(b) The transitions between energy levels of largest values of $|m|$ have second moments due to like-spin exchange and like-spin dipole-dipole interactions, which are smaller than the second moment of the line shape without quadrupole broadening.

(2) We find experimental agreement with the interaction distance dependence in the exchange constant derived by Anderson. The electronic wave-function densities at A and B nuclear positions are determined using Anderson's exchange constant, an assumed effective mass equal to the free-electron mass, and the experimental exchange second moments.

(3) The broadening of the resonance line shapes of each nuclear spin-system as the magnetic field is rotated from $\langle 001\rangle$ directions is explained as due to anisotropic dipole-dipole and anisotropic quadrupole interactions. The quadrupole second moments are due to a distribution of field gradients, which are characterized by a root-mean-square field gradient. The experimental quadrupole second-moment anisotropy and the magnitude of the mean-square field gradient agree with an explanation that the electric field gradients are due to the electric fields of the ionized impurities. The tensor component R_{14} is estimated at the nuclear positions, and the ratios of the antishielding factors between In, Sb, Ga, and As nuclear positions are determined.

ACKNOWLEDGMENTS

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Relaxation Effects in Antiferromagnetic Ferrous Carbonate†

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Mössbauer studies of antiferromagnetic $FeCO_3$ below and above the Néel temperature show an asymmetric line broadening, and a constant value of 184 kOe of the magnetic hyperfine field from 0 to $\frac{1}{2}T_N$. These phenomena are explained using an Ising model with slow electron relaxation. The relaxation rate decreases with decreasing temperature, suggesting a spin-lattice relaxation. The Néel temperature was found to be (38.3 ± 0.3)°K, which is 3.3°K higher than that measured by neutron diffraction.

INTRODUCTION

RECENTLY, electron-spin relaxation phenomena have been observed by many investigators[1–8] using Mössbauer technique. However, most of these studies in iron compounds were restricted to the Fe^{3+} ions, and to my knowledge no relaxation effects in the Fe^{2+} ions in an antiferromagnetic material have been observed. The purpose of this paper is to present the Mössbauer spectra of antiferromagnetic $FeCO_3$ at low temperatures, and to explain the observed phenomena in terms of slow electron relaxation between two lowest states of the Fe^{2+} ions.

Ferrous carbonate, occurring naturally as the mineral siderite, has a rhombohedral (calcite) structure[9] with a bimolecular unit cell which has the dimensions $a_0=5.795$ Å, $\alpha=47°45'$. Its structure may be visualized as an NaCl-type lattice contracted along a body diagonal, and, therefore, we may expect the ferrous ion to be under the influence of a crystalline electric field of cubic symmetry in the first approximation, and of the trigonal field in the second approximation. Magnetic susceptibility[10–12] and neutron diffraction[13] measurements have established antiferromagnetic behavior at low temperatures with the Fe^{2+} spins pointing along the trigonal c axis, in alternating (0 0 0 1) ferromagnetic

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TABLE I. Magnetic hyperfine field and quadrupole splitting of $FeCO_3$ at various temperatures.

T (°K)	H (kOe)	$e^2qQ/2$ (mm/sec)
4.24	184±3	2.02±0.03
8.65	184±3	2.02±0.03
14.7	183±3	2.01±0.03
19.6	183±3	2.01±0.03
24.4	177±3	2.04±0.03
28.3	167±3	2.04±0.03
32.2	148±3	2.01±0.03
36.1	110±3	2.03±0.03
37.5	78±3	2.05±0.03
43.8	0	2.09±0.01
60	0	2.08±0.01
79	0	2.05±0.01
102	0	2.03±0.01
124	0	2.00±0.01
148	0	1.97±0.01
194	0	1.92±0.01

sheets. Metamagnetism of $FeCO_3$ was also studied by Jacobs,[12] who found that the metamagnetic transition toward ferromagnetism was nearly complete at 4.2°K with an external magnetic field of 200 kOe. Kanamori[14] investigated the crystalline field origin of the Fe^{2+} anisotropy in $FeCl_2$ and noted its applicability to $FeCO_3$. He concluded that an Ising model is a good low-temperature approximation. This model is supported by the jump in the specific heat[15] on crossing the transition temperature from paramagnetic to antiferromagnetic ordering. Kalinkina and Kostryukov[15] measured the specific-heat jump as 12.9±0.5 J/mole deg, and calculated the theoretical value 12.5 J/mole deg by using the effective spin $\frac{1}{2}$. Mössbauer studies of $FeCO_3$ originally carried out by Ono and Ito,[16] did not show any relaxation effects because they studied Mössbauer spectra only at two very low temperatures.

