

Electron-Nuclear Double Resonance of  $Mn^{2+}$  in  $Al_2O_3$ 

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(Received 5 August 1965)

The electron paramagnetic resonance and electron-nuclear double resonance spectra of  $Mn^{2+}$  in  $Al_2O_3$  have been examined at 4.2°K. The spin-Hamiltonian parameters are  $g_{||} = 2.0025 \pm 0.0006$ ,  $g_{\perp} = 2.0010 \pm 0.002$ ,  $D = +235.5 \pm 0.4$  G,  $a-F = +24.7 \pm 0.6$  G,  $A = -240.42 \pm 0.05$  Mc/sec,  $B = -234.79 \pm 0.35$  Mc/sec, and  $Q' = +2.686 \pm 0.013$  Mc/sec. The quadrupole parameter  $Q'$  agrees with the value deduced from analysis of the "forbidden"  $Mn^{2+}$  spectrum and confirms the validity of that analysis. The axial crystal-field parameter increased significantly from the room-temperature value, and its absolute sign was shown to be positive.

## INTRODUCTION

IN recent years there has been a considerable amount of interest aroused by the observation of so-called "forbidden" transition lines<sup>1</sup> in the electron paramagnetic resonance (EPR) spectra of a number of materials. Because of the large electronic and nuclear spins of divalent manganese ( $S=I=\frac{5}{2}$ ), these transitions are especially prominent with respect to normal allowed transitions.<sup>1</sup> The "forbidden" transitions involve a change in the nuclear quantum number ( $\Delta m \neq 0$ ) and hence their position depends on the nuclear Zeeman and quadrupole interactions in contrast to the allowed ( $\Delta m = 0$ ) transitions. This fact has been used by a number of authors to obtain information about the size of the quadrupole interaction of  $Mn^{2+}$  in a variety of crystal hosts.<sup>2-8</sup> Because of the small size of this interaction in comparison with other terms in the spin Hamiltonian, it has been necessary to carry the perturbation calculations to third order to evaluate terms which give shifts of the same order of magnitude in the line positions. For  $Mn^{2+}$  in  $Al_2O_3$ , the size of the quadrupole interaction parameter  $Q'$  was large enough to measure with some accuracy at  $K$ -band frequencies.<sup>3</sup> The value found contrasted strongly with the much smaller values of  $Q'$  found for the  $3d^3$  isoelectronic series  $V^{2+}$ ,  $Cr^{3+}$ , and  $Mn^{4+}$  in  $Al_2O_3$ .<sup>9</sup> These facts prompted us to undertake an electron-nuclear double resonance (ENDOR) study of  $Mn^{2+}$ -doped  $Al_2O_3$ . Succinctly stated, our experimental results, although much more accurate, confirm the value obtained<sup>3,4</sup> from an analysis of the "forbidden" lines. In addition, accurate values of the hyperfine coupling constants are reported.

<sup>1</sup> B. Bleaney and R. S. Rubins, Proc. Phys. Soc. (London) **77**, 103 (1961); **78**, 778 (1961).

<sup>2</sup> H. G. Andresen, J. Chem. Phys. **35**, 1090 (1961).

<sup>3</sup> V. J. Folen, Phys. Rev. **125**, 1581 (1962).

<sup>4</sup> J. Schneider and S. R. Sircar, Z. Naturforsch. **17a**, 651 (1962).

<sup>5</sup> F. Waldner, Helv. Phys. Acta **35**, 756 (1962).

<sup>6</sup> M. Odehnal, Czech. J. Phys. **B13**, 566 (1963).

<sup>7</sup> R. W. Kedzie, Bull. Am. Phys. Soc. **8**, 259 (1963).

<sup>8</sup> B. C. Cavenett, Proc. Phys. Soc. (London) **84**, 1 (1964).

<sup>9</sup> N. Laurance and J. Lambe, Phys. Rev. **132**, 1029 (1963).

