We take the trigonal field to be of the form[11]

$$V_{\text{trig}}=aP_2(\cos\theta). \tag{5}$$

There can, in principle, be a fourth-order contribution to the potential, but this is neglected, being a higher order term in the potential expansion. (The origin of the potential is at a distance large compared to the size of the Fe^{2+} ion.) Inserting (5) in (4), and using the functions (1) yields

$$a=-7\delta/6\Delta. \tag{6}$$

Using this result for a first-order perturbation calculation of the functions ϕ_1, ϕ_2, ϕ_3, and ϕ_4, we can again write the eigenfunctions as in (1), but now

$$\alpha=\arccos[(\sqrt{\tfrac{2}{3}})(1-\delta/3\Delta)]. \tag{7}$$

Following Okiji and Kanamori,[12] we write

$$eq(\text{doublet})/eq(\text{singlet})=-\tfrac{3}{2}\cos^2\alpha+\tfrac{1}{2},$$

so that

$$eq(\text{doublet})=eq(\text{singlet})(-\tfrac{1}{2}+2\delta/3\Delta). \tag{8}$$

(We neglect $\delta^2/9\Delta^2$ since it is of the order of 10^{-3}.) Therefore the thermal averaging now gives[13]

$$eq(T)=eq(0)\frac{1-[1-(4\delta/3\Delta)](\exp(-\delta/kT))}{1+2\exp(-\delta/kT)}. \tag{9}$$

By fitting the parameter δ to the experimental data as shown in Fig. 1 (solid line), we get: $\delta=(1650\pm50)$°K, which is somewhat higher than the result $\delta=1020$ cm^{-1} (1470°K) given by Imbert.[14]

ACKNOWLEDGMENTS

We would like to thank Professor S. Alexander and R. Hornreich for helpful discussions.

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[11] J. Smit *et al.*, J. Phys. Soc. Japan **17**, Suppl. BI, 270 (1962), express the trigonal field potential as $V_{\text{trig}}\propto(xy+yz+zx)$ in cubic axes, which is equivalent to (5) in our choice of the z axis.

[12] A. Okiji and J. Kanamori, J. Phys. Soc. Japan **19**, 908 (1964).

[13] The direct contribution of neighboring ions (including the antishielding of the electronic core) to the EFG have been neglected in this discussion.

[14] P. Imbert (to be published).

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Nuclear Magnetic Resonance of Fe^{57} in Single-Crystal Hematite*

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Experimental results are presented for the Fe^{57} resonance in the internal field of two natural hematite (α-Fe_2O_3) crystals; results on two polycrystalline samples are also reported for comparison purposes. The intensities of the samples decrease and ultimately approach zero as the temperature is decreased. This is interpreted as due to the weak ferromagnetic-to-antiferromagnetic transition with attendant loss of NMR enhancement. Deviations from the expected transition temperatures are explained in terms of the effect of known titanium impurities. The fractional change in frequency is found to be closely proportional to $T^{5/2}$ for all samples. In one of the crystals a very weak resonance is observed at 73.596±0.015 Mc/sec at 4.0°K, and is in good agreement with the extrapolated values of all four samples. This low-temperature value, apparently representative of the weak ferromagnetic or canted state, corresponds to a total field at Fe^{57} of $H=-534.93\pm0.42$ kOe at 0°K. This leads to a zero-point spin deviation of $(1.9\pm1)\%$ for α-Fe_2O_3, which is in reasonable agreement with theoretical estimates. Experimental studies of the dependence of intensity on field and orientation are presented and analyzed in terms of an enhancement model based upon the Dzialoshinsky-Moriya theory of weak ferromagnetism in α-Fe_2O_3. These results, together with a comparison with a magnetization curve from the principal crystal, lead to the conclusion that both domain-rotation and wall-enhancement processes occur in this crystal of α-Fe_2O_3, with the domain-rotation process predominating. It is suggested that either domain rotation, wall enhancement, or both may be operative in α-Fe_2O_3, depending upon the value (or range of values) of the basal-plane anisotropy energy. The observed decrease of intensity with decreasing particle size is attributed to an increase in coercivity and decrease in domain-wall volume with decreasing particle size.

I. INTRODUCTION

OVER the years there have been numerous studies of the magnetic properties of α-Fe_2O_3 (hematite). Generally speaking most of these studies were related to the fact that at room temperature α-Fe_2O_3 always had a weak ferromagnetic moment even though the material was believed to be antiferromagnetic. Furthermore, at ~250°K the weak moment was observed to essentially vanish, and below this temperature[1] α-Fe_2O_3 exhibited antiferromagnetic behavior. The crystal

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* This work was supported by the U. S. Atomic Energy Commission.

[1] Often called the Morin transition temperature; see F. J. Morin, Phys. Rev. **78**, 819 (1950).

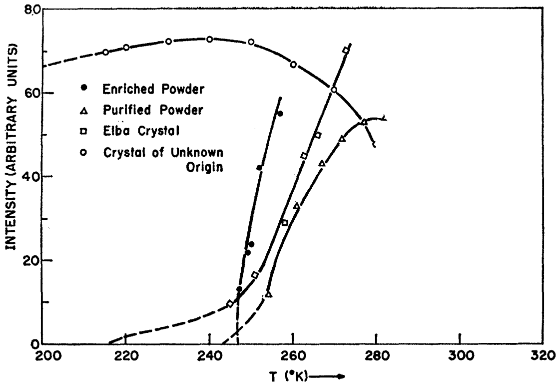

FIG. 1. The NMR intensity versus temperature for four samples of α-Fe_2O_3.

structure of α-Fe_2O_3 is rhombohedral with the Fe^{+3} ions lying along the body diagonal of the unit rhombohedron.[2] Neutron diffraction studies[3] established that the spin configuration in α-Fe_2O_3 is essentially antiferromagnetic. However, above ~250°K the spin direction is in the basal plane (perpendicular to the rhombohedral *c* axis) while below ~250°K the spins are oriented along the *c* axis. Dzialoshinsky[4] consolidated this information in a theory based upon thermodynamic and symmetry considerations. He showed that when the spins were in the basal plane the sublattices would cant with respect to each other, yielding a net weak magnetic moment. On the other hand, when the spins were along the *c* axis the symmetry conditions would not allow canting. Moriya[5] later showed that the physical basis for this phenomenon in α-Fe_2O_3 was anisotropic superexchange. Thus a weak magnetic moment in the basal plane is considered an intrinsic property of α-Fe_2O_3 above the transition temperature; below the transition temperature α-Fe_2O_3 is believed to be completely antiferromagnetic.

