APPENDIX

In the linearized Boltzmann equation

$$\frac{\partial f_1}{\partial t}+\mathbf{v}\cdot\boldsymbol{\nabla} f_1+\frac{e}{m}\left(\mathbf{E}_1\cdot\frac{\partial f_0}{\partial \mathbf{v}}+\mathbf{E}_0\cdot\frac{\partial f_1}{\partial \mathbf{v}}\right)+\frac{e}{m}(\mathbf{v}\times\mathbf{B}_0)\cdot\frac{\partial f_1}{\partial \mathbf{v}}=0,$$

we wish to neglect the term containing the static field $\mathbf{E}_0$. In a positive column of an active discharge, $\mathbf{E}_0$ has both axial and radial components. The axial component is required to maintain the plasma, but we ignore it in Eq. (2) because it does not play a role in our problem. The component of interest is the radial electric field E_{r0} which accompanies the steady-state diffusion to the walls of the column. For our purposes it is sufficient to assume that the diffusion to the insulating walls is ambipolar. Then E_{r0} is given by[20]

$$E_{r0}=\frac{(1+\mu_-^2B^2)\boldsymbol{\nabla}(D_+N)-(1+\mu_+^2B^2)\boldsymbol{\nabla}(D_-N)}{(1+\mu_+\mu_-B^2)(\mu_++\mu_-)N}, \qquad \text{(A1)}$$

where $\mu_\pm$ and $D_\pm$ are the ion (or electron) mobilities and diffusion coefficients, respectively. Under conditions of the present experiment, $\mu_+B\ll 1$, $\mu_-B\gg 1$ and $\mu_+\mu_-B^2\gtrsim 1$. Then (A1) reduces to

$$E_{r0}\sim\left(T_+-\frac{T_-}{1+\mu_+\mu_-B^2}\right)\boldsymbol{\nabla}N/N, \qquad \text{(A2)}$$

where T_- and T_+ are the electron and ion temperatures (in eV), respectively. In deriving (A2) we used the Einstein relation, $D_\pm/\mu_\pm=T_\pm$. Consequently, in order that the term $\mathbf{E}_0\cdot(\partial f_1/\partial\mathbf{v})$ be negligible compared to, say, $(\mathbf{v}\times\mathbf{B}_0)\cdot(\partial f_1/\partial\mathbf{v})$, we must have

$$\left|\frac{T_+}{T_-}-\frac{1}{1+\mu_+\mu_-B^2}\right|\frac{r_c|\boldsymbol{\nabla}N|}{N}\ll 1, \qquad \text{(A3)}$$

where r_c is the electron Larmor radius. In the present experiments, the neutral gas pressure is relatively high (0.1–0.5 Torr) so that $\mu_+\mu_-B^2\simeq 1$, and the inequality (A3) becomes

$$r_c|\boldsymbol{\nabla}N|/N\ll 1. \qquad \text{(A4)}$$

The lower the pressure of the neutral gas, the easier it becomes to satisfy the inequality (A3).

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Fe^{57} Mössbauer Effect in Nickel Oxide*

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The Fe^{57} Mössbauer effect in antiferromagnetic NiO, used as a source, has been studied over a wide range of temperatures below as well as above its Néel temperature (523°K). The aftereffects of decay produce only ferrous and ferric states, which have been identified by their characteristic hyperfine fields and isomer shifts. These observations are similar to those reported on CoO. The temperature dependence of the hyperfine field at the nuclei of Fe^{2+} and Fe^{3+} ions, although almost identical, deviates from the sublattice magnetization of NiO as well as from the Brillouin function for the Ni^{2+} state ($S=1$). The spectrum at liquid-nitrogen temperature indicated the presence of an electric field gradient at the ferrous nucleus. The intensity of the ferrous peak is highly temperature-dependent, decreasing with an increase in temperature finally vanishing above about 466°K. This dependence has been qualitatively explained in terms of the electron-capture mechanism. It has been concluded that the temperature dependence of the capture cross section of the ferric ion is mainly responsible for the observed behavior.

