(with a large CW rf field on). The changes of magnitude of the Zeeman and secular dipolar terms of the Hamiltonian by factors of, respectively, $\mathbf{H}_{\text{eff}}/\mathbf{H}_0$ and $-1/2$ just cause irrelevant changes in the corresponding spin temperatures. Turning the CW rf field off after a time τ and immediately applying a 90° pulse around the Y axis result in similar rotations of the state and Hamiltonian of the spin system around the Y axis by, respectively, $+90°$ and $-90°$.

We have performed experiments C and D with a rotating component $\mathbf{H}_1$ of the rf field of about 25 G (the local fields in CaF_2 are of the order of a few gauss) and durations τ between 20 μsec and 13 msec (the free precession signal of CaF_2 dies out in about 50 μsec.) Our results are in complete agreement with the above predictions: The "90°–long pulse–90°" irradiation decreases the magnitude of the observed free precession signals by less than 13%; it changes the sign of the Zeeman signal and not that of the dipolar signal; the duration τ of the rf irradiation has no influence on the final state of the spin system; no mixing between Zeeman and dipolar energy in the rotating frame is observed.

Pulse sequence E was used to measure the magnitude of the rf magnetic fields from the frequency of the free precession in the effective field.

Experiment F is the rotating-frame analog of the Strombotne-Hahn experiment.[10] In the rotating frame, the spin system is first prepared in a state of order in zero effective field (dipolar order in the laboratory frame). A constant effective field is then turned on suddenly and, exactly as in the laboratory-frame experiment, the energy oscillates for a time of the order of T_2 back and forth between the Zeeman and the dipolar terms of the effective Hamiltonian, at about twice the Larmor frequency ω_1 in the effective field (the oscillations at ω_1 are absent in the case of strong irradiation at the exact NMR frequency ω_0). The sudden suppression of the effective field after a time τ destroys this Zeeman energy, but does not change the dipolar energy which then rearranges itself in the absence of rf field and is measured later on by means of the 45° information pulse. A straightforward calculation (see Ref. 8), using the hypothesis of two independent spin temperatures in the rotating frame, predicts that the laboratory-frame dipolar order recovered after a long and strong irradiation should be $\frac{1}{4}$ of the initial dipolar order, in good agreement with our experimental results.

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Electron-Spin-Resonance Spectrum of Mn^{2+} in β-Ga_2O_3*

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The electron-spin-resonance spectrum of Mn^{2+} has been investigated in monoclinic β-Ga_2O_3 at 24 kMc/sec. It was found that the spectrum consists of a set of lines corresponding to a single type of environment. This spectrum (including the fine and $\Delta m=0$ hyperfine structure) is satisfactorily described by the spin Hamiltonian for Mn^{2+} in a rhombic crystal field with the following derived constants: $A_z=-87.7\pm0.2$ G; $A_y=-85.6\pm0.2$ G; $g_z=2.002$; $g_y=2.007$; $D=545.0$ G; $E=124.3$ G. The y crystal-field axis is along the monoclinic axis (b) and the z crystal-field axis makes an angle of 18° with the c crystal axis ($a>c$). Forbidden $\Delta m=\pm1$, ±2 hyperfine transitions were also observed. From the separations between the $\Delta m=\pm1$ doublets, a value of $Q'=+0.9\pm0.2$ G was obtained. On the basis of the axial crystal fields inferred from the measured values of Q' in β-Ga_2O_3 and in other oxide materials, it appears that the calculated crystal-field contribution to the D parameter of Mn^{2+} does not explain the experimental results.

INTRODUCTION

THE origin of the ground-state splitting of the $3d^5$–$^6S_{5/2}$ ions (Mn^{2+} and Fe^{3+}) has been the object of a considerable number of theoretical and experimental investigations. Such investigations have indicated that these splittings may arise from the combined action of the spin-orbit interaction (W_{so}) and the crystal field,[1–5] or from the intra-ionic spin-spin interaction (W_{ss}) and the crystal field,[2,4–6] or from overlap and covalency between the S-state cation and its

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ligands combined with the W_{s0} or W_{ss} terms.[7] However, the degree to which these various mechanisms or their combinations apply and thus the origins of the various crystal-field terms in the spin Hamiltonian have not been determined.