Since α-Fe_2O_3 is a magnetic material there is the possibility of observing the zero-field resonance of Fe^{57}, and some studies on polycrystalline α-Fe_2O_3 have been reported.[6–8] Although some experiments on polycrystalline hematite are presented here, this paper is primarily concerned with the study of the resonance of Fe^{57} in single-crystal hematite. The results of these studies are of interest from a number of standpoints. The temperature dependence of the intensity gives information regarding the mechanism of the weak ferromagnetic to antiferromagnetic transition, and demonstrates the significant effect titanium impurities have upon the transition. Studies of the temperature dependence of the resonance frequency allow us to draw conclusions about the temperature dependence of the sublattice magnetization in the α-Fe_2O_3 lattice. Also, a precise value of the Fe^{57} resonance frequency is obtained at 4°K, presumably representative of the canted state. This is of interest for estimates of the zero point spin deviation in the antiferromagnetic lattice of α-Fe_2O_3. Experiments on the orientation dependence of the intensity show the importance of magnetic anisotropy energy in such observations and provide a means of confirming the magnetic structure of the canted state. Studies of the field dependence of the intensity give us criteria for deciding whether the nuclear-resonance enhancement occurs by domain rotation or wall motion. This is facilitated by a comparison with the magnetization curve obtained from the same crystal. Finally, the role which particle size plays in such experiments is considered.[9]

II. EXPERIMENTAL SAMPLES

The single-crystal studies were made on two natural crystals of a few cm^3 each in volume. Analysis of the first crystal (of unknown origin) showed 0.4% Ti with less than 0.1% Cr and Mn. The second crystal, which was from Elba, showed 0.02% Ti and less than 0.1% Cr, Mn, Co, and Ni. Back-reflection x-ray examination showed that both samples had good single-crystal characteristics. (The x-ray reflections are, of course, only characteristic of a surface layer. Also, α-Fe_2O_3 has a layer-like growth habit, with the layers or platelets perpendicular to the *c* axis. In consideration of these factors, it is possible that the order perpendicular to the *c* axis, observed in the back reflection studies, is not necessarily maintained throughout the bulk of the crystal.) Studies were also performed upon two polycrystalline samples. The first[10] was isotropically enriched to 91% in Fe^{57} and contained less than 0.02% Ti with less than 0.05% Cr and Ni. The second was prepared in our laboratory and contained 0.004% Ti with less than 0.005% Mn and Cr.

III. EXPERIMENTAL PROCEDURES

Experiments were performed with a conventional frequency-modulated marginal oscillator. For improved sensitivity the temperature-dependence experiments were performed in a Dewar constructed with electrical leads inserted through its walls for direct connection from the oscillator to the coil. Later studies utilized a marginal oscillator and a Dewar which could be directly inserted into the sample coil with the sample at liquid-He temperature. In the field-dependence experiments, the coil was attached to the oscillator with a

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[2] A. F. Wells, *Structural Inorganic Chemistry* (University Press, Cambridge, England, 1950), 2nd ed., p. 379.

[3] C. G. Shull, W. A. Strauser, and E. O. Wollan, Phys. Rev. **83**, 333 (1951).

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[7] Le Dang Khoi and F. Bertaut, Compt. Rend. **254**, 1584 (1962).

[8] M. Matsuura, H. Yasuoka, A. Hirai, and T. Hashi, J. Phys. Soc. Japan **17**, 1147 (1962).

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[10] Obtained on loan through the courtesy of Oak Ridge National Laboratory.

TABLE I. A summary of the temperature dependence of the NMR frequencies of Fe^{57} for four samples of α-Fe_2O_3.

Sample	T range (°K)	Slope of $\log\{[\nu(0°K)-\nu(T)]/\nu(0°K)\}$ versus $\log T$	$\nu(0°K)$ Mc/sec
Crystal (unknown origin)	73–466	2.58±0.01	73.54
Crystal (Elba)	218–299	2.59±0.01	73.56
Polycrystalline (Fe^{57} enriched)	259–395	2.47±0.06	73.54
Polycrystalline (especially purified)	250–297	2.53±0.03	73.58

one-half-wavelength transmission line. Helmholtz coils and an electromagnet with a $2\frac{3}{4}$-in. gap were used for the magnetic-field studies of the signal intensity. In the magnetization experiment, performed with a ballistic galvanometer, a large Helmholtz configuration solenoid was utilized.

IV. EXPERIMENTAL RESULTS

1. Temperature Dependence of the Intensity

The temperature variation of intensity (as measured by peak height) was most pronounced in the vicinity of 250°K and is shown in Fig. 1. Although all samples except the crystal of unknown origin showed a drop in intensity in that region they differed with respect to the temperature at which the signal was no longer observable. The signal from the crystal of unknown origin could be observed from room temperature down to 77°K, although the intensity gradually weakened in the low-temperature region. Careful studies at 4°K on the crystal of unknown origin in the Dewar which could be placed directly into the sample coil gave an extremely weak signal at 73.596±0.015 Mc/sec. The signal of the Elba crystal could be observed to approximately 215°K, while that of the enriched power disappeared at about 248°K. The intensity of the purified power was observable down to about 243°K.

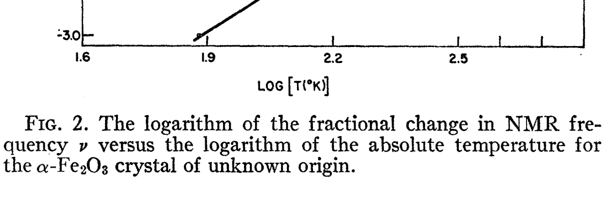

FIG. 2. The logarithm of the fractional change in NMR frequency ν versus the logarithm of the absolute temperature for the α-Fe_2O_3 crystal of unknown origin.

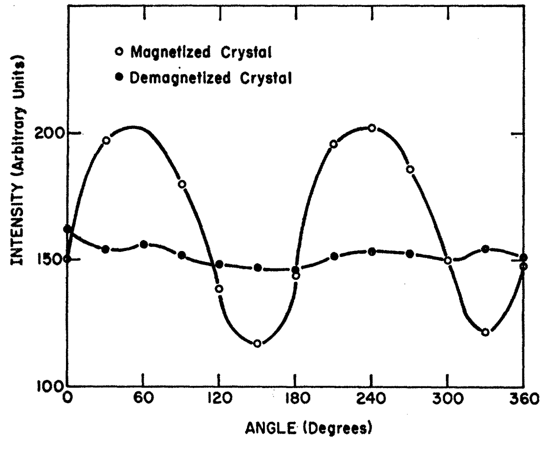

FIG. 3. The NMR intensity versus the angle between the direction of the radiofrequency field and an arbitrary direction in the plane perpendicular to the c axis in the α-Fe_2O_3 crystal of unknown origin.

2. Temperature Dependence of the Resonant Frequency

The results of the studies of the temperature dependence of the resonant frequency are summarized in Table I. The values of $\nu(0°K)$ were obtained by extrapolating plots of ν versus $T^{5/2}$ (which were all quite linear) to $T=0°K$. As observed there is good agreement leading to an average value of $\nu(0°K)=73.56\pm0.02$ Mc/sec. (The averaging procedure is assumed to be valid since the values of ν at given temperatures agree to within about 0.03%.) In Table I the slope of $\log\{[\nu(0°K)-\nu(T)]/\nu(0°K)\}$ versus $\log T$ is reported. Here we utilized the value of $\nu(0°K)$ which was obtained by extrapolating plots of $\nu(T)$ versus $T^{5/2}$ to 0°K. The tabulated slope was arrived at by a least-squares analysis of the data over the indicated temperature range. The average deviation from the least-squares slopes is also shown. A plot of the $\log\{[\nu(0°K)-\nu(T)]/\nu(0°K)\}$ versus $\log T$ for the crystal of unknown origin is shown in Fig. 2 for illustration.

