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Study of Pure and Doped Cobaltous and Nickelous Oxide*

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We give results for a number of "critical" tests intended to eliminate some of the structural models which have been proposed for nickelous and cobaltous oxide prepared at temperatures of order 300 to 400 °C. For the case of cobaltous oxide we are able to eliminate all of the proposed models, leaving us with no completely satisfactory explanation of the striking properties of this material. The importance of the semiconducting properties of these oxides is demonstrated by measurements of the ratio of Fe^{2+}/Fe^{3+} observed in the Mössbauer patterns as a function of the p-type dopant lithium and the n-type dopants chromium and gallium. When the Li doping is raised sufficiently, it is possible to completely suppress the Fe^{2+} resonance at room temperature.

I. INTRODUCTION

The highly ideal Mössbauer isotope Fe^{57} has opened extensive study of the transition-metal oxides in recent years.[1-12] The physical properties of samples prepared at low and high temperatures have been radically different, and considerable debate has taken place over the structure of the low-temperature preparations. Anion and cation vacancies, microcrystals, and pores have been invoked to account for the observations. None of these taken by themselves is adequate to account for all of the experimental data, and it would appear from our present data that even a combination of these suggestions is not capable of satisfactorily accounting for the striking properties of cobaltous oxide.

Much of the focus for the model debate has been the paper which we published,[9] where we attempted to correlate a large amount of data taken by x-ray, chemical, and Mössbauer techniques. To contrast the low-temperature preparation from the high, we adopted the notation forms I and II for the high- and low-temperature preparations, respectively. We tried to explain the then-existing data by assuming a very high Schottky-defect density, where Fe^{3+} is stabilized by the transfer of an electron from iron to an anion vacancy. Although we noted that the x-ray patterns precluded the possibility for any long-ranged order to the proposed Schottky defects, the model was interpreted by many as a two-phase model, a term which was not used in our original publications.[9] This was probably due to our speculation that there might be short-range order to the vacancy arrangement, and also because of an error[9] which we made in calculating the densities of our form-II samples. Our model was not a two-phase model, however, but rather a point-defect model where we assumed that all of the observed properties could be accounted for by assuming a large and equal density of anion and cation vacancies. Shortly after the publication of our paper, Schroeer and Triftshäuser[10] gave an alternative explanation of our results by assuming that our low-temperature samples consisted of microcrystals. Although their arguments had some quantitative difficulties,[11] they seemed sufficiently plausible to warrant further tests to differentiate which model was correct. These experiments[12] indicated that neither model was completely satisfactory, but suggested that a synthesis of the models might account for all of the observations. Although this synthesis, which assumes both anion and cation vacancies and pores, is the best model to data, it appears to be incompatible with some quantitative aspects of the experimental results. Specifically, we will show that cobaltous oxide II possesses properties which have not been satisfactorily explained thus far.[13]

We shall continue to use our original notation CoO(I), CoO(II), CoO(I, II) for the pure stoichiometric oxides showing only Mössbauer resonances of Fe^{2+}, only Fe^{3+}, and a combination of Fe^{2+} and Fe^{3+}, respectively. A similar notation will be used for differentiating NiO samples. The reason for this notation goes beyond the empirical differences indicated for these preparations of cobaltous and nickelous oxide. We find that not all low-temperature preparations lead to stoichiometric cobaltous oxide or nickelous oxide. If the anneal temperature is too low, or the anneal time is too short, a poorly characterized nonstoichiometric material is formed, and although we have studied these materials[14] in considerable detail, we shall not discuss them at length in the present paper. Thus, while we obtained many densities for nonstoichiometric samples, which we shall refer to as CoO* and NiO*, the well-characterized stoichiometric CoO(II) and NiO(II) gave reproducible values for the density, in the first case 25% less than CoO(I), and in the second case 12% less than NiO(I). Because we did not exhaustively explore the possibility of preparing stoichiometric samples having other densities and yet exhibiting only Fe^{3+} in the Mössbauer effect resonance, however, the present notation should be regarded as primarily a convenience for distinguishing our samples prepared at high and low temperatures.