I. INTRODUCTION

NICKEL OXIDE is an antiferromagnetic substance[1] with a Néel temperature of 523°K, and is one of the most extensively studied monoxides of the iron group. It has a crystal structure characterized by an fcc lattice of the positive ions. Below the Néel temperature, the lattice contracts along one of its body diagonals, the corner angle becoming $\pi/2\pm\Delta$. The cube edges contract by an amount $\delta a/a$. The new geometry is rhombohedral.[2] The interaction of individual magnetic ions with the crystalline electric field from the distorted oxygen octahedra quenches the orbital angular momentum of the Ni^{2+} ions. Hence, in this substance the anisotropy energy responsible for the observed magnetic ordering (of the second kind) is mainly dipolar in origin.[3,4] Further, the exchange forces con-

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strain the spins to point parallel to the distortion axis,[5] the ferromagnetic sheets being {111} planes.

The semiconductive properties of NiO have been studied by many authors.[6,7] The conduction mechanism in this type of oxidic semiconductors has also been discussed in the literature,[8–11] following a suggestion by Mott,[9] who predicted a "valence exchange" in these compounds.

In the present investigation the antiferromagnetic properties of NiO have been studied by probing the lattice with Mössbauer isotope Fe^{57}, produced by the electron capture of Co^{57} atoms. Radioactive Co^{57} ions are introduced in NiO lattice to replace Ni^{2+} ions. The after-decay effects produce various valence states of iron, but the ones that have been observed in the present work are only the Fe^{2+} and Fe^{3+} states. The states have been identified by their characteristic isomer shifts and the time-averaged hyperfine fields at their nuclei. These measurements are in many respects similar to those reported by Wertheim on CoO.[12]

The temperature dependence of the hyperfine fields for the Fe^{2+} and Fe^{3+} ions have been found to deviate from the sublattice magnetization of NiO. The intensity of the Fe^{2+} state is also observed to be highly temperature-dependent. This result has been used to discuss the stability of higher charged states and their relation to the conduction properties of the material.

To study the possibility of various charged states in α-Fe_2O_3, spectra have been taken with α-Fe_2O_3 containing radioactive Co^{57} as a source. No trace of higher or lower charged states other than Fe^{3+} was observed.

II. EXPERIMENTAL

Nearly stoichiometric NiO was prepared by repeated oxidation of spongy nickel with high-temperature steam (around 600°C). The x-ray powder photographs showed no trace of nickel or its higher oxides. The starting materials to obtain spongy nickel were of good purity and no chemical analysis of the final product has been made.

The radioactive sources were prepared by coating NiO powder with Co^{57} from an aqueous solution. The samples were then air-fired at 900°C for 5 h. This powder was sandwiched into a thin layer, between half-mil-thick aluminum foils, and was pressed onto a copper block.

The source assembly was taken to high temperatures in a miniature nichrome furnace. The sample was cooled to liquid-nitrogen temperature in a Thermocole Dewar.

The radioactive Co^{57} was introduced in α-Fe_2O_3 powder in essentially the same way as in NiO.

The absorber used in the investigation was an enriched 310 stainless steel which gave a linewidth of 0.70±0.02 mm/sec against a good chromium source. The absorber was at 298°K in all the observations.

A constant-velocity drive, described elsewhere, was used to impart relative velocity between the source and the absorber. This drive was precalibrated with a standard Fe_2O_3 absorber.

III. RESULTS AND DISCUSSION

A. Hyperfine Interactions

Some typical transmission curves taken at various temperatures have been given in Fig. 1. The spectrum at room temperature (298°K) is similar in many respects to the spectra obtained by Wertheim[12] for CoO, below its Néel temperature, 291°K. It can be seen that the spectrum is made up of two sets of six-finger hyperfine patterns. Further, the intensities of the corresponding lines of the two sets are more or less equal. The centroids of the two sets are widely separated and are situated at 1.40±0.05 mm/sec and 0.50±0.05 mm/sec velocities. These shifts of the centroids from the zero velocity, i.e., the isomer shifts, are characteristic of those corresponding to the divalent and the trivalent states of iron.[13] Thus, we can determine that the two sets correspond to two distinct valence states of iron, the one closer to the center of the spectrum being that of the ferrous ion. Arguments similar to those given by Wertheim for the CoO case can be applied here to rule out the possibility of the two sets of hyperfine patterns being due to ions with the same valence occupying different sites.

