Density Effects Due to Impurities and Local Moments in Metals in Hyperfine Interactions*, edited by A. J. Freeman and R. B. Frankel (Academic Press Inc., New York, 1967).

[2] G. K. Wertheim, V. Jaccarino, J. H. Wernick, and D. N. E. Buchanan, Phys. Rev. Letters **12**, 24 (1964).

[3] M. B. Stearns and S. S. Wilson, Phys. Rev. Letters **13**, 313 (1964).

[4] M. B. Stearns, Phys. Rev. **147**, 439 (1966).