The present experiments were designed to answer the following questions. Does NiO(II) have analogous properties to CoO(II)? What changes in the ratios of Fe^{2+}/Fe^{3+} occur as acceptors (Li) and donors (Ga and Cr) are added to NiO and CoO, and what light does this shed on the semiconducting and structural properties of these materials? What is the best explanation of the great differences in the physical properties of forms I and II?

II. EXPERIMENTAL TECHNIQUE

The velocity spectrometer system was of the crank type and has been described earlier.[15] Temperature was controlled to within ± 1 °K in the experiments above room temperature. Unsplit sodium ferrocyanide absorbers were used throughout this work.

Samples were prepared by techniques described earlier.[9] Starting materials of Co and Ni were 99.999% pure. NiO(II) was prepared[14] by forming the nitrate and then the oxide by annealing at 400 °C under an argon atmosphere for 5 to 10 h. Specimens were handled with much caution using a large glove box facility. Doped samples were made by adding the dopant in the form of a nitrate to nickelous or cobaltous nitrate solution prior to annealing. Carrier-free Co^{57} in a chloride solution was also added prior to annealing. To avoid additional defects in the doped samples, they were all annealed at elevated temperatures (~ 1000 °C). Mössbauer spectra indicated that the dopants dispersed into their host lattices, and other investigators have indicated that the dopants occupy substitutional sites randomly dispersed within the host lattice. X-ray diffraction patterns of the doped and undoped samples indicated that the crystal structure was unaffected by the dopants.

III. X-RAY AND CHEMICAL MEASUREMENTS

All of the samples discussed in this section were verified[14] to be stoichiometric within 2% by procedures developed in our earlier work.[9] Nonstoichiometric samples can be prepared at low temperatures and our studies[14] showed that they had much different properties than CoO(II) or NiO(II).

The origin of some of the controversy about low-temperature preparations may be due to some investigators not determining the stoichiometry of their samples. We found by analytical analysis that inadequately annealed samples contained undecomposed nitrate of carbonate, and hence, they are poorly characterized.

Our earlier work indicated that CoO(II) had a density of 4.8 ± 0.5 g/cm^3, 25% less than the value predicted from the lattice parameter and crystal structure, and also 25% less than the density of 6.4 ± 0.1 g/cm^3 found experimentally for CoO(I). Similar measurements, on NiO(II), using carbon tetrachloride as a nonreactive liquid in which the sample was immersed in a volumetric flask, gave a density of 6.0 ± 0.2 g/cm^3, 12% less than the expected value of 6.8 g/cm^3. When we attempted to carry out a density measurement with inert gases, it was found that gas adsorption was too great to permit a measurement by this approach.

We have measured the room-temperature adsorption of argon and neon for CoO(II)[12] and NiO(II),[14] using a direct gravimetric technique. The quantity of gas adsorbed was sufficiently great that we could account for our observed broadening of the

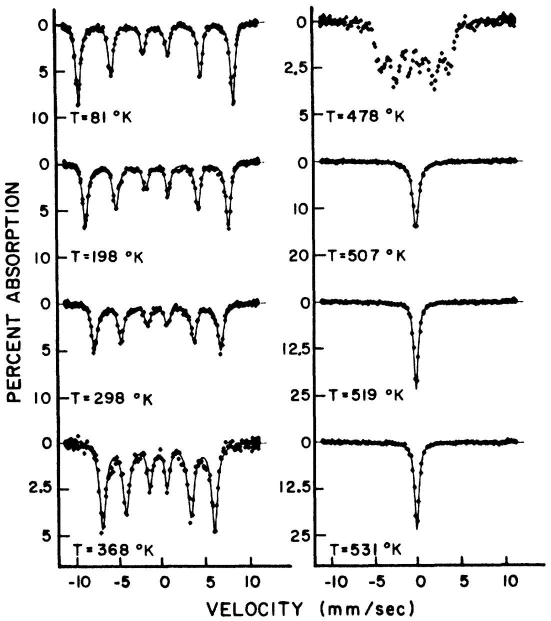

FIG. 1. Temperature dependence of Mössbauer spectra for NiO(II) prepared at 400 °C. A 1.0-mg/cm^2 sodium ferrocyanide absorber was used.

x-ray patterns in terms of porosity effects if we assumed 1% of the surface to be covered in the case of argon adsorption. In contrast to the oxygen uptake by CoO(II), the adsorption of argon and neon by CoO(II) and NiO(II) was reversible, and these inert gases could be removed from the surface by evacuating the sample holder.