The observed valence states are the products of the Auger cascades which follow the electron capture by the Co^{57} nucleus. As has been shown by Pollak,[14] a variety of charged states of iron up to Fe^{7+} are possible through the cascade processes. However, states with high valence decay after capturing electrons from the neighborhood in the lattice and only those states having a lifetime of the order of 10^{-7} sec (which is the lifetime of the excited state of Fe^{57} yielding the resonance radiation) are observed. Indeed, the intensities of the resultant lines of the higher valence states will depend on the structural and electronic properties of the solid. This will be discussed in some detail later.

The hyperfine fields at the nucleus of the Fe^{2+} and Fe^{3+} ions have been determined using the ground-state splitting, as well as the excited-state splitting of the nuclear levels obtained from the spectra. The values obtained in these two ways are close to each other. This

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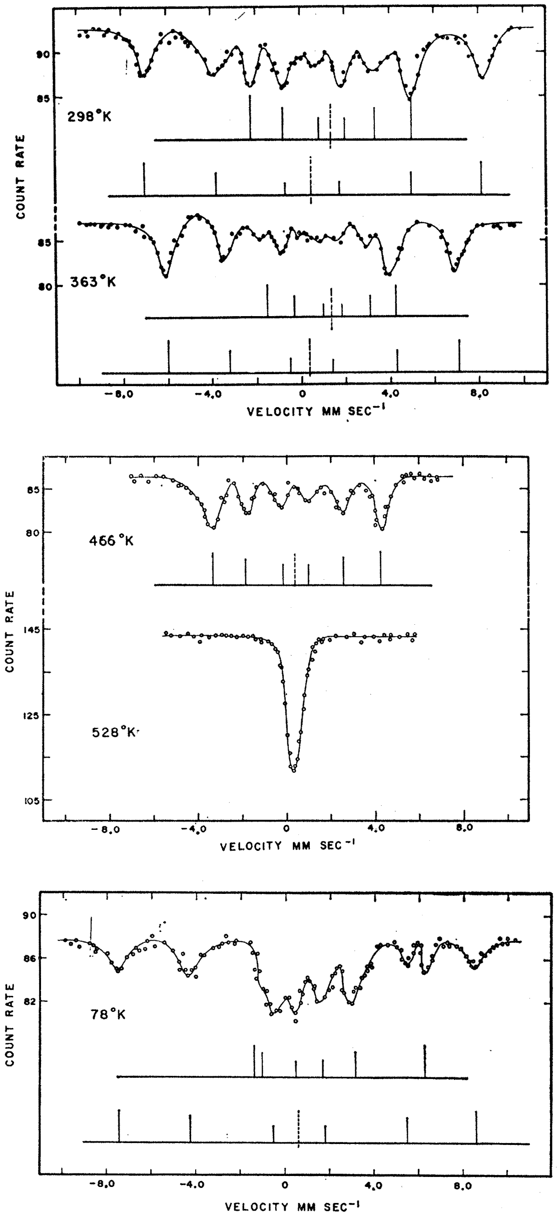

FIG. 1. Typical transmission curves, taken with Co^{57} in NiO as source and enriched 310 stainless steel as absorber, at various source temperatures. The various line positions of the ferrous and ferric states have been shown. Note that above 466°K, ferrous lines completely disappear. The spectrum taken at 528°K, which is above the Néel temperature of NiO (523°K), shows zero hf field at the nucleus. The spectrum taken at 78°K shows large quadrupolar interaction at the ferrous ion.

indicates that the quadrupole interaction at both Fe^{2+} and Fe^{3+} is negligibly small (<1 Mc/sec). Similar results have been reported on CoO and are to be expected because of the near-cubic symmetry of the lattice in this group of monoxides, even below their Néel temperatures. The room-temperature values of the fields at the nuclei, obtained from the two sets of six-finger patterns, are 471 ± 5 and 221 ± 4 kOe. These values are within 5 to 6% of their low-temperature limit. Clearly, the former value characterizes a ferric ion (450 to 550 kOe)[15] while the latter is characteristic of a ferrous ion (180 to 400 kOe).[15] Indeed, the identification of the charged states carried out this way is confirmed by that done through the isomer-shift systematics.