3. Dependence of the Intensity upon Crystal Orientation

Here our results were obtained primarily on the crystal of unknown origin, which was larger in size and of better crystal quality than the Elba crystal. Studies on the Elba crystal, although not as extensive, yielded similar results. When the radiofrequency field ($\mathbf{H}_1$) was parallel to the crystallographic c axis a minimum signal (very close to zero intensity) was obtained. The results obtained when $\mathbf{H}_1$ was in the plane perpendicular to c are shown in Fig. 3. Here we have plotted the peak-to-peak intensity in arbitrary units, versus the angle made between $\mathbf{H}_1$ and an arbitrary direction in the c

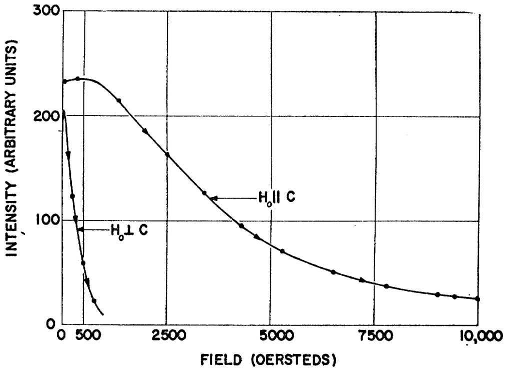

FIG. 4. The NMR intensity versus applied static field (H_0) for the α-Fe_2O_3 crystal of unknown origin. The static and radiofrequency fields are perpendicular in each case; the radiofrequency field is in the plane perpendicular to the c axis.

plane. The "demagnetized state" was obtained by applying a 60-cps field in the c plane and varying the field from 100 Oe down to 0 Oe. The "magnetized state" was achieved by placing a 1200-Oe field in the c plane for about 10 sec, and then removing the crystal from the field to the spectrometer. These results were reproducible.

4. Dependence of the Intensity upon Magnetic Field Strength

Here the results reported were obtained only from studies on the crystal of unknown origin. In this experimental arrangement (large electromagnet and transmission lines) it was not possible to obtain a satisfactory signal-to-noise ration on the Elba crystal. Figure 4 shows the dependence of intensity on field strength when the applied field $\mathbf{H}_0$ was parallel and perpendicular to the c axis. In each case $\mathbf{H}_1$ was perpendicular to $\mathbf{H}_0$, and the crystal was initially in the "demagnetized state" as defined in Sec. IV 3. Because of the scale in Fig. 4 it is difficult to observe that when $\mathbf{H}_0$ was perpendicular to c, the intensity at first rose with field, reached a maximum at about 50 Oe, and then fell off rapidly. This dependence was examined more carefully because it was felt some anisotropies might be observed. These results are shown in Fig. 5. Here $\mathbf{H}_0$ was given the indicated angles in the plane perpendicular to the c axis. The angles chosen were 0°, 30°, $\cdots$, 150°. Because of the symmetry of α-Fe_2O_3, 0°, 60°, and 120° corresponded to twofold axes and 30°, 90°, and 150° corresponded to mirror planes. The intensities were scaled as shown to allow plotting on a single figure. Figure 6 shows the analogous dependence when $\mathbf{H}_1$ was parallel to $\mathbf{H}_0$, at the same orientations as above.

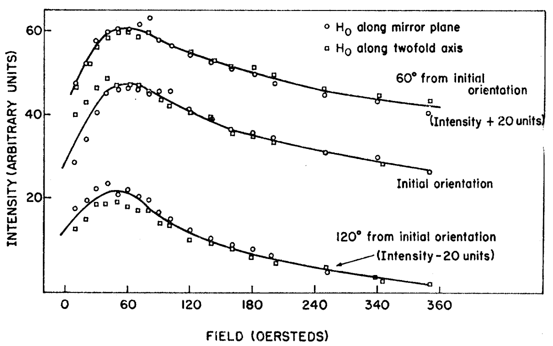

FIG. 5. The NMR intensity versus applied static field for the α-Fe_2O_3 crystal of unknown origin. The applied static field (H_0) is perpendicular to the radiofrequency field in each case. The orientation of the static applied field in the plane perpendicular to the c axis is as indicated in the figure and the intensities have been scaled as shown to allow plotting on a single figure.

5. Dependence of the Magnetization upon Field Strength

In order to ascertain the specific magnetic properties of the crystal of unknown origin a magnetization curve was obtained and is shown in Fig. 7. Calibration of the galvonmeter was achieved with a nickel foil arranged in a configuration similar to the crystal. The Helmholtz field was calibrated with a Hall probe.

6. Intensity Dependence upon Particle Size

Early in the course of this work a large difference was noted in the intensities of finely powdered samples and large crystallite samples. The intensity of a fairly large natural crystal (from the same lot as that of unknown origin) was first measured, and then the crystal was pulverized. Next the powder was separated through standard sieves into three batches, and the intensity of each measured. The results are plotted in Fig. 8. Here the particle size corresponds to the mesh size through which the powder was able to pass.

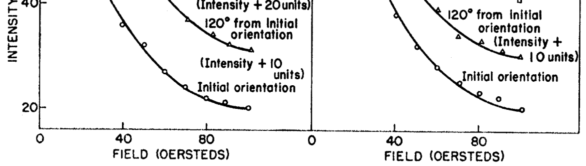

FIG. 6. The NMR intensity versus applied static field for the α-Fe_2O_3 crystal of unknown origin. The applied static field (H_0) is parallel to the radiofrequency field in each case. The orientation of the static applied field in the plane perpendicular to the c axis is as indicated in the figure and the intensities have been scaled as shown to allow plotting on a single figure.

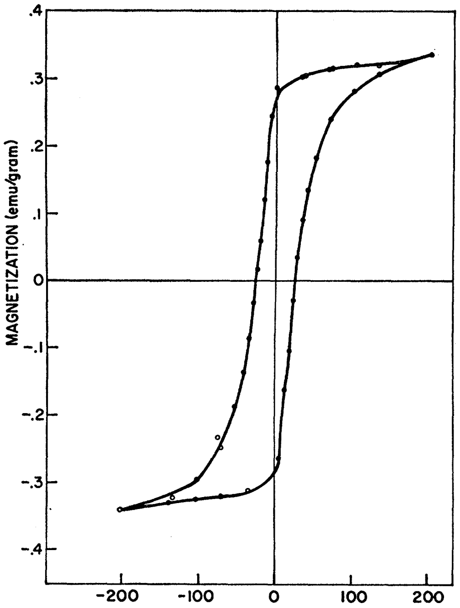

FIG. 7. The magnetization in the plane perpendicular to the c axis versus field for the crystal of unknown origin of α-Fe_2O_3 at room temperature.

V. DISCUSSION

1. Temperature Dependence of the Intensity

In Fig. 1 we observed that, with the exception of the case of the crystal of unknown origin, the intensity approached zero in the vicinity of 250°K. This is expected to be the approximate temperature for the spin reorientation for fairly pure materials.[11] Consequently, the observed, strong NMR signal is attributed to the weakly ferromagnetic state and the absence of a signal to the antiferromagnetic state. In order to observe a strong signal in the low abundance (~2%), low moment (~0.09 nm) Fe^{57} at room temperature, an enhancement mechanism of the type usually associated with ferromagnets[12] would presumably be necessary. Here the enhancement may involve domain rotation or domain-wall displacement. To understand the results on the temperature variation of the intensity, therefore, we must first consider the enhancement mechanism. The situation is analogous to that in $KMnF_3$,[13] except that the signal of the magnetic nucleus is observed directly, and also to that in $CrCl_3$,[14] except that in this case the weak moment is permanent and not field induced. First, consider domain rotation in the α-Fe_2O_3 spin system depicted in Fig. 9.