Additional information on the origin of the axial crystal-field parameter (D) in the Mn^{2+} spin Hamiltonian may be obtained from measurements of both D and the nuclear electric-quadrupole-interaction parameter (Q') in a series of materials. Such measurements of Q' provide information on the axial crystal fields that are utilized in crystal field calculations of D.

In the present paper, the electron spin resonance (ESR) spectrum of Mn^{2+} in β-Ga_2O_3 is investigated. Values of D and Q' as well as other spin-Hamiltonian parameters are obtained from the measurements, and an analysis is given of the crystal-field contribution to the D parameter on the basis of the axial crystal fields inferred from the measured values of Q' in β-Ga_2O_3, Al_2O_3,[8] ZnO,[9] and $CaWO_4$.[10] β-Ga_2O_3 possesses a monoclinic crystal structure (the most probable space group being $C_{2h}^3 - C2/m$)[11,12] and, among other things, is of interest because the cation sites have large distortions from cubic symmetry making possible the observation of a nuclear electric quadrupole interaction.

THEORY

The ESR measurements on β-Ga_2O_3 were analyzed using the spin Hamiltonian appropriate for Mn^{2+} in a rhombic crystalline electric field[13]

$$\begin{aligned}\mathcal{H}=\beta(g_xH_xS_x+g_yH_yS_y+g_zH_zS_z)&\\ +D[S_z^2-\tfrac{1}{3}S(S+1)]+E(S_x^2-S_y^2)&\\ +\text{Quartic Terms }(a,F)+A_xS_xI_x&\\ +A_yS_yI_y+A_zS_zI_z-g_N\beta_N\mathbf{H}\cdot\mathbf{I}&\\ +Q'[I_z^2-\tfrac{1}{3}I(I+1)]+Q''(I_x^2-I_y^2)\,,&\qquad(1)\end{aligned}$$

where

$$Q'=3eqQ/4I(2I-1)\quad\text{and}\quad Q''=eq\eta Q/4I(2I-1)\qquad(2)$$

are the axial and rhombic part of the nuclear quadrupole interaction, respectively, Q is the nuclear electric quadrupole moment, and η is the asymmetry parameter in the field-gradient tensor. The quantity q in Eqs. (2) is related to the quadratic axial crystal electric-potential coefficient A_2^0 by the equation

$$q=(1-\gamma_\infty)(5/\pi)^{1/2}A_2^0\,,\qquad(3)$$

where γ_∞ is the Sternheimer antishielding factor.

For measurements with H parallel to z, the eigenvalues (to second order) of Eq. (1) are given by

$$\begin{aligned}E_{M,m}={}&g_z\beta HM+D[M^2-\tfrac{1}{3}S(S+1)]+A_zMm+Q'[m^2-\tfrac{1}{3}I(I+1)]-g_N\beta_NHm\\ &+\frac{A^2}{4}\left[\frac{[R'-m(m+1)][R-M(M-1)]}{H+D(2M-1)+A(m-M+1)}-\frac{[R'-m(m-1)][R-M(M+1)]}{H+D(2M+1)+A(m-M-1)}\right]\\ &+\frac{E^2}{8}\left[\frac{[R-M(M-1)][R-(M-1)(M-2)]}{H+2D(M-1)+Am}-\frac{[R-M(M+1)][R-(M+1)(M+2)]}{H+2D(M+1)+Am}\right]\\ &+\text{ Quartic terms}\,,\qquad(4)\end{aligned}$$

where $R'=I(I+1)$ and $R=S(S+1)$. Here the hyperfine constant A is assumed isotropic for the second-order terms. The eigenvalues for H parallel to the y crystal-field axis are obtained by replacing in Eq. (4) the quantities g_z, A_z, Q', D and E by g_y, A_y, $\frac{1}{2}(-Q'-3Q'')$, $\frac{1}{2}(-D-3E)$, and $\frac{1}{2}(D-E)$, respectively. Using Eq. (4) with appropriate expansions of the second-order terms, one obtains the following relation for the resonant values of H corresponding to $M,m \leftrightarrow M-1,m$ transitions:

