IV. HIGH TEMPERATURES

The resistivity of some of the stabilized delta phases reaches a minimum somewhere around 300° to 400°C and then increases with temperature. At these temperatures the kT spread at the top of the Fermi distribution is a substantial fraction of the width of the $5f$ band and thus, the usually omitted terms in T^4 have to be included in Eq. (2). It appears that in order to account for the observed behavior the absolute value of d^2N/dE^2 has to increase with increasing E. This can be done by slightly modifying the parabolic $N(E)$ curve proposed above. Any more detailed analysis of the behavior of resistivity at high temperature will require correlation with the thermal expansion coefficient which in many delta alloys is anomalous in this range of temperatures.

It appears thus that, at least qualitatively, the whole resistivity pattern of α and δ plutonium can be made understandable in terms of a band model. There is little doubt, however, that more detailed and especially numerical speculation as to the band shapes in plutonium can be made only with caution.[16,26] The underlying formalism, while rather simple and intuitively attractive, is based on very radical, well-known approximations. There is some hope that the band structure for delta plutonium will be sooner or later calculated in sufficient detail to verify some of the conclusions here reached. There is, unfortunately, very little hope that the same will be possible for the exceedingly complicated alpha phase in which an anomaly in the Hall constant has been recently[27] observed.

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"Forbidden" Transitions in the Paramagnetic Resonance of Mn^{++} in Al_2O_3

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"Forbidden" hyperfine transitions were observed in the electron paramagnetic resonance spectrum of divalent Mn^{55} in Al_2O_3. The intensities and positions of these lines were found to be in good agreement with theory. From measurements of the unequal separations between the $M=\frac{1}{2}\leftrightarrow-\frac{1}{2}$, $\Delta m=\pm1$ transitions in the spectrum, evidence was obtained for a nuclear electric quadrupole interaction in the S-state Mn^{++} ion.

INTRODUCTION

FORBIDDEN hyperfine transitions ($\Delta m\neq0$) have been observed in the electron paramagnetic resonance spectra of Mn^{++} in $ZnSiF_6{:}6H_2O$,[1,2] $(NH_4)_2Zn(SO_4)_2{:}6H_2O$[1], and $CaCO_3$.[3] The intensity of these transitions has been explained[2,4,5] by perturbation expressions involving the combined action of the fine structure D term and the hyperfine A term. On the basis of this theory and recently measured[6] values of the D and A parameters for Mn^{++} in Al_2O_3, "forbidden" transitions should be observable for Mn^{++} in single crystals of this material.

In the present paper, observations of the "forbidden" transitions in the paramagnetic resonance spectrum of Mn^{++} in Al_2O_3 are reported and compared with theory. From measurements of the separations between the $M=\frac{1}{2}\leftrightarrow-\frac{1}{2}$, $\Delta m=\pm1$ transitions in the spectrum, evidence is obtained for the existence of a nuclear electric quadrupole interaction in the S-state Mn^{++} ion.

THEORY

The spin Hamiltonian appropriate for an Mn^{++} ion at a trigonal cation site in Al_2O_3 is given by[7]

$$\begin{aligned}\mathcal{H}=&g\beta\mathbf{H}\cdot\mathbf{S}+D[S_z^2-\tfrac{1}{3}S(S+1)]\\&+(a/6)[S_\xi^4+S_\eta^4+S_\zeta^4-\tfrac{1}{5}S(S+1)(3S^2+3S-1)]\\&+(1/180)F[35S_z^4-30S(S+1)S_z^2+25S_z^2\\&-6S(S+1)+3S^2(S+1)^2]+AS_zI_z+B(S_xI_x+S_yI_y)\\&-\gamma\beta_N\mathbf{H}\cdot\mathbf{I}+Q'[I_z^2-\tfrac{1}{3}I(I+1)],\end{aligned}\quad(1)$$

where z is the trigonal axis and $\xi\eta\zeta$ refer to the cubic axes.

