

Nuclear Magnetic Dipole Coupling in Al_2O_3

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An investigation of the five nuclear magnetic resonance lines in Al_2O_3 shows a partially resolved structure for each of the five lines. This structure can properly be described in terms of a two-spin Hamiltonian with dipole-dipole coupling. The dipole coupling constant d is 0.3998 kc/sec and the linewidths are approximately $10d$. The analysis of the line shapes shows that the sign of the quadrupole coupling constant eqQ is positive.

THE nuclear magnetic resonance (NMR) spectrum of Al^{27} in an Al_2O_3 single crystal was first explained by Pound.¹ Pound observed the spectrum in a strongly colored natural crystal and interpreted the spectrum in terms of the nuclear electric quadrupole interaction. This spectrum is a classic example of nuclear quadrupole splitting in high-field NMR.² It consists of five lines near the nuclear Larmor frequency ν_0 . The spacing is a function of the crystalline orientation in the external magnetic field and the nuclear quadrupole coupling constant.

We have made a careful study of the shape and width of the five Al^{27} lines in several samples of Cr^{3+} doped Al_2O_3 (Ruby). Each line shows partially resolved structure which varies as the crystal is rotated in the magnetic field. An analysis of the spectrum in terms of nuclear dipole-dipole coupling gives satisfactory agreement with the experiment. A further result of this measurement is the determination of the sign of the quadrupole coupling constant.

The spectra were observed with a Pound-Watkins type marginal detector. The measurements were made at fixed field using frequency scan and conventional recording techniques. The magnetic field modulation was 280 cps with 2-gauss amplitude and the derivative of the absorption curve was observed on the recorder. Frequency measurements were made with a frequency counter.

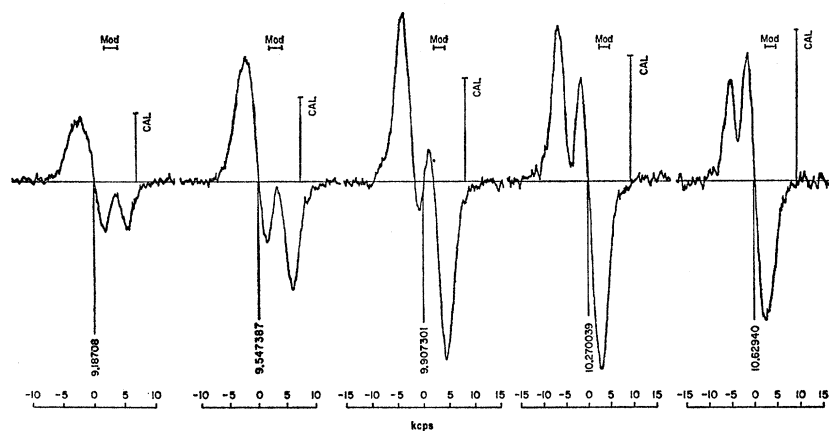
Figure 1 shows the five-line spectrum observed at

room temperature in 0.1% ruby. The magnetic field was aligned along the trigonal axis of the sample by rotating the sample for maximum splitting of the outer lines. Each of the resonance lines shows a partially resolved splitting in the derivative curve. Particular notice is taken of the position of the structure on the five lines. The central line shows a symmetric splitting.

The satellite resonances are not symmetric lines. However the entire spectrum is symmetric about ν_0 . A similar spectrum was observed for another sample of 0.1% ruby and 0.01% ruby. The spectrum at this orientation was also reproduced at a lower magnetic field with the same shape. If the magnetic field is rotated from the direction of the trigonal axis the splitting diminishes and becomes unobservable.

Since the original splitting of the spectrum into five lines is due to the electric quadrupole interaction one might assume that this further splitting is due to a twinning of the crystal with a resultant misalignment of the trigonal axis at different Al positions. This explanation can be discounted for two reasons. The identical spectrum in several independent samples is very improbable on this basis. More conclusive is the angular dependence of the quadrupole splitting and the relative size of the effect on the central and satellite lines. Since the quadrupole splitting has an extremum when the magnetic field is along the crystalline axis, the effect of twinning would increase as the field is rotated away from the trigonal axis.³ The opposite is observed. Fur-

FIG. 1. Nuclear resonance spectrum of Al^{27} in a single crystal of Al_2O_3 (0.1% Cr). The magnetic field is parallel to the trigonal axis. The vertical lines marked CAL next to each resonance line indicate the relative sensitivity of the spectrometer.



¹ R. V. Pound, Phys. Rev. **79**, 685 (1950).

² M. H. Cohen and F. Reif, *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 5.

³ A. H. Silver and P. J. Bray, J. Chem. Phys. **31**, 247 (1959).

