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Properties of Cobaltous Oxide: Effects of Gas Absorption and External Magnetic Fields*

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We have extended our earlier studies of cobaltous oxide, form II,[1] investigating the oxidation properties in greater detail and examining the effects of large external applied magnetic fields. We find that CoO(II) strongly picks up oxygen at room temperature, with excess oxygen exceeding 60% after long exposures. By contrast, N_2, Ar, and Ne are only slightly adsorbed by this material. The effect of applying a 47.5-kG magnetic field is to selectively broaden the hyperfine pattern. We discuss these results in relation to recent proposed models on the structure of cobaltous oxide. We conclude that none of the simpler models suggested for this material is completely satisfactory in explaining all of the data. The data appear to require a high porosity as well as a significant concentration of point defects, and suggest a spongelike structure possibly resulting from sintered microcrystals. The way in which CoO(II) selectively absorbs oxygen may make it a useful material in applications requiring a room-temperature oxygen getter.

I. INTRODUCTION

RECENT studies on CoO and NiO, using primarily the Mössbauer effect, have indicated that radically different properties can be observed for specimens prepared by different techniques. For example, in the case of CoO, the charge state of Fe resulting from the decay of Co^{57} can be either 2+ or 3+, and Mössbauer characteristic temperatures differ drastically for the low- and high-temperature preparations of CoO. Similar differences have been found in physical properties for NiO. Despite many of the similarities of Mössbauer results, explanations advanced to explain these results[1–5] in CoO and NiO are quite different, and various models and combinations of models have been advanced by different investigators. Some workers such as Ando *et al.*[2] ascribe the differences in properties observed in NiO to differences in particle size. This idea has also been advanced by Schroeer and Triftshäuser[3] to explain results on CoO, although, as we have already noted, their qualitative arguments have serious difficulties.[4] Some of the observations have been attributed to excess cation vacancies, as by Triftshäuser and Craig,[5] and this model has then been combined with the microcrystal model of Schroeer and Triftshäuser.[3] We have described the results of our observations on CoO by viewing the high- and low-temperature preparations as two forms of CoO,[1] which we labeled as CoO(I) and CoO(II). Based on our observation that the relative densities ρ_{II}/ρ_{I} was of the order of 0.75, the relative Debye temperatures Θ_{II}/Θ_{I} was 0.61, and CoO(II) was observed to absorb more than 60% excess O_2 at room temperature, we postulated that CoO(II) was a highly vacated structure. Also, thermal hysteresis and quenching experiments supported this view.

The area of controversy relates to the nature of CoO(II), the form obtained in preparing CoO at low temperatures. Thus, the purpose of this paper is to describe in detail new results on CoO(II), and to amplify our earlier remarks[4] on the various models which have been proposed, showing that none of the simpler models appears to give a completely satisfactory quantitative explanation of the observed properties. Specifically, we wish to give the most recent results of our studies of the oxidation and magnetic properties of CoO(II), and to discuss the question of the structure of CoO(II) in the light of these experiments.

II. EXPERIMENTAL TECHNIQUES

The oxidation properties of CoO(II) were studied with the same general procedures used in our earlier work. Specimens were handled in a sealed plexiglass glove box, using only high-purity gases. As before,[1] CoO(II) was prepared by annealing $CoCO_3$ in vacuum at 300°C for a period of 1 h (larger samples required longer annealing), and the sample was sealed in a capsule under gaseous Ar to prevent atmospheric oxidation. The x-ray pattern of this particular sample was not taken, although identical procedures for earlier samples always indicated a domain size of about 50 Å. Mössbauer spectra were taken with a crank system,[6] with multichannel data storage in the time mode of a 400-channel analyzer. Sodium ferrocyanide single-line absorbers, enriched in Fe^{57}, were used throughout the experiments.

The studies of the effects of an applied field were carried out with a superconducting magnet designed by Eastern Scientific Co. with a Dewar made by Janis Co., which permitted the observation of the emitted γ rays

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[3] D. Schroeer and W. Triftshäuser, Phys. Rev. Letters **20**, 1242 (1968).

