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Hyperfine Spectrum of Chromium 53 in Al_2O_3

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Electron nuclear double-resonance techniques were used to observe the hyperfine spectrum of Cr^{53} in Al_2O_3. Through analysis of the spectrum at zero degrees a positive value of 48.5 ± 0.1 Mc/sec was obtained for the hyperfine coupling constant and -0.85 ± 0.04 Mc/sec for the quadrupole coupling constant. From this a value of -0.03 barn was deduced for the quadrupole moment of Cr^{53}.

INTRODUCTION

THE electron nuclear double-resonance (ENDOR) techniques developed by Feher[1] permit direct measurement of transitions between hyperfine levels in paramagnetic resonance spectra. Through these techniques a great deal of new information about the interaction of paramagnetic ions with their surroundings has been obtained.[2-4] One can measure values of interaction parameters with much greater precision than through observation of hyperfine structure in paramagnetic resonance spectra.

We have carried out similar double resonance experiments with ruby ($Al_2O_3:Cr^{3+}$).[5] We were able to observe directly the hyperfine interaction of the Cr^{53} nuclei with the crystalline electric field as well as the surrounding electrons responsible for the paramagnetic resonance. From these measurements we were able to deduce a value for the sign and magnitude of the nuclear electric quadrupole moment and hyperfine coupling constant of Cr^{53}.

We also observed the interaction of the paramagnetic chromium ions with the aluminum nuclei throughout the lattice. A separate paper describing several experiments carried out to better understand the coupling mechanisms between the electron and nuclear spins has been prepared.[6] Details of our experimental procedure will be given in that paper. This paper will be mainly concerned with our measurements and analysis of the $(Cr^{53})^{3+}$ hyperfine spectrum.

All of our experiments were performed at 4.2°K with Linde pink ruby, i.e., $Al_2O_3:0.05\%\ Cr^{3+}$. The chromium ions enter the crystal substitutionally for the Al^{3+} ions. Each metal ion is surrounded by six oxygen ions which form a distorted octahedron around the metal ion site resulting in a local crystalline electric field of trigonal symmetry. The ground state of the Cr^{3+} ion is an orbital singlet with $S=\frac{3}{2}$. The $(Cr^{53})^{3+}$ ions which are 9.5% abundant have a nuclear spin of $\frac{3}{2}$. All the other stable isotopes of chromium have zero nuclear spin. The splittings in the ground state of the $(Cr^{53})^{3+}$ ions should be describable by the following Hamiltonian.[7,8]

$$\begin{aligned}H={}&g_{\parallel}\beta H_zS_z+g_{\perp}\beta[H_xS_x+H_yS_y]+D[S_z^2-\tfrac{1}{3}S(S+1)]\\&+AI_zS_z+B[S_xI_x+S_yI_y]\\&-\gamma_n\beta_n[H_xI_x+H_yI_y+H_zI_z]+Q'[I_z^2-\tfrac{1}{3}I(I+1)],\end{aligned}$$

where g is isotropic to better than 1% and equals approximately 1.99^{9-11}; $2D$ at $4.2°K=-11.447\pm0.005$ kMc/sec[12,13]; the magnitude of A is approximately 50 Mc/sec[14]; $\gamma_n\beta_n$ is 2.406 kc/gauss; and Q' is the nuclear quadrupole interaction constant. The above Hamiltonian neglects lattice distortions and interactions with the Al^{27} nuclei. Also, additional terms related to possible anisotropic nuclear g values have been neglected.[5]

In the present work the values of A and Q' were obtained by observing the ENDOR spectrum with the magnetic field along the crystalline c axis. In this case the energy levels to second order in the hyperfine interaction are given by

$$\begin{aligned}W_{M,m}={}&g\beta HM+D[M^2-\tfrac{1}{3}S(S+1)]\\&+AMm-\gamma_n\beta_nHm+Q'[m^2-\tfrac{1}{3}I(I+1)]\\&+\tfrac{1}{4}B^2\frac{[S(S+1)-M(M+1)][(I+1)-m(m-1)]}{-g\beta H-D(2M+1)+A(M-m+1)}\\&+\tfrac{1}{4}B^2\frac{[S(S+1)-M(M-1)][I(I+1)-m(m+1)]}{g\beta H+D(2M-1)+A(m-M+1)},\end{aligned}$$