We studied the x-ray powder patterns for nickelous oxide by the same procedure described earlier for cobaltous oxide.[9,12] As with cobaltous oxide we found broadened lines for form II as compared with form I. The broadening indicated that the region of order was about 200 Å for NiO(II), which is comparable to the 50-Å value obtained for CoO(II).

IV. MÖSSBAUER MEASUREMENTS

The temperature dependence of the Mössbauer spectrum for NiO(II) is shown in Fig. 1. The Néel temperature was not as sharp as for form I, and we estimated it to be (515 ± 5) °K. The temperature dependence of the hyperfine field was found empirically to approximately follow a Brillouin function for $S=\frac{5}{2}$ with the low-temperature hyperfine field being 550 kG. There was no evidence for a quadrupole interaction in the hyperfine pattern, which is believed to be due to the randomness of the point defects in this material. It should be noted that no noticeable broad single component is observed, as was found to be the case for CoO(II). When we reduced the anneal temperature to 300 °C we did see such a broad resonance, superimposed on a resolved hyperfine structure, but this material was not the well-characterized stoichiometric form II.[14]

We carried out a series of measurements on a sample of cobaltous and nickelous oxide prepared at elevated temperatures with *p*-type (Li) and *n*-type (Ga, Cr) dopants. The purpose of these experiments was to see if the thermodynamic equilibrium of Fe^{2+}/Fe^{3+} could be altered by the addition of electron acceptors and donors. Our earlier proposal that charge compensation in form II was due to electron trapping at anion vacancies, would require that additions of other electron traps such as lithium should suppress that Fe^{2+} and enhance the Fe^{3+} Mössbauer resonance. This result is illustrated for NiO in Fig. 2, where we observed a progressive enhancement of the Fe^{3+} resonance with increasing lithium concentration. The effect is very noticeable at 81 °K and is even more pronounced at room temperature. Although the line positions for the Fe^{3+} resonance in the doped sample are the same within about 2% as for NiO(II), the linewidths for the doped specimen are much narrower (~ 0.2 mm/sec). A similar effect was observed for cobaltous oxide doped with lithium, and because the Néel temperature is less than room temperature for this material the suppression of the Fe^{2+} line makes it possible to use this technique for preparing a nearly ideal single-line source with the isomer shift of either the 2+ or the 3+ Möss-

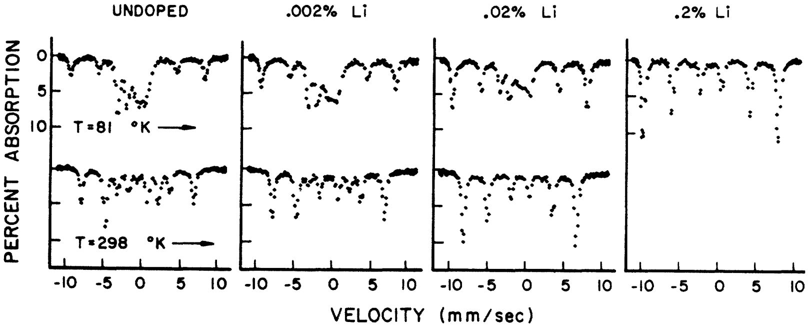

FIG. 2. Effect of substitutionally doping with Li^{1+} on the Mössbauer spectra of NiO(I, II) prepared at 800 °C. A 1.0-mg/cm^2 sodium ferrocyanide absorber was used.

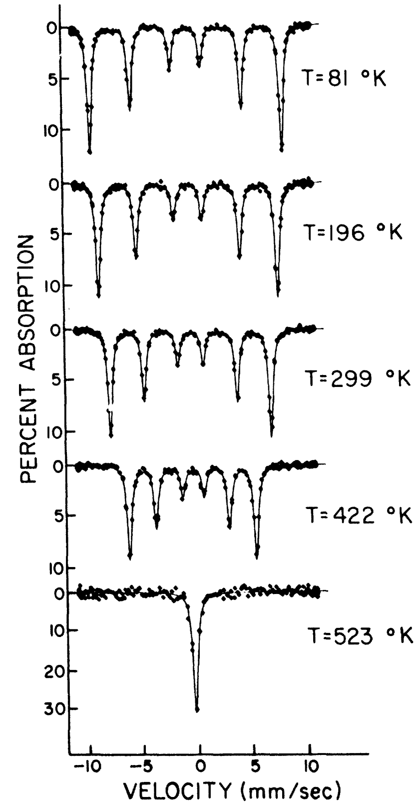

FIG. 3. Temperature dependence of Mössbauer spectra for NiO prepared at 1000 °C with a 1% Li^{1+} doping. A 1.0-mg/cm^2 sodium ferrocyanide absorber was used.

bauer resonance.