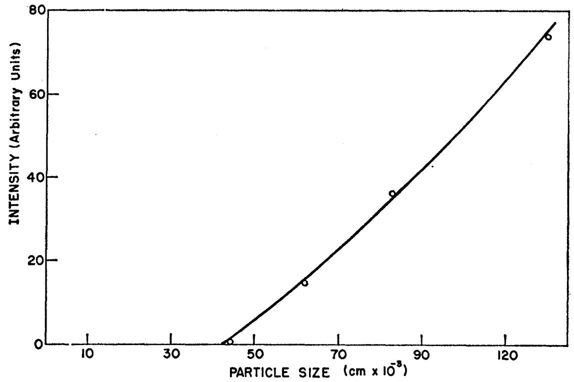

FIG. 8. The NMR intensity versus particle size (in terms of mesh size) for a sample of α-Fe_2O_3 from the same lot as the crystal of unknown origin. The highest intensity point is from a large crystallite and has been arbitrarily placed on the curve.

The energy of the system may be written as

$$E = -MH \sin\varphi + K \sin^2 3\theta. \tag{1}$$

Here φ is the angle between the total applied field $\mathbf{H}$ and the sublattice direction and $\mathbf{M}$ is the weak moment. (For clarity the change in angle of the sublattice moments due to canting has been exaggerated in Fig. 9; the actual change is $\sim 10^{-3}$ deg. For simplicity we also approximate $-\mathbf{M}\cdot\mathbf{H}$ as $-MH \sin\varphi$.) An anisotropy energy in the basal plane, $K \sin^2 3\theta$, has also been assumed since it has been observed in many α-Fe_2O_3 crystals.[11] K is the anisotropy constant and θ the angle between the easy axis of magnetization and the direction of the sublattice moment. At equilibrium $dE/d\theta = 0$, and using the relation $\varphi = \alpha + \theta$,

$$MH \cos\varphi = 3K \sin 6\theta. \tag{2}$$

We define the enhancement factor η as

$$|\eta| = |H_{1\,\mathrm{eff}}/H_1|, \tag{3}$$

where $\mathbf{H}_1$ is the applied radiofrequency field and $\mathbf{H}_{1\,\mathrm{eff}}$ the effective transverse radiofrequency field at the Fe^{57} nucleus. In the case where $\mathbf{H} = \mathbf{H}_1$, that is zero applied static field, $\Delta\theta$ is defined as the change in θ produced by the application of a field on the system.

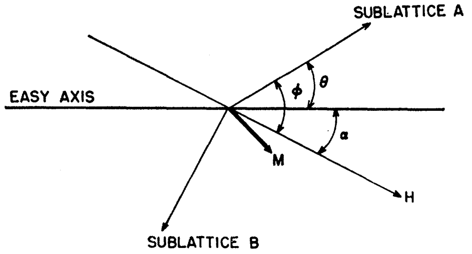

FIG. 9. A schematic diagram of the magnetic-spin system in α-Fe_2O_3. The crystallographic c axis is perpendicular to the plane of the figure. H represents the applied field, and M the weak moment.

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[11] P. J. Flanders and J. P. Remeika, Phil. Mag. **11**, 1271 (1965).

[12] A. M. Portis and A. C. Grossard, J. Appl. Phys. Suppl. **31**, 205S (1960).

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[14] A. Narath, Phys. Rev. **131**, 1929 (1963).

Since $\Delta\theta\approx H_{1\ \mathrm{eff}}/H_{\mathrm{hfs}}$

$$|\eta|\approx\left|\frac{H_{\mathrm{hfs}}}{H_1}\Delta\theta\right|, \tag{4}$$

where $\mathbf{H}_{\mathrm{hfs}}$ is the hyperfine field at the Fe^{57} nucleus. If $H_{\mathrm{hfs}}\gg H_1$

$$|\eta|\approx\left|H_{\mathrm{hfs}}\left(\frac{d\theta}{dH_1}\right)\right|. \tag{5}$$

By differentiating Eq. (2) with respect to H_1 and using $d\varphi/dH_1=d\theta/dH_1$

$$|\eta|\approx\left|\frac{H_{\mathrm{hfs}}M\cos\varphi}{MH_1\sin\varphi+18K\cos6\theta}\right|. \tag{6}$$

In conditions of zero static field $\theta=0$ and if $H_1\approx0$, then

$$|\eta|\approx\left|\frac{H_{\mathrm{hfs}}M\cos\varphi}{18K}\right|. \tag{7}$$

Letting $H_{\mathrm{hfs}}=5\times10^{-5}$ Oe, $M=0.3$ emu/g, and $\varphi=0$ we find

$$|\eta|\approx\left|\frac{4\times10^4}{K}\right|. \tag{8}$$

Choosing $K=10$–100 erg/cm^3, which are typical observed values,[11] $|\eta|\approx4\times10^2$ to 4×10^3 which compares with that observed in cobalt[12] ($|\eta|\approx1.8\times10^3$). [From the magnetization curve of the crystal of unknown origin, Fig. 7, we see that $H_c\approx26$ Oe, and since $H_c\approx18\,K/M$, $K\approx1$ erg/cm^3. Since the magnetization curve (Fig. 7) is quite constricted, our crystal undoubtedly has a range of K values extending above 1 erg/cm^3.] Thus, large values of the enhancement can be reasonably expected for α-$\mathrm{Fe_2O_3}$ from the domain-rotation mechanism.

We are now in a position to consider the temperature variation of the NMR intensity shown in Fig. 1. From Eq. (7) the enhancement factor is directly proportional to the weak moment M. A decrease in intensity could arise if the value of the weak moment M decreased with temperature uniformly over the sample or if the volume of crystal having the fixed value of M decreased with temperature. Since Matsuura *et al.*[8] find that the enhancement factor stays constant with temperature this implies that the spin transition takes place gradually over the bulk of the sample. This is reasonable when the effect of impurities on the transition temperature is considered, especially when they may be rather inhomogeneously distributed throughout the sample. These conclusions follow naturally when domain rotation is considered the predominant enhancement mechanism. (However, it is not obvious that domain-wall enhancement processes would be consistent with the experimental observations.)

The disappearance of the signals of the three samples at about 250°K correlates quite well with their known impurities. Flanders and Remeika[11] showed that, of various impurities, Ti and Sn affected the spin transition temperature most drastically. Ignoring the effect of Sn, since our materials did not contain a significant amount, we see that the purified powder, which contained the least Ti, had the highest transition temperature and that the Elba crystal and enriched powder, having more Ti, had a lower transition temperature. From the work of Flanders and Remeika[11] as well as that of Kaye,[15] the transition of the crystal of unknown origin would be expected to be much lower than the above samples. Kaye's work would indicate that 0.4% Ti could depress the transition to 0°K, thus accounting for our observation of a weak signal at 4°K. (The considerations of Artman *et al.*[16] suggest that the phase transition in α-$\mathrm{Fe_2O_3}$ occurs because the effective fields due to single ion terms and magnetic dipolar interactions are almost equal and opposite in sign, but that the competing fields have different temperature dependencies.) In arriving at the above conclusions and in referring to Eq. (7) it was assumed that the basal-plane anisotropy K remained essentially constant with temperature. There is no independent evidence for this, but the correspondence between our Fig. 1 and the magnetization-versus-T curves in Flanders and Remeika[11] suggest that K remains relatively constant.