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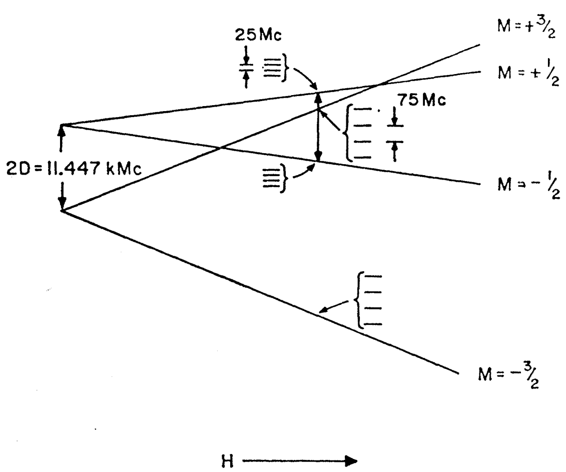

FIG. 1. Energy levels for Cr^{3+} in Al_2O_3 at $\theta=0$ deg.

where M and m are the quantum number specifying the orientation of the electron spin S and the nuclear spin I, respectively. The term AMm is much larger than the other hyperfine terms so that for $M=\pm\frac{1}{2}$, the four hyperfine levels are split by approximately 25 Mc/sec and for $M=\pm\frac{3}{2}$ by approximately 75 Mc/sec as indicated in Fig. 1.

The X-band spin resonance transition which we observed in our experiments is also indicated in Fig. 1. One would expect to see four hyperfine components in the electron spin resonance spectrum. However, the details of the Cr^{53} hyperfine structure are obscured by the absorption of the other isotopes. The electron spin resonance line associated with the other isotopes is inhomogeneously broadened to a half-width of 50 Mc/sec. One does observe the two outer lines of the Cr^{53} hyperfine spectrum as small bumps on the wings of the main absorption.

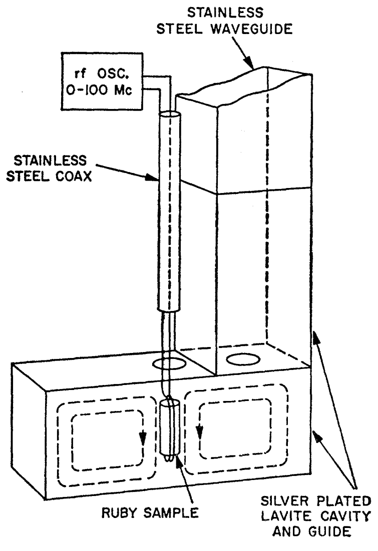

FIG. 2. Schematic of electron-spin-resonance cavity and sample holder for double-resonance experiments.

EXPERIMENTAL TECHNIQUES AND DATA

The cavity in our electron-spin-resonance spectrometer was such that we could insert samples into the cavity from above when the cavity was immersed in liquid helium. As indicated in Fig. 2, we had only to place a coil around the sample and use a stainless steel coaxial line for a sample rod to perform double resonance experiments.

Magnetic field modulation at 5 kc/sec was used to observe the edge of the $(+\frac{1}{2}\rightleftarrows-\frac{1}{2})$ electron-spin-resonance transition near 9 kMc/sec with a microwave power level well above saturation. The spectrum shown in Fig. 3 was then obtained by scanning the frequency of a low-power rf oscillator connected to the coil around the samples while observing changes in the electron-spin-resonance signal. As indicated in Fig. 3, the nuclear magnetic resonance spectrum of the host aluminum nuclei throughout the crystal was observed in the 3-Mc/sec region. That is, when the oscillator was tuned to one of the aluminum nuclear resonance transitions a large decrease in the electron spin resonance signal was observed.

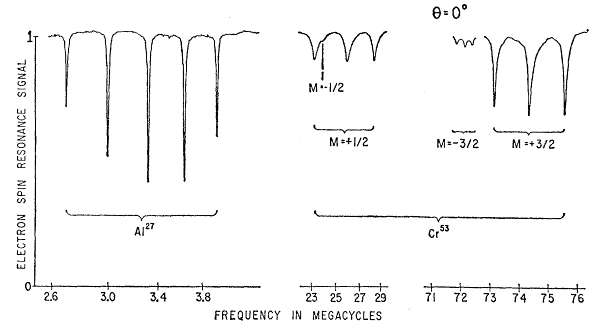

FIG. 3. Spectrum obtained by observing the $(+\frac{1}{2}\rightleftarrows-\frac{1}{2})$ electron-spin-resonance signal from ruby under saturation conditions and scanning the frequency of an rf generator connected to a coil around the crystal ($H=3285$ gauss, $\nu=9160$ kMc/sec, $T=4.2$°K).