In Fig. 3 we show the temperature dependence of the Mössbauer effect for a sample of nickelous oxide which was doped with 1% lithium and annealed at 1000 °C. It is apparent that the Fe^{2+} resonance is completely suppressed in the temperature interval studied (81–523 °K). The line positions are the same as for the Fe^{3+} resonance in NiO(II) within about 2%, but the width of the lines is narrower by 0.2 mm/sec.

Assuming a single spin axis for CoO(I) and NiO(I), an analysis by Smart[16] gives

$$T_N = C_1 Z_2 J_2, \qquad (1)$$

where Z_2 is the number of second-nearest neighbors of a Ni or Co ion, J_2 is the exchange interaction between second neighbors, and C_1 is a constant. This relation can give us a basis for estimating the density of vacancies in our form-II samples if we perform an average over Z_2 and assume that the reduction in Z_2 is proportional to the cation vacancy density. In this way we can estimate what fraction of the measured reduction in density from the ideal value is due to single vacancies and what fraction is due to microscopic pores.

We first tested the proposed analysis based on Eq. (1) by observing the reduction in T_N for a controlled quantity of Li ions in the NiO and CoO lattices. Even though the accuracy of determination of T_N was only of order 1 °K the relative precision of T_N in a comparative measurement was considerably better than this value. For NiO we found that a 0.9% doping of Li^{1+} resulted in a lowering in T_N from (525.5 ± 1) °K to (521.2 ± 1) °K or 0.8%. The doping of CoO with 1.1% Li resulted in a 1.2% reduction in the Néel temperature. Our earlier work[9] showed a 6% reduction in T_N for CoO(II) compared with CoO(I). The above analysis would then lead to the conclusion that one-fourth of the observed 25% reduction in density found for CoO(II) is due to dispersed Schottky defects. For NiO(II) we found the Néel temperature to be (515 ± 5) °K, which would indicate on the basis of the present analysis that one-sixth of the 12% reduction in density observed for NiO(II) is due to dispersed anion and cation vacancies.

Two difficulties with the above analysis should be noted with respect to its application to CoO(II) and NiO(II). First, the vacancy density is so high that the average over Z_2 cannot be considered rigorous. Second, the substantial porosity implies a large surface area, with a significant fraction of the cobalt ions on or very near a surface pore. Such surface effects are clearly not included in the analysis given.

The temperature dependence of the recoil-free fraction f, which is proportional to the area under the Mössbauer absorption spectrum, is related to the binding of ions in the lattice and may be characterized through the Mössbauer characteristic temperature Θ_M.[17] Values of Θ_M which we have determined for several Mössbauer resonances are given in Table I. The significance of these results is that the Mössbauer characteristic temperature

TABLE I. Observed values of the Mössbauer characteristic temperature.

Mössbauer resonance	Θ_M(°K)
Fe^{3+} in CoO(II)	230 ± 10^a
Fe^{3+} in NiO(II)	350 ± 10
Fe^{3+} in NiO(1%Li)	420 ± 10^b
Fe^{3+} in CoO(1%Li)	410 ± 10^b
Fe^{2+} in CoO(I)	410 ± 10^a

[a] In calculating Θ_M from the temperature dependence of the area under the Mössbauer absorption curve, a computer program was employed which calculated the exact value of the Debye integral when needed, rather than making the low-temperature approximation. Thus, these values should be more accurate than the earlier ones which we reported (Ref. 9).

[b] NiO (1% Li) and CoO (1% Li) denote high-temperature preparations of CoO or NiO with a 1% Li^{1+} doping.