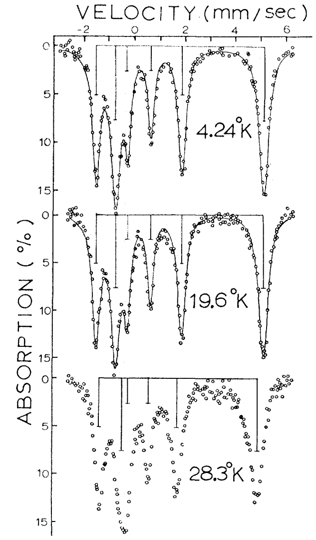

FIG. 1. Mössbauer spectra of $FeCO_3$ at very low temperatures.

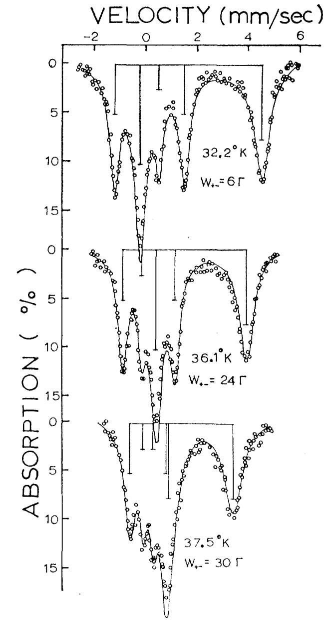

FIG. 2. Mössbauer spectra of $FeCO_3$ just below T_N.

EXPERIMENTAL PROCEDURES

Since natural siderite is usually impure (impurities of order of 10%), the $FeCO_3$ sample for the present Mössbauer studies was prepared by heating a mixture of a solution of $FeSO_4$ (99.5% pure) and $NaHCO_3$ (99.8% pure) in a high pressure of CO_2 (~200 atm) at 160°C for 18 h. In order to prevent oxidation caused by atmospheric oxygen, the preparation (mixing, high-purity (99.99%) CO_2 atmosphere, where water distilled twice in high-purity nitrogen gas was used. A part of the sample was examined by x-ray diffraction technique (Cr $K\alpha$ line), showing only $FeCO_3$ diffraction peaks. The particle diameter of 800 Å was determined using the Scherrer formula[17] and quartz diffraction peaks as the standard linewidth not affected by size effects. The particle size of 800 Å is big enough to exclude any superparamagnetic relaxation effects[18,19] which may exist in ultrafine particles (less than 200 Å in diameter). A Mössbauer spectrometer with an electromechanical drive system manufactured by Elron Co. and stabilized[20] up to ±0.001 mm/sec was used with 10-mCi Co^{57} source in Pd which was kept at room temperature. Temperature measurement and control were carried out by a platinum resistance and a heater above 50°K with an accuracy of 0.5°K. A carbon resistance

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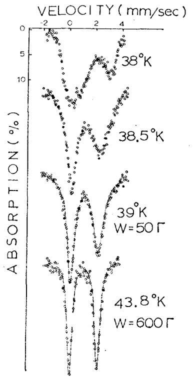

FIG. 3. Mössbauer spectra of $FeCO_3$ near and above the transition temperature.

thermometer calibrated at liquid-nitrogen, liquid-hydrogen, and liquid-helium temperatures was used for temperature measurement and control below 50°K with an accuracy of 0.1°K. The temperature near the antiferromagnetic transition temperature was controlled manually with a stability of 0.01°K using a highly sensitive galvanometer and a heater.