## EXPERIMENTAL

The samples used in this investigation were grown from a  $PbO$ - $PbF_2$  flux doped with Mn impurity and were made available to us by V. J. Folen. The mole fraction of  $Mn^{2+}$  in the samples was approximately  $2 \times 10^{-4}$ . Optical absorption studies showed the presence<sup>10</sup> of  $Mn^{3+}$  in addition to  $Mn^{2+}$ . This is to be expected since  $Mn^{2+}$ , which is substitutional<sup>11</sup> for  $Al^{3+}$ , has an improper valence for its location and no attempt was made to charge compensate the crystal as grown. The problem of charge compensation in these crystals has been discussed previously,<sup>11</sup> but it was not possible to decide whether or not the compensation was local. An EPR spectrum of  $Al_2O_3:Mn^{2+}$  at room temperature and  $X$ -band frequency ( $\approx 9400$  Mc/sec) is shown in Fig. 1. The noticeable broadening of the outer hyperfine sets causes the derivative peaks to fail to have the expected 5:8:9:8:5 ratios. This can be attributed to a spatial variation in the value of the spin Hamiltonian parameter  $D$  within the crystal. Using the expressions of Feher<sup>12</sup> we find that the rms deviations of  $D$  from the average value is 1 to 2% for typical crystals. Since the amount of variation changes somewhat from crystal to

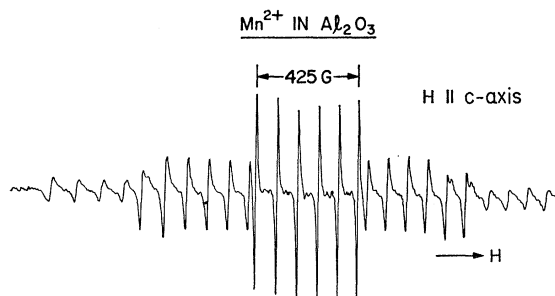


FIG. 1. EPR spectrum of  $Mn^{2+}$  in  $Al_2O_3$  at room temperature and  $X$ -band frequency ( $\approx 9400$  Mc/sec).

<sup>10</sup> H. A. Weakliem and D. S. McClure, J. Appl. Phys. Suppl. **33**, 347 (1962); D. S. McClure, J. Chem. Phys. **36**, 2757 (1962).

<sup>11</sup> J. J. Krebs, Phys. Rev. **135**, A396 (1964).

<sup>12</sup> E. R. Feher, Phys. Rev. **136**, A145 (1964).

TABLE I. Spin Hamiltonian parameters for  $Mn^{2+}$  in  $Al_2O_3$ .

	4.2°K	300°K <sup>a</sup>
$g_{11}$	$2.0025 \pm 0.0006$	$2.0028 \pm 0.001$
$g_{\perp}$	$2.0010 \pm 0.002$	$2.0019 \pm 0.002$
$D(G)$	$+235.5 \pm 0.4$	$+207.3 \pm 1.0$
$(a-F)(G)$	$+24.7 \pm 0.6$	$+23.7 \pm 0.5$
$A(G)$	$-85.7 \pm 0.2$	$-85.2 \pm 0.6$
$B(G)$	$-84.0 \pm 0.5$	$-83.5 \pm 0.6$

<sup>a</sup> See Ref. 3.

crystal, the effect may well be due to charge-compensating centers which are some distance away from the  $Mn^{2+}$  ion.