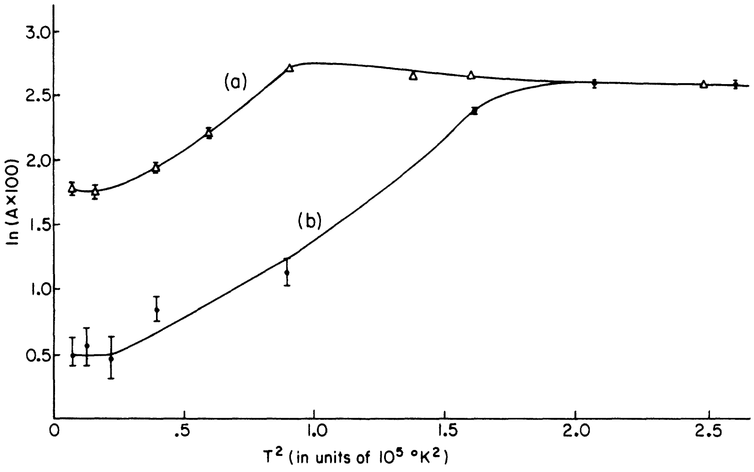

FIG. 4. Temperature dependence of ln*A* for Fe^{3+} in (a) CoO(I, II) with a 0.1% Li^{1+} doping and (b) CoO(I, II).

Θ_M is significantly higher for the Fe^{3+} resonance induced by Li^{1+} doping in the high-temperature preparations than for the Fe^{3+} resonance in CoO(II) and NiO(II). The Fe^{3+} resonance induced by Li^{1+} in high-temperature samples has a Mössbauer characteristic temperature which is essentially the same as that of the Fe^{2+} resonance in CoO(I).

Since the Fe^{3+} ion is smaller [18–20] than the Fe^{2+} ion, the lower Θ_M of the Fe^{3+} resonance in CoO(II) and NiO(II) as opposed to that of Fe^{2+} in high-temperature preparations might be explained on the basis of ion size effects. If the impurity ion is smaller than the ion it substitutionally replaces, it may have a large mean-square displacement, which would cause a lower Θ_M. This effect will tend to be offset by the tendency of the extra charge of the Fe^{3+} to draw the oxygen ions closer, thereby reducing $\langle x^2 \rangle$. If ion size or charge effects of this type are dominant, we should see the same Θ_M for Fe^{3+} in low-temperature forms and for the Fe^{3+} resonance in high-temperature preparations by lithium. In fact, Θ_M for Fe^{3+} in high-temperature preparations is essentially the same as for Fe^{2+} in high-temperature preparations, and is significantly higher than for Fe^{3+} in low-temperature preparations. Thus, a comparison of Θ_M for CoO (1% Li) and CoO(I) shows no evidence for ion size effects within experimental error, in that the Fe^{2+} and Fe^{3+} resonances in high-temperature samples have the same Θ_M. Schroeer and Triftshäuser[10] attempted to explain the lower value found for Θ_M in CoO(II) or NiO(II) by a microcrystal model, assuming modifications of the lattice vibrational spectrum. We[11] showed, using an analysis by Rich,[20] that this effect is much smaller than required to account for the observed lowering of Θ_M. It is noteworthy, however, that the fractional reduction in Θ_M from high-temperature forms for CoO(II) is about three times that of NiO(II) and the density of Schottky defects estimated for these materials from the Néel temperature lowering is in the ratio 3:1, which supports the idea that Schottky defects cause the lowering of Θ_M.

We had previously observed[9] an unusual increase in the recoil-free fraction with increasing temperature for Fe^{57} in CoO(I, II), the form which gives both Fe^{2+} and Fe^{3+} in the Mössbauer pattern. In Fig. 4 we see a plot of the natural logarithm of the area *A* under the curve for the Fe^{3+} resonance in CoO(I, II) and CoO(I, II) doped with 0.1% Li^{1+}. The initial value of ln*A* is higher for the Fe^{3+} resonance in the second sample because of the lithium doping. The curves have different turning points, but they show basically the same type of dependence of area with temperature. We had initially put forward the hypothesis that the increase in $f(T)$ was due to a dispersion of anion vacancies.[9] Our present estimate of the Schottky-defect density, based on the observed reductions in the Néel temperature would not be compatible with this original hypothesis. The similar increase in $f(T)$ for Li-doped samples as compared with undoped ones also rules out our earlier hypothesis. An alternative explanation which is in harmony with all of the data thus far accumulated is that both lithium ions and anion vacancies serve as electron traps. The observed temperature dependence could then result from a temperature dependence to the equilibrium ratio of Fe^{2+}/Fe^{3+}. A detailed knowledge of the band structure of cobaltous and nickelous oxide and the energy levels of the impurities Fe^{2+} and Fe^{3+} will be required before this new hypothesis can be put to a critical quantitative test.

