

But for each vertical link the two spins are *independently* described in ψ . Thus

$$\begin{aligned} \langle \psi | \text{one vertical link} | \psi \rangle &= -\frac{1}{2} \langle \psi | \sigma_x | \psi \rangle \langle \psi | \sigma_x' | \psi \rangle \\ &\quad - \frac{1}{2} \langle \psi | \sigma_y | \psi \rangle \langle \psi | \sigma_y' | \psi \rangle \\ &\quad - \frac{1}{2} \Delta \langle \psi | \sigma_z | \psi \rangle \langle \psi | \sigma_z' | \psi \rangle \\ &= -\frac{1}{2} \Delta [\langle \psi | \sigma_z | \psi \rangle]^2 \\ &= -\frac{1}{2} \Delta y^2. \end{aligned}$$

(32) follows. (33) can be similarly proved.

For suitable y and Δ (for example, $y=0$, Δ =large negative) Theorem (12) gives more stringent upper bounds for f^{II} and f^{III} than (26).

Theorem 13:

$$\begin{aligned} \frac{\partial f}{\partial y} \Big|_{y=1} &= 0 && \text{for } \Delta \geq 1, \\ &= -\frac{1}{2}(\Delta-1) && \text{for } \Delta \leq 1. \end{aligned}$$

Proof: Use (26), (27) and Theorem 10.

This theorem yields the $T=0$ magnetic field \mathcal{H} necessary to produce 100% magnetization.

$$\begin{aligned} \mathcal{H} = z \frac{\partial f}{\partial y} &= 0, && \text{for } \Delta \geq 1; \\ &= z \frac{1}{2}(1-\Delta), && \text{for } \Delta \leq 1. \end{aligned}$$

Temperature-Dependent Lifetimes of Nonequilibrium Fe^{3+} Ions in CoO from the Mössbauer Effect*

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The lifetime of the nonequilibrium Fe^{3+} state in a $\text{CoO}:\text{Co}^{57}$ source has been determined in the temperature range 78 to 1000°K. The intensity of the ferrous state is highly temperature-dependent and was hardly detectable above 800°K. The width of the nuclear excited level of the nonequilibrium state is determined by the nuclear decay time τ and the atomic decay time θ (3). The expected changes in the linewidth of the nonequilibrium Fe^{3+} state in the Mössbauer spectra have been observed. The observed deviation of the temperature variation of the hf magnetic field at the nuclei of both Fe^{2+} and Fe^{3+} ions from that expected by the molecular-field theory may be due to a possible biquadratic exchange interaction in CoO, with $j/J_z \approx 0.022$.

1. INTRODUCTION

IN the electron-capture decays of nuclei various highly ionized atomic states are produced as a consequence of Auger electron emission.¹ It has been shown earlier² that the Mössbauer effect offers a possibility of detecting some of these nonequilibrium charge states whose lifetimes are comparable with that of the excited state of the nucleus producing the Mössbauer emission. In metallic lattices these highly charged nonequilibrium states relax to the stable state in a time very much smaller as compared to the nuclear lifetime and hence only the stable state is observed in the Mössbauer spectrum. However, employing dielectric source lattices in which the relaxation times can be of the order of the nuclear lifetime, some of the non-

equilibrium charge states can be detected. Indeed, nonequilibrium Fe^{3+} state has been observed in cobalt oxide³ and nickel oxide⁴ using the Fe^{57} Mössbauer effect.

In nickel oxide we have reported⁴ a strong temperature dependence of the intensity of the ferrous state which indeed vanished above about 466°K. The present paper deals with the temperature dependence of the lifetime and the linewidth of the nonequilibrium Fe^{3+} state in CoO over the temperature range, 78 to 1000°K. Wertheim³ has reported earlier Fe^{57} Mössbauer measurements in CoO used as a source over the range 78°K to room temperature. Our observations, in this range of temperature, pertaining to the hf magnetic fields at the Fe^{2+} and Fe^{3+} nuclei are in agreement with those reported by Wertheim.³ Above the room temperature, and indeed even below this, we observed a decrease in the intensity of the ferrous peak with increasing temperature to almost negligible value above about 800°K. This behavior is seen to be closely connected with the semiconducting properties of this oxide

* Work done under the auspices of the U. S. National Bureau of Standards, Washington, D. C.