$$\begin{aligned}H_{M,m}={}&H_0-(2M-1)D-A_zm-(A^2/2H)[I(I+1)-m^2+(2M-1)m]\\ &+(A^2D/2H^2)\{3[I(I+1)-m^2](2M-1)-m[2S(S+1)+3(-2M^2+2M-1)]\}\\ &-(A^3/2H^2)\{[2I(I+1)-3m^2](2M-1)+m[-S(S+1)-I(I+1)+3M^2-3M+m^2+2]\}\\ &-(E^2/2H)[2S(S+1)-6M^2+6M-3]\\ &+(E^2D/H^2)\{(2M-1)[3S(S+1)-5M^2+5M-6]\}\\ &+(E^2Am/2H^2)[2S(S+1)-6M^2+6M-3]\,,\qquad(5)\end{aligned}$$

where $H_0=h\nu/g\beta$ and the spin-Hamiltonian parameters are now divided by $g\beta$. In regard to the third-order terms in Eq. (5), the A^2D and A^3 are in agreement with those obtained by Schneider and Sircar.[14] The E^2D and E^2A terms have been calculated in the present work.

On the basis of pure-crystal field theory, Watanabe[2] has shown that the D-parameter for Mn^{2+} is related to

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the A_2^0 coefficient as follows:

$$D=-9.90\Delta^2\times10^{-10}+3.62M'\Delta\times10^{-5}\ \mathrm{cm}^{-1}\,, \qquad (6)$$

where $\Delta=\frac{1}{4}(5/\pi)^{1/2}\langle r^2\rangle A_2^0$ and $M'\approx0.2$. The first term in Eq. (6) is due to a fourth-order process quadratic in the axial crystal potential $[V_{\mathrm{ax}}=A_2^0r^2Y_2^0(\theta,\varphi)]$ and quadratic in W_{so} and the second term results from a second-order process linear in V_{ax} and linear in W_{ss}. The quantity M' represents the radial part of a matrix element of W_{ss} between the ground state and the $3d^44s$ excited state in Mn^{2+}. The two terms in Eq. (6) have been recalculated by Germanier *et al.*[4] who obtained two additional terms, one being due to a process linear in V_{ax} and cubic in W_{so} and a second process linear in V_{ax}, W_{ss}, and W_{so}. Recently, Leushin[5] has performed another crystal field calculation of the W_{ss} and W_{so} contributions to D. Using a procedure in which the strong cubic field and electron electrostatic interactions are taken into account in the same order of perturbation, he found that the ground-state splitting of the $^6S_{5/2}$ multiplet when calculated this way is almost the same as that obtained by Watanabe's procedure. In all these calculations, D is linearly and/or quadratically dependent on A_2^0. From Eqs. (2) and (3), it is seen that Q' is linearly dependent on A_2^0. Thus, one may obtain the value of A_2^0 from Q' measurements on a particular material and use this value to predict the crystal field contribution to D in the same material.

The Q' parameter can be readily obtained from measurements of the separations of the forbidden $\Delta m=\pm1$ doublets which occur between the $M=\frac{1}{2}\leftrightarrow-\frac{1}{2}$, $\Delta m=0$ transitions as was done previously for Mn^{2+} in Al_2O_3[8] and ZnO.[9] The separation between these doublets is given by

$$\begin{aligned}\Delta H_d&=H_{M=\frac{1}{2},\,m+1\,\rightarrow\,M=-\frac{1}{2},m}-H_{M=\frac{1}{2},\,m\,\rightarrow\,M=-\frac{1}{2},\,m+1}\\&=17A^2/2H+(2g_N\beta_N/g\beta)H-\{(Q'-4A^2D/H^2)\\&\quad\times(3\cos^2\theta-1)+3(Q''-4A^2E/H^2)\\&\quad\times\sin^2\theta\cos2\varphi+25A^3/2H^2\}(2m+1)\,, \qquad (7)\end{aligned}$$

where θ is the angle that the z crystal-field axis makes with H and φ is the angle between the x crystal-field axis and the projection of H on the x-y plane.