[4] H. N. Ok and J. G. Mullen, Phys. Rev. Letters **21**, 823 (1968); H. N. Ok and J. G. Mullen, Phys. Rev. **168**, 550 (1968); **168**, 563 (1968); **181**, 986(E) (1969).

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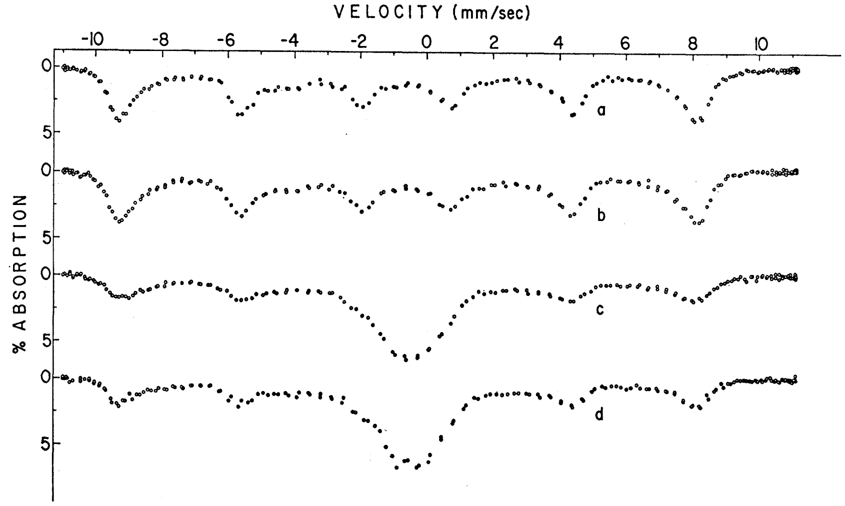

FIG. 1. Effects of N_2 and O_2 absorption in CoO(II) on Mössbauer spectra. The actual sequence of experiments is (a)–(d). After the sample was exposed to N_2 and O_2 at room temperature, Mössbauer spectra were taken at the sample (source) temperature of 77°K. A 1.0 mg/cm^2 $Na_4Fe(CN)_6 \cdot 10H_2O$ absorber was used at room temperature in these experiments. Mössbauer spectra (a) of the original CoO(II), (b) after exposure to N_2 for $1\frac{1}{2}$ h, (c) after exposure to O_2 for 10 h (in this case, the weight gain corresponded to $n=0.23$), CoO(II)$\cdot n$O, and (d) after exposure to N_2 for 3 h.

along a horizontal axis. The absorber was moved in a direction parallel to the direction of the magnetic field applied at the CoO(II) source.

III. GAS-ABSORPTION RESULTS

Because the model controversy concerning CoO(II) centers largely on the question of the relative fraction of the CoO(II) structure which is porous as compared to that fraction which is dispersed point defects, we studied the pickup of O_2, N_2, Ar, and Ne, to look for adsorption as well as absorption effects. There was a qualitative and quantitative difference between the effects of exposure of the samples of CoO(II) to O_2 compared to any of the other above mentioned gases. This contrast is illustrated in Fig. 1, where we show Mössbauer spectra after exposing CoO(II) to pure N_2 gas and subsequently to pure gaseous O_2. While gaseous N_2 had very little effect on the sample, the O_2 picked up was very large, as in our earlier measurements. In a large nonradioactive sample of mass 2181.75 mg, the mass increased only 0.45 mg after $\frac{1}{2}$ h exposure to high-purity N_2 gas, but the quantity of O_2 absorbed after $\frac{1}{2}$ h was 101.30 mg. These combined Mössbauer and gravimetric measurements show that the O_2 pickup cannot be a physical adsorption[7] but must be either a chemical adsorption or a process where the O_2 diffuses into CoO(II), as we had suggested earlier.