MÖSSBAUER SPECTRA

The Mössbauer spectra of $FeCO_3$ at various temperatures are shown in Figs. 1–3. Below 38.3°K, the spectra consist of six lines, which can be easily analyzed by diagonalizing the 4×4 magnetic hyperfine and quadrupole-interaction matrix[21] for the first excited state of Fe^{57} to give magnetic hyperfine field and quadrupole splitting. The results are shown in Table I and Fig. 4. The line positions and relative intensities calculated for $\theta=0$ and $\eta=0$ (θ is defined to be the angle between the magnetic hyperfine field and the direction of the maximum electric field gradient, η is defined to be asymmetry factor of the electric field gradient) are shown by vertical lines in Figs. 1 and 2. There are three noteworthy things in these spectra: First, as is evident in Fig. 1, the spectra did not change as the temperature increased from 4.2 to 20°K. The magnetic hyperfine field remained essentially the same (184 kOe) for both 4.2 and 19.6°K, even though the Néel temperature T_N was 38.3 ± 0.3°K. Ono and Ito[16] observed Mössbauer spectra of natural $FeCO_3$ (siderite) at both liquid-helium and liquid-hydrogen temperature, and found 172 ± 15 and 171 ± 15 kOe, respectively, as magnetic hyperfine field. These values are substantially lower than our value of 184 ± 3 kOe. However, their spectra were not as sharply resolved as ours. These authors interpreted the invariance of the magnetic hyperfine field as evidence of a high value of the Néel temperature without actually measuring it. Our measured value of T_N ($=38.3$°K) makes this interpretation doubtful. As discussed in the next section, the correct interpretation may be connected with relaxation phenomena. Another interesting point in Figs. 1 and 2 is that as the temperature increases above 20°K towards T_N the highest-energy line (the extreme right line) broadens much more than the other lines. Before proceeding any further, it must be emphasized that this asymmetric broadening did not come from a nonuniform temperature distribution across the sample or from any other instrumental effects. To prove this point a $FeCO_3$ sample five times smaller than the previous one ($\frac{5}{8}$ in. diameter) was mounted with stopcock grease in a copper sample holder to give better thermal conduction. The Mössbauer spectra of this much smaller sample at 37.5°K showed exactly the same spectra and the same line broadening as the bigger sample. An iron foil mounted in the same place as the $FeCO_3$ sample did not show any asymmetric broadening, thereby eliminating any instrumental effects on the line broadening. The third noteworthy point is the asymmetric line broadening of the doublet in the paramagnetic state above T_N, as shown in Fig. 3. This kind of asymmetric line broadening of a doublet has been observed for paramagnetic Fe^{3+} ions in some materials,[7] and was interpreted as slow electron-spin relaxation as compared to the nuclear-precession frequency.

RELAXATION EFFECTS

Before discussing relaxation effects we will look for the electronic levels which may participate in relaxation phenomena at low temperatures. The ground-orbital state of Fe^{2+} ($3d^6$,^5D) in cubic-octahedral crystal field is the orbital triplet (T_{2g}). When we take the trigonal axis of $FeCO_3$ crystal as the quantization z axis, the orbital wave functions of the triplet may be written as[22]

$$\psi_1=(\tfrac{2}{3})^{1/2}Y_2^{-2}+(\tfrac{1}{3})^{1/2}Y_2^{1},$$
$$\psi_0=Y_2^{0},$$
$$\psi_{-1}=(\tfrac{2}{3})^{1/2}Y_2^{2}-(\tfrac{1}{3})^{1/2}Y_2^{-1},$$

where Y_2^m ($m=0$, ±1, ±2) represent the spherical harmonics of order 2. This triplet splits into a singlet (ψ_0) and a doublet (ψ_1, ψ_{-1}) in a trigonal field. Since

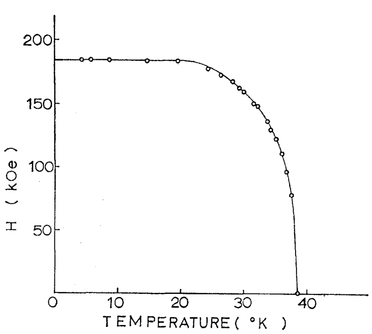

FIG. 4. Temperature dependence of the magnetic hyperfine field.