¹ I. Bergström, in *Beta- and Gamma-Ray Spectroscopy*, edited by K. Siegbahn (North-Holland Publishing Company, Amsterdam, 1955), p. 624.

² H. Frauenfelder and R. Steffen, in *Alpha, Beta and Gamma Ray Spectroscopy*, edited by K. Siegbahn (North-Holland Publishing Company, Amsterdam, 1964), Vol. 2, p. 1182. G. K. Wertheim, *Mössbauer Effect: Principles and Applications* (Academic Press Inc., New York, 1964), p. 100.

³ G. K. Wertheim, *Phys. Rev.* **124**, 764 (1961).

⁴ V. G. Bhide and G. K. Shenoy, *Phys. Rev.* **143**, 309 (1966).

and to the mechanism of electron capture by the non-equilibrium charge states.

Neutron-diffraction^{5,6} and Mössbauer measurements^{4,7} on the antiferromagnetic oxides of the 3d transition metals giving temperature dependence of the sublattice magnetization and the hf field at the nuclei, respectively, have indicated the necessity of an additional biquadratic exchange interaction to explain the observed behavior in terms of the molecular field theory. Below the Néel temperature (292°K), the temperature variation of the hf fields at the nuclei of Fe^{2+} and Fe^{3+} ions in CoO deviates from the Brillouin function with $S = \frac{3}{2}$, characteristic of the Co^{2+} ion, indicating the possible presence of a biquadratic exchange interaction in CoO .

2. EXPERIMENTAL

Two different methods were employed in the preparation of the CoO sources. The first was similar to that described by Wertheim³ in which the activity was introduced in CoO powder. In the second method, Co^{57} was diffused in thin foils of cobalt metal. These foils were subsequently oxidized to CoO by heating them in air at 900°C. The sources prepared either way gave similar spectra which were also similar to those reported by Wertheim.³ The sources prepared by the latter method were, however, more convenient to handle and gave lesser background in the 14.4-keV counting channel. X-ray studies were carried out on these sources to assure their chemical composition.

Two single-line absorbers were used in the study. The first was a 60-mg/cm² $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ single-crystal absorber and the second was an enriched 310 stainless steel absorber. A constant-velocity-type Mössbauer spectrometer was used in the investigation.

3. RESULTS

We have shown in Fig. 1 some typical Mössbauer emission spectra of $\text{CoO}:\text{Co}^{57}$ at various temperatures, above the Néel temperature, obtained against the $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ absorber. The spectra below the room temperature down to 78°K are similar to those reported by Wertheim.³ In the room-temperature spectrum we have two well-resolved peaks of nearly equal intensity. These two peaks have been assigned to the divalent and trivalent states of iron³ using the isomer-shift systematics.⁸ This assignment was also checked by observing the spectra below the Néel temperature (two sets of six-finger pattern) and using the hf field systematics.⁹ The line positions and the intensities of the two peaks in the room temperature spectrum are in good

⁵ D. S. Rodbell, I. S. Jacobs, J. Owen, and E. A. Harris, Phys. Rev. Letters **11**, 10 (1963).

⁶ M. E. Lines and E. D. Jones, Phys. Rev. **139**, A1313 (1965).

⁷ D. E. Cox, G. Shirane, P. A. Flinn, S. L. Ruby, and W. J. Takei, Phys. Rev. **132**, 1547 (1963).

⁸ L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961).

⁹ R. E. Watson and A. J. Freeman, Phys. Rev. **123**, 2027 (1961).