To study the possibility of a pure chemical adsorption on the surface of CoO(II), we measured both the Mössbauer and the x-ray patterns as a function of O_2 pickup, as is illustrated in Figs. 2 and 3. Figure 2 shows that there is a systematic conversion of the six-line hyperfine pattern toward the two-line pattern as O_2 is added to the sample. If this were interpreted as a chemical reaction, then it is possible from the relative areas under the two types of absorption spectra to

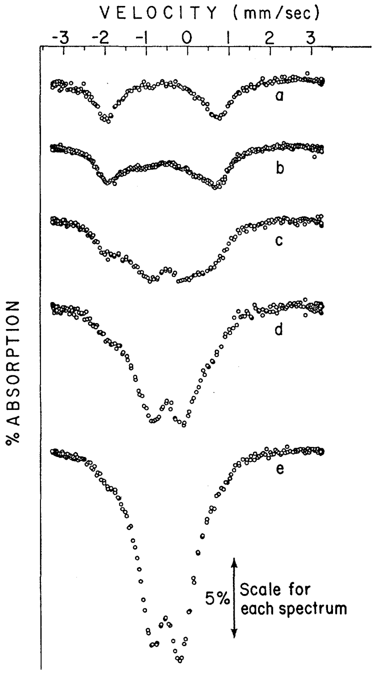

FIG. 2. Effects of room-temperature O_2 absorption of CoO(II) on Mössbauer spectra at 77°K. The experiments were carried out in the sequence of (a)–(e). Mössbauer spectra were taken only over the region of prime interest, ranging from −3.15 to +3.15 mm/sec. Mössbauer spectra (a) before O_2 absorption, after exposure to O_2, (b) for 8 min (the weight increase corresponded to $n=0.1$), (c) for 28 min ($n=0.19$), (d) for 21 h ($n=0.34$), and (e) for a week ($n=0.504$). Additional experiments, not shown, over a wider velocity range indicated that the six-line hyperfine pattern for CoO(II), Fig. 1(a), decreased in area as the doublet pattern increased in area in such a way that the total area was essentially a constant.

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[7] Surface adsorption can be of two types, usually referred to as physical adsorption and chemical adsorption. Physical adsorption is related to such things as surface area exposed, gas critical temperature, etc. The properties of N_2, O_2, and Ar are sufficiently alike with respect to these properties that their physical adsorption is always very similar. For comparison of the adsorption of these gases on charcoal and silica gel, see, e.g., S. Brunauer, *The Adsorption of Gases and Vapors* (Princeton University Press, Princeton, N. J., 1945), pp. 81 and 157.

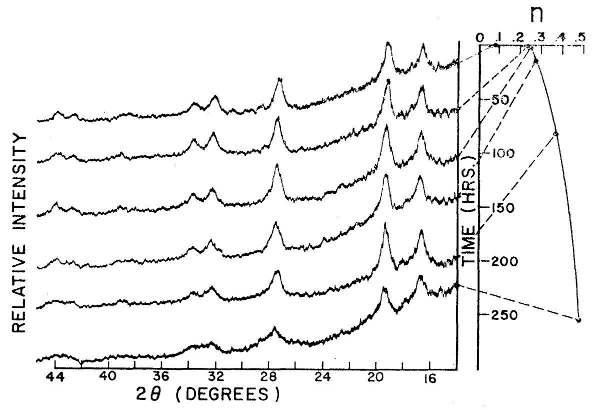

FIG. 3. The x-ray powder pattern for $CoO(II)\cdot nO$ as a function of n. The curve on the right is a plot of the time dependence of the O_2 pickup.

extrapolate what the chemical composition would have to be in order to completely convert the six-line pattern into the two-line pattern. Although the sample after 400-h exposure to O_2 had a 60% O_2 weight gain, there still was a large component to the six-line CoO(II) pattern (not shown). In Fig. 2(e) we see the Mössbauer pattern for the doublet associated with O_2 pickup of approximately 50% of the original O_2 content. For this case the Mössbauer pattern over the entire spectrum indicated that the amount of pure CoO(II) resonance observed, as measured by a comparison of the areas at 77°K, was comparable to that of the doublet component. This would require the surface oxidation state to be at least CoO_2. In view of the lack of evidence for such an oxidation state, the model of simple oxidation of a microcrystal or porous surface appears to be ruled out.

