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Some Properties of Supported Small α-Fe_2O_3 Particles Determined with the Mössbauer Effect*

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Mössbauer spectra of Fe^{57} in α-Fe_2O_3 have been measured as a function of particle size and temperature. Bulk α-Fe_2O_3 shows a change in the sign of the quadrupole interaction in going through the Morin transition temperature, 263°K. Analyses of the spectra show that the magnetization vector is in the c plane above the transition temperature and parallel to the c axis below it. In contrast, finely divided α-Fe_2O_3 particles, supported on a high-area silica, do not undergo a Morin transition. The spectra show that the magnetization vector remains perpendicular to the c axis at least down to 10°K. It is evident that the spins are pinned by the surface in small particles. When the particle size is less than 135 Å, the room-temperature spectrum consists only of a quadrupole-split center line corresponding to superparamagnetic α-Fe_2O_3. As the particle size is gradually increased, a 6-line hyperfine spectrum of increasing intensity appears. This transition from superparamagnetic to ferromagnetic behavior, coupled with a measurement of the average particle size by x-ray line broadening, leads to a calculated value of the crystalline anisotropy constant in the c plane of $(4.7\pm1.1)\times10^4$ erg per cm^3. A sample with an average particle size just below that required for ferromagnetic behavior at room temperature, when cooled, displays an increasing fraction of ferromagnetic material as the temperature is decreased. From these data the particle size distribution of the α-Fe_2O_3 is determined. In addition, these data are used to calculate an independent value of the anisotropy constant of $(4.1\pm1.1)\times10^4$ erg per cm^3. Careful measurements on the series of samples with varying particle sizes show that the quadrupole splitting increases from the bulk value of 0.42 mm sec^{-1} to a value of 0.98 mm sec^{-1} for particles with an undetermined average size of less than 100 Å.

INTRODUCTION

THE unusual magnetic behavior of α-Fe_2O_3 has been the subject of numerous investigations. Dzyaloshinsky[1] formulated a thermodynamic theory explaining the magnetism of α-Fe_2O_3, which has the corundum structure $D^6{}_{3d}$. According to this theory, which is based mainly on the neutron-diffraction data of Shull *et al.*,[2] and on various magnetic measurements,[3,4] the following picture was developed. Between the Morin transition temperature ($T_M=263$°K) [5] and the Néel temperature ($T_N=961$°K),[5] the spins lie in one of the vertical planes of symmetry, making a small angle with the basal plane. Above T_M, α-Fe_2O_3 shows a weak ferromagnetism due to a slight angle between the spins of the two magnetic sublattices. At temperatures below the Morin transition, the spins are aligned along the [0001] axis and the oxide is a pure antiferromagnet. If the oxide is in the form of finely divided particles, the sample exhibits a thermal remanence magnetization, as shown by Cohen *et al.*[6] These results were explained by Néel[7] in terms of superantiferromagnetism.

Finely divided α-Fe_2O_3 particles supported on high-area materials offer a controlled system with which to examine the behavior of α-Fe_2O_3 as a function of both temperature and particle size by means of the Mössbauer effect.[8] Nakamura and Shimizu[9] have shown that particles of unsupported α-Fe_2O_3, with a reported size of about 50 Å, have, at room temperature, a Mössbauer spectrum which consists of a doublet similar to the samples studied by us. On cooling to 120°K, their spectrum consisted of a 6-line hyperfine split line similar to that of bulk α-Fe_2O_3. In extending our previous measurements to varying particle sizes and lower temperatures, we have amplified them as well as those of Nakamura and Shimizu.

In this work the use of the Mössbauer effect to examine the Morin transition in α-Fe_2O_3 is described. In addition, the transition from superparamagnetic to ferromagnetic behavior on increasing the particle size, or lowering the temperature, is quantitatively studied. The data are used to calculate the anisotropy constant at two temperatures and to obtain a size distribution for the α-Fe_2O_3 particles. Finally, variations in the quadrupole splitting and isomer shift as the particle size is decreased are demonstrated.