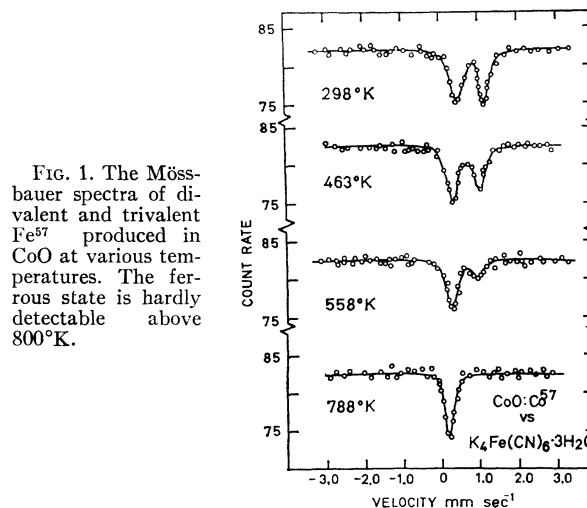


FIG. 1. The Mössbauer spectra of divalent and trivalent Fe^{57} produced in CoO at various temperatures. The ferrous state is hardly detectable above 800°K.

agreement with those reported by Wertheim.³ These observations are, however, in disagreement with those of Bearden *et al.*¹⁰ who have reported only the Fe^{2+} state in CoO .

With increasing temperature the ferrous peak intensity decreased and finally above about 800°K, the ferrous peak was hardly detectable (see Fig. 1). Our measurements (as well as those reported in Ref. 3) indicate that even below the Néel temperature, the intensities of the ferrous peaks in the split spectra show a decrease with increasing temperature. It may be mentioned that the temperature cycling of the source had no influence on the intensity of the ferrous and ferric states. Further, no anomalous changes were observed at the Néel temperature showing that the intensities are mainly governed by the semiconducting properties of the samples, as discussed in Sec. 4.

In Fig. 2 we have plotted the temperature variation of the intensity of the ferric peak relative to the ferrous peak, defined by the equation

$$I(3) = 100g(3)[g(3) + g(2)]^{-1}. \quad (1)$$

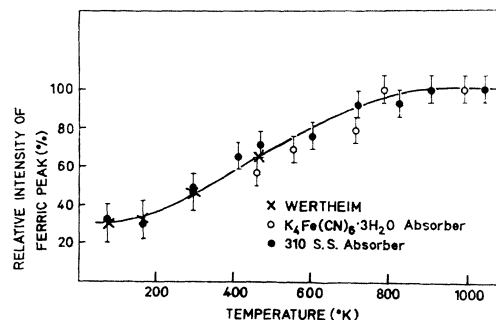


FIG. 2. The intensity of the ferric peak relative to the ferrous peak, defined by Eq. (1), as a function of temperature.

¹⁰ A. J. Bearden, P. L. Mattern, and T. R. Hart, Rev. Mod. Phys. **36**, 470 (1964).

In this equation $\mathcal{I}(3)$ and $\mathcal{I}(2)$ are the "row dips" (background-corrected intensity at the peaks) of the ferric and ferrous peaks, respectively. Below the Néel temperature, where both states yield a six-finger pattern, the row dips of the extreme ferric and ferrous peaks which are well separated have been measured to compute $I(3)$. The figure includes the data obtained using both the absorbers. With a 310 stainless-steel absorber, which gives a broad line (of half-width 0.70 ± 0.04 mm/sec against a good Cr:Co⁵⁷ source), the ferrous and ferric peaks were not resolved above the Néel temperature. The composite spectra were analyzed by fitting two Lorentzians with unequal half-widths and intensities, the ferric Lorentzian being broader.

The ferric lines observed with $K_4Fe(CN)_6 \cdot 3H_2O$ absorber clearly showed a larger width as compared to the ferrous lines (see Fig. 1). At room temperature the ferric and ferrous linewidths were 0.45 ± 0.04 and 0.30 ± 0.04 mm/sec, respectively. The ferric linewidth decreased with increasing temperature approaching 0.30 mm/sec at about 800°K. Similar behavior was also evident in the resolved peaks of the spectra obtained with 310 stainless steel absorber. This temperature dependence of the linewidth of the ferric peak is also intimately connected with the lifetime of the charge state as discussed in the next section.