If acceptors such as lithium enhance the Fe^{3+} resonance while diminishing the Fe^{2+} resonance, it would be expected that donors such as chromium and gallium would have the opposite effect or a very small effect depending on the relative values of the respective donor levels. Figure 5 shows the effect of adding Cr^{3+} to nickelous oxide prepared at 800 °C

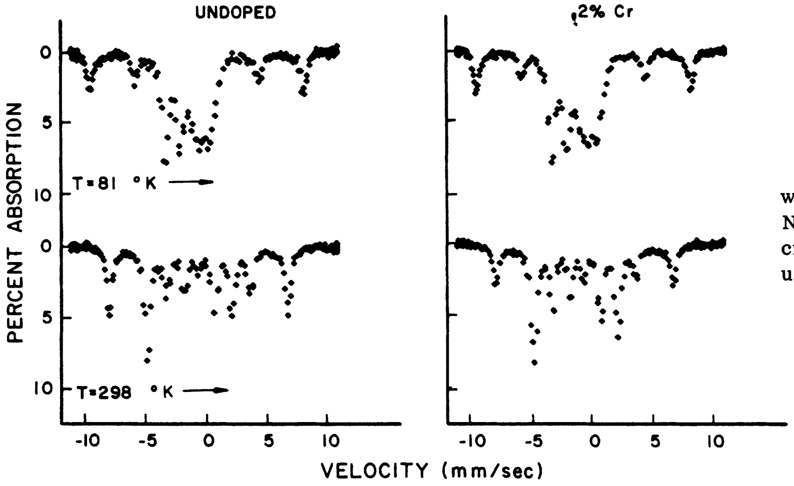

FIG. 5. Effect of substitutionally doping with Cr^{3+} on the Mössbauer spectra of NiO(I, II) prepared at 800 °C. A 1.0-mg/cm^2 sodium ferrocyanide absorber was used.

in air. A reduction in the Fe^{3+}/Fe^{2+} ratio was observed at 298 °K, while the ratio remained approximately the same at 81 °K. Figure 6 shows similar results for CoO(I, II) prepared at 1000 °C in air, where adding Li^{1+} caused the Fe^{3+}/Fe^{2+} ratio to increase at both 81 and 298 °K. Adding Ga^{3+} caused the ratio Fe^{3+}/Fe^{2+} to decrease slightly at 298 °K, while the pattern was essentially unchanged at 81 °K.

As another critical test of the Schroeer-Trift-shäuser[10] proposal, that our form II consists of microcrystals, we extended our earlier search[12] for superparamagnetism. With fields of order 50 Kg we have thus far found no evidence for superparamagnetism, except in the poorly characterized material NiO*, which is prepared at a very low anneal temperature (300 °C). An observation of a partial conversion of unresolved hyperfine pattern into resolved pattern suggested that microcrystals which are weakly coupled may be formed in the early stages of annealing NiO(II), but that sintering has already occurred by the time the stoichiometric form II has been prepared. For the details of these experiments the reader is referred to Ref. 14.

V. CONCLUSIONS

Since CoO and NiO are II-VI compounds we may expect that their electronic behavior will lie somewhere between the ionic behavior of I-VII compounds and the covalent behavior of III-V compounds. In ionic compounds there is a complete transfer of electronic charge, and in purely covalent compounds there is a sharing of electrons. The effects of the Li^{1+}, Cr^{3+}, and Ga^{3+} dopants can be explained by a band model for these semiconducting oxides. Other investigators have found that lithium acts as an acceptor, increasing the conductivity significantly, and gallium or chromium act as donors, decreasing the conductivity.[21-25] Regarding Fe^{2+} as a donor, we obtain a conversion from 2+ to 3+ upon substitutionally inserting an acceptor such as lithium, as shown in Figs. 2–4. This is