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† Also at North American Aviation Science Center, Thousand Oaks, California.
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THEORY

The hyperfine structure in the Mössbauer spectrum is a result of the nuclear magnetic dipole and the electric quadrupole interaction. The electric field gradient is a 3 by 3 tensor which can be reduced to diagonal form so that it can be specified by the three components $\partial^2V/\partial x^2$, $\partial^2V/\partial y^2$, and $\partial^2V/\partial z^2$. These are abbreviated here to V_{xx}, V_{yy}, and V_{zz}, respectively. Since the charge density vanishes at the nucleus, the components obey the Laplace equation: $V_{xx}+V_{yy}+V_{zz}=0$. The charge density of the s electrons at the nucleus is finite, it does not contribute significantly to the electric-field gradient at the nuclear site because, to a first approximation, the orbitals are spherically symmetric. In an axial crystal the field is specified by V_{zz} only, with $V_{xx}=V_{yy}=-\frac{1}{2}(V_{zz})$. The interaction energy E between the nuclear moment of a state with spin I, and V_{zz} is

$$E=-g\mu_N H(0)m_I+(-1)^{1/2+|m_I|}eQV_{zz}/4\,, \qquad (1)$$

when $H(0)$, the direction of the magnetization vector, is parallel to V_{zz}. When the direction is perpendicular

$$E=-g\mu_N H(0)m_I-(-1)^{1/2+|m_I|}eQV_{zz}/8\,. \qquad (2)$$

In these equations g is the nuclear g factor, μ_N the nuclear magneton, m_I the magnetic quantum number, and Q the quadrupole moment. α-Fe_2O_3 does not undergo a phase transition when it is taken through the Morin transition. Therefore, it is to be expected that the magnitude of V_{zz} is not affected in going through the transition temperature. The position of Mössbauer lines, determined above and below the transition temperature, can be used to test Eqs. (1) and (2) for consistency in the calculated value of the electric-field gradient. This establishes which equation applies and hence leads to a determination of the angle between $H(0)$ and the c axis. The values used in Eqs. (1) and (2) for Fe^{57} are[10,11]

$$\mu_{\text{gd}}=+(0.0903\pm0.0007)\mu_N\,,$$
$$\mu_{\text{excited}}=-(0.1549\pm0.0013)\mu_N\,,$$
$$Q_{\text{excited}}=+(0.29\pm0.02)\text{ b}\,.$$

These considerations apply to bulk α-Fe_2O_3.

We now turn to a discussion of the magnetic properties of the finely divided form of the oxide. In the following treatment, it is assumed that the particles are spherical and not stressed by external forces so that shape and strain anisotropy can be neglected. The magnetization vector in a single-domain particle is held in an easy direction by the crystalline field. Above the Morin transition temperature, the easy axis of magnetization in α-Fe_2O_3 is perpendicular to the c axis. The anisotropy energy density in the c plane may be written as $K\cos(3\psi)$, where ψ is the angle between the magnetization vector and the vertical reflection plane, and K is the anisotropy constant. The energy required to go from one easy direction to another in the c plane is $2K$. At any finite temperature thermal fluctuations cause the magnetization vector to undergo a kind of Brownian rotational motion around the easy axis. In an assembly of particles, each with a volume v, there is a finite probability proportional to $\exp(-2Kv/kT)$ (where k is the Boltzmann constant) that the magnetization vector will spontaneously change its direction. The relaxation time τ_0, which indicates how rapidly this transition occurs, may be written as

$$\tau_0=(1/af)e^{2Kv/kT}\,, \qquad (3)$$

where a is a geometrical factor. This is the number of different directions the magnetization vector can flip. For trigonal α-Fe_2O_3, $a=2$, since M can flip either clockwise or counterclockwise into another easy direction. This is only approximately correct because after one spin flip there still exists some "memory" of the previous direction of magnetization. The frequency factor f is the Larmor frequency of the magnetization vector M in an effective field H_{eff} defined as

$$H_{\text{eff}}=2Kv/M\,. \qquad (4)$$

The frequency factor is then

$$f=(2Kv/M)(n_{\text{eff}}\mu_B/h)\,, \qquad (5)$$

where n_{eff} is the number of Bohr magnetons μ_B per Fe atom, and h is Planck's constant. Using

$$M=2n_{\text{eff}}\mu_B\rho N_L v/A\,, \qquad (6)$$

one obtains

$$f=KA/\rho N_L h=7.7\times10^8 K\text{ cm sec g}^{-1}\,, \qquad (7)$$

where A is the molecular weight and ρ is the density of α-Fe_2O_3, and N_L is Avogadro's number.