2. Temperature Dependence of the Resonant Frequency

Since the theoreis of internal fields in magnetic materials[17] involve terms proportional to the unpaired spin density on the atom, the resonant frequency ν would be expected to be essentially proportional to the sublattice magnetization σ_s. More precisely,

$$\nu=A\sigma_s, \tag{9}$$

where A is the hyperfine coupling constant. Thus, $\nu(T)$ would be proportional to $\sigma_s(T)$ if $dA/dT=0$. If this is a valid assumption, theories of the temperature dependence of the sublattice magnetization $\sigma_s(T)$ of an antiferromagnet, which α-$\mathrm{Fe_2O_3}$ represents to a first approximation, should provide an interpretation of $\nu(T)$.[18]

One way to attempt this is to use the spin-wave theory of the antiferromagnetic state. Since our measurements were made at temperatures much less than the Néel temperature ($T_N\approx960$°K) noninteracting spin-wave theory would presumably be valid. A treatment of this type was recently made on MnO by Lines and Jones.[19] Here they compared their experimentally determined relation of $\{\nu(0)-\nu(T)/\nu(0)\}T^2$

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[16] J. O. Artman, J. C. Murphy, and S. Foner, Phys. Rev. **138**, A912 (1965).

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[18] For a molecular field interpretation see K. Ono and A. Ito, J. Phys. Soc. Japan **17**, 1012 (1962); S. Freier, M. Greenshpan, P. Hillman, and H. Shechter, Phys. Letters **2**, 191 (1962).

[19] M. E. Lines and E. D. Jones, Phys. Rev. **139**, A1313 (1965).

versus T with the theoretical plot of $\{\bar{S}(0)-\bar{S}(T)/\bar{S}(0)\}T^2$ versus T where $\bar{S}$ is the sublattice spin. (The relations utilize T^2 in the denominator because a simple power law is not generally expected for complex magnetic materials.) To arrive at an analogous theoretical comparison for α-Fe_2O_3 a knowledge of both the magnetic anisotropy energies and exchange parameters is required. Let us first consider the effect of anisotropy energy in α-Fe_2O_3. In the canted or weakly ferromagnetic case, which is the one relevant to our measurements, two anisotropy energies are involved. One is the basal-plane anisotropy energy (K), which was discussed above; the other is the out-of-plane anisotropy energy. In work on α-Fe_2O_3 Williamson and Foner[20] found that the flop field H_c was 6.5 kOe at 0°K for pure crystals and that H_c decreases with temperature. Impurities generally also reduce this value and Ti has been shown to have a drastic effect.[21] In any event we can utilize the pure crystal value to estimate an upper limit for the out-of-plane anisotropy since $H_c=(2H_{\text{ex}}H_A)^{1/2}$, where H_A is the out-of-plane anisotropy field and H_{ex} is the exchange field. Assuming $H_{\text{ex}}\approx 10^6$ Oe we find an upper limit for $H_A\approx 2.1\times 10^3$ Oe at 0°K. In considering the importance of anisotropy on antiferromagnetic properties Eisele and Keffer[22] define an anisotropy temperature T_{AE} and in this case $kT_{AE}=g\mu_0 SH_c$, where g is the electronic g factor ($g\approx 2.0$), μ_0 the Bohr magneton, and S the spin quantum number of the iron atom. Consequently $T_{AE}\approx 43$°K for the out-of-plane anisotropy. (The in-plane anisotropy temperature is much less: $T_{AE}'\approx 10^{-3}$ °K.) Since this is an upper limit and all of our measurements were made above 77°K (with the exception of the 4°K value), the effects of anisotropy should be negligible as demonstrated in the work of Eisele and Keffer.[22]

Unfortunately there is no good information available on the exchange interactions in α-Fe_2O_3. From the structure, however, it appears that an approximate model involving two exchange parameters (for interlayer and intra-layer exchange) may be applicable. Davis[23] has performed such a calculation and concludes that the $T^{5/2}$ dependence results in the spin-wave formalism if zone boundary effects are taken into account. On the other hand the long-wavelength approximation would predict a T^2 dependence.[24]

Using $+0.9024\pm 0.00007$ nm [25] for the value of the magnetic moment of Fe^{57} and the 4.0°K value for $\nu(0°\text{K})=73.596\pm 0.015$ Mc/sec, $H_{\text{int}}=-534.93\pm 0.42$ kOe [26] for the value of the total internal field at Fe^{57} at 0°K. (Since the Fe^{57} nuclei are not very concentrated and the temperature is not extremely low, we expect no frequency pulling of the type discussed by de Gennes *et al.*[27]) This value agrees well with the extrapolated Mössbauer value of Shirane *et al.*[28] (535 kOe), but disagrees somewhat with that of Forester *et al.*[29] (548±5 kOe). (However, see the discussion in the next paragraph.) A precise value at $T=0$°K is necessary to estimate the zero-point spin deviation for the antiferromagnetic state of α-Fe_2O_3. (The reader is referred to the work of Locher and Geschwind[25] for a discussion of this point.) In essence, the spin-wave theory for $S=\frac{5}{2}$ predicts a zero-point spin deviation of 2 to 3%.[30] In an attempt to estimate the deviation for α-Fe_2O_3 Locher and Geschwind[25] used their value of the magnetic moment of Fe^{57} ($\mu=0.09024\pm 0.00007$ nm), Forester *et al.*'s value[29] of the internal field at 0°K (-548 ± 5 kOe), and Wertheim and Remeika's value[31] of the hyperfine field of Fe^{57} in Al_2O_3 (-549 ± 5 kOe). They also added $+5$ kOe for the dipolar field contribution in α-Fe_2O_3. In this case they utilized the calculation of Tachiki and Nagamiya[32] which agreed with their independent calculation.[25] This value also agrees with the recent calculation of Artman, Murphy, and Foner.[16] (There seems to be a slight discrepancy here, however, since the work of Artman *et al.*[16] yields a dipolar field of -6.70 kOe parallel to the c axis rather than the -5 kOe mentioned above.) This gave a hyperfine field of -543 ± 5 kOe which, when compared to the value of -549 ± 5 kOe for Fe^{+3} in Al_2O_3, yielded a zero-point spin deviation of only (1 ± 1)%. Thus they concluded that there was a discrepancy between the theory and the experimental observations.

In our case at 4°K the natural crystal apparently has a small volume which is still in the weak ferromagnetic state where the spins are perpendicular (rather than parallel) to the c axis. Presumably a signal is observed from only this small volume of sample. For this configuration the approximate dipolar field contribution is $+3.35$ kOe,[16] which yields a hyperfine field of -538.3 ± 0.4 kOe. When compared to -549 ± 5 kOe for Fe^{+3} in Al_2O_3, a zero-point spin deviation of (1.9 ± 1)% is obtained. [If the observed signal were appropriate to the antiferromagnetic state where the spins are parallel to the c axis, the dipolar contribution would be -6.70 kOe.[16] This yields a hyperfine field of -528.2 ± 0.4 kOe, which when compared as above,

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[20] S. J. Williamson and S. Foner, Phys. Rev. **136**, A1102 (1964).