ENDOR data were taken at  $X$  band and  $Ku$  band (17 000 Mc/sec) at 4.2°K. However, only the  $Ku$ -band data were used in the analysis since for that case the convergence of the perturbation expressions is significantly better. ENDOR transitions were obtained on each of the EPR transitions shown in Fig. 1 with the magnetic field parallel to the  $c$  axis ( $\theta=0$ ) and were also obtained on the  $\frac{1}{2} \leftrightarrow -\frac{1}{2}$  EPR transitions with the magnetic field perpendicular to the  $c$  axis ( $\theta=90^\circ$ ). These latter data were taken in order to obtain an accurate value of the hyperfine constant  $B$ . The error in a typical ENDOR frequency determination was  $\approx 6$  kc/sec. The  $\theta=0$  alignment was checked by noting the disappearance of the "forbidden" spectrum. A description of the spectrometer and details of the experimental technique have been given previously.<sup>9</sup>

## RESULTS

The spin Hamiltonian used to analyze the data was<sup>13</sup>

$$\begin{aligned} \mathcal{H} = & g_{11}\beta H_x S_x + g_{\perp}\beta(H_y S_x + H_z S_y) \\ & + D(S_z^2 - 35/12) + AS_z I_z + B(S_x I_x + S_y I_y) \\ & + \frac{1}{6}a(S_1^4 + S_2^4 + S_3^4 - (707/16)) + (7F/36) \\ & \times [S_z^4 - (95/14)S_z^2 + 81/16] \\ & - \gamma \mathbf{H}_0 \cdot \mathbf{I} + Q'(I_z^2 - 35/12). \quad (1) \end{aligned}$$

Since there are some changes in the parameters of the Hamiltonian between 4.2°K and room temperature, these parameters were redetermined from the EPR spectrum. The values obtained are given in Table I and compared there with Folen's<sup>3</sup> room-temperature values. By measuring the EPR spectra at liquid-helium temperature, it was possible to determine the absolute value of the axial crystal field parameter  $D$  as positive. Previous investigators<sup>3,13</sup> had inferred this by assuming that the hyperfine constant  $A$  was negative.

In evaluating the parameters  $A$ ,  $B$ , and  $Q'$ , 70 ENDOR frequencies were used. The values of the parameters were obtained by comparing the measured frequencies with energy-level perturbation expressions calculated to third order.<sup>4</sup> These perturbation expressions for  $\theta=0$  were recalculated and found to be correct

<sup>13</sup> W. Low and J. T. Suss, Phys. Rev. **119**, 132 (1960).

and they were extended to cover the  $\theta=90^\circ$  case. The results of this analysis of the ENDOR data are given in Table II. Also shown are the corresponding direct EPR determinations and the value of  $Q'$  obtained previously from the "forbidden" lines.<sup>3,4</sup>

## DISCUSSION

As is seen in Table II, the quadrupole interaction parameter as measured by the ENDOR technique is considerably more accurate than that obtained from the analysis of the "forbidden" spectra. It agrees, however, with the earlier measurement within the quoted error. From this fact, we can conclude that the analysis of the "forbidden" spectra of  $Mn^{2+}$  is capable of yielding results of reasonable accuracy for  $Q'$  in cases where third-order terms are smaller than  $Q'$ . Since we used the same perturbation expressions as were used for the analysis of the "forbidden" spectra, the reason for the improved accuracy is the much greater resolution of the ENDOR spectra. Drumheller and Rubins<sup>14</sup> have recently pointed out that there is a small contribution of order  $aB^2/H^2$  which should be taken into account in analyzing the "forbidden" spectra. However, for  $Mn^{2+}$  this term is typically one order of magnitude less than terms of the type  $AB^2/H^2$  and can normally be neglected except in work of extreme accuracy. It is important to note, however, that their work shows that the  $\Delta m = \pm 1$  lines may occur even in the case where  $D=0$  (cubic symmetry).

The quadrupole-interaction parameter  $Q'$  can be written as

$$Q' = \frac{3e^2 Q q_u (1 - \gamma_\infty)}{4I(2I - 1)}, \quad (2)$$

where  $eQ$  is the quadrupole moment of the nucleus,  $I$  is the nuclear spin,  $eq_u$  is the electric field gradient produced by the lattice, and  $\gamma_\infty$  is the antishielding factor which reflects the modification of the "bare" electric field gradient by the electrons of the ion. In addition to  $Mn^{2+}$ , the quadrupole interaction has been measured for the excited state of  $^{57}Fe^{3+}$  in  $Al_2O_3$  by the Mössbauer technique.<sup>15</sup> The values for these isoelectronic ions are shown in Table III where the nuclear-magnetic-resonance results<sup>16</sup> for  $Al^{3+}$  in  $Al_2O_3$  are also listed for

TABLE II. Quadrupole and hyperfine constants for  $Mn^{2+}$  in  $Al_2O_3$ .