In the measurement of the magnetic properties of single-domain particles what is observed depends on the ratio of the time required for the measurement, τ_{obs}, to the relaxation time, τ_0. For $\tau_{\text{obs}}\ll\tau_0$, the particles will show ferromagnetic behavior. If the reverse is true, the particles will be superparamagnetic. With the Mössbauer effect, the nuclear Zeeman splitting caused by the magnetic field at the site of the nucleus, $H(0)$, can be observed. However, the magnetic quantum numbers are well defined only if the Larmor frequency ν_I of the nuclear spin around $H(0)$ is larger than $1/\tau_0$. Therefore, in a Mössbauer experiment τ_{obs} corresponds to $1/\nu_I$. For an Fe^{57} nucleus in the first excited state and in a typical field of 500 kOe, the Larmor frequency is 4×10^7 sec^{-1}. (The frequency of the excited state is considered here since its nuclear g factor is smaller than that of the ground state.) Thus, if τ_0 is $\gg2.5\times10^{-8}$ sec the Zeeman splitting will be observed. For $\tau_0\ll2.5\times10^{-8}$ sec, the particles will appear to be superparamagnetic and the Zeeman splitting will disappear. Using these

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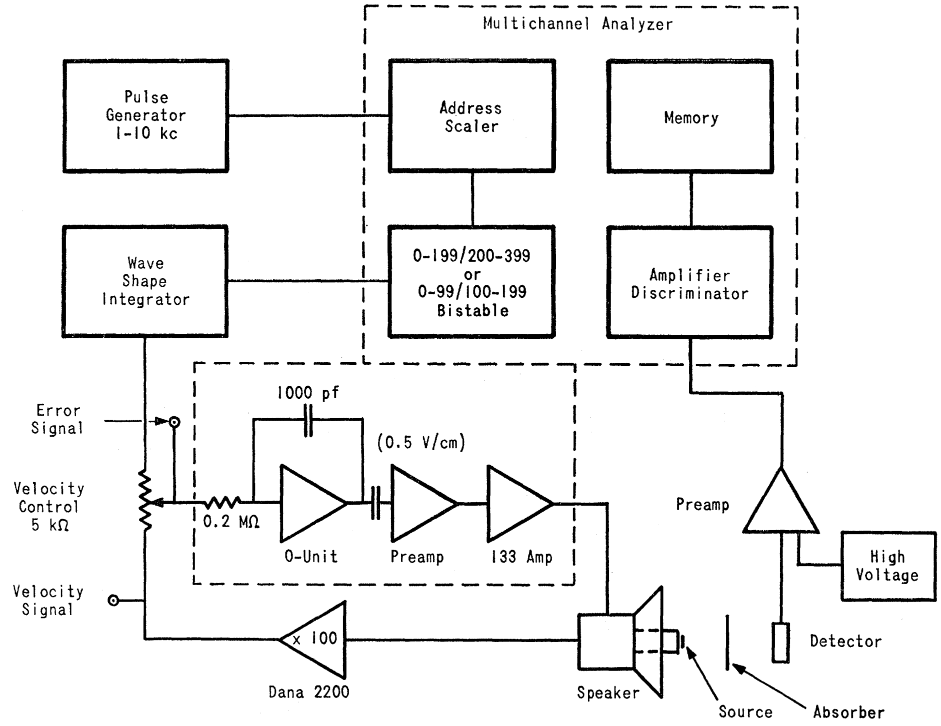

FIG. 1. Schematic of the Mössbauer spectrometer.

values, Eq. (3) can now be written

$$\ln(4\times 10^{-4}K)=2K\bar{v}/kT. \tag{8}$$

Since all samples used here have a distribution of α-Fe$_2$O$_3$ particle sizes, K can be determined experimentally in two independent ways from Eq. (8). However, both depend on an independent evaluation of the average volume $\bar{v}$. The first method involves measuring the spectra at one temperature for a series of samples with known average particle sizes which encompass the transition region between superparamagnetic and ferromagnetic behavior. From the spectra the average size that contains equal amounts of both types of particles can be estimated. This size is the proper value to insert into Eq. (8).

In the second method, a sample is selected with a particle size such that the particles are mostly superparamagnetic at room temperature. Spectra are taken at progressively lower temperatures. From these, the temperature at which the particles are half-superparamagnetic and half-ferromagnetic can be estimated. This value used in Eq. (8) gives another value of K. It is to be noted that this technique yields a particle size distribution if it is assumed that K does not vary greatly with temperature. In addition, it is clear that if K is independent of particle size, this technique can be used to establish a particle size and size distribution in the sub-x-ray region.