The above analysis has been extended to all the spectra taken at different temperatures. Various line positions and the centroid of the set of six-finger patterns have also been shown in Fig. 1. The analysis was quite straightforward in all the cases except for the spectrum taken at liquid-nitrogen temperature. This case has been discussed separately. It is interesting to observe from Fig. 1 that as the temperature is increased, the intensity of the ferrous lines decreases, and above 466°K only the ferric-ion spectrum is obtained. On further increasing the temperature the six-finger pattern of the ferric state collapses, finally yielding a single-line spectrum above 523°K, which is the Néel temperature of NiO.

To locate exactly the antiferromagnetic-paramagnetic transition temperature, we have measured the count rate at the centroid of the ferric spectrum at various temperatures. The constant-velocity spectrometer was set at the centroid by adding to the isomer shift the necessary temperature shift. The observations are shown in Fig. 2. As we approach the transition temperature the count rate falls sharply, whereas above the transition temperature it is hardly dependent on the temperature. The transition temperature located this way matches well with the reported Néel temperature of NiO. This is to be expected in view of the fact that the magnetic ordering in the lattice vanishes above the Néel temperature.

As mentioned above, the spectrum taken at liquid-nitrogen temperature showed a behavior considerably different from the rest of the spectra. The ferric lines could be analyzed with ease and did not incidate the presence of any quadrupole interaction. But the ferrous

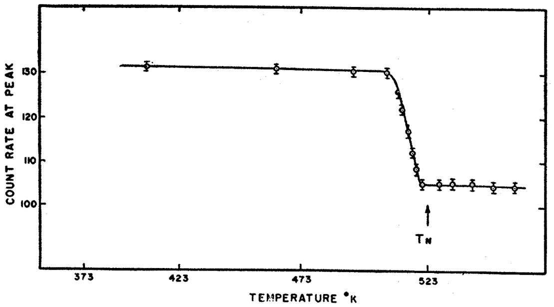

FIG. 2. Count rate at the centroid of the ferric spectrum, plotted as a function of temperature. The sharp variation at the Néel temperature of NiO indicates the antiferromagnetic-paramagnetic transition.

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lines showed a large amount of quadrupole interaction. Similar observations have been made by Wertheim on CoO at 78°K, which he has assigned to the possible Jahn-Teller distortion. An alternative possibility of its origin has been proposed by Marshall.[16] He argues that at low temperature there may be an alignment of the charge cloud due to the spin-orbit coupling.

Our observations indicate a quadrupole coupling of 33 Mc/sec. This was obtained by fitting the excited-state splitting with Parker's calculations.[17] The best fit was obtained for $\lambda=0.3$ and $\theta=0°$, where λ represents the ratio of the quadrupole coupling to the magnetic coupling and θ is the angle between the electric-field-gradient (EFG) axis and the magnetic spin direction. However, because of broad absorber used in the present work, there was difficulty in obtaining the exact splitting of the excited state, and our values of λ and θ could be in some error. The hyperfine field for the ferrous ion was found from the above analysis to be 236 ± 12 kOe, while it was 496 ± 7 kOe for the ferric ion. On extrapolating these values to 0°K we obtain a value of 500 ± 7 kOe for the ferric ion and 238 ± 12 kOe for the ferrous ion. These values may be compared with those for Fe^{3+} and Fe^{2+} ions in CoO at 78°K, which are 557 and 180 kOe, respectively.

Watson and Freeman[15] have computed the fields at the nucleus of the ferric ion ($S=\frac{5}{2}$, ^6S state) and the ferrous ion ($S=2$, ^5D state) to be -630 and -550 kOe, respectively. However, these free-ion values would greatly decrease in the solid state because of (1) covalency effects and (2) positive contributions from the unquenched orbital angular momentum and the interatomic dipolar interaction. These factors, however, cannot be separately computed with any accuracy for the present case and we shall discuss them only qualitatively.