	ENDOR	EPR
$Q'$ (Mc/sec)	$+2.686 \pm 0.013$	$+2.94 \pm 0.56^a$
$A$ (Mc/sec)	$-240.42 \pm 0.05$	$-240.2 \pm 0.6^b$
$B$ (Mc/sec)	$-234.79 \pm 0.35$	$-235.3 \pm 1.4^b$

<sup>a</sup> See Refs. 3 and 4.

<sup>b</sup> This work.

<sup>14</sup> J. E. Drumheller and R. S. Rubins, Phys. Rev. **133**, A1099 (1964).

<sup>15</sup> W. J. Nicholson and G. Burns, Phys. Rev. **129**, 2490 (1963).

<sup>16</sup> W. J. Veigle, A. W. Bevan, Jr., and W. H. Tanttila, J. Chem. Phys. **38**, 1596 (1963).

TABLE III. Quadrupole interaction parameters in  $Al_2O_3$ .

Ion	$e^2qQ$ (Mc/sec)	$Q$ ( $\bar{b}$ )	$1-\gamma_\infty$	$e^2q_u$ (Mc/sec $\bar{b}$ )	Ref.
$Mn^{2+}$	+35.8	+0.35	12.4	+8.3	This work, a, b
$Fe^{3+}$	11.6	+0.28	10.14	4.1	c, d, b
$Al^{3+}$	+ 2.38	+0.149	3.59	+4.4	e, f, g

<sup>a</sup> H. Walther, Z. Physik **170**, 507 (1962).

<sup>b</sup> R. M. Sternheimer, Phys. Rev. **130**, 1423 (1963).

<sup>c</sup> See Ref. 15.

<sup>d</sup> R. Ingalls, Phys. Rev. **133**, A787 (1964).

<sup>e</sup> See, Ref. 16.

<sup>f</sup> H. Lew and G. Wessel, Phys. Rev. **90**, 1 (1953).

<sup>g</sup> T. P. Das and R. Bersohn, Phys. Rev. **102**, 360 (1956).

comparison. As can be seen, the  $e^2q_u$  values for the S-state ions  $Mn^{2+}$  and  $Fe^{3+}$  agree with that for  $Al^{3+}$  within a factor of 2. This fact argues against local charge compensation of the  $Mn^{2+}$  ion.

Thus, as has been pointed out<sup>9,17</sup> the deduced  $e^2q_u$  values for  $V^{2+}$  and  $Mn^{4+}(3d^3)$  as well as for  $Cu^{3+}(3d^8)$  appear to be anomalously small. In the case of  $V^{2+}$ , the recent redetermination of the  $V^{51}$  quadrupole moment<sup>18</sup> removes the anomaly for this ion, since the new value is some 40 times smaller than the previous one<sup>19</sup> and possibly of opposite sign. As a result the value of  $|e^2q_u|$  is found to be 6.3 Mc/sec  $\bar{b}$  for this ion. In addition, the necessity of charge-compensating<sup>9</sup> the  $Mn^{4+}$ -doped  $Al_2O_3$  crystals with  $Mg^{2+}$  makes it difficult to interpret the results for this ion.<sup>20</sup> For  $Cu^{3+}$ , however, the reason for the small quadrupole interaction is still not clear.