For the fraction of the particles in a sample which are superparamagnetic, the observed spectrum will consist of a pure quadrupole-split center line, the splitting of which is given by

$$E=\tfrac{1}{2}eQV_{zz}. \tag{9}$$

EXPERIMENTAL

A series of samples containing various levels of α-Fe$_2$O$_3$ supported on a high-area silica was made by the impregnation of Davison grade 70 silica gel (obtained from Davison Division of W. R. Grace and Company, Baltimore, Maryland) with unenriched iron nitrate solutions of different concentrations. The grade 70 silica gel has an average pore radius of 70 Å, in contrast to the silica previously used,[8] which has an average pore radius of 20 Å. This latter sample will be designated X in the discussion below. After the impregnated samples were dried at 200°C, they were calcined at 500°C for 2 h in dry air. They were then potted in a polyester resin in the form of disks 24 mm in diameter and 3 mm thick. The average particle size was determined where possible from x-ray line broadening using a method described by Klug and Alexander.[12] The α-Fe$_2$O$_3$ content and the average particle size in the samples is given in Table I. In the experiments carried out on unsupported oxide bulk α-Fe$_2$O$_3$, calcined at 1500°C in air, was used.

The Mössbauer spectra were obtained with the spectrometer indicated schematically in Fig. 1. In this, the address scaler of a RIDL 400-channel analyzer is advanced by a pulser. A square wave is taken from the

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[12] H. P. Klug and L. E. Alexander, *X-Ray Diffraction Procedures* (John Wiley & Sons, Inc., New York, 1954), pp. 504–509.

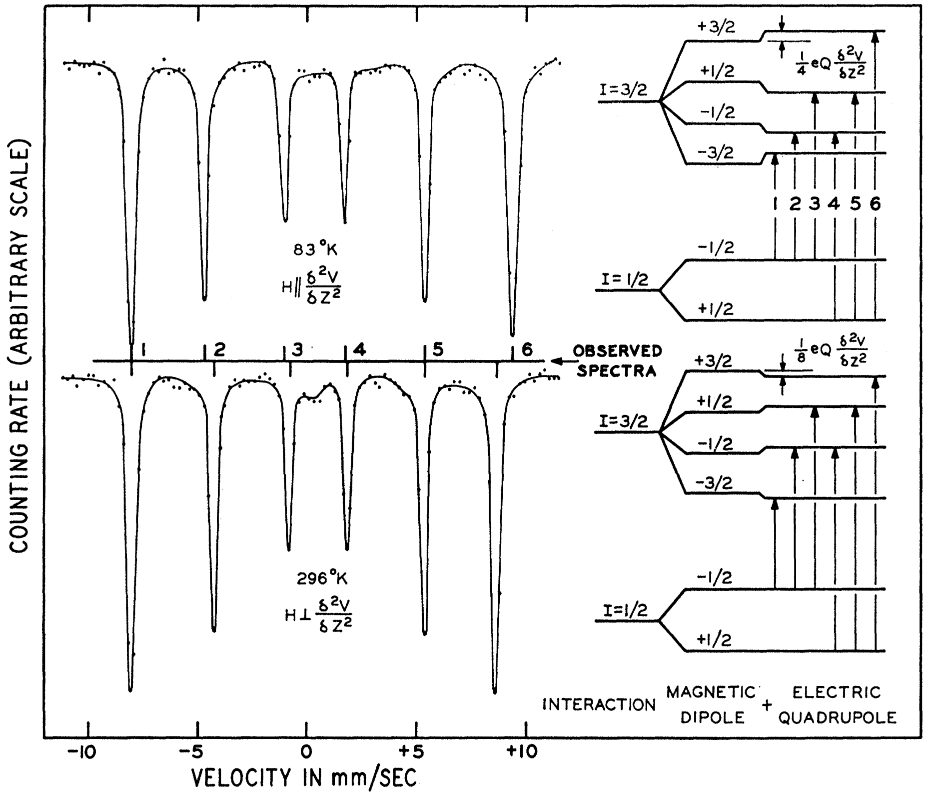

FIG. 2. Mössbauer spectra below and above the Morin transition.

hundred bistables of the address scaler. The square wave is shaped and integrated into a triangular wave by a circuit similar to the one described by Kankeleit.[13] The triangular wave drives a University C-8HC two-voice coil speaker. One coil is used as the driver and the other as a velocity sensor. The velocity can be controlled either by the potentiometer or by a change in the frequency of the pulse generator. With this system, which permits the use of velocities up to 50 mm/sec, a highly reliable instrument, which is fairly easily assembled, is readily available. The present instrument has an error signal (peak-to-peak) of less than 0.2% of the velocity signal with a deviation from linearity, as detected with an Fe absorber of less than one quarter of a channel.