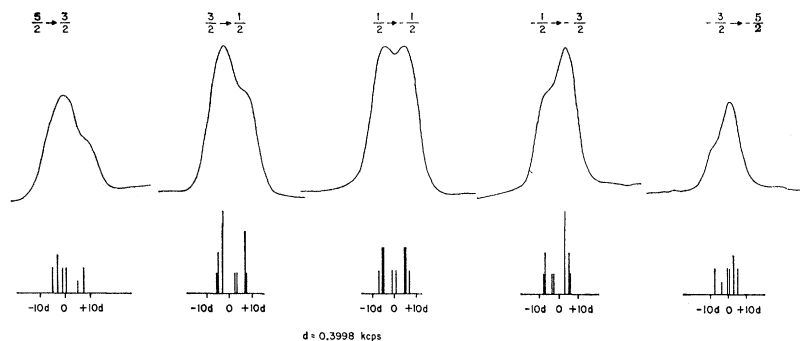


FIG. 2. Theoretical and experimental absorption spectrum of Al^{27} in Al_2O_3 . The angle between \mathbf{H}_0 and the crystal-line axis is 0° . The curves represent the integrals of the derivative lines in Fig. 1 and the line spectra are the corresponding theoretical spectra.

thermore the quadrupole shift on the central line would be much smaller than that on the satellite lines and would be inversely proportional to the magnetic field.

The high-field Hamiltonian for a nuclear spin in the presence of a polarizing magnetic field and an electric field gradient can be written²

$$\mathcal{H}_0 = \gamma \hbar H_0 I_z + \frac{eqQ}{4I(2I-1)}(3I_z^2 - \mathbf{I}^2), \quad (1)$$

where γ is the nuclear magnetogyric ratio and eqQ is the quadrupole coupling constant. The quadrupole interaction in Al_2O_3 is small compared with the magnetic energy so the z direction is chosen as the direction of the external magnetic field \mathbf{H}_0 . The dipole-dipole coupling constant between any two Al spins is

$$d = (\gamma/2\pi)^2 \hbar r^{-3} \left(\frac{3}{2} \cos^2 \theta - \frac{1}{2} \right), \quad (2)$$

where r is the internuclear distance and θ is the angle between \mathbf{r} and \mathbf{H}_0 . All the aluminum atoms are equivalent and lie along the trigonal axis of the unit cell. When θ is 0° the value of d for the nearest neighbor is 0.3998 kc/sec, 2.5 times as large as the next largest contribution, and should have a dominating influence on the line shape.

The Hamiltonian for two identical spins in a polarizing magnetic field with the same quadrupole interaction and direct dipole-dipole coupling is

$$\mathcal{H} = \gamma \hbar H_0 (I_{1z} + I_{2z}) + \frac{eqQ}{4I(2I-1)} \times (3I_{1z}^2 + 3I_{2z}^2 - \mathbf{I}_1^2 - \mathbf{I}_2^2) + d(\mathbf{I}_1 \cdot \mathbf{I}_2 - 3I_{1z}I_{2z}). \quad (3)$$

The z direction is determined by \mathbf{H}_0 and the representation which we choose is $\mathbf{I}_1^2, \mathbf{I}_2^2, I_{1z}, I_{2z}$. In the absence of the dipole term those states which correspond to an interchange of I_z are degenerate. The dipole interaction through the terms $I_{1x}I_{2x}$ and $I_{1y}I_{2y}$ removes the degeneracy from those states where $|I_{1z} - I_{2z}| = 1$. In a manner analogous to that of Pake⁴ we calculate the energy levels and wave functions for the new states of this combined Hamiltonian. The square

of the matrix elements of $(I_{1x} + I_{2x})$ connecting the eigenstates of \mathcal{H} gives the relative intensities of the component lines. The calculated line spectrum is presented in Fig. 2 and compared with the experimental absorption curves. The predicted spectrum consists of five groups of transitions which correspond to the five observed resonance lines. The sums of the transition probabilities for each of the five groups are in the ratio of 5:8:9:8:5 in agreement with the ratio for the single-spin case. In calculating the spectrum we have used a positive value for the nuclear γ and for the quadrupole coupling constant. Change of either sign interchanges the satellite line shapes, i.e., the $m \rightarrow m-1$ and $-m \rightarrow (m-1)$ transitions are interchanged. This produces an inversion of the asymmetric satellite lines.

The calculated spectrum is compared with the observed absorption spectrum in Fig. 2. The absorption curves were obtained by electronically integrating the derivative curves presented in Fig. 1. Each of the five groups of transitions, which now corresponds to one of the five magnetic dipole resonances, has a vanishing first moment calculated from the position of the resonance line without dipole interaction. Hence the theoretical and observed spectra may be compared by aligning the positions for which the first moment is zero. The second moments for each of the five calculated line spectra shown in Fig. 2 are:

$$\begin{aligned} \frac{1}{2} \leftrightarrow -\frac{1}{2}, & \quad 4.28 \text{ (kc/sec)}^2; \\ \pm \frac{1}{2} \leftrightarrow \pm \frac{3}{2}, & \quad 3.12 \text{ (kc/sec)}^2; \\ \pm \frac{3}{2} \leftrightarrow \pm \frac{5}{2}, & \quad 2.51 \text{ (kc/sec)}^2. \end{aligned}$$

The total second moment for the central resonance line is 7.897 (kc/sec)^2 when computed by the Van Vleck method⁵ for the entire Al_2O_3 lattice. The contribution of the nearest neighbor when computed by this method gives the same result which we calculate from the detailed spectrum. By subtracting the contribution of the nearest neighbor atom from the total second moment, we derive that the second moment for each component line in the calculated spectrum is 3.62 (kc/sec)^2 for the central resonance line. We assume that the rms line-width for the component lines in the other resonances is

⁴ G. E. Pake, J. Chem. Phys. 16, 77 (1948).