[21] P. J. Besser and A. H. Morrish, Phys. Letters **13**, 289 (1964).

[22] J. A. Eisele and F. Keffer, Phys. Rev. **96**, 929 (1954).

[23] H. L. Davis, Annual Progress Report of Metals and Ceramics Division of Oak Ridge National Laboratory, 1965, p. 51 (unpublished).

[24] See the discussion in V. Jaccarino, in *Magnetism, A Treatise on Modern Theory and Materials*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA, p. 319 ff.

[25] P. R. Locher and S. Geschwind, Phys. Rev., **139**, A991 (1965).

[26] We will uniformly use the negative sign. See A. J. Freeman and R. E. Watson, in *Magnetism, A Treatise on Modern Theory and Materials*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA, p. 167.

[27] P. G. de Gennes, P. A. Pincus, F. Hartmann-Boutron, and J. M. Winter, Phys. Rev. **129**, 1105 (1963).

[28] G. Shirane, D. E. Cox, and S. L. Ruby, Phys. Rev. **125**, 1158 (1962).

[29] D. W. Forester, F. E. Obenshain, L. D. Roberts, and J. O. Thomson, Bull. Am. Phys. Soc. **8**, 558 (1963).

[30] P. W. Anderson, Phys. Rev. **86**, 694 (1952).

[31] G. K. Wertheim and J. P. Remeika, Phys. Letters **10**, 14 (1964).

[32] M. Tachiki and L. Nagamiya, J. Phys. Soc. Japan **13**, 452 (1958).

gives a zero-point spin deviation of (3.8±1)%.] Both of these values are more in line with estimates of spin-wave theory[30] and are in the proper direction to remove the apparent discrepancy. Although the low-temperature signal was observed in the least pure sample, the value was in good agreement with the extrapolated values of the pure samples. (See Table I.) Consequently, the signal is probably representative of pure α-Fe_2O_3 in the canted state. However, the validity of the procedure whereby an ordered concentrated material is compared to a dilute paramagnetic material still remains an open question.

A recent paper[33] has reported the observation of the Fe^{57} resonance in an enriched sample of α-Fe_2O_3 at 4°K. The resonance frequency was given as 74.61 Mc/sec which corresponds to a total field at the nucleus of -542.37 kOe. Our value at 4°K corresponds to -534.93 kOe, and leads to a difference of -7.44 kOe. This is fairly close to the calculated difference (-10.0 kOe) in dipolar fields for the two magnetic configurations based upon the point dipolar approximation.[16] This may also be evidence that the weak signal observed in the natural crystal at 4°K is representative of the canted state.

3. Dependence of the Intensity upon Crystal Orientation

α-Fe_2O_3 has small anisotropy energy in the c plane, but relatively large anisotropy energy out of the c plane. Consequently little or no signal would be expected when $\mathbf{H}_1$ was parallel to c, as observed. That is, the small applied $\mathbf{H}_1$ would not lead to a rocking of the sublattice moments, when applied to the c direction. However, as predicted by Eq. (7), a large enhancement factor is expected when $\mathbf{H}_1$ is in the c plane. In Fig. 3 the intensity variation characteristic of the "demagnetized state" is essentially independent of the angle between $\mathbf{H}_1$ and arbitrary angle in the c plane. (The slight deviations can undoubtedly be accounted for by strains and/or other imperfections.) To obtain the enhancement factor for the "demagnetized state" $|\eta|_D$ a random distribution for φ is assumed in Eq. (7) and

$$|\eta|_D=\left|\frac{H_{\mathrm{hfs}}M}{18K}\left[\left(\frac{1}{\pi}\right)\int_{-\pi/2}^{\pi/2}\cos\varphi\, d\varphi\right]\right| \tag{10}$$

and

$$|\eta|_D=\left|\frac{H_{\mathrm{hfs}}M}{18K}\left(\frac{2}{\pi}\right)\right|. \tag{11}$$

In Fig. 4 the dependence for the "magnetized state" shows a $\cos\varphi$ dependence in accord with Eq. (7). If it is assumed that the crystal is magnetically saturated and that $\varphi=0$, then

$$|\eta|_S=\left|\frac{H_{\mathrm{hfs}}M}{18K}\right|, \tag{12}$$

where $|\eta|_S$ is the maximum enhancement factor for the magnetically saturated crystal.

Assuming that the intensity is proportional to $|H_{1\,\mathrm{eff}}|^2$,

$$\left|\frac{I_S}{I_D}\right|=\left|\left(\frac{\eta_S}{\eta_D}\right)^2\right|=\left|\left(\frac{\pi}{2}\right)^2\right|=2.47. \tag{13}$$

If saturation effects are neglected this would be expected to correspond roughly to the maximum ratio of intensities of the "magnetized" to "demagnetized." However, the observed ratio is only about 1.3. We will comment on this and related matters in the next section.

4. Dependence of the Intensity upon Magnetic Field Strength

Figure 4 shows the gross field dependence of the intensity; $\mathbf{H}_1$ is perpendicular to $\mathbf{H}_0$ in each case. Because of the large anisotropy energy, very large fields (on the order of 10^4 Oe) would be required to move the moments out of the c plane. Consequently, only a small effect was observed with $\mathbf{H}_0 \| c$. The fall off above ~1000 Oe can readily be accounted for by a few degree misalignment of the crystal axis with respect to the field.

The most interesting field dependence occurs when $\mathbf{H}_0$ is in the plane perpendicular to the c axis. Here we have two cases: (1) when the radiofrequency field ($\mathbf{H}_1$) is parallel to the static field ($\mathbf{H}_0$), and (2) when $\mathbf{H}_1$ is perpendicular to $\mathbf{H}_0$.

When $\mathbf{H}_1 \| \mathbf{H}_0$ and $\mathbf{H}_0 \gg \mathbf{H}_1$ the enhancement factor is proportional to $d\theta/dH$, and as in Eq. (6) becomes

$$|\eta|_{\|}\approx\left|\frac{H_{\mathrm{hfs}}M\cos\varphi}{MH_0\sin\varphi+18K\cos6\theta}\right|. \tag{14}$$

In the case $\mathbf{H}_1 \perp \mathbf{H}_0$ geometrical arguments in Fig. 9 show that $\eta \approx (H_{\mathrm{hfs}}/H_0)(d\theta/d\alpha)$. When $d\theta/d\alpha$ is evaluated from the equilibrium relation [Eq. (2)] with $\varphi=\alpha+\theta$ we obtain

$$|\eta|_{\perp}=\left|\frac{H_{\mathrm{hfs}}M\sin\varphi}{MH_0\sin\varphi+18K\cos6\theta}\right|. \tag{15}$$

In order to compare the predictions of these equations with the experimental observations shown in Figs. 5 and 6, the value of θ is required. This represents the angular deviation of the direction of sublattice magnetization from the "easy axis," i.e., the easiest direction of sublattice magnetization. In a perfect crystal at equilibrium and $H_0=0$, $\theta=0$. That being the case different results would be expected for different orientations of $\mathbf{H}_0$ with respect to the easy axis. To compare with observations the appropriate value of α would be used to calculate the corresponding value of φ from Eq. (2). Then, using known values for H_{hfs} and M, η could be calculated for given values of K, the anisotropy constant. The intensity would be assumed to be propor-