As indicated in Fig. 3 we also observed all the transitions between the hyperfine levels of $(Cr^{53})^{3+}$. Note that even though we were observing the $(+\frac{1}{2}\rightleftarrows-\frac{1}{2})$ electron spin transition our electron-spin-resonance signal was strongly affected when hyperfine transitions were induced in ions in the $M=+\frac{3}{2}$ states. A triplet is observed for each electron spin state corresponding to the three allowed transition between the four hyperfine levels. The splitting of the triplet results from the second-order hyperfine interaction and the nuclear quadrupole term. The frequencies at which these transitions occurred are given in Table I.

Figure 4 illustrates the rapid change in the hyperfine splittings of the $(Cr^{53})^{3+}$ ions as the angle of the dc magnetic field is varied. The crystalline field splitting is of the same order as the electron spin Zeeman energy so that one has considerable mixing of electron spin states as the angle of dc magnetic field relative to the crystalline c axis is changed. This mixing is particularly apparent with the $M=+\frac{1}{2}$ and $+\frac{3}{2}$ states, as inspection of Fig. 1 shows that our observations were made near a crossover point of these energy levels. The crystalline c axis was aligned with the dc magnetic field to better than a tenth of a degree in order to obtain the data in Table I.

We were also able to observe the chromium hyperfine spectrum at 0 deg while saturating both the high and low magnetic field $(+\frac{3}{2}\rightleftarrows+\frac{1}{2})$ electron spin transitions. In addition we traced the hyperfine splittings as the angle of dc magnetic field relative to the crystalline axis was varied between 0 and 90 deg. Figure 5 shows the spectrum which we obtained at 90 deg.

ANALYSIS AND DISCUSSION

Agreement between the observed and predicted spectra at 0 deg to better than 0.1 Mc/sec for all lines was obtained with $A=B=48.5$ Mc/sec and $Q'=-0.21$ Mc/sec. The only feature of the spectrum which we could not explain was the unequal spacing of the triplet for the $M=\frac{3}{2}$ state, i.e., 0.240 and 0.267 Mc/sec. This could not be accounted for by considering the third order perturbation of the hyperfine interaction. The value of Q' was determined from the splittings and the unexplained unequal spacing limits the accuracy of the determination of its value to about ±0.01 Mc/sec. Comparison of the 90-deg data with approximate calculations supported the assumption that $A=B$. We were able to obtain the sign of both A and Q' by comparison with the second-order hyperfine interaction term.[3,6] From the above value of Q', a value of 0.84±0.04 Mc/sec is obtained for the quadrupole coupling constant which equals $\frac{4}{3}I(2I-1)Q'$.

TABLE I. Observed hyperfine splitting in Mc/sec for Cr^{53} in Al_2O_3 with $\theta=0°$ and electron-spin-resonance frequency of 9152 Mc/sec.

Hyperfine transitions	Electron spin states			
	$M=-\frac{3}{2}$	$M=-\frac{1}{2}$	$M=+\frac{1}{2}$	$M=+\frac{3}{2}$
$+\frac{3}{2}\rightleftarrows+\frac{1}{2}$	72.298		23.08	75.566
$\frac{1}{2}\rightleftarrows-\frac{1}{2}$	72.058	23.75[a]	25.65	74.320
$-\frac{1}{2}\rightleftarrows-\frac{3}{2}$	71.790		28.112	73.140

[a] Unresolved triplet centered at 23.75 Mc/sec.

One can deduce an approximate value for the magnitude of the nuclear electric quadrupole moment of Cr^{53} by comparing the quadrupole interaction constants for the $(Cr^{53})^{3+}$ ion with that for the $(Al^{27})^{3+}$ ion in Al_2O_3.[13] Q' for the $(Al^{27})^{3+}$ ion in $Al_2O_3=0.180$ Mc/sec and its nuclear electric quadrupole moment is 1.49 barns. The quadrupole interaction constant Q' is related to the nuclear electric quadrupole moment Q by