TABLE I. Particle size and Fe concentration in the different samples.

Sample	α-Fe_2O_3 content, wt%	Average particle diameter in Å
X^a	1.63	<100
A	2.57	<100
B	6.39	135±10
C	12.41	150±10
D	20.52	180±10

[a] Reference 8.

RESULTS

The change in the magnetic behavior of bulk α-Fe_2O_3 in going through the Morin transition, as reflected in the Mössbauer spectrum, is shown in Fig. 2. The energy-level diagrams for Fe^{57} in the right-hand part of the figure depict the levels for the two cases of the magnetic field being either parallel or perpendicular to the electric-field gradient. At 83°K the energy difference between lines 1 and 2, Δ_{12}, is less than that between lines 5 and 6, Δ_{56}; $\Delta_{12}-\Delta_{56}$ is negative. The reverse is true above the Morin transition at 296°K. The measured values for $\Delta_{12}-\Delta_{56}$ are shown in the upper-half of Table II. If the value for the 83°K spectrum is used in Eq. (1), it is found that V_{zz} is $+1.14\times10^{17}$ V cm^{-2}; Eq. (2) yields a value of -2.28×10^{17} V cm^{-2}. Similarly, for the room-temperature spectrum, Eq. (1) gives a value of -0.70×10^{17} V cm^{-2}; Eq. (2) $+1.40\times10^{17}$ V cm^{-2}. It is evident that the perpendicular case applies to the room-temperature spectrum and the parallel case to the 83°K spectrum. This shows that above the Morin transition $H(0)$ is perpendicular to the c axis and parallel to it below. This is in agreement with neutron-diffraction data.[2] The values for the magnetic field at the nucleus, the electric-field gradient, and the estimated errors are given in Table II, along with the observed isomer shift. These data extend those given by other investigators.[14,15]

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[13] E. Kankeleit, Rev. Sci. Instr. 35, 194 (1964).

[14] J. Gastebois and J. Quidort, Compt. Rend. 253, 1257 (1961).

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TABLE II. $H(O)$, V_{zz}, isomer shift with temperature for bulk and 180-Å particle α-Fe_2O_3.

Sample	T °K	H[a] kOe	$\Delta_{12}-\Delta_{56}$[b] mm sec^{-1}	V_{zz} 10^{17} V cm^{-2}	IS[c] mm sec^{-1}	$\sphericalangle(H,c)$[d] rad
bulk	296	518±6	+0.42±0.03	+1.40±0.15	+0.39±0.02	$\pi/2$
α-Fe_2O_3	83	542±6	−0.69±0.03	+1.14±0.15	···	0
180 Å	296	503±6	+0.44±0.03	+1.44±0.15	+0.38±0.03	$\pi/2$
(sample D)	80	527±6	+0.39±0.03	+1.30±0.15	···	$\pi/2$
	10	531±6	+0.37±0.03	+1.21±0.15	···	$\pi/2$

[a] The error in H comes mainly from calibration uncertainties. Relative values of H are correct to within 0.2%.
[b] $\Delta_{12}-\Delta_{56}$ is the splitting between lines 1 and 2 of the spectrum minus the splitting between lines 5 and 6.
[c] IS is the isomer shift relative to Fe metal.
[d] $\sphericalangle(H,c)$ is the angle between the magnetization vector and the c direction.

The room-temperature spectra for the supported α-Fe_2O_3 samples of Table I are shown in Fig. 3. (The spectrum for bulk α-Fe_2O_3 is included for comparison.) Sample A, with the lowest α-Fe_2O_3 content, gives a spectrum consisting of only the quadrupole-split center line. The average particle size is small enough so that the behavior is completely superparamagnetic. As the particle size is increased in going from samples A to D, the Zeeman lines become progressively more preponderant over the quadrupole-split center line. In sample D the average particle size has increased to a value which almost corresponds to a pure ferromagnet.