We were able to establish by a careful gravimetric measurement that surface effects were of greater consequences than our earlier proposed model[4] would indicate. Using 99.998% pure Ar and 99.995% pure Ne we were able to measure the surface adsorption of these gases on CoO(II). A 14.4-g sample adsorbed about 4 mg of Ar and of the order of 0.1 mg of Ne. In contrast to the O_2 pickup we found that the Ar and Ne adsorbed by the sample could be removed by reducing the gas pressure sufficiently with a vacuum system. Thus, this observation can almost certainly be attributed to a process of physical adsorption in contrast to the O_2 adsorption measurement. Although it is hard to estimate the particle or pore size from this data, as the fraction of the surface covered is not known, an assumption of about 1% of the surface containing adsorbed Ar leads to an estimate of particle size of the correct order of magnitude required to explain the x-ray broadening of the powder pattern.

In Fig. 3 we see the effects of O_2 pickup at room temperature on the x-ray powder patterns for this material. It should be mentioned that these experiments require considerable caution in the early stages of O_2 pickup, as direct exposure to 1 atm of O_2 in the initial stages produces such a strong exothermic reaction that Co_3O_4 is produced. A gradual increase in the O_2 pressure avoids this difficulty. It is seen in Fig. 3 that in the earlier stages of O_2 pickup the x-ray pattern is practically unchanged within the experimental errors, although in the latter stages ($n \gtrsim 0.3$) the relative intensities and positions of the lines do shift slightly and the lines begin to broaden. It should also be noted that the point where the x-ray pattern begins to change corresponds to a rather sharp knee in the curve representing the time dependence of the O_2 pickup. The sharp knee in the $n(t)$ curve with the accompanying x-ray pattern changes seems to indicate that the O_2 pickup is a two stage process. The results appear to be consistent with an initial surface oxidation followed by a slower diffusion of the O_2 into dispersed defects within the sample. Even this rather involved picture, however, is unable to explain the large remnant CoO(II) Mössbauer pattern after the O_2 content has increased by 50 to 60%, without making the dubious postulate that the surface oxide is an amorphous form of CoO_2. Also, it is not clear why the changes in the Mössbauer pattern upon oxidation of CoO(II) do not appear to reflect a two stage process, although this might be accountable on the basis of a resolution problem in the first stage of O_2 pickup.

IV. RESULTS FOR APPLIED MAGNETIC FIELDS

Mössbauer experiments on CoO(II) at 249, 221, and 102°K at an external magnetic field of 47.5 kG were performed. The results at 249 and 102°K are shown in Figs. 4 and 5, along with the corresponding Mössbauer spectra, without an external applied field, for comparison. As shown in our earlier papers, CoO(II) has a complex temperature dependence to the internal hyperfine field, even in the absence of any external applied field. Below 77°K a clear six-line pattern was observed, but as the temperature increased, a broad unresolvable

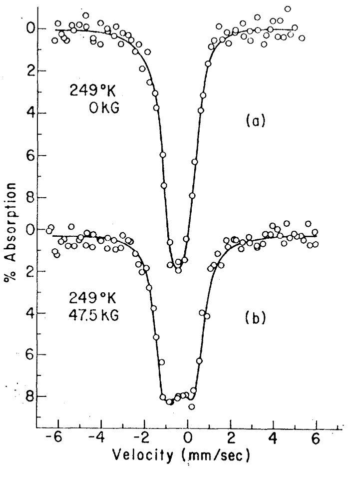

FIG. 4. Mössbauer spectra for CoO(II) at 249°K (a) before and (b) after the application of the external magnetic field of 47.5 kG. A 1.5 mg/cm^2 $Na_4Fe(CN)_6\cdot 10H_2O$ absorber was used in these experiments.