At an angle θ relative to the z axis, the energy (apart

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from fine structure terms) for a state M, m is

$$\begin{aligned}\mathcal{E}_{M,m}=&KMm+(B^2/2g\beta H)\\&\times\{-S(S+1)m+M^2m+M[I(I+1)-m^2]\}\\&-\gamma\beta_N Hm+\tfrac{1}{2}Q'(3\cos^2\theta-1)[m^2-\tfrac{1}{3}I(I+1)]\\&+(3D\sin 2\theta/4g\beta H)^2[M^2-\tfrac{1}{3}S(S+1)]^2(2Bm/M)\\&+[B^2D(3\cos^2\theta-1)/8(g\beta H)^2]\\&\times\{[S(S+1)-M(M+1)][I(I+1)-m(m-1)]\\&\times[(M+1)^2-\tfrac{1}{3}S(S+1)]+[S(S+1)-M(M-1)]\\&\times[I(I+1)-m(m+1)]\\&\times[(M-1)^2-\tfrac{1}{3}S(S+1)]\},\end{aligned}\quad(2)$$

where $K^2=A^2\cos^2\theta+B^2\sin^2\theta$. Here the second-order quadrupole terms are neglected and the approximation $A\cong K$ is used for all terms except the first. The fifth term was obtained by Bleaney and Rubins,[5] and the sixth term was calculated in an investigation of the unequal spacings between the $\Delta m=\pm1$ transitions which were found in the present measurements.

For the central ($M=\frac{1}{2}$) transitions in the spectrum one obtains from Eq. (2) the following magnetic fields which are to be added to the fine structure resonance field equations:

$\frac{1}{2},m\leftrightarrow-\frac{1}{2},m$

$$\begin{aligned}H_{m;m}'=&-Km-(B^2/2H)[35/4-m^2]\\&-32B(D\sin 2\theta/H)^2m\\&-(14/3H^2)B^2D(3\cos^2\theta-1)m,\end{aligned}\quad(3)$$

$\frac{1}{2},m+1\leftrightarrow-\frac{1}{2},m$

$$\begin{aligned}H_{m+1;m}'=&-K(m+\tfrac{1}{2})+(B^2/2H)[m(m+1)+\tfrac{1}{4}]\\&+(\gamma\beta_N/g\beta)H-16B(D\sin 2\theta/H)^2(2m+1)\\&-[(Q'/2)+(6B^2D/H^2)]\\&\times(3\cos^2\theta-1)(2m+1),\end{aligned}\quad(4)$$

$\frac{1}{2},m\leftrightarrow-\frac{1}{2},m+1$

$$\begin{aligned}H_{m;m+1}'=&-K(m+\tfrac{1}{2})+(B^2/2H)[m(m+1)-67/4]\\&-(\gamma\beta_N/g\beta)H-16B(D\sin 2\theta/H)^2(2m+1)\\&+[(Q'/2)+(4B^2D/3H^2)]\\&\times(3\cos^2\theta-1)(2m+1),\end{aligned}\quad(5)$$

where all the parameters except $(\gamma\beta_N/g\beta)$ are now in units of gauss.

The intensity of the $M,m+1\leftrightarrow M-1,m$ and $M,m\leftrightarrow M-1,m+1$ transitions relative to the $\Delta m=0$ transitions is given by[4,5]

$$\begin{aligned}&(3D\sin 2\theta/4g\beta H)^2[1+S(S+1)/3M(M-1)]^2\\&\times[I(I+1)-m^2-m].\end{aligned}\quad(6)$$

It is seen that this ratio is maximum at $\theta=45°$ and that the intensities of the $\Delta m=\pm1$ doublets are in the ratio 5:8:9:8:5 for $m=-\frac{5}{2},-\frac{3}{2},-\frac{1}{2},\frac{1}{2}$, and $\frac{3}{2}$, respectively.

EXPERIMENTAL

The Al_2O_3 single crystals, containing about 0.05 wt.% Mn, were synthesized using the flux[8] technique. A combined PbO and PbF_2 flux and a lowering rate of 1.4°C per hour from 1300°C were used in the crystal synthesis.

The single crystals were x-ray oriented on polystyrene rods with the c axis perpendicular to the rod axis, and the rods were positioned along the cylindrical axis of a TE_{011} mode cylindrical transmission cavity. This arrangement enabled rotation of the crystals in the magnetic field. A Pound stabilized klystron (operating at 24 kMc/sec) was used for the microwave power. The output of the cavity was detected with a 1N26 silicon diode, amplified in a narrow-band 1000-cps amplifier, phase detected and finally displayed as the first derivative of an absorption curve on an x-y recorder. The dc magnetic field was sinusoidally modulated at 1000 cps and was measured using proton and lithium resonances.