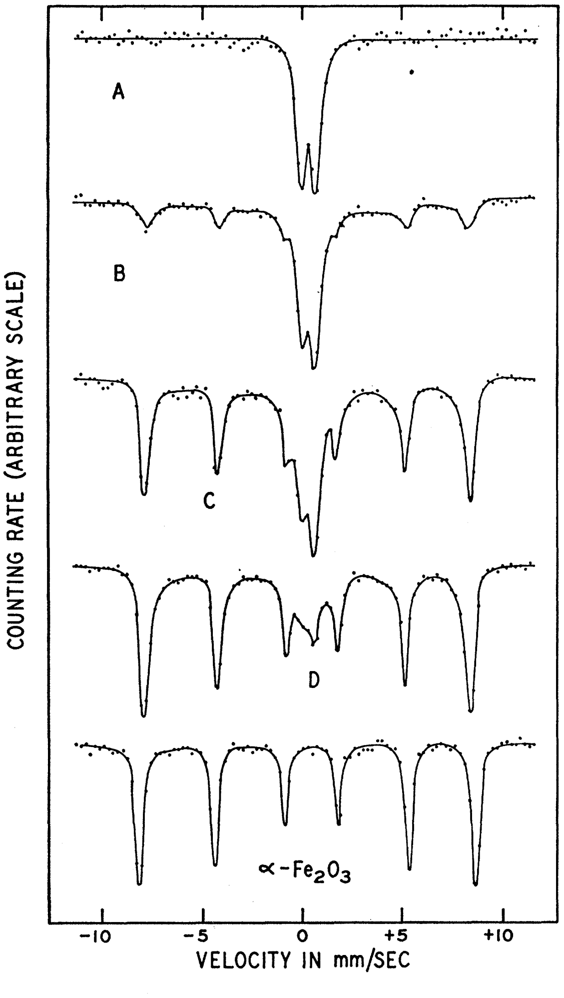

FIG. 3. Mössbauer spectra of α-Fe_2O_3 as a function of the average particle size. The size increases from A to D.

Because the amount of Fe in the samples is low, self-absorption is negligible. This is borne out by the fact that the relative intensities of the Zeeman lines are in the ratio of 1:2:3, as would be expected from the transition probabilities. Therefore, the ratio of the superparamagnetic fraction of α-Fe_2O_3 particles to the ferromagnetic fraction can be obtained directly by integration of the absorption lines. The ratios so obtained are plotted in Fig. 4 against the average particle volume. The errors indicated were estimated from point scatter in duplicate spectra. The figure shows that 50% of the particles are ferromagnetic when the average volume is $(1.3\pm0.2)\times10^{-18}$ cm^3. Using this value in Eq. (8), one finds that $K=(4.7\pm1.1)\times10^4$ erg/cm^3.

Turning now to the second method for the evaluation of K discussed above, spectra were measured for sample B at various temperatures. These are shown in Fig. 5, which shows the increasing ferromagnetic content as the temperature is lowered. The ratios of ferromagnetic and superparamagnetic fractions obtained from Fig. 5 are plotted in Fig. 6. This indicates that the temperature at which 50% of the particles are ferromagnetic is 206°K. This value, when used with the average particle diameter in Eq. (8), gives the second

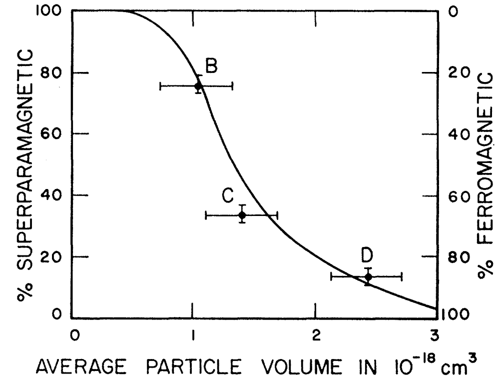

FIG. 4. Percentage of superparamagnetic fraction in samples of Fig. 3 as a function of the average volume obtained from x-ray line broadening.