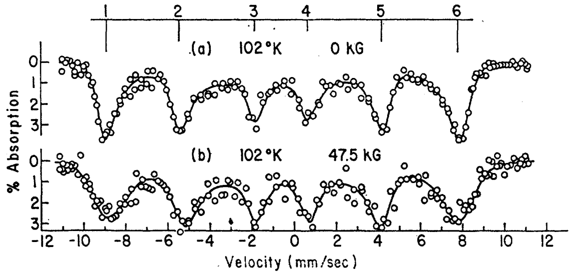

FIG. 5. Mössbauer spectra for CoO(II) at 102°K (a) before and (b) after the application of the external magnetic field of 47.5 kG.

line grew in addition to the resolvable six-line pattern. As the temperature was increased, the resolvable six-line pattern gradually coalesced and nearly disappeared by 242°K. The broad unresolved line became narrower up to a temperature of 270°K. At 270°K, the single line has maximum intensity at the resonance peak. As shown in Fig. 4(a), the Mössbauer spectrum at 249°K with no external magnetic field applied consists of a broad single line with a width of 1.6 mm/sec, which becomes broader under the external applied field of 47.5 kG, without showing any resolvable magnetic hyperfine pattern [Fig. 4(b)]. The line shape is not of the Lorentzian type observed at lower temperatures, with no external magnetic field, but it is flattened at the peak of the resonance. The width of this magnetically broadened absorption line is 2.4 mm/sec. On the other hand, the spectrum at 102°K and zero field consists of a resolvable six-line pattern in addition to a small amount of the unresolvable line [Fig. 5(a)]. The magnetic hyperfine field associated with the resolvable pattern is 519 kG and the linewidths of all six lines are 1.0 ± 0.1 mm/sec. The relative intensities of the six lines are roughly as expected, i.e., 3:2:1:1:2:3. Under an applied field of 47.5 kG the linewidths change, however, as shown in Fig. 5(b), in such a way that the outermost lines, one and six, broaden the most and the innermost lines, three and four, broaden the least. The linewidths of each line before and after the application of the external field are given in Table I. The line positions did not change noticeably, and the unresolvable part of the spectrum was not significantly changed by the application of the 47.5-kG field. At 221°K (not shown), the resolvable and unresolvable parts of the spectrum showed about equal area under the absorption curve for the zero field case. The Mössbauer spectrum did not change noticeably with the application of the 47.5-kG field, although the absorption dips of the six-line pattern were too small in this case to permit a definitive conclusion.

V. DISCUSSION OF FIELD EFFECTS ON ANTIFERROMAGNETIC CoO(II)

Below the Néel temperature antiferromagnetic materials under external magnetic fields show quite different behavior, depending on the strength of the external magnetic field. Van Vleck[8] has calculated the susceptibility of a simple two sublattice antiferromagnet with nearest-neighbor interactions only. Since $\chi_\perp > \chi_\parallel$, the minimum energy configuration in an external magnetic field will occur with the antiferromagnetic axis perpendicular to the external field. Consequently, for the simple Heisenberg model, we would expect the moments to rotate until they are in a perpendicular configuration to the applied field. In real materials, however, such rotations are opposed by an anisotropy field, which tends to keep moments aligned along a particular crystal axis.[9,10] It is not until the applied field reaches a critical value $\sim(2H_eH_a)^{1/2}$, where H_e and H_a are the effective exchange molecular field and the anisotropy field, respectively, that the moments flip into the perpendicular configuration. If the applied field is further increased to a magnitude of the order of the effective exchange field, then the antiferromagnetic ordering will be destroyed, and all spins will be aligned parallel to the applied magnetic field.

We would expect three distinct cases possibly to obtain, for the Mössbauer spectra of antiferromagnetic materials, under various external magnetic field strengths. If the external magnetic field is high enough to destroy the antiferromagnetic ordering, we would expect a magnetic hyperfine field at the Fe^{57} nuclei of a strength $H_{\mathrm{mhf}}'\pm H_0$, where H_{mhf}' is the magnetic hyperfine field at a Fe^{57} nucleus due to the electrons outside the nucleus, and H_0 is the external magnetic field, without any line broadening in the Mössbauer spectra, such as is observed for CoO(II) at 102°K in Fig. 5(b). On the other hand, if the external magnetic field is comparable to the critical value of magnetic sublattice flipping $\sim(2H_eH_a)^{1/2}$, we would expect to observe a magnetic hyperfine field at Fe^{57} of magnitude $(H_{\mathrm{mhf}}^2+H_0^2)^{1/2}$, again without any line broadening of the type observed. It is obvious in Fig. 5 that the applied field $H_0=47.5$ kG is not large enough to cause either magnetic sublattice flipping or the destruction of antiferromagnetic ordering, because of the unequal line broadening of each of the resonance peaks and the observance of very little shift of the line positions of the six lines. Thus, we

TABLE I. Linewidths of the six-line Mössbauer pattern at 102°K before and after the application of an external magnetic field of 47.5 kG.