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[33] M. Rubinstein, G. H. Strauss, and David H. Anderson, Bull. Am. Phys. Soc. **11**, 172 (1966).

tional to η^2, and a cutoff value would be utilized to take into account the fact that saturation would take place at some value of η. Obviously this would occur physically and is not taken into account in Eqs. (14) and (15). However, apparently there is no well-defined easy axis for our crystal. This is shown by the fact that no anisotropies were observed in Figs. 5 and 6. (Actually these experiments were performed in the hope of measuring anisotropy energy by the NMR technique. Although positive results were not obtained here it still seems that the concept might be applicable to other suitable materials and/or crystals.) It should perhaps be emphasized here that the existence of an *intrinsic* basal-plane anisotropy in α-Fe_2O_3 is still a controversial question. That is, even though many crystals display a definite triaxial basal-plane anisotropy, it is found to vary depending on the purity, state of perfection, etc. The reader is referred to the work of Flanders and Remeika[11] for more information on this point. However, whatever its source, our crystal has an *effective* basal-plane anisotropy and from the magnetization curve in Fig. 7, a lower limit would be $K\approx MH_c/18\approx 0.20$ erg/g.

In order to compare our experimental observations with theoretical models of enhancement, while recognizing that a well-defined value of θ apparently did not exist for our crystal, it was assumed that α had a distribution in the basal plane. Specifically, the calculations were performed as follows on the Sandia Laboratory computer: One thousand equally spaced values of α, all weighted equally, were selected in the interval from 0° to 90°. From Eq. (2) and the relation $\varphi=\alpha+\theta$ the corresponding value of φ was then calculated for each value of θ. Then η and η^2 could be obtained for each value of H_0, assuming a given value of K. To obtain appropriate values for comparison with the experimental results, the values of η^2 obtained from the 1000 values of θ were averaged. Here a maximum value of $\eta=2\times10^4$ was assumed in order to compensate for saturation effects. This value seemed reasonable from earlier enhancement measurements[8] on polycrystalline α-Fe_2O_3, and also gave a shape which was in qualitative agreement with the experimental results. The calculations for three different values of K as well as their superposition are shown in Figs. 10, $\mathbf{H}_1\perp\mathbf{H}_0$, and 11, $\mathbf{H}_1\|\mathbf{H}_0$. Although the intensities are in arbitrary units they have the same scale factor, so that a comparison of the curves for different values of K is valid.

Considering the nature of our model and the intrinsic difficulty of intensity measurements the agreement between Figs. 5 and 6 and Figs. 10 and 11 is probably satisfactory in the high-field region. However, there is some evidence of an additional enhancement process in the low-field region (also in Sec. V 3), which leads us to a consideration of domain-wall motion. Here we believed that we might qualitatively demonstrate the existence of domain-wall contributions by field-reversibility studies of the intensity. With $\mathbf{H}_1\|\mathbf{H}_0$ a maximum of irreversibility would be expected since the walls which are created and annihilated would be parallel to the rf field; conversely, with $\mathbf{H}_1\perp\mathbf{H}_0$ a minimum of irreversibility would be anticipated. The results are shown in Figs. 12 and 13. (The results of only one orientation are shown for each case; other orientations gave essentially the same dependence.) In the parallel case (Fig. 12) we have pronounced irreversibility with the maxima occurring at about 20–30 Oe, which agrees rather well with the coercive force ($H_c\approx 26$ Oe) derived from Fig. 7. Qualitatively speaking, Fig. 12 shows the expected reversibility for the perpendicular case. Consequently, the existence of some domain-wall enhancement in our crystal is consistent with the observations.

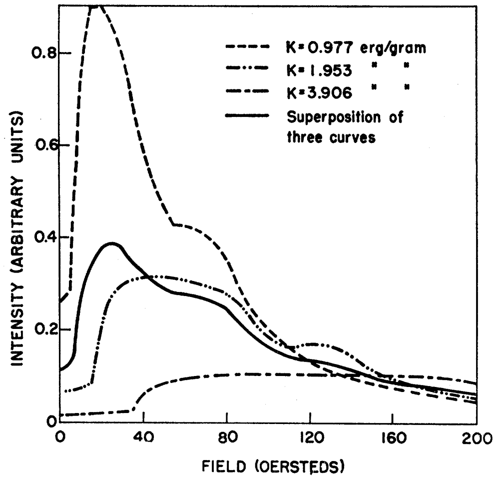

FIG. 10. A theoretical plot (see text) of the NMR intensity versus field for α-Fe_2O_3 when the applied static and radiofrequency fields are perpendicular and in the plane perpendicuar to the c axis. Curves are shown for three different values of the basal-plane isotropy energy K, as well as their superposition.

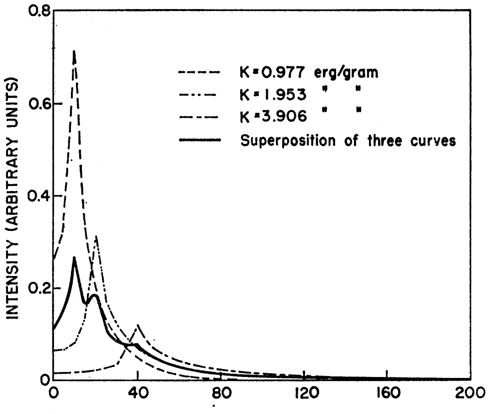

FIG. 11. A theoretical plot (see text) of the NMR intensity versus field for α-Fe_2O_3 when the applied static and radiofrequency fields are parallel and in the plane perpendicular to the c axis. Curves are shown for three different values of the basal-plane isotropy energy K as well as their superposition. Both the applied static and radiofrequency fields are in the plane perpendicular to the crystallographic c axis.

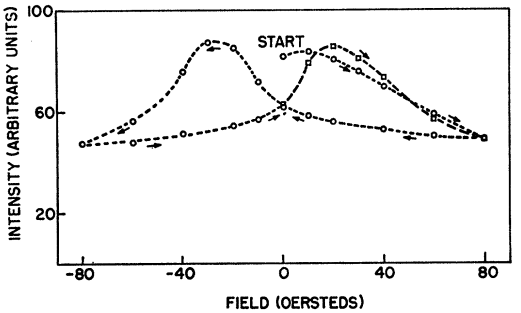

FIG. 12. The NMR intensity versus field for the crystal of unknown origin of α-Fe_2O_3. At the point denoted "start" the crystal is in the demagnetized state discussed in the text. The arrows indicate the direction of the change in field. The applied static and radiofrequency fields are parallel and mutually perpendicular to the crystallographic c axis.

Thus in our crystal of α-Fe_2O_3 we have evidence for both domain-rotation and domain-wall enhancement. This situation is not unreasonable because, as we have observed, the anisotropy energy apparently varies throughout the crystal. In regions of low K where the formation of domain walls is not energetically favorable domain-rotation enhancement would be the most important, as shown in Eq. (8). On the other hand, in high-K regions, where domain-wall formation would be favorable, the enhancement from domain rotation would be reduced [see Eq. (8)] and wall enhancement would prevail. Consequently the mechanism of enhancement depends upon the anisotropy state of the material. For α-Fe_2O_3 the anisotropy energy depends upon such variables as degree of purity, degree of strain, particle size and shape (see Sec. V 6), and possibly others. Therefore, depending on the state of the sample, α-Fe_2O_3 may exhibit domain-rotation enhancement, wall enhancement, or a combination of both.