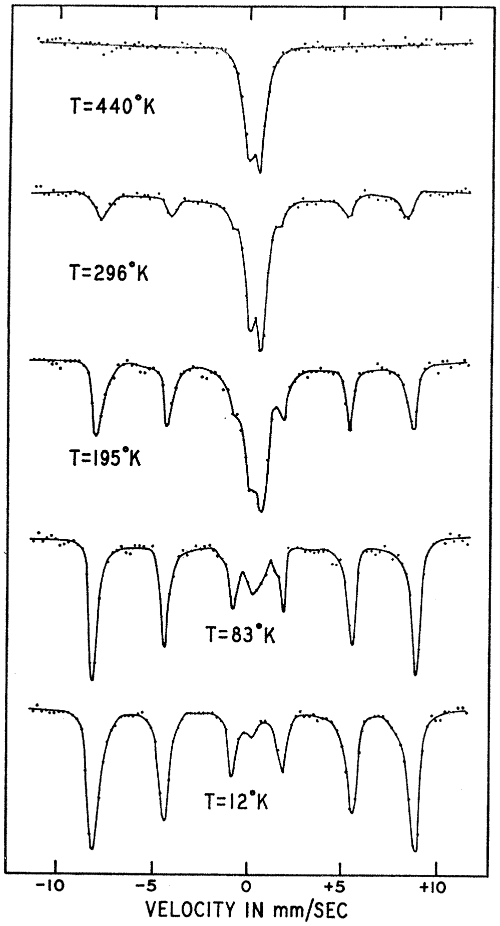

FIG. 5. Mössbauer spectra of sample B at various temperatures.

value of $K=(4.1\pm1.2)\times10^4$ erg/cm^3. The volume scale of the histogram shown in Fig. 5 was calculated using this value of K and the ferromagnetic to superparamagnetic ratio. It is seen that the particle size distribution is slightly skewed, which indicates that use of the 50% ratio for the calculation of K is not exactly correct, but is probably well within the estimated error in K.

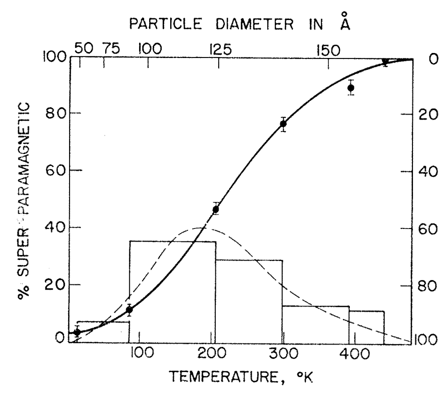

FIG. 6. Percentage of superparamagnetic fraction in sample B as a function of the temperature. The histogram is obtained from this data and the calculated anisotropy constant.

The spectra for sample D, also measured at progressively lower temperatures, are shown in Fig. 7. It is observed that at least down to 10°K, lines 5 and 6 remain closer than 1 and 2. Clearly, for the small α-Fe_2O_3 particles no Morin transition is observed in the temperature range used, and the magnetization vector stays perpendicular to the c axis. It is most likely that the surface, which, for such particles, represents a huge solid-state defect, pins the spins. This is analogous to the spin pinning by impurities observed by Morin.[3] Parameters calculated from this data are included in the lower half of Table II in order to contrast them to the values obtained for bulk α-Fe_2O_3.

A preliminary analysis of the spectra for samples A to C (Fig. 3) indicated an increase in the quadrupole splitting of the center line as the particle size decreased.

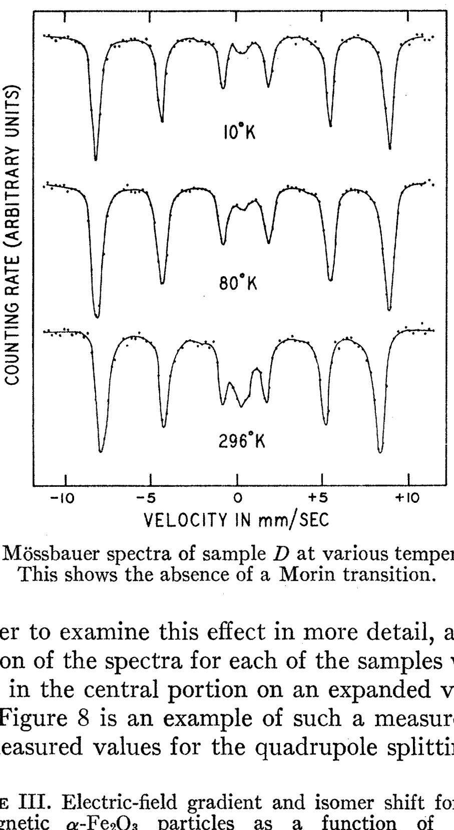

FIG. 7. Mössbauer spectra of sample D at various temperatures. This shows the absence of a Morin transition.

In order to examine this effect in more detail, a determination of the spectra for each of the samples was repeated in the central portion on an expanded velocity scale. Figure 8 is an example of such a measurement. The measured values for the quadrupole splitting and

TABLE III. Electric-field gradient and isomer shift for superparamagnetic α-Fe_2O_3 particles as a function of the Fe concentration.