$$Q'=\frac{3eQ(\partial^2V/\partial z^2)}{4I(2I-1)}.$$

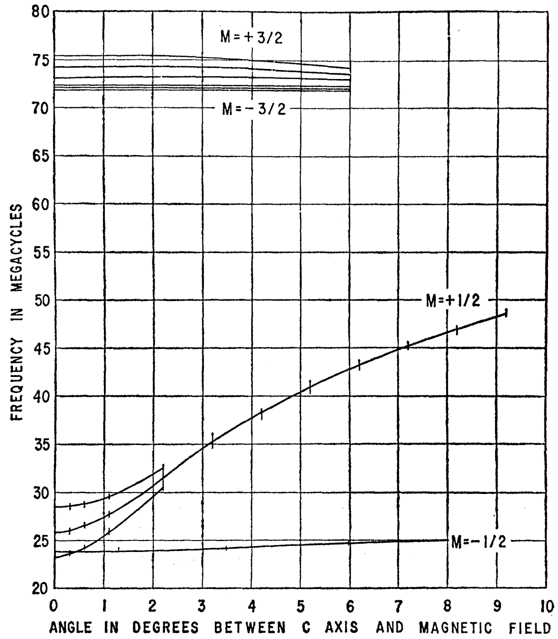

FIG. 4. Experimental data on angular dependence of hyperfine splittings of the electron spin states of the Cr^{53} ion in ruby. The change in frequency with angle results from the mixing of electron spin states ($\nu=9160$ kMc/sec, $T=4.2°K$).

By comparing values of Q' for Al^{27} and Cr^{53} and using the above one finds that

$$Q_{Cr^{53}}=-0.05\frac{\partial^2V/\partial z^2 \text{ at the } Al^{27} \text{ site}}{\partial^2V/\partial z^2 \text{ at the } Cr^{53} \text{ site}}.$$

The problem then is to determine the relative values of the electric field gradient at the two ion sites.

Bersohn[15] has computed the crystalline electric field at the metal ion sites in Al_2O_3 assuming nonoverlapping ions and neglecting polarization of the lattice. Correcting this field gradient for the calculated antishielding of the closed electron shells of the $(Al^{27})^{3+}$ ion, $(1-\gamma_\infty)=3.59$, he obtained a value of 0.247 b for $Q_{Al^{27}}$. This

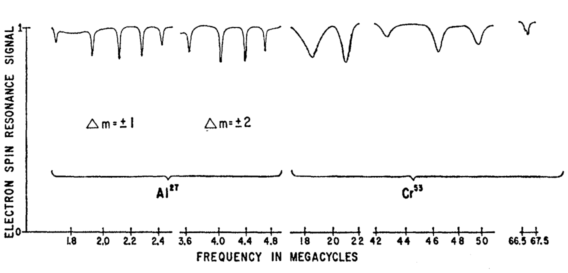

FIG. 5. Spectrum observed with $\theta=90°$ ($\nu=9160$ kMc/sec, $T=4.2°K$).

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compares reasonably well with the atomic beam value of 0.149 b, indicating that the ionic crystal model is reasonably good but that there is some covalent bonding.

The negative sign in the formula for $Q_{\mathrm{Cr}^{53}}$ follows from the assumption that $Q'_{\mathrm{Al}^{27}}$ is positive in $\mathrm{Al_2O_3}$. Bersohn made this assumption on the basis of his calculations of the sign of the crystalline field gradient.

For paramagnetic ions in solids the gradient of the electric field at the nuclei contains a contribution from the distorted electron cloud and from the crystalline electric field. However, in the case of the Cr^{3+} ion the electronic g value is almost isotropic and, according to Abragam and Pryce,[16] the electronic contribution to the electric field gradient is negligible. Thus, as a first approximation, the electric field gradients at both the Al^{27} and Cr^{53} nuclei are associated with the same crystalline electric field. The ratio of the field gradients at the two nuclear sites would then be equal to the ratio of $(1-\gamma_\infty)$ for the two ions. Recently Burns and Wikner[17] calculated antishielding factors for Fe^{3+} and Mn^{2+} using contracted wave functions. On the basis of these calculation Burns[18] estimated that γ_∞ for Cr^{3+} to be about -5. From this, one would conclude that the effective field gradient at the Cr^{53} sites was 1.7 times that at the Al^{27} sites.

With the reasoning outlined above one deduces that the Q for Cr^{53} is -0.03 b. According to the plot of Townes, Foley, and Low,[19] one would expect Q for Cr^{53}, which has 29 neutrons, to have the same sign and magnitude as the Q's for Cu^{63} and Cu^{65}, which have 29 protons. The values of Q for Cu^{63} and Cu^{65} have been determined to be about -0.15 b.[20] Thus, the deduced sign for the Q of Cr^{53} agrees with those of the copper isotopes but the value appears low. The significance of the difference in magnitude is difficult to evaluate as very few quadrupole moments of odd-neutron nuclei have been measured. Also, the moments for Cu^{63} and Cu^{65} have not been corrected for shileding of the closed electron shells.

While the accuracy of this determination of Q for Cr^{53} is quite limited, this method appears promising for obtaining nuclear quadrupole moments of the iron group elements, many of which have not been measured. Studies of systems such as vanadium in $\mathrm{Al_2O_3}$, where ions of several different valence states can be observed, would be of particular importance in reducing many of the uncertainties.

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