Line number	Linewidth before application of 47.5-kG field (mm/sec)	Linewidth after application of 47.5-kG field (mm/sec)	Net change of linewidth (mm/sec)
1	1.0 ± 0.1	1.8 ± 0.1	0.8
2	1.0 ± 0.1	1.5 ± 0.1	0.5
3	1.0 ± 0.1	1.1 ± 0.1	0.1
4	1.0 ± 0.1	1.1 ± 0.1	0.1
5	1.0 ± 0.1	1.5 ± 0.1	0.5
6	1.0 ± 0.1	1.8 ± 0.1	0.8

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[8] J. H. Van Vleck, J. Chem. Phys. **9**, 85 (1941).

[9] J. S. Smart, *Effective Field Theories of Magnetism* (W. B. Saunders Co., Philadelphia, 1966).

[10] T. Nagamiya, Progr. Theoret. Phys. (Kyoto) **6**, 342 (1951).

will restrict our argument to the case of an external magnetic field which is smaller than the critical value $(2H_eH_a)^{1/2}$ required for sublattice flipping. Since there is no definite relationship between the directions of H_{mhf} and H_0, in this case the magnetic hyperfine field at Fe^{57} nuclei will be the vector sum of the two fields. If we take the z axis along the external magnetic field, and denote the polar and azimuthal angles of H_{mhf} by θ and φ, respectively, the total magnetic hyperfine field at Fe^{57} nuclei under the external magnetic field will be

$$H_T=(H_{\mathrm{mhf}}^2+H_0^2+2H_{\mathrm{mhf}}H_0\cos\theta)^{1/2}.$$

Since CoO(II) is assumed to consist of numerous domains of order of 50-Å size, the direction of the magnetic hyperfine field in each domain should be different, thereby causing a distribution of values for H_T. The average value of H_T can be obtained by averaging the above expression over all directions, i.e.,

$$\langle H_T\rangle=\frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi}(H_{\mathrm{mhf}}^2+H_0^2+2H_{\mathrm{mhf}}H_0\cos\theta)^{1/2}d\varphi\,\sin\theta d\theta$$
$$=H_{\mathrm{mhf}}+H_0^2/3H_{\mathrm{mhf}}.$$

The standard deviation in the energy when the field is applied is

$$\Delta E=[\langle E^2\rangle-\langle E\rangle^2]^{1/2}$$
$$=|m_1g_1\mu_N+m_2g_0\mu_N|\Delta H,$$

where

$$\Delta H=[\langle H_T^2\rangle-\langle H_T\rangle^2]^{1/2}=(\tfrac{1}{3}H_0^2-H_0^4/9H_{\mathrm{mhf}}^2)^{1/2},$$

and where E refers to energy of the particular transition in question, and m_1 and m_2 are the magnetic quantum numbers for the specified excited and ground states, respectively. This spread of H_T, however, does not broaden the six lines of the Mössbauer magnetic hyperfine pattern equally. In Table II the spread of each line is tabulated, where g_1 and g_0 are the absolute values of the g factors of the first excited state and ground state of Fe^{57}, respectively, and μ_N is the nuclear magneton. In the column 2 of Table II, the energy, or relative line position, of each line is proportional to the total magnetic hyperfine field, but the proportionality constant is different from line to line. Therefore, even for an equal amount of spread in H_T, the spread in energy of each line is different, as shown in column 3. The proportionality constant of line 1 and line 6 is largest and that of line 3 and 4 is smallest. In column 4, the calculated values of the line broadening for $\Delta H=27.4$ kG are shown, which is calculated using the above formula with $H_0=47.5$ kG and $H_{\mathrm{mhf}}=519$ kG. Comparing these values with the experimental values listed in Table I, the agreement is within experimental errors. The total average magnetic hyperfine field $\langle H_T\rangle$ is also calculated to be 519+1.45 kG, using the above formula. This implies a line shift of only 0.28%, which is also in agreement with the experimental data within the error limits (see Fig. 5).