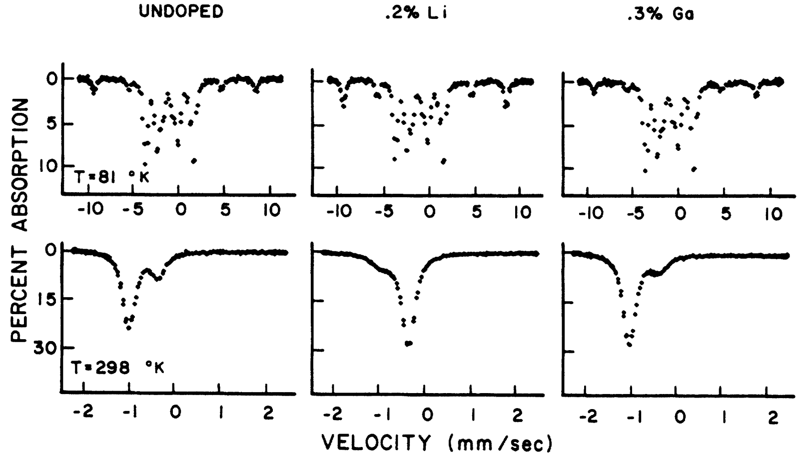

FIG. 6. Effect of substitutionally doping with Li^{1+} and Ga^{3+} on the Mössbauer spectra of CoO(I, II) prepared at 1000 °C. A 1.0-mg/cm^2 sodium ferrocyanide absorber was used at 81 °K and a 0.5-mg/cm^2 absorber at 298 °K.

based on the assumption that the lithium level lies lower in the band gap than the iron level. The equilibrium ratio Fe^{2+}/Fe^{3+} goes in the opposite direction when donors such as chromium or gallium are added, as shown in Figs. 5 and 6. This is based on the assumption that the chromium and gallium levels lie higher in the band gap than the iron level. A monotonic dependence of the ratio Fe^{2+}/Fe^{3+} upon the concentration of the dopant was found, as illustrated in Fig. 2. Our results indicate that Mössbauer measurements on these oxides can be a useful tool for studying their semiconducting properties, and optical measurements of impurity and band levels in these materials should permit a quantitative comparison with our Mössbauer data.

Considering all the data taken thus far on these systems, the structural model for NiO(II) and CoO(II) which seems most compatible with experiment involves a combination of point defects, or vacancies, and small pores. This picture, however, does not explain the large oxygen pickup of CoO(II). This latter phenomenon is very striking, and we have no satisfactory explanation for it, thus far. The results indicate that the CoO(II) and NiO(II) samples definitely have significant structural differences from high-temperature samples. The low-temperature preparations, stoichiometric CoO(II) and NiO(II), may be viewed as a sponge-like structure formed from sintered microcrystals, with a large concentration of dispersed vacancies. The main features of our original model[9] are still indicated in that vacancies of both cation and anion types appear to be the primary cause for most of the observed differences between high- and low-temperature preparations of these oxides. The data are consistent with the mechanism of charge stabilization for the Fe^{3+} ion proposed earlier, i.e., electron trapping by oxygen vacancies, analogous to *F* centers in the alkali halides. (Centers of this type have been observed and studied in MgO.[26]) While our data indicate that small stoichiometric variations may be possible in CoO(II) and NiO(II), these do not appear to be the main cause of their differences in physical properties.

Unfortunately, we still do not have a completely satisfactory explanation of our results, and further research should be done in this area. There are two questions which need to be answered by further experimental and theoretical work.

(i) What is responsible for CoO(II) picking up greater than 60% excess oxygen? This is an exothermic reaction and the reaction has be slowed in order to prevent excessive heating and the formation of Co_3O_4. The oxygen uptake at room-temperature is so great that it would have to completely fill the anion vacancies and the pores to account for our observations. If the phenomenon is basically a surface adsorption, it is very mysterious why the Mössbauer pattern continuously converts[12] from a 6-line to a 2-line pattern at 77 °K in proportion to the oxygen uptake at room temperature.

(ii) Can the ratio of Fe^{2+}/Fe^{3+} observed in our experiments be quantitatively explained on a band picture of these oxides? Additional data on the band gap and impurity levels will be required before this test can be made.