The hf magnetic fields at the nuclei of the ferric and ferrous ions were determined from both the ground- and the excited-state splittings and are in agreement with those reported earlier.³ We have also observed at 78°K the presence of quadrupole interaction at the ferrous ion, with the EFG axis perpendicular to the direction of the hf field at the nucleus. The values obtained are 31 Mc/sec for the quadrupole coupling and 180 kOe for the hf field. This quadrupolar interaction at the ferrous ion may arise out of the Jahn-Teller distortion or alternatively from the alignment of the charge cloud due to the spin-orbit coupling.¹¹ Figure 3 shows the variation of the field at the nuclei of ferrous and the ferric ions as a function of reduced

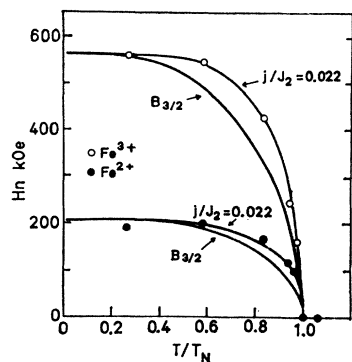


FIG. 3. The hyperfine field at the nuclei of ferrous and ferric ions produced in CoO as a function of reduced temperature, T/T_N . The Brillouin function with $S = \frac{3}{2}$ has also been shown.

temperature T/T_N . It is normally expected that the hf field at any temperature will be proportional to the sublattice magnetization.^{12,13} Unfortunately, no sublattice-magnetization measurements on CoO are available. However, the sublattice magnetization can be described in the molecular-field approximation by a Brillouin function. In Fig. 3 we have also plotted the Brillouin function with $S = \frac{3}{2}$ for the cobaltous ion. We observe that, as in the case of NiO,⁴ the variation of the hf field at the nuclei is slower than that predicted by the molecular field theory.

4. DISCUSSION

Temperature Dependence of Lifetime of Ferric State in CoO

The radioactive Co⁵⁷ atoms transform into Fe⁵⁷ atoms through the *K* or the *L* electron capture. The consequent readjustment of electrons in the various electronic shells is accompanied by the Auger electron emission which gives rise to a variety of ionized states of iron. The intensities of these charge states depend upon the valence of the starting cobalt ion, as well as on the various Auger-transition probabilities.¹⁴ However, when Co⁵⁷ decays in a solid, the resulting highly ionized states of iron soon decay to the lower ionized states by the capture of electrons from the neighboring atoms in the solid. The detectability of these ionized states in the Mössbauer spectrum depends upon their lifetimes relative to the lifetime of the 14.4-keV excited state of Fe⁵⁷ ($= 10^{-7}$ sec) and only those charge states which have lifetimes 10^{-8} sec or greater can be observed in a Mössbauer spectrum.¹⁵

When these nonequilibrium charge states are formed in a metallic lattice, they decay to the lower stable state by capturing electrons from the conduction band within a time much shorter than 10^{-8} sec and hence only the lowest charge state is observed in the Mössbauer spectrum. In ionic salts,¹⁵⁻¹⁷ however, the relaxation process is slower; the electrons being available only from the ligand orbitals. The lifetimes of the ionized state, being dependent on the degree of overlap, are expected to be longest in ionic compounds and shortest in strong-crystal-field covalent complexes.

In the oxidic semiconductors, such as CoO³ and NiO,⁴ we believe that the electrons necessary for the relaxation of the highly charged states are available from the cation neighbors of the decaying ion. If we assume that the initial charge on Co⁵⁷ ion is 2+, then according to Pollak,¹⁴ charge states Fe⁷⁺ to Fe²⁺ with varying intensities are produced by the Auger processes. However, as the Mössbauer spectra do not reveal charge

¹² W. Marshall, Phys. Rev. **110**, 1280 (1958).

¹³ G. B. Benedek and T. Kushida, Phys. Rev. **118**, 46 (1960).

¹⁴ H. Pollak, Phys. Status Solidi **2**, 720 (1962).

¹⁵ G. K. Wertheim and H. J. Guggenheim, J. Chem. Phys. **42**, 3873 (1965).