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$\frac{1}{2}e^2qQ>0$ in Table I, the doublet is lower than the singlet, because both ψ_1 and ψ_{-1} give $(2/7)e\langle r^{-3}\rangle$ for the electric field gradient, while ψ_0 gives $-(4/7)e\langle r^{-3}\rangle$, where e is taken as positive. As shown in Table I, the quadrupole splitting is nearly constant (2.05 ± 0.05 mm/sec) over the temperature range from 0 to 120°K. Since the quadrupole splitting of 2.05 mm/sec is positive and is almost the maximum value[23] that the doublet (ψ_1, ψ_{-1}) can give, it may be concluded that the energy separation between the doublet (ψ_1, ψ_{-1}) and the singlet is much larger than the spin-orbit coupling energy. Thus, if we neglect in our low-temperature discussion the secondary effects from the singlet state, the spin-orbit coupling $\lambda\mathbf{L}\cdot\mathbf{S}$ ($\lambda\simeq-150$°K) splits the ground-orbital doublet having a spin degeneracy of 5 into five spin-orbit doublets. The lowest of these doublets has the wave functions $\psi_1\chi_{-2}$ and $\psi_{-1}\chi_2$, and the first excited doublet separated by $|\lambda|$ from the ground doublet has the wave functions

$$\phi_1=(\psi_1\chi_{-1}-\psi_{-1}\chi_1)/\sqrt{2},$$

and

$$\phi_2=(\psi_1\chi_{-1}+\psi_{-1}\chi_1)/\sqrt{2},$$

where χ_m ($m=0, \pm1, \pm2$) are the spin-wave functions of $S=2$. The electric field gradients and magnetic-hyperfine fields of these levels are now calculated using the above wave functions and the following expressions[21] for the magnetic hyperfine field and the electric field gradient:

$$H=2\mu_B\langle r^{-3}\rangle\langle L_z\rangle+\tfrac{1}{2}H_c\langle S_z\rangle-\tfrac{1}{2}\mu_B\langle 3z(\mathbf{S}\cdot\mathbf{r})r^{-2}-S_z\rangle\langle r^{-3}\rangle,$$
$$V_{ij}=-e\langle r^{-3}\rangle\langle 3x_ix_jr^{-2}-\delta_{ij}\rangle,$$

where x_1, x_2, and x_3 are the x, y, and z coordinates of the unpaired $3d$ electron, and i, $j=1$, 2, 3. μ_B is the Bohr magneton, and H_c is the contact-term effective field. The calculated results are shown in Table II. It is noteworthy that $\psi_1\chi_{-2}$ and $\psi_{-1}\chi_2$ of the ground doublet give the same quadrupole splitting but opposite magnetic field $\pm H_0$ ($H_0\equiv(16/7)\mu_B\langle r^{-3}\rangle+H_c$), while the first excited state gives a zero magnetic hyperfine field. Taking[24] $\langle r^{-3}\rangle=4.78$ a.u., and using[25] $H_c=-500$ kOe, we can obtain $H_0=184$ kOe from the above expression. Since the energy separation $|\lambda|$ between the ground doublet and the first excited doublet is about 150°K, it may be assumed that only the ground doublet is occupied at temperatures below 50°K. This assumption is supported by the metamagnetic character[12] of FeCO₃ and by the discontinuity of specific heat[13] across T_N that was explained by taking the effective spin $\frac{1}{2}$ as mentioned before. When the temperature decreases below T_N, the exchange interaction will appear to split the ground doublet. The exchange interaction for a typical iron spin $\mathbf{S}$ can be written as

$$-2J_1\textstyle\sum_i\mathbf{S}\cdot\mathbf{S}_i+2J_2\sum_i\mathbf{S}\cdot\mathbf{S}_i.$$

TABLE II. Magnetic hyperfine fields and electric field gradients of the lowest two spin-orbit doublets of FeCO₃.