At the nucleus of a ferric ion, since there is no orbital current contribution, the deviation from the free-ion value could come mainly through the dipolar contribution and the covalency effects. The dipolar contribution cannot exceed 10 kOe (it is 7.67 kOe in MnO [18]). Also, if the isomeric shift can be taken as a measure of covalency, our large shift of 0.50 ± 0.05 mm/sec indicates less than 10% covalency factor.[13,19] [The shift is close to that obtained with $Fe_2(SO_4)_3$]. Since there is no other known mechanism which makes a positive contribution to the field, the observed low value cannot be easily understood from above considerations. In CoO, on the other hand, a large covalency is indicated by the isomer shift (0.30 mm/sec), while the observed field is higher than that in NiO. (The dipolar contribution will not be much different in the two compounds.) These results clearly indicate that the isomer shifts, especially of the impurity nucleus, should not always be taken to signify covalency. A smaller field for Fe^{3+} ion in NiO than in CoO is probably determined by the cation-anion bond length which is, indeed, smaller in NiO than in CoO. Such systematics of bond length and the field have previously been observed in yttrium iron garnet (YIG).[15]

At the ferrous ion a large unquenched orbital angular momentum is known to exist, as in FeO. According to Freeman[20] this unquenched angular momentum is evidenced through the spectra taken at low temperatures and greatly reduces the field at the nucleus of the ferrous ion. Apart from this, the spin-orbit coupling can also decrease the effective value of the average spin $\langle S_z\rangle$ on the ferrous ion, which in turn decreases the core-polarization term (i.e., the free-ion value).

Okiji and Kanamori[21] have computed the orbital contribution for Fe^{2+} ion in a nearly cubic environment to be about $+266$ kOe. They also expect the average spin on Fe^{2+} ion to decrease from 2 to $\frac{3}{2}$, because of the spin-orbit coupling. These effective positive contributions along with the covalency effects would bring the free-ion value of Freeman and Watson closer to the observed one.

B. Temperature Dependence of the Field at the Nucleus

In an antiferromagnetic salt, the field at the nucleus of an ion can be written as

$$H_n=(A^{\text{core}}+A^{\text{orbital}}+A^{\text{dipolar}})\langle S_z\rangle\,,$$

where

$$A^{\text{core}}=(8\pi/3)g\mu_B\delta(\bar{r})\,,$$
$$A^{\text{orbital}}=2\mu_B\langle1/r^3\rangle(g_z-2)(1-\xi)\,,$$
$$A^{\text{dipolar}}=(\mu_B/2)\langle(3z^2-r^2)/r^5\rangle(1-\xi)\,,$$

where the usual notations have been used, and ξ represents the covalency factor. It is interesting to see that the A's are temperature-independent and hence the field at the nucleus and the sublattice magnetization $\langle S_z\rangle$ should vary proportionally with temperature. Indeed, similar behavior has been predicted in ferromagnetic substances also.

However, the experimental data on the temperature dependence of H_n and $\langle S_z\rangle$ obtained at constant pressure cannot be compared as they are, since the thermal-expansion effects of the lattice can influence the value of H_n and $\langle S_z\rangle$ differently. Such corrections have been made in the NMR study of ferromagnets like

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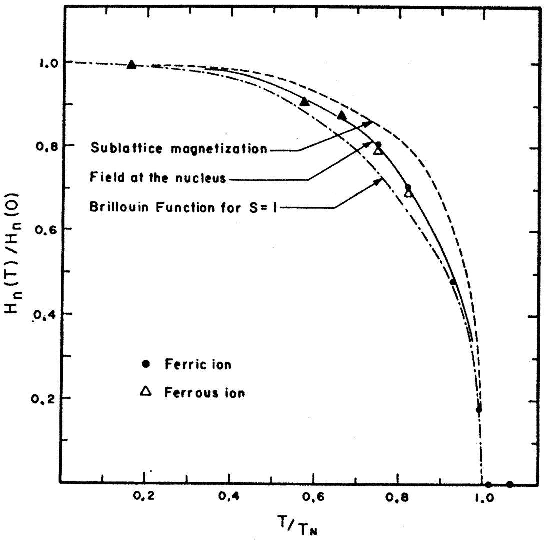

FIG. 3. Reduced field, $H_n(T)/H_n(0)$, at the nucleus of the ferrous and ferric ions as a function of reduced temperature, T/T_N. Also shown in the figure are the Brillouin function for $S=1$, and the sublattice magnetization obtained from the neutron-diffraction data (Ref. 25).

iron[22] and nickel,[23] and the effects have been found to be large in the case of iron. In antiferromagnets, an attempt to include such corrections has been made only on MnF_2 through F^{19} NMR study,[24] and the corrections have been found to be small.