Sample	α-Fe_2O_3 content, wt%	Quadrupole splitting, mm sec^{-1}	V_{zz} 10^{17} V cm^{-2}	IS mm sec^{-1}
X[a]	1.63	0.98±0.01	+3.24±0.10	+0.32±0.02
E	0.37	0.77±0.01	+2.55±0.10	+0.305±0.005
F	0.14	0.77±0.01	+2.55±0.10	+0.308±0.005
A	2.57	0.68±0.01	+2.25±0.10	+0.300±0.005
B	6.39	0.57±0.01	+1.88±0.10	+0.322±0.004
C	12.41	0.55±0.02	+1.82±0.15	+0.327±0.011
D[b]	20.52	0.44±0.03	+1.44±0.15	+0.38±0.03

[a] Reference 8.

[b] Calculated from hfs splitting.

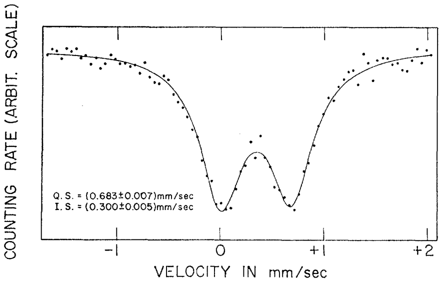

FIG. 8. Mössbauer spectra of sample *A* measured on an expanded velocity scale. The line is a least-squares fit to two Lorentzian curves defined by the points.

isomer shift, as well as the electric-field gradient calculated from Eq. (9) are given in Table III. Data for sample *X* are included.[8] The results show a definite increase in the splitting, and hence the electric-field gradient, as the α-Fe_2O_3 content of the samples is decreased. Although samples *A*, *E*, *F*, and *X* do not give an x-ray diffraction pattern (in itself an indication of very small particles), the evidence presented above is strongly indicative that these samples do indeed still have the iron present as α-Fe_2O_3, rather than some other species. In addition, it will be recalled that sample *X* was prepared using a 40-Å pore diameter silica, approximately one-third the diameter used for the other samples in Table III. This is confirmatory evidence that sample *X* contains much smaller α-Fe_2O_3 particles than sample *B*.

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Pulsed-NMR Study of Protonic Relaxation in Paramagnetic and Antiferromagnetic $CoCl_2\cdot 6H_2O$†

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Protonic spin-lattice relaxation times have been measured in crystalline $CoCl_2\cdot 6H_2O$ in the temperature range 4.2–1.24°K, which includes the Néel transition region. Spin-echo experiments have also been carried out over this temperature range to determine the homogeneous transverse relaxation time T_2 and the extent of the inhomogeneous broadening. All experiments in this series were performed with the position of the external field along the intermediate anisotropy axis (*b*). In the paramagnetic region, the spin-lattice relaxation time T_1 and T_2 became increasingly temperature-dependent below 3°K, changing most rapidly in the range 2.30–2.20°K. Moriya has pointed out that such rapid fluctuations in relaxation rates are to be associated with critical fluctuations in the electronic spin system. Below the Néel temperature T_N, the protonic T_1 is found to have a very strong temperature dependence. Below 2°K, $T_1 \propto T^{-7}$. The observed temperature dependence of T_1 in the antiferromagnetic state is in accord with theoretical predictions based on a magnetoelastic coupling between magnon and phonon modes. T_2 exhibits much weaker temperature dependence below T_N.

INTRODUCTION

NUCLEAR magnetic relaxation provides a means for studying the dynamical behavior of an antiferromagnetically ordered system.[1] Excitations of the spin system produce fluctuating local fields at the nuclear sites via hyperfine and dipolar coupling. The Fourier component of the fluctuating field at the NMR frequency transverse to the direction of the effective field is responsible for spin-lattice relaxation. Experiments on MnF_2 [2,3] and CoF_2 [4] indicate that spin-spin relaxation is produced by indirect nuclear coupling through the electronic excitations.

NMR-pulse techniques provide a convenient method for measurement of relaxation times, spanning the range from microseconds to minutes. In addition, by using echo techniques one can recover the homogeneous transverse relaxation time T_2 in the presence of inhomogeneous broadening. This is particularly useful for studying relaxation near the antiferromagnetic transition temperature.

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[*] Now with Solid State Research Group, Xerox Corporation, Webster, New York.

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