CRYSTALLOGRAPHY AND EXPERIMENTAL METHODS

Geller[12] has shown that the unit cell of β-Ga_2O_3 contains four molecules of Ga_2O_3 and that the ions are located in five sets of special positions $4i$: $(000,\ \frac{1}{2}\frac{1}{2}0$ $\pm(x0z)$, each site having an m point symmetry. This mirror plane is perpendicular to the monoclinic b axis. According to Geller, the cation sites are either tetrahedrally or octahedrally coordinated, the former sites having considerably smaller dimensions than the latter. The a and c crystal axes are perpendicular to the monoclinic axis and the angle (β) between the a and c axes is 103.7°.

The ESR measurements were made on β-Ga_2O_3 single crystals containing about 0.05 wt.%Mn. These crystals were synthesized using the flux method.[15] A combined PbO and PbF_2 flux and a lowering rate of 1.5°C per hour from 1250°C were used in the crystal synthesis. Although many of the crystals were twinned, several untwinned crystals were found, and these were used for the ESR measurements.

A 24-kMc spectrometer described earlier[8] was used in ESR measurements. Except for the forbidden hyperfine doublet spacings which were measured at 77°K, all the ESR data were obtained at room temperature.

RESULTS AND DISCUSSION

Measurements of the angular dependence of the $\Delta M=1$, $\Delta m=0$, ±1, ±2 ESR transitions in Mn^{2+} showed that the spectrum consists of a single set of lines corresponding to one type of environment. Since the octahedral sites are considerably larger than the tetrahedral sites in β-Ga_2O_3, it is probable that this spectrum is due to Mn^{2+} ions in octahedral sites. The earlier measurements[16,17] on β-Ga_2O_3 doped with Cr^{3+} indicate that the Cr^{3+} ions reside in the octahedral sites. In contrast with the results on Mn^{2+} and Cr^{3+}, our measurements on the Fe^{3+} in β-Ga_2O_3 (to be published) show that two types of sites are occupied by the Fe^{3+}.

From measurements of the Mn^{2+} spectra with H in the a-c, b-c, and b-a crystal planes, it was found that the y crystal-field axis is along the b crystal axis (i.e., the monoclinic axis) and that the z crystal-field axis makes an angle of 18° with respect to the c crystal axis as shown in Fig. 1. The spectrum for H along the z crystal-field axis is shown in Fig. 2. The transitions in this spectrum are the allowed $\Delta M=1$, $\Delta m=0$ transitions. From a comparison of the relative intensities of the transitions in the five hyperfine sextets shown in this figure, it was found that the inhomogeneous broadening in the $M=\pm\frac{5}{2}\leftrightarrow\pm\frac{3}{2}$ and $M=\pm\frac{3}{2}\leftrightarrow\pm\frac{1}{2}$ sextets was not significantly larger than in the central $M=\frac{1}{2}\leftrightarrow-\frac{1}{2}$ transitions, indicating high crystalline perfection. The extra lines shown in the vicinity of the $M=\frac{5}{2}\leftrightarrow\frac{3}{2}$,

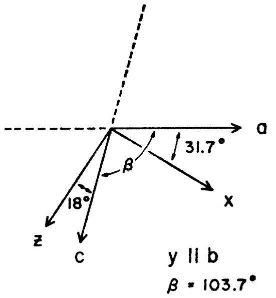

FIG. 1. Orientation of the crystal field axes (x,y,z) with respect to the crystallographic axes (a,b,c) for Mn^{2+} in β-Ga_2O_3. The b and y axes are perpendicular to the plane of the figure and β is the angle between the a and c axes.

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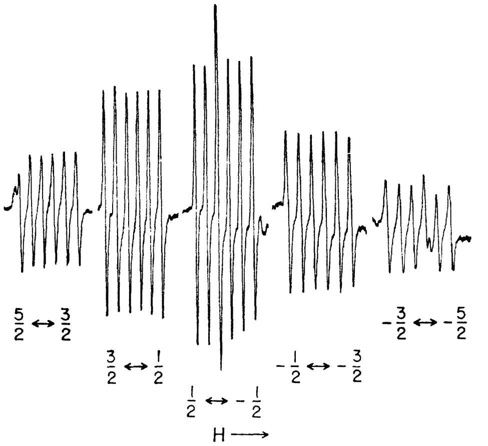

FIG. 2. Electron-spin-resonance spectrum at 300°K of Mn^{2+} in β-Ga_2O_3 with the magnetic field H parallel to the z crystal-field axis. Values of M are given for the initial and final states.