EXPERIMENTAL RESULTS

Measurements of the fine and hyperfine structure in the spectrum of Mn^{++} in Al_2O_3 parallel and perpendicular to the c axis yielded the following values for some of the parameters in Eq. (1): $D=+207.3\pm1$ gauss, $a-F=+23.7\pm0.5$ gauss (assuming a negative A as found in previous measurements on other single-crystal materials); $g_{\parallel}=2.0028\pm0.001$ and $g_{\perp}=2.0019\pm0.002$; $A=-85.2\pm0.6$ gauss and $B=-83.5\pm0.6$ gauss. These parameters are in very good agreement with those obtained by Low and Suss[6] for Mn^{++} in Al_2O_3.

At values of θ between 0° and 90°, doublets appeared between the $\frac{1}{2},m\leftrightarrow-\frac{1}{2},m$ transitions, as illustrated in Fig. 1 for which $\theta=10°$. The intensities of the doublets

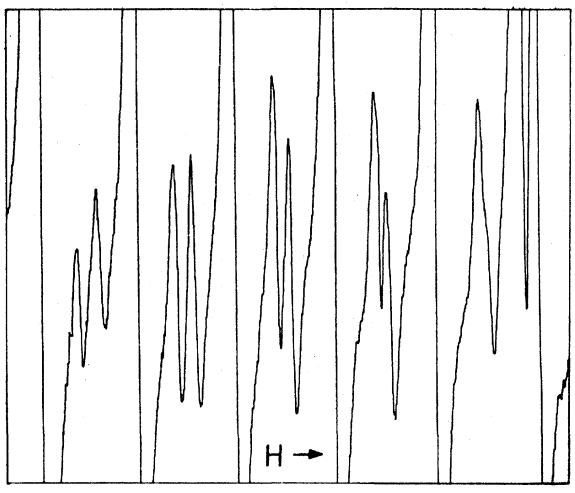

FIG. 1. "Forbidden" transition ($\Delta m=\pm1$) doublets between the $\Delta m=0$ transitions in the EPR spectrum of Al_2O_3:Mn^{++} for $\theta=10°$.

[8] J. W. Nielsen and E. F. Dearborn, J. Phys. Chem. Solids **5**, 202 (1958).

were zero for $\theta=0°$ and 90° and maximum at 45° where they were about one-third the intensity of the $\frac{1}{2}$, $m\leftrightarrow-\frac{1}{2}$, m transitions. In Fig. 1, it is seen that the doublets occur approximately in the ratios of 5:8:9:8:5. All these results are in agreement with the predictions of Eq. (6).

As shown in Fig. 1, the separations of the lines in the doublets decrease with increasing magnetic field. In the order of increasing magnetic field in this figure, the separations of the lines in each doublet are 20, 16, 13, 10, and 6 gauss, respectively. This asymmetry was found to be maximum in the vicinity of $\theta=0°$ and very small at $\theta=55°$, varying with angle approximately as $(3\cos^2\theta-1)$. The separation of the lines in a doublet is

$$\Delta H_d=(17B^2/2H)+2(\gamma\beta_N/g\beta)H -[Q'+(22B^2D/3H^2)](3\cos^2\theta-1)(2m+1), \quad (7)$$

which is obtained by subtracting Eq. (5) from Eq. (4). The first two terms in this equation give an essentially equal doublet separation, but the third term can cause the asymmetry and its angular dependence. It was found that the B^2D quantity in this term was about 7 times too small to account for the experimental results. Thus it appears that a small nuclear electric quadrupole interaction exists which amounts to $Q'=+0.7\pm0.2$ gauss. From measurements of the $(m=-\frac{1}{2})$ doublet spacing, the ratio $(\gamma\beta_N/g\beta)=0.37\pm0.02\times10^{-3}$ was deduced. This value can be compared with 0.377×10^{-3} for which $\gamma=1.387$ as determined[9] by nuclear resonance measurements.