⁵ N. Laurance, E. C. McIrvine, and J. Lambe, J. Phys. Chem. Solids (to be published).

approximately the same as the value for the central line. The over-all linewidth for each resonance line is about $10d$.

Analysis of the Al^{27} NMR spectrum in Al_2O_3 using a two-spin Hamiltonian with dipole-dipole coupling predicts the correct shape and width of the resonance lines assuming a positive value for the magnetic moment μ and the quadrupole coupling constant eqQ . Since both μ and Q have been measured as positive,⁶ q is positive. This is in agreement with a calculation by Bersohn.⁷

An accurate determination of the magnitude of eqQ from the splitting of the NMR spectrum requires that the line separation be measured from the center of gravity of the line. This is not coincident with the position of zero slope for the satellite lines.

⁶ D. Strominger, J. M. Hollander, and G. T. Seaborg, *Rev. Mod. Phys.* **30**, 585 (1958).

⁷ R. Bersohn, *J. Chem. Phys.* **29**, 326 (1958).

The relative position of the dipolar splitting on each of the resonance lines can be understood in terms of a simple physical model. One nearest neighbor nucleus with $I' = \frac{5}{2}$ would be expected to split each resonance into six equally spaced dipole transitions due to the six equally probable orientations of I'_z . However, those transitions for which the two nuclei can resonate via spin-spin interaction will be broadened and split further apart. Thus the splitting of the $\frac{5}{2} \rightarrow \frac{3}{2}$ resonance occurs when the neighboring spin is in the $\frac{5}{2}$ or $\frac{3}{2}$ states. Since μ is positive this must occur on the high-frequency side of the $\frac{5}{2} \rightarrow \frac{3}{2}$ resonance. Hence we can assign the $\frac{5}{2} \rightarrow \frac{3}{2}$ transition to the observed low-frequency resonance line and determine that eqQ is positive.⁸

⁸ After completion of this research we learned this effect was independently observed by Verber and interpreted in terms of the physical model which we outline here. See, C. M. Verber, H. P. Mahon, and W. H. Tanttla, following paper [*Phys. Rev.* **125**, 1149 (1962)], and C. Verber, thesis, University of Colorado, 1961 (unpublished).

Nuclear Resonance of Aluminum in Synthetic Ruby*

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The linewidth, line shape, and spin-lattice relaxation time T_1 have been measured as a function of temperature in single crystals of $(\text{Al}^{27})_2\text{O}_3$ having nominal Cr_2O_3 concentrations of 0%, 0.01, 0.1, 1.5, and 4% by weight. Of the two important contributions to the linewidth, the nuclear spin-spin interaction is 7 gauss and temperature-independent. The contribution from the paramagnetic ions increased from zero at 300°K to as much as 42 gauss, depending upon concentration, temperature, and static magnetic field. An anomalous structure in the aluminum resonance was evident in both the steady-state and pulsed nuclear induction data. The $\frac{1}{2}$ to $-\frac{1}{2}$ transition has a splitting of 2.84 gauss with a $3 \cos^2\theta - 1$ dependence on the angle between the c axis and H_0 . The splitting is independent of the observation frequency and chromium ion concentration. T_1 was observed to vary from 150 sec to 1.5 msec as a function of ion concentration and temperature, and to vary in a manner not correctly given by existing theory. Many of the samples were observed to have a nonunique T_1 .

I. INTRODUCTION

ONE of the most persistent problems in the field of nuclear magnetic resonance has been that of predicting the spin lattice relaxation times of nuclei in a crystalline lattice. Original theoretical work¹ yielded predictions which were off by many orders of magnitude. It was not until the realization that, for nuclei with $I < 1$, paramagnetic ions, if present, are the basis for the primary relaxation mechanism, that there was even qualitative agreement between experiment

and theory. The importance of paramagnetic impurities was noticed by Rollin and Hatton² who observed the dependence of the relaxation time of fluorine in CaF_2 upon the number of F centers present, and by Bloembergen³ who investigated a variety of materials and whose theoretical treatment forms the basis for most of the more recent work. In particular, the role of spin diffusion in determining the recovery rate of nuclear magnetization after saturation has been examined in detail by Blumberg.⁴ The shape of the free induction signal in solids has been discussed by Lowe and Norberg⁵ and related, through the Fourier

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I. Waller, *Z. Physik* **79**, 370 (1932).

² B. V. Rollin and J. Hatton, *Phys. Rev.* **74**, 346 (1948).

³ N. Bloembergen, *Physica* **15**, 386 (1949).

⁴ W. E. Blumberg, *Phys. Rev.* **119**, 84 (1960).

⁵ I. J. Lowe and R. E. Norberg, *Phys. Rev.* **107**, 46 (1957).