$M=\frac{1}{2}\leftrightarrow-\frac{1}{2}$ and $M=-\frac{3}{2}\leftrightarrow-\frac{5}{2}$ sextets are due to a trace of Fe^{3+} in the crystals.

Measurements of the spectra with H along the z and y crystal-field axes yielded [with the aid of Eq. (5)] the following values of the spin-Hamiltonian parameters:

$$A_z=-87.7\pm0.2\ \text{G};\quad A_y=-85.6\pm0.2\ \text{G};\quad g_z=2.002;$$
$$g_y=2.007;\quad D=545.0\ \text{G};\quad E=124.3\ \text{G}.$$

Here the A parameters are assumed to be negative because in all materials where the sign has been determined, the A's were found to be negative.

From measurements of the unequal separations between the forbidden $\Delta m=\pm1$ doublets (those occurring between the $M=\frac{1}{2}\leftrightarrow-\frac{1}{2}$, $\Delta m=0$ transitions), a value of $Q'=+0.9\pm0.2$ G was obtained using Eq. (7). For this measurement H was directed in the z-y plane at an angle of 7° from the z axis. It was necessary to make measurements at this small angle in order that the perturbation calculations used to obtain Eq. (7) are sufficiently convergent. When H was oriented at large angles with respect to z, it was necessary to take into account the large deviation of the orientation of the nuclear magnetic moment from that of the applied magnetic field in order to obtain agreement with the experimental line positions. For example, when H was applied 45° from the z direction, the nuclear moment was calculated to be oriented at an angle of approximately 30° with respect to H. Bir and Sochava[18] found that the large deviation of the direction of the nuclear moment from H had to be included in their intensity calculations also in order to obtain good agreement with the ESR experimental results on Mn^{2+} in $SrCl_2$.

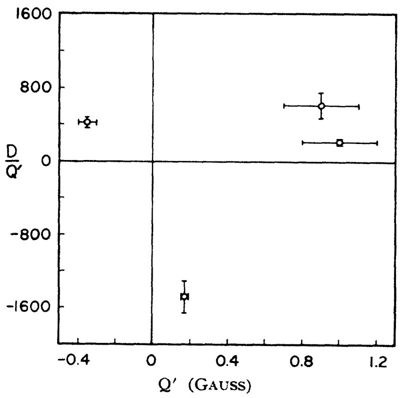

FIG. 3. Absence of linear dependence of D/Q' on Q'.

A comparison of the values of A, D, Q' and D/Q' for Mn^{2+} in $CaWO_4$, β-Ga_2O_3, Al_2O_3 and ZnO is given in Table I. The materials are listed in the order of increasing covalency which is indicated[19] by the values of A shown in the second column. From a crystal-field calculation of the form of Eq. (6), it is seen with the use of Eqs. (2) and (3) that D/Q' is linearly related to Q'. However, it appears from Fig. 3 that such a relationship is not consistent with the experimental results.[20] A possible explanation of these results may be obtained from overlap and/or covalent mechanisms. Kondo[7] has calculated overlap and covalent contributions to D resulting from W_{so} and W_{ss}. His results show that D should be of the form $D\propto(S^2-\lambda^2)$, where S is the overlap integral between the Mn^{2+} $3d$ orbital and the ligand orbital, and λ is the degree of covalency. Since the axial crystal field is not involved explicitly in this model, such a model could explain the experimental results on the D parameter.

TABLE I. Comparison of experimental values of A, D, Q' and D/Q' for Mn^{2+} in various host lattices.

Host lattice	A (G)	D (G)	Q' (G)	D/Q'
$CaWO_4$	−95.24[a]	−147.4[a,b]	−0.35±0.05[b]	+421±60
β-Ga_2O_3	−87.7[c]	+545[c]	+0.9 ±0.2[c]	+606±135
Al_2O_3	−85.2[d,e]	+207[d,e]	+1.0 ±0.2[e]	+207±41
ZnO	−79.3[f]	−252.7[f]	+0.17±0.02[f]	−1486±175

[a] C. F. Hempstead and K. D. Bowers, Phys. Rev. **118**, 131 (1960).
[b] See Ref. 10.
[c] Present work.
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[e] See Ref. 8.
[f] See Ref. 9.

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