No such correction has been made in the present investigation, which therefore requires the study of the pressure dependence of both H_n and $\langle S_z\rangle$. We have compared in Fig. 3 the temperature dependence of the normalized field at the nucleus, $H_n(T)/H_n(0)$, of ferric ion and ferrous ion, with the temperature dependence of the normalized sublattice magnetization, $M_s(T)/M_s(0)$, of NiO obtained from the neutron-diffraction measurements.[25] Also we have plotted in the same figure the Brillouin function for $S=1$ (Ni^{2+} ion). From the figure we observe the following:

(1) The sublattice magnetization obtained from the neutron-diffraction measurements considerably deviates from the Brillouin function. This anomalous behavior, which has also been observed in MnO, has been assigned to a possible biquadratic exchange term by Rodbell *et al.*[26] The validity of this picture has recently been discussed in detail by Lines and Jones,[18] who have shown that even though the absence of a biquadratic term cannot be proved, with certainty, the bilinear exchange term along with the lattice distortion effects can predict the observed behavior if the description of the Green's-function model is adopted.

(2) The field at the nucleus considerably deviates from the measured sublattice magnetization and also from the Brillouin function.

(3) The fields at the nuclei of the ferrous and ferric ions, within experimental error, fall more or less on the same curve.

The deviation of the temperature dependence of $H_n(T)/H_n(0)$ and $M_s(T)/M_s(0)$ would arise from many sources, such as: (a) The volume expansion effects for the two variations may be different, as was pointed out earlier. (b) The proportionality constants (i.e., A's) may have an explicit temperature dependence. Such dependence has been observed in ferromagnetic substances. Using the band theory of solids, Benedek and Armstrong[22] have shown that in ferromagnets A's are proportional to T^2, but the validity of this theory in the present case is uncertain. (c) In Fig. 3, the comparison is made of the field at the nucleus of the impurity ion with the magnetization of the host sublattice. This may not be justified, since the sublattice magnetization as detected by the impurity may have a different temperature dependence from that of the host sublattice magnetization. We shall now see how this actually occurs. The sublattice magnetization, in a molecular-field approximation, has a temperature dependence given by

$$M_s(T)/M_s(0)=B_s[g\mu_B S H_{\mathrm{eff}}/kT],$$

where H_{eff} is the effective field acting on a sublattice. For an antiferromagnet like NiO, which has ordering of the second kind, this becomes

$$M_s(T)/M_s(0)=B_s[6S\bar{S}J_2/kT],$$

where J_2 is the exchange integral between the next-nearest-neighbor spins. If the lattice distortion effects are taken into account, following Lines and Jones,[18] this expression becomes

$$M_s(T)/M_s(0)=B_s\{6S\bar{S}[J_2+2j(\bar{S})^2]/kT\},$$

where j is a constant. When our interest is in the temperature dependence of the sublattice magnetization as detected by the impurity, in the above expression, J_2 will have to be replaced by J_2', where J_2' represents the exchange integral between the impurity spins and the next nearest host spins, i.e., in the present case, between Fe^{2+} or Fe^{3+} spins and next nearest Ni^{2+} spins. If J_2 and J_2' are different, the host sublattice magnetization and the impurity-detected sublattice magnetization could have different temperature dependences. Indeed, such a mechanism has been proposed by the authors[27] in the case of ferromagnets containing impurities.

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C. Temperature Dependence of the Intensity of Ferrous Peak

As already mentioned, one of the significant observations of the present study is the temperature dependence of Fe^{2+} intensity, which completely vanishes above about 466°K. This rapid change in the intensity should not be mistaken as the change in the Lamb-Mössbauer factor, even though these reductions in the intensity include a variation from the Lamb-Mössbauer factor. To see whether a similar change occurs in CoO, we made measurements on CoO also up to high temperatures. Indeed, above about 800°K in CoO, the Fe^{2+} line vanished. The details of this study will be reported separately.