Doublet	Wave functions	$\langle V_{zz}\rangle$	η[a]	H
2	ϕ_1	$(2/7)e\langle r^{-3}\rangle$	0	0
	ϕ_2	$(2/7)e\langle r^{-3}\rangle$	0	0
1	$\psi_1\chi_{-2}$	$(2/7)e\langle r^{-3}\rangle$	0	$-(16/7)\mu_B\langle r^{-3}\rangle-H_c$
	$\psi_{-1}\chi_2$	$(2/7)e\langle r^{-3}\rangle$	0	$(16/7)\mu_B\langle r^{-3}\rangle+H_c$

[a] Asymmetry factor was calculated from the expression

$$\eta=(\langle V_{xx}\rangle-\langle V_{yy}\rangle)/\langle V_{zz}\rangle.$$

The first sum is the ferromagnetic interaction within the same hexagonal layer, and the second sum represents the antiferromagnetic interlayer interactions. Using the molecular field approximation the above expression can be written as

$$-2Jx\langle S_z\rangle S_z,$$

where x is the number of the neighbors of the ferrous ion, and J is a molecular field constant. $\langle S_z\rangle$ is the statistical average value of the z component of a ferrous ion spin. Thus, the two states of the ground doublet are separated by $8Jx\langle S_z\rangle$. Since in this approximation both $\psi_1\chi_{-2}$ and $\psi_{-1}\chi_2$ are still eigenstates of $-2Jx\langle S_z\rangle S_z$ they give $-H_0$ and $+H_0$, respectively, as the magnetic hyperfine field, while they give same electric field gradient $(2/7)e\langle r^{-3}\rangle$. As long as the energy separation between the two states $\psi_1\chi_{-2}$ and $\psi_{-1}\chi_2$ is small compared to $|\lambda|$ ($\simeq150$°K), the primary contributions to the magnetic hyperfine field and the electric field gradient come from $\psi_1\chi_{-2}$ and $\psi_{-1}\chi_2$. Using the metamagnetic properties of FeCO₃ Jacobs[12] obtained the saturation magnetic moment per Fe²⁺ ion of $6\mu_B$ by applying an external magnetic field at 4.2°K. Using one of the two wave functions $\psi_1\chi_{-2}$ and $\psi_{-1}\chi_2$, one can calculate the saturation magnetic moment as follows:

$$\langle\psi_{-1}\chi_2|(L_z+2S_z)\mu_B|\psi_{-1}\chi_2\rangle=5\mu_B,$$

which is a little smaller than the above experimental value. However, the natural siderite sample used by Jacobs[12] contained about 17% impurities. Thus far, using the crystal field theory, the specific-heat jump across T_N, and the metamagnetic properties, we have tried to establish the existence of two low states ($\psi_1\chi_{-2}$ and $\psi_{-1}\chi_2$) which are well separated from excited states, and which give the magnetic hyperfine fields $+H_0$ and $-H_0$, and the same electric field gradient $(2/7)e\langle r^{-3}\rangle$. Slow fluctuation between these two states will give a fluctuating magnetic field between $+H_0$ and $-H_0$ with fixed electric field gradient. The probabilities of occupation of these two states are the same in the paramagnetic state, but they are not the same in the antiferromagnetic state because of the energy separation between the two states.

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An explicit expression for a static electric field gradient with randomly fluctuating magnetic field between $+H_0$ and $-H_0$ parallel to the axis of the maximum electric field gradient was derived by Blume and Tjon[3] using the stochastic model. The shape of the Mössbauer emission (or absorption) spectra is given by

$$W(\mathbf{k})=\frac{2}{\Gamma}\operatorname{Re}\int_0^\infty dt\exp\left(i\omega t-\frac{\Gamma}{2}t\right)(\langle\mathcal{H}^{(-)}\mathcal{H}^{(+)}(t)\rangle)_{\mathrm{av}},$$

where $\mathcal{H}^{(+)}$ is the operator for emission of a γ ray by the nucleus. Γ is the linewidth, ω and $\mathbf{k}$ are the frequency and wave vector of the gamma photon. The $(\ )_{\mathrm{av}}$ denotes the average over the stochastic degrees of freedom in the Hamiltonian