¹⁶ R. Ingalls and G. DePasquali, Phys. Letters **15**, 262 (1965).

¹⁷ J. G. Mullen, Phys. Rev. **131**, 1415 (1963).

¹¹ W. Marshall, in *The Mössbauer Effect*, edited by D. M. E. Compton and A. H. Schoen (John Wiley & Sons, Inc., New York, 1962), p. 141.

states higher than Fe^{3+} , it is expected that the lifetimes of the Fe^{7+} to Fe^{4+} states are shorter than 10^{-8} sec. Indeed, these higher valence states decay by the capture of electrons from the neighboring Co^{2+} ions of the host lattice, which goes over to the Co^{3+} state. This process of electron transfer, known as the "valence exchange" mechanism, is used to describe the semiconducting properties of these oxides.¹⁸

The decay of any nonequilibrium charge state to a lower one can be described by the equation

$$I(n) = I_0(n)e^{-\tau/\theta(n)}, \quad (2)$$

where $I_0(n)$ is the Auger-produced intensity of the ionic state of valence n . These intensities are determined entirely by the Auger-process transition probabilities and have been computed by Pollak.¹⁴ τ is the lifetime of the excited state producing the Mössbauer radiation ($=10^{-7}$ sec in the present case), and $\theta(n)$ describes the relaxation time of the charge state Fe^{n+} . If the decay to lower charge states takes place monotonically, the intensity of the given charge state (r), after the time interval τ , is given by

$$I(r) = [I_0(r) + \sum_{n=r+1}^7 I_0(n) \prod_{n>r+1} (1 - e^{-\tau/\theta(n)})] e^{-\tau/\theta(r)}. \quad (3)$$

In the Mössbauer spectra, over the range of temperatures investigated, no states with $n \geq 4$ have been observed. This means that for states with $n \geq 4$, the lifetimes are much shorter than 10^{-7} sec, and based on the detectability limit we can put the upper limit as 10^{-8} sec. It therefore appears that all the higher charge states decay over to Fe^{3+} state in a time period much shorter than 10^{-8} sec, giving at $t \approx 0$, $I_0(3) = 95\%$ and $I_0(2) = 5\%$. However, in the observed spectrum at room temperature, which reflects the relative intensities at the end of time interval τ , we have $I(3) = 47\%$ and $I(2) = 53\%$. This means that during the lifetime τ , Fe^{3+} decays from 95% to 47%, and Fe^{2+} increases from 5% to 53%. Using Eq. (2), we can compute the decay time $\theta(3)$ at room temperature to be 1.4×10^{-7} sec.¹⁴ Following similar reasoning, $\theta(3)$ can be computed at various temperatures and it is found that $\theta(3)$ is highly temperature-dependent. Thus, at 78°K, $\theta(3)$ is 8.7×10^{-8} sec. This increases to about 10^{-6} sec above 800°K. The variation of $\theta(3)$ (on log scale) with temperature is given in Fig. 4. It must at this stage be mentioned that in computing $\theta(3)$ from the observed intensities, we have assumed that the Lamb-Mössbauer factors for both the ferrous and ferric ions in CoO are equal, at all the temperatures. This may in fact cause some error.

We have previously described⁴ the temperature-dependent behavior of $\theta(r)$ in terms of various parameters. Confining our attention to $\theta(3)$, one can write $\theta_T(3) = [n(T)\sigma_3(T)v(T)]^{-1}$, where $n(T)$ is the carrier

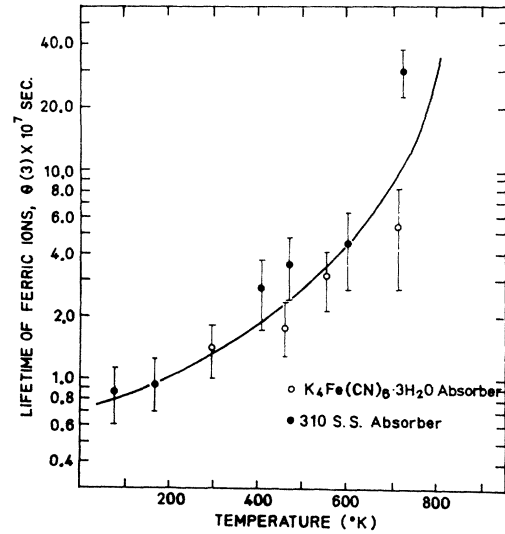


FIG. 4. The lifetime of nonequilibrium ferric ions in CoO at various temperatures.