Pollak[14] has recently predicted the intensity of various valence states resulting out of the Auger cascades. In these cascades, the hole from the K shell moves out to the outermost shell within about 10^{-14} sec. The intensities of these states, at the end of the above time interval, depends on the charged state of the starting cobalt ion, and have been given in Table I for Co^{2+} and Co^{3+} cases. In the present work it is quite uncertain whether Ni^{2+} ions are replaced by Co^{2+} or Co^{3+} ions. As is well known, in NiO the cation sites are occupied by both Ni^{2+} and Ni^{3+} ions, and this fact is generally used to explain the conduction mechanism in this compound, i.e., by valence exchange between cations. This behavior is strongly supported by the observation that NiO is usually cation-deficient and exhibits p-type conduction. Thus, it is normally to be expected that the starting ionic state of the cobalt ions in NiO (and probably in CoO also) could be both divalent and trivalent. At the same time, unlike the situation in FeO, since the nonstoichiometry in NiO could be kept small, the possibility of Co^{3+} ions is small compared with that of Co^{2+} ions.

It is tempting to think of the possibility of having an EFG in the presence of Co^{3+} ions at the sites in its neighborhood. This is especially to be expected in the light of Shirane's work[28] on Fe_xO. However, in the present study—firstly because NiO is nearly stoichiometric, and secondly because the Mössbauer probe is an impurity and the chance of having another probe in the vicinity of Co^{3+} ions therefore small—no EFG due to charge difference should be expected. Indeed, this is in keeping with the observations. Further, the significant observation of the change in the $Fe^{2+}:Fe^{3+}$ ratio with temperature suggests that the Fe^{3+} state is not due to Co^{3+} introduced with charge compensation but appears because of the aftereffects of decay.

TABLE I. Percentage intensities $I_0(n)$ of various possible ionized states n resulting at the end of the Auger cascades from Co^{2+} and Co^{3+} ions. (Taken from Ref. 14.)

Ionized state of iron n	Percentage intensity $I_0(n)$ % Co^{2+}	Co^{3+}
2	5.0	...
3	21.5	5.0
4	25.3	21.5
5	29.5	25.3
6	14.2	29.5
7	4.1	14.2
8	...	4.1

It appears that the relative intensities of the various valence states of iron as indicated by the Mössbauer spectra are determined more by the relaxation effects rather than by the initial intensities of the valence states of the Co^{57} Mössbauer isotope. Thus in Fe_2O_3, although the valence state of Co^{57} is equally uncertain, the spectra we obtained using it as a source showed only one single six-finger pattern characteristic of the Fe^{3+} state, at exactly the same positions as obtained with Fe_2O_3 as an absorber. The higher charge states such as Fe^{7+} produced by Auger cascades de-excite immediately to the lower states by capturing electrons from the neighborhood. In this type of oxidic semiconductors the sources of these electrons for the relaxation are the following:

(1) Auger-produced electrons which escape in the lattice.

(2) The cations in the neighborhood of the decaying atom themselves. This is particularly so, because a divalent ion such as Ni^{2+} can donate an electron to the neighboring decaying atom and go to the Ni^{3+} state. This process, in principle, is the same as that responsible for conduction.

With increasing temperature the energy required to transfer an electron from a Ni^{2+} ion would reduce. Hence, if the latter mechanism is mainly responsible for the relaxation processes, it is to be expected that the higher states decay faster and the intensity of the lower valence states should increase with increasing temperature. However, we observe that (1) even at low temperatures no states higher than Fe^{3+} are observed, (2) the states lower than Fe^{2+} (such as Fe^0, which has been found in Ge [29]) are not present over the entire range of temperature studied, and (3) the Fe^{2+} intensity decreases with increasing temperature.

The first observation indicates that the higher states of iron decay in a time much shorter than 10^{-7} sec (which is the lifetime of the excited state of the nucleus) to lower states such as Fe^{2+} and Fe^{3+}. The second observation is to be expected since the lowest charged state of starting cobalt ion was 2. Further, in these divalent compounds the most stable charged state is Fe^{2+}. However, states like Fe^{3+} are observed in CoO and NiO. This is because, as proposed by Pollak,[14] the cavity available for the Fe^{2+} ion in CoO is smaller than in FeO, and in the smaller cavity the iron ion stabilizes

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in the trivalent state. The cavity in NiO is smaller yet, and it is not surprising to see Fe^{3+} ions. The last observation of decreasing intensity of Fe^{2+} states with increasing temperature, however, cannot be understood from the above picture. The following model has been proposed to explain the observed facts.