TABLE II. Average line positions and line broadening of the six magnetic hyperfine lines for CoO(II) under the external field.

Number of lines	Average line position	Spread of lines	Calculated values of the spread (mm/sec)
1	$(\frac{3}{2}g_1+\frac{1}{2}g_0)\mu_N\langle H_T\rangle$	$2(\frac{3}{2}g_1+\frac{1}{2}g_0)\mu_N\Delta H$ [a]	0.88
2	$\frac{1}{2}(g_1+g_0)\mu_N\langle H_T\rangle$	$2(\frac{1}{2}g_1+\frac{1}{2}g_0)\mu_N\Delta H$	0.51
3	$\frac{1}{2}(-g_1+g_0)\mu_N\langle H_T\rangle$	$2(-\frac{1}{2}g_1+\frac{1}{2}g_0)\mu_N\Delta H$	0.14
4	$\frac{1}{2}(g_1-g_0)\mu_N\langle H_T\rangle$	$2(-\frac{1}{2}g_1+\frac{1}{2}g_0)\mu_N\Delta H$	0.14
5	$\frac{1}{2}(-g_1-g_0)\mu_N\langle H_T\rangle$	$2(\frac{1}{2}g_1+\frac{1}{2}g_0)\mu_N\Delta H$	0.51
6	$(-\frac{3}{2}g_1-\frac{1}{2}g_0)\mu_N\langle H_T\rangle$	$2(\frac{3}{2}g_1+\frac{1}{2}g_0)\mu_N\Delta H$	0.88

[a] We use g_1 to represent the magnitude of g_1 only as the sign is explicitly taken into account in these formulas. The factor of 2 is required to give the total spread in the linewidth.

Our model, which assumed a random distribution of magnetic domains, explains both the temperature and field dependence of the observed Mössbauer spectra, assuming that the external magnetic field is small compared to the critical value for spin flipping. In their recent letter[3] Schroeer and Tritfshäuser suggested that the temperature-dependent behavior of the magnetic hyperfine pattern of CoO(II) was the result of superparamagnetism. According to the theory of superparamagnetism, the spin orientation of a small particle can change because of thermal relaxation. If the superparamagnetic relaxation time is long compared to the Larmor precession time of the first excited state of Fe^{57}, we can observe a six-line magnetic hyperfine pattern, but otherwise a broadened single line should be observed. When we applied a field of 47.5 kG to a sample of CoO(II) at 249°K, which is just above the temperature where we see a disappearance of the completely resolved six-line pattern, and also at 221°K, at which the strengths of the resolved six-line pattern and the unresolved broad single line are almost equal, we would expect that the external magnetic field would increase the superparamagnetic relaxation time, thereby converting some of the unresolved pattern into the resolved pattern. This is because fine particles have permanent magnetic moments, which are generally parallel to the alignment of antiferromagnetic spin system.[11] These permanent moments result from an imperfect compensation of the magnetic sublattices. The origin of such a moment depends on the lack of internal structural perfection and on the surface form of the particle. Such a moment would be relatively larger when the particle is smaller. Even though the magnitude of the permanent magnetic moment of a 50-Å CoO particle is not known, we may use the magnetization data[12] of 50-Å NiO particles to estimate the order of magnitude of the

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[11] I. S. Jacobs and C. P. Bean, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1963), Vol. III.

[12] J. Cohen, K. M. Creer, R. Pauthenet, and K. Srivastava, J. Phys. Soc. Japan Suppl. **17**, 685 (1962).