Tables I–III show the experimental and theoretical values of the differences $H_{m+1;m'}-H_{m;m'}$ and $H_{m;m+1'}-H_{m;m'}$ for measurements at $\theta=10°$, 37°, and 45°, respectively. In Table I, comparison of the theoretical values, using $Q'=+0.7$ gauss and $Q'=0$, with experiment shows that very good agreement is obtained only when the quadrupole interaction is included.

TABLE I. Comparison of the experimental magnetic field differences $H_{m+1;m'}-H_{m;m'}$ and $H_{m;m+1'}-H_{m;m'}$ with theory using $Q'=+0.7$ gauss and $Q'=0$. $\theta=10°$.

	$H_{m+1;m'}-H_{m;m'}$ (gauss)			$H_{m;m+1'}-H_{m;m'}$ (gauss)		
m	Exp.	Theor.	Theor. ($Q'=0$)	Exp.	Theor.	Theor. ($Q'=0$)
$-\frac{5}{2}$	53	52	49	33	32	35
$-\frac{3}{2}$	51	51	49	35	34	35
$-\frac{1}{2}$	49	49	49	36	36	36
$\frac{1}{2}$	49	48	49	39	38	37
$\frac{3}{2}$	45	47	50	39	40	37

TABLE II. Comparison of the experimental magnetic field differences $H_{m+1;m'}-H_{m;m'}$ and $H_{m;m+1'}-H_{m;m'}$ with theory using $Q'=+0.7$ gauss. $\theta=37°$.

	$H_{m+1;m'}-H_{m;m'}$ (gauss)		$H_{m;m+1'}-H_{m;m'}$ (gauss)	
m	Exp.	Theor.	Exp.	Theor.
$-\frac{5}{2}$	51	51	35	34
$-\frac{3}{2}$	49	50	35	35
$-\frac{1}{2}$	50	50	37	36
$\frac{1}{2}$	51	49	39	38
$\frac{3}{2}$	50	49	39	39

TABLE III. Comparison of the experimental magnetic field differences $H_{m+1;m'}-H_{m;m'}$ and $H_{m;m+1'}-H_{m;m'}$ with theory using $Q'=+0.7$ gauss. $\theta=45°$.

	$H_{m+1;m'}-H_{m;m'}$ (gauss)		$H_{m;m+1'}-H_{m;m'}$ (gauss)	
m	Exp.	Theor.	Exp.	Theor.
$-\frac{5}{2}$	50	50	35	35
$-\frac{3}{2}$	48	50	35	36
$-\frac{1}{2}$	49	50	35	36
$\frac{1}{2}$	50	50	38	37
$\frac{3}{2}$	51	50	39	38

DISCUSSION

All of the experimental aspects of the "forbidden" $\Delta m=\pm1$ transitions in the paramagnetic resonance spectrum of Mn^{++} in Al_2O_3 are very satisfactorily described by theory. Because of the relatively large intensity of the "forbidden" transitions, it is possible that Al_2O_3:Mn^{++} can be used in the dynamical polarization of Mn nuclei.

From the experimental evidence for a nuclear electric quadrupole interaction in Mn^{++}, it appears that the crystalline electric field gradient that exists at the cation sites in Al_2O_3 distorts the spherically symmetric (^6S) electron cloud in Mn^{++}, and produces an electric field gradient at the Mn^{55} nucleus. It is reasonable to expect this distortion (providing it doesn't arise because of the valence differences between Mn^{++} and Al^{3+}) to occur for Mn^{++} in $ZnSiF_6$:$6H_2O$ which has a D parameter[1] comparable in magnitude to the D in Al_2O_3. However, Friedman and Low[2] were able to obtain good agreement between experiment and theory for the positions of the Mn^{++} "forbidden" transitions in $ZnSiF_6$:$6H_2O$ without using terms in the theory that give the $2m+1$ asymmetry [see Eq. (7)] for the "forbidden" doublet spacings. In view of Eq. (7), this could be explained by a possible cancellation of the quadrupole interaction term by the B^2D term since the D parameter in the fluorosilicate is negative, and the B^2D term ($H\approx3300$ gauss in the measurements on the fluorosilicate) is comparable with the quadrupole interaction deduced from the present measurements in Al_2O_3.

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