The relatively large (13%) increase in  $D$  on going from room temperature to 4.2°K deserves comment. This change is in contrast with the behavior of iso-electronic  $Fe^{3+}$ , for which  $D$  increases<sup>21</sup> by only 2.4% on going to 4.2°K. At the same time, the magnitude of  $eq_u$  as seen by an  $Al^{3+}$  ion decreases<sup>16</sup> by 1.5% in this same temperature interval. Since the local environment is very likely distorted by the presence of the impurity ion, the importance of being able to measure both  $D$  and  $eq_u$  on the same ion is evident.<sup>15</sup> If the quadrupole interaction at 300°K were known with comparable accuracy to the low-temperature ENDOR value, it would provide

<sup>17</sup> W. E. Blumberg, J. Eisinger, and S. Geschwind, Phys. Rev. **130**, 900 (1963).

<sup>18</sup> H. Nagasawa, S. K. Takeshita, and Y. Tumono, J. Phys. Soc. Japan **19**, 764 (1964).

<sup>19</sup> H. Murakawa and T. Kamei, Phys. Rev. **92**, 325 (1953).

<sup>20</sup> M. D. Sturge, Phys. Rev. **133**, A795 (1964).

<sup>21</sup> G. S. Bogle and H. F. Symmons, Proc. Phys. Soc. (London) **73**, 531 (1959).

a means of determining the dependence of  $D$  on the axial crystal field<sup>22</sup> which is proportional to  $eq_u$ .

The size of the unshielded electric field gradient at the paramagnetic ion is of help in estimating the change in the  $D$  parameter with an applied electric field. This is because the relative change in the  $D$  parameter with applied field can be written as<sup>11</sup>

$$\frac{1}{D} \frac{\partial D}{\partial E} = \frac{1}{V_{ax}^0} \left( \frac{\partial V_{ax}}{\partial x} \right)_0 \left[ \frac{D_1 + 2D_2 V_{ax}^0}{D_1 + D_2 V_{ax}^0} \right] k, \quad (3)$$

when the predominant mechanism for the electric field effect involves the displacement of the paramagnetic ion relative to the neighboring ions. In this expression  $V_{ax}^0$  is the axial field at the normal site of the ion,  $x$  is the relative displacement along the  $c$  axis,  $k$  is the relative displacement of the ion per unit applied field, and

$$D = D_1 V_{ax} + D_2 V_{ax}^2 \quad (4)$$

for S-state ions.<sup>22</sup> It was found previously<sup>11</sup> that the experimental results for the electric field effect indicated that  $(V_{ax}^0)^{-1}(\partial V_{ax}/\partial x)_0$  is roughly 9 times as large for  $Mn^{2+}$  as for  $Fe^{3+}$ . If we assume that the electric field gradient is the dominant term in  $V_{ax}$ , then by referring to Table III we see that  $V_{ax}^0$  is twice as large for  $Mn^{2+}$  as for  $Fe^{3+}$ . This result indicates that  $(\partial V_{ax}/\partial x)_0^{Mn} \approx 18(\partial V_{ax}/\partial x)_0^{Fe}$ . This is consistent with the fact that the temperature dependence of  $D$  in  $Al_2O_3$ ,  $D^{-1}(\partial D/\partial T)$ , is some five times greater for  $Mn^{2+}$  than for  $Fe^{3+}$ . In making this comparison,  $k$  and the quantity in square brackets in (3) have been assumed to be the same for the two ions which is probably true to within a combined factor of 2. However, since the effect on the electronic charge cloud distribution of the applied electric field may also contribute to  $D^{-1}(\partial D/\partial E)$ , this factor<sup>23</sup> would also have to be taken into account to clarify the situation.

#### ACKNOWLEDGMENTS

We would like to thank V. J. Folen for making available the  $Mn^{2+}$ -doped  $Al_2O_3$  crystals grown by R. A. Becker. We are happy to thank Richard Ager for his excellent assistance in the experimental aspects of this work.

<sup>22</sup> H. Watanabe, Progr. Theoret. Phys. (Kyoto) **18**, 405 (1957).

<sup>23</sup> E. B. Royce and N. Bloembergen, Phys. Rev. **131**, 1912 (1963).