$$\mathcal{H}=\mathcal{H}_0+Q'(3I_z^2-I^2)+g\mu H_0I_zf(t),$$

where $Q'=e^2qQ/4I(2I-1)$, and $f(t)$ is a random function of time, which takes on the values ± 1. The function f is specified by giving the matrix of probabilities per unit time, W_{ij} for a transition of $f(t)$ from the value i to the value j $(i\neq j)$. The final expression for the line shape in terms of W_{ij} is

$$W(\mathbf{k})=\frac{2}{\Gamma}\operatorname{Re}\sum_{m_0m_1}\tfrac{1}{4}|\langle I_0m_0|\mathcal{H}^{(+)}|I_1m_1\rangle|^2,$$
$$\times\sum_{ij}P_i\langle j|(P-\mathbf{W}-i\alpha\mathbf{F})^{-1}|i\rangle,$$

where

$$P=-i[\omega-\omega_0-Q'(3m_1^2-15/4)]+\tfrac{1}{2}\Gamma,$$
$$\alpha=(g_0m_0-g_1m_1)\mu H_0,$$
$$\mathbf{W}=\begin{pmatrix}-W_{+-}, & W_{+-}\\ W_{-+}, & -W_{-+}\end{pmatrix},$$

and

$$\mathbf{F}=\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}.$$

$|I_0m_0\rangle$ and $|I_1m_1\rangle$ $(m_0=\pm\frac{1}{2},\ m_1=\pm\frac{1}{2},\ \pm\frac{3}{2})$ represent the ground and the first excited states of Fe^{57}, respectively. g_0 and g_1 are the g factors of the ground and the first excited states of Fe^{57}. μ is the nuclear magneton. P_i is the *a priori* probability of the value i at $t=0$. ω_0 is the 14.4 keV for Fe^{57}. Since the above expression shows only the emission (or absorption) probability, it is necessary to carry out the integration

$$A(v)=\int_{-\infty}^{\infty}W(\omega)F(\omega-\omega_0-(\omega_0/c)v)d\omega$$

in order to fit the theoretical curve to the Mössbauer spectra. $F(x)$ is a single-line source spectrum (in the present case Co^{57} single line in Pd), c is the velocity of light, and v is the Doppler velocity of the source.

In the paramagnetic state above 38.3°K, one can put $P_i=\frac{1}{2}$ and $W_{+-}=W_{-+}=W$. However, in the antiferromagnetic state, the energetically lower state[26] of $\psi_1\chi_{-2}$ and $\psi_{-1}\chi_2$ is more likely to be occupied than the higher state. In this case P_i may be obtained in the following way:

$$H=P_+H_0+P_-(-H_0),$$
$$1=P_++P_-,$$

where H is the magnetic hyperfine field in case of no slow relaxation. W_{ij} may be determined by the relationship $W_{+-}/W_{-+}=P_-/P_+$. Using these relations, the line-shape function $A(v)$ was calculated for each Doppler velocity v using an IBM 7094 computer, and the results are shown as solid lines through the data points in Figs. 2 and 3 with corresponding W_{ij} values. The relaxation rate (W or W_{+-}) decreased as the temperature decreased, suggesting that the nature of relaxation might be of spin-lattice type. Below 20°K, the solid lines through the points in Fig. 1 are simple superpositions of six Lorentzians, with the relative intensity values calculated without taking into account any line broadening due to relaxation effects except thickness broadening.[27] This suggests that at temperatures below 20°K the relaxation rate is so slow that the nucleus can see the full magnetic hyperfine field ($+H_0$ or $-H_0$) during a nuclear-precession period that is 0.7×10^{-7} sec for $H_0=184$ kOe. This may also explain the unusual observed constant value of the magnetic hyperfine field between 0 and 20°K in Fig. 4. Finally, it must be mentioned that our measured Néel temperature of 38.3°K is 3.3°K higher than that determined by Alikhanov[13] using neutron diffraction technique. However, our value is very close to the ~38°K found by Jacobs[12] using magnetic susceptibility measurements. Both Alikhanov and Jacobs used natural impure siderite samples.[28]

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