concentration at temperature T given by

$$n_0 \exp(-E_d/kT),$$

where E_d is the activation energy. $\sigma_3(T)$ is the capture cross section given in the Coulomb approximation by $(\pi e^4/k^2 e^2)(3/T)^2$, and $v(T)$ is the thermal velocity of the charge carriers given by $(2k/m)^{1/2} T^{1/2}$. No measurements on the capture cross section are available for the oxidic semiconductors. However, some data are available for some impurities in elemental semiconductors, such as Ge and Si. Thus, for Au impurities in Si ,¹⁹ and Sb in Ge,²⁰ the capture cross section varies as T^{-4} . In general we may write $\sigma_3(T) = AT^{-x}$.

In addition to these parameters which are discussed above, there is yet one more factor which may affect $\theta(3)$, and that is the size of the cavity available for the ion, as it is known that in the smaller cavity iron ion stabilizes in the trivalent state. This dependence is reflected in the range of temperatures over which ferrous ion is seen in various oxide lattices, namely NiO , CoO , and FeO . The sizes of the oxygen octahedra surrounding the metal ion are in the following order: $\text{FeO} > \text{CoO} > \text{NiO}$, and indeed we observe that the ferrous state vanishes in NiO at about 466°K, in CoO at about 800°K, and should be seen even up to very high temperatures in stoichiometric FeO . Thus one can express $\theta(3)$ by the equation

$$\theta(3) = [AT^{-x} n_0 e^{-E_d/kT} (2k/m)^{1/2} T^{1/2}]^{-1} f(r), \quad (4)$$

where $f(r)$ is the cavity size factor. Assuming that $f(r)$ for a given lattice does not appreciably change with temperature, the temperature dependence of $\theta(3)$ can

¹⁸ N. F. Mott, Proc. Phys. Soc. (London) **A62**, 416 (1949).

¹⁹ G. Bemski, Phys. Rev. **111**, 1515 (1958).

²⁰ S. Koenig, J. Phys. Chem. Solids **8**, 227 (1959).

be expressed as follows:

$$\theta(3) = cT^{(x-1/2)} \exp(E_d/kT). \quad (5)$$

The factor $\exp(E_d/kT)$ decreases with increasing temperature, whereas the factor $T^{(x-1/2)}$ causes an increase of $\theta(3)$ if $x > \frac{1}{2}$. Indeed, in the Coulomb approximation $x=2$ and in some cases^{19,20} $x=4$ has also been reported. Thus, Eq. (5) qualitatively describes the observed temperature dependence of $\theta(3)$ for small E_d .

Half-widths of Ferric Line

We have observed a gradual decrease in the width of the ferric line with increasing temperature. This behavior can be understood from the following considerations. The Auger-produced ferric ion along with its nucleus in the 14.4-keV excited state, forms a system which decays either by the capture of an electron with the lifetime $\theta(3)$ or by the gamma emission with the lifetime τ . The lifetime T_0 of such a system can be expressed as

$$1/T_0 = 1/\tau + 1/\theta(3). \quad (6)$$

Consequently, the total excited level width Δ is given by

$$\begin{aligned} \Delta &= \hbar[1/\tau + 1/\theta(3)] \\ &= \Gamma[1 + \tau/\theta(3)], \end{aligned} \quad (7)$$

where $\Gamma = \hbar/\tau$, the natural linewidth.