Let $\lambda(n)$ represent the relaxation constant for the nth ionized state and τ the lifetime of the Fe^{57} nucleus, which is the time during which our observations are made. If the intensity distribution of various charged states, $I_0(n)$, occurs at time $t=0$, as predicted by Pollak, then the observed intensity of ferric and ferrous lines at any temperature is

$$I(3)=\left[I_0(3)+\sum_{n=4}^{7} I_0(n)\prod_{n\geq 4}(1-e^{-\lambda(n)\tau})\right]e^{-\lambda(3)\tau},$$

and

$$I(2)=\left[I_0(2)+\sum_{n=3}^{7} I_0(n)\prod_{n\geq 3}(1-e^{-\lambda(n)\tau})\right].$$

These expressions have been derived with the assumption that the Lamb-Mössbauer factor is the same for all the ions and is independent of temperature (over the range of study). The relaxation constant $\lambda(n)$ can be formally defined as

$$\lambda(n)=N\sigma_n v_0,$$

where N represents the number of charged carriers per unit volume, σ_n is the capture cross section for the ion of valence state n, and v_0 is the thermal velocity of the carriers. Since σ_n is large for ions with $n\geq 4$, we can assume that λ_n for these ions is large compared with $1/\tau$, and we then have

$$I(3)=\sum_{n=3}^{7} I_0(n)e^{-\lambda(3)\tau},$$

and

$$I(2)=I_0(2)+\sum_{n=3}^{7} I_0(n)(1-e^{-\lambda(3)\tau}).$$

It is clear from these expressions that the relative intensities of the ferrous and ferric lines would depend upon the value of $\lambda(3)$. In the extreme situation when $\lambda(3)\ll 1/\tau$ we have

$$I(2)=I_0(2),$$

and

$$I(3)=\sum_{n=3}^{7} I_0(n).$$

In such a case, since $I_0(2)$ is small (only 5%), the ferrous peak would vanish. The observed variation of the decreasing intensity of the ferrous line with increasing temperature thus seems to arise out of the decrease in $\lambda(3)$ with increasing temperature. Our explanation would be complete if we can show that the parameters governing $\lambda(3)$ decrease with increasing temperature. However, no measurements are available on the temperature variation of σ_n in oxidic semiconductors for any impurity. But in a Coulomb approximation it can be shown that

$$\sigma_n=(\pi e^4/k^2\epsilon^2)(n^2/T)^2,$$

where ϵ is the dielectric constant of the host. In certain cases of impurities in Si,[30] where measurements are available, it has been observed that σ_n is even inversely proportional to T^4. Thus we feel that since N and v_0 have a slower dependence on temperature, the temperature dependence of σ_n governs the observed decrease in the intensity of the ferrous peak. No exact computations have been made in the present case, especially because of the large errors that may be involved in the measurement of the intensity in a spectrum.

It may be of interest at this stage to refer to the recent work of Ingalls and Depasquali[31] who report the observation of higher nonequilibrium charge states in addition to the normal Fe^{2+} state in various hydrated cobalt compounds. They suggest that the protons in the hydrated compounds polarize the water molecules in such a way that there is less overlap between the iron ion and its ligands than in the anhydrous cases. Wertheim and Guggenheim[32] have extended this idea in their studies on the lifetime of nonequilibrium Fe^{3+} ions in some ionic solids using the Mössbauer effect. They suggest that the lifetime of the nonequilibrium charge states reflects the degree of overlap and that it should be longest in ionic compounds and shortest in strong-crystal-field covalent complexes. It appears that in addition to the mechanism discussed above for the semiconductor NiO, the overlap of the iron ion and its surrounding ligands offers an alternative mechanism for the relaxation of higher charge states to the equilibrium charge state.

IV. CONCLUSIONS

Although, in general, the use of a dielectric material as a source in Mössbauer studies gives rise to numerous difficulties in the interpretation of the results, the present study has shown that using NiO and CoO sources very useful information regarding their magnetic behavior can be obtained. Further, the information obtained from the temperature dependence of the intensities of the two valence states, Fe^{2+} and Fe^{3+}, can be used to understand some of the semiconducting properties of these oxides.

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