We might add a comment here regarding possible field dependencies of the resonant *frequency* as opposed to the intensity. It is observed (see Fig. 9) that when the crystal is saturated the weak moment **M** is parallel to the field and therefore, to first order, does not change the field at the nucleus since the sublattice spins are essentially perpendicular to the weak moment. Consequently no shift in frequency with field is expected under these conditions. At the other extreme with the nuclei in a domain wall, the coercive force allows a field up to about 30 Oe along the sublattice direction. This would lead to a maximum shift in frequency of ~4 kc/sec for the nuclei in the wall. Considering the linewidth (~30 kc/sec for the crystal of unknown origin) and the fact that only some of the nuclei are affected, this shift would be difficult to observe. These expectations were borne out by our experiments, since no frequency shifts with field were observed within experimental error.

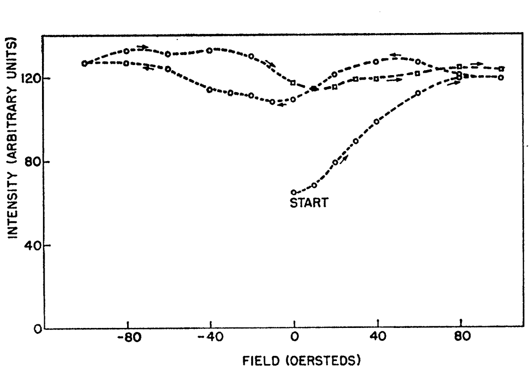

FIG. 13. The NMR intensity versus field for the crystal of unknown origin of α-Fe_2O_3. At the point denoted "start" the crystal is in the demagnetized state discussed in the text. The arrows indicate the direction of the change in field. The applied static and radiofrequency fields are perpendicular and mutually perpendicular to the crystallographic c axis.

5. Dependence of the Magnetization upon Field Strength

From Fig. 7 we obtain $\sigma_s = 0.314$ emu/g and $H_c = 26.8$ Oe. The saturation magnetization is somewhat lower than most natural crystals of hematite, which usually fall in the range of 0.40±0.05 emu/g.[11] Possibly the limited field available with the large Helmholz configuration prevented complete saturation. The coercive field falls within the range reported for natural crystals of hematite.[11]

6. Dependence of the Intensity upon Particle Size

As a result of varying the particle size a decrease in signal intensity would be expected in moving from an optimally oriented signal crystal to a randomly oriented polycrystalline sample. This follows from the geometrical considerations discussed in the previous sections. However, as shown in Fig. 8, the intensity continues to decrease as the particle size decreases after it is initially polycrystalline and randomly oriented. Here it should be recalled that the particle size plotted in Fig. 8 represents the largest particle size of the material. Because of our procedure there is presumably a distribution of sizes ranging up to the plotted value. From a domain-wall-enhancement point of view the dependence shown in Fig. 8 could be explained by asserting that the volume of domain walls (and hence the intensity) decreases as we reduce the particle size toward single domain dimensions. However, as was shown, domain-rotation enhancement processes are perhaps the most significant in our crystal of α-Fe_2O_3, which is the same material used in the particle-size experiment. It is felt that the decrease in intensity with decreasing particle size is a result of the known increase of coercive force as the particles approach single domain dimensions.[34] Here the main effects are expected from the shape anisotropy, longitudinal stress, and the general depend-

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[34] C. Kittel and J. K. Galt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 3, p. 437.

ence of coercive force on particle size. Of course we would also expect some decrease in intensity due to a decrease in domain-wall volume as the particle size decreases. From Fig. 8 it can be seen that a weak signal is still observed when the largest particle size is $\sim 4\times 10^{-2}$ cm. Presumably the single domain size is an order of magnitude or so smaller and very approximately would be $\sim 10^{-3}$ cm. Since the single domain size is expected to be orders of magnitude larger than that of iron,[35] and the single domain size in iron is estimated to be $\sim 10^{-6}$ cm;[36] these results are reasonable.

At this point an incidental note might be added which may be of practical value in the study of similar polycrystalline systems. By tapping and shaking the polycrystalline samples in the presence of a high static field we would expect to orient many of the particles along the field direction. After removing the sample from the static field after this procedure and applying the radiofrequency field in a direction perpendicular to the static field, an order of magnitude increase in signal to noise was observed. Again this would be expected from domain-rotation enhancement but not necessarily from a domain-wall process.

VI. SUMMARY AND GENERAL CONCLUSIONS

The studies of the Fe^{57} resonance in α-Fe_2O_3 have a number of interesting aspects. The disappearance of the signals with decreasing temperature is understood in terms of the weak ferromagnetic to antiferromagnetic transition. Deviations from the expected transition temperatures can be explained on the basis of the effect of known titanium impurities. The field and orientation studies show that the magnetization is anisotropic, with the weak ferromagnetic and sublattice moments in the c plane and virtually perpendicular. The existence of domains and domain walls is qualitatively confirmed. All of the above results are consistent with the Dzialoshinsky-Moriya model of weak ferromagnetism in α-Fe_2O_3. In addition, all samples showed a fractional change of resonance frequency which was closely proportional to $T^{5/2}$. The work of Davis[23] suggests that this dependence will result for α-Fe_2O_3 if zone-boundary effects are taken into account. A very weak resonance was observed at 73.596±0.015 Mc/sec in the crystal of unknown origin at 4.0°K. This value was apparently representative of the canted state, and, using certain subsidiary information, yielded a zero spin deviation of $(1.9\pm 1)\%$. In field and orientation studies of the intensity of single crystals, it was concluded that both domain rotation and wall enhancement mechanisms were operative. It was suggested that both enhancement processes were likely to occur when the value of the basal-plane anisotropy energy varied throughout the material. The decrease of intensity of the signal with reduction of particle size was interpreted in terms of an increase in coercivity and decrease in wall volume.

A few general observations based upon this work are perhaps worth considering. Obviously, nuclear-magnetic-resonance techniques would generally be applicable to the study of other weak-ferromagnetic to antiferromagnetic transitions with the signal intensity playing the important role. The study of sublattice magnetization in many antiferromagnets would be facilitated if the material could be converted to a weak ferromagnet with the attendant signal enhancement. Our results show that small amounts of doping can drastically change the transition temperature to allow study in a different temperature regime. It would also seem that proper doping might change an antiferromagnet to a weak ferromagnet if the material had the proper symmetry. This would facilitate experiments and perhaps not seriously affect the phenomena to be studied. Finally, although not successful here, magnetic anisotropy energy and sublattice spin directions could possibly be determined from such relatively simple experiments.

ACKNOWLEDGMENTS

The author is grateful to A. Narath for many interesting and valuable discussions, especially those regarding enhancement mechanisms. Discussions with H. L. Davis and E. D. Jones were also beneficial. Thanks are also due to R. Aden for excellent experimental assistance.

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[35] T. Moriya, in *A Treatise on Modern Theory and Materials*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. 1, p. 85.

[36] R. M. Bozorth, *Ferromagnetism* (D. Van Nostrand, Inc., New York, 1951).