The linewidth of the ferric resonance peak with an atomic relaxation lifetime 10^N times the nuclear lifetime τ is then given by

$$\Delta = \Gamma(1 + 10^{-N}). \quad (8)$$

When $N = -1$, i.e. $\theta(3) = 10^{-8}$ sec, we have $\Delta = 11\Gamma$, and of course, the intensity of the line, as per Eq. (2), is hardly 1% of the main line. Indeed, this corresponds to the limit of the lifetime of a nonequilibrium charge state which can be observed in a Mössbauer experiment as discussed by Wertheim and Guggenheim.¹⁵ On the other hand, if $N = +1$, i.e., $\theta(3) = 10^{-6}$ sec, we obtain $\Delta = 1.1\Gamma$. Thus, it is seen that if $\theta(3)$ changes from 10^{-8} to 10^{-6} sec, the Δ varies from 11Γ to 1.1Γ . Indeed, in

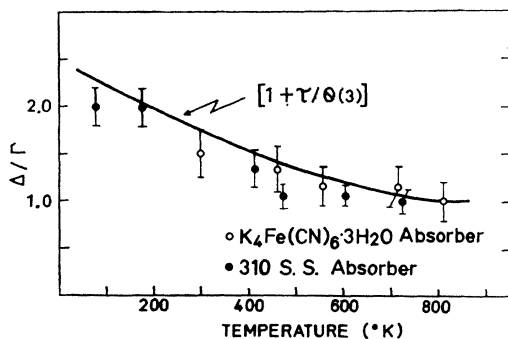


FIG. 5. Variation of Δ/Γ with temperature. The curve is obtained from Eq. (7), while the points represent the experimental values. The value of Γ is assumed to be the ferrous linewidth.

CoO we have a situation where the lifetime $\theta(3)$ of the ferric ion varies from 8.7×10^{-8} sec at 78°K to 3.4×10^{-6} sec at 723°K , and hence there should be a corresponding variation in the linewidths of the ferric state. In Fig. 5 we plot Δ/Γ as a function of temperature. The continuous curve has been obtained using Eq. (7), in which the value of $\theta(3)$ at any temperature was obtained from the smoothly drawn curve of Fig. 4. Taking Γ to be the ferrous linewidth, the experimentally observed values of Δ/Γ for the ferric line have been shown by points. The close agreement between the observed and the computed values is satisfactory, particularly in view of the fact that $\theta(3)$'s are not known with great accuracy and the assumptions implied in Eq. (2).

Biquadratic Exchange Term in CoO

Our observations on the hf magnetic fields at the nuclei of ferrous (180 kOe at 78°K) and ferric (560 kOe at 78°K) ions in CoO are in close agreement with those reported by Wertheim and need no comment. However, it may be pointed out that the temperature variation of the hf field of the ferrous and ferric ions do not follow the Brillouin function for $S = \frac{3}{2}$ characteristic of the Co^{2+} ion. No neutron-diffraction measurements on the temperature dependence of the sublattice magnetization of CoO are available. But if we assume that the hf fields are proportional to the sublattice magnetization, then the observed deviation from the Brillouin function for $S = \frac{3}{2}$ implies a deviation of the sublattice magnetization from the Brillouin function, and this may be attributed to the presence of a possible biquadratic exchange term, as suggested by Rodbell *et al.*⁵ They have reported that the deviation of the sublattice magnetization in MnO and NiO from the corresponding Brillouin function may be attributed to the presence of a biquadratic exchange term of the type $j(\mathbf{S}_a \cdot \mathbf{S}_b)^2$ in addition to the usual bilinear term $J_2(\mathbf{S}_a \cdot \mathbf{S}_b)$. If we assume that the observed deviation in the present case is due to the presence of a biquadratic term, then we find that the value $j/J_2 = 0.022$ gives a fairly good fit with the experimental results as shown in Fig. 3. It may, however, be necessary to point out that as discussed in Ref. 4, the observed deviation may be caused by several factors such as the implicit and explicit temperature dependence of the constant coupling the hf field and the sublattice magnetization, difference between the exchange energy between the host $\text{Co}^{2+}:\text{Co}^{2+}$ ions and that between impurity and the host ions such as $\text{Fe}^{3+}:\text{Co}^{2+}$ and $\text{Fe}^{2+}:\text{Co}^{2+}$.

ACKNOWLEDGMENTS

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