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[13] We have modified our original model of CoO(II) from a simple point-defect model to one which includes both Schottky defects and porosity. This modification seems necessary to account for the results described in Ref. 12 and in the present paper.

[14] For the details of these studies see W. R. Helms, Ph. D. thesis (Purdue University, 1970) (unpublished), which is also described in AEC Report No. COO-AT (11-1)-1616-14 (unpublished).

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Exchange Effects in the Optical-Absorption Spectrum of Fe^{3+} in Al_2O_3

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The polarized optical-absorption spectrum of Fe^{3+}-doped Al_2O_3 has been measured at room, liquid-nitrogen, and helium temperatures as a function of Fe^{3+} concentration (0.02–2 at.%). At low concentrations, the single-ion spectra are fit using the parameters $B = 660\ \text{cm}^{-1}$, $C/B = 4.75$, and $Dq = 1510\ \text{cm}^{-1}$. At liquid-nitrogen temperature and above, there is a marked concentration dependence of the intensities of the ${}^4A_1$, ${}^4E^a$; ${}^4E^b$; and ${}^4T_1^b$ bands which indicates the importance of exchange enhancement. In particular, the ${}^4E^b$ band has a partially resolved component whose temperature and concentration dependence shows that it arises from exchange-coupled pairs of Fe^{3+} ions. The vanishing of this component at liquid-helium temperature indicates that it involves $\Delta S = 0$ transitions analogous to those observed for Mn^{2+}. At 2% Fe^{3+}, the exchange-enhanced bands dominate the optical spectrum at room temperature, and one can anticipate a similar effect in most iron-rich oxides. Owing to the good (for Fe^{3+}) resolution obtained at 77 K, we are able to discuss some of the band details. A point-charge static odd crystal-field calculation of the electric dipole ${}^6A_1 \rightarrow {}^4A_1$ intensities is in very poor agreement with experiment, indicating the need to take lattice vibrations into account. Because of the existence of a strong spin-allowed Fe^{2+} transition in our samples, the two lowest-lying bands of Fe^{3+} in Al_2O_3 are not observed, but their positions are taken from the recent work of Lehmann and Harder.

INTRODUCTION

This paper is concerned with determining the low-temperature polarized optical spectra arising from Fe^{3+} ions in Al_2O_3 and establishing the importance of exchange-coupled pairs to the spectra observed for moderate ($\geq 0.5\%$) Fe^{3+} concentrations at 77 K and above. Quite reasonable values of the intraionic and cubic crystal-field parameters explain the observed spectra. The report also represents the discovery of a distinct exchange-coupled pair line in the optical spectrum of Fe^{3+}.

Until very recently, there has been a paucity of good data on the optical-absorption spectrum of trivalent iron. This fact is associated with the doubly (parity and spin) forbidden nature of transitions from the ${}^6S$ ground state of Fe^{3+} to any of the crystal-field-split quartet states. When the iron concentration is increased to overcome the inherent weakness of the Fe^{3+} bands, a strong absorption edge tends to mask all but the lowest-lying states. Further, the simultaneous existence of both octahedral and tetrahedral Fe^{3+} sites in many of the more interesting iron-bearing compounds has been a bar to interpreting the spectra found. Wickersheim and Lefever[1] reviewed the problem in 1962 and found an anomalous situation in which the technologically most important transition-metal ion had perhaps the most poorly understood energy-level scheme.

In 1967, Wood and Remeika,[2] in the process of examining the infrared optical window in yttrium iron garnet (YIG), were able to detect a substantial number of optical bands and successfully assign them to both octahedrally and tetrahedrally coordinated Fe^{3+}. By growing mixed gallium iron yttrium garnets, they were also able to determine the dependence of some of the band intensities on iron concentration and show that Beer's law is violated. More recently, the discovery that $FeBO_3$ and FeF_3 are transparent room-temperature canted antiferromagnets has stimulated study[3,4] of their optical and magneto-optical properties although no detailed band assignments exist as yet. The extensive work of Kahn *et al.*[5] on the rare-earth orthoferrites has altered the picture significantly. In this study, the ultraviolet region of the spectrum was examined using the complex polar Kerr effect. In particular, the nature of the strong absorptions which arise from parity and spin-allowed charge-