permanent magnetic moment of a 50-Å CoO microcrystal. Since the magnetization curves for superparamagnetic particles follow a Langevin function[13] closely, we carried out a least-square fitting of a Langevin function with the permanent magnetic moment as a parameter to the data on NiO of Cohen *et al.*,[12] and found $\mu = 5.044V$ cgs emu, where μ and V are the permanent magnetic moment and the volume, respectively, of a 50-Å NiO particle. In order to see a remarkable change of relaxation time of microcrystals in an external field of H_0, the magnetic energy μH_0 must be of the same order of magnitude as the thermal energy kT. The magnetic energy μH_0 in a field of 47.5 kG is calculated to be 1.57×10^{-14} erg, while the values of kT at 249, 221, and 102°K are 3.44×10^{-14}, 3.05×10^{-14}, and 1.41×10^{-14} erg, respectively, which are of the same order of magnitude as μH_0. Therefore, if CoO(II) consists of "free" microcrystals of size 50 Å, we would expect to see a significant change in the superparamagnetic relaxation time in an external field of 47.5 kG. As shown in Fig. 4, however, the unresolved line at 249°K did not split into six lines even under a field as great as 47.5 kG. Furthermore, at 221°K, where the superparamagnetic relaxation time should be comparable to the Larmor precession time of the first excited state under no external field, we did not observe any measurable conversion from the single unresolved line to the six resolved lines with a 47.5-kG external field. Also, it is evident in Fig. 5 that the unresolved line at 102°K did not change before and after the application of an external magnetic field. At 249°K the Mössbauer line broadened only from 1.6 to 2.4 mm/sec. This small broadening and the non-Lorentzian line shape suggests that this broadening comes from the direct interaction of Fe^{57} nuclei with the external magnetic field, because the unresolved line at a temperature just below 249°K does not have a flattened peak and the external field of 47.5 kG corresponds to a 1.5-mm/sec splitting if there is no quadrupole splitting. In CoO(II), we have assumed the existence[1] of a small quadrupole interaction due to defect structure and trapped charges in vacancies. Thus, failure to observe a splitting of the unresolved line under the external magnetic field suggests that CoO(II) does not consist of superparamagnetic particles. On the other hand, this phenomenon may be explained quite satisfactorily in terms of our static domain model,[1] because, even though each domain may have incomplete compensation of spins, the spins near the domain wall would not have the freedom possessed by the spins of isolated superparamagnetic particles, due to the interaction with the nearby spins in the adjoining domain.

In view of our finding the density of CoO(II) higher than first expected,[4] along with our gas-adsorption measurements with gaseous Ar and Ne, however, it would be consistent with our present results to view the domains formed as sintered microcrystals. This would account for our failure to see relaxation effects evidence for superparamagnetism in our samples of CoO(II), and at the same time this model would be consistent with the observations suggesting a relatively large porosity and defect structure. We have initiated studies along these lines with NiO, and it might be noted that we find evidence for substantial magnetic broadening effects in samples prepared at low temperatures with very short anneals, while we appear to obtain results similar to CoO(II) for intermediate anneals. These results may well indicate that microcrystals were indeed formed in the early stages of sample preparation but that sintering has already occurred in the anneal periods used for our samples.

VI. SUMMARY AND CONCLUSIONS

Our present results indicate that the simple defect model which we first proposed to explain our results on CoO(II) is not adequate to explain some of our present results, such as the large gas adsorption of Ar and the two-stage nature of O_2 pickup as revealed by our more detailed x-ray studies. The microcrystal model of Schroeer and Triftshäuser also seems inadequate to quantitatively account for all of the results obtained. A sponge structure for CoO(II), formed from sintered microcrystals and having a substantial concentration of dispersed vacancies, appears to best account for the vast majority of the data, although even this model leaves some quantitative aspects of the data, such as the extremely large amount of O_2 pickup, in need of still further investigation.

Our results indicate that the internal fields at Fe^{57} nuclei are only a simple superposition of the internal hyperfine fields and the applied fields, for applied fields under 50 kG, which are the largest fields readily available in the laboratory at the present time. This result may be explained by a static domain model and does not require an assumption of superparamagnetism.

The property of selective O_2 pickup may give a practical application for CoO(II), in that this material could be used as a good room-temperature O_2 getter. The capacity of this material to absorb O_2 is such that more than 60% excess O_2 compared to the ideal stoichiometric value can be achieved in periods of order 400 h. The striking differences and similarities in the properties of CoO(I) and CoO(II) should make possible still further interesting studies of CoO.

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[13] C. P. Bean and J. D. Livingston, J. Appl. Phys. Suppl. **30**, 120 (1959).