

REINTERPRETATION OF DATA ON MULTIPLE CHARGE STATES OF Fe IN CoO†

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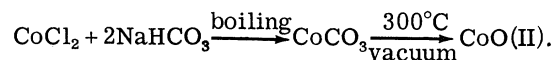
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It is suggested that the samples studied in recent Mössbauer experiments on CoO doped with ^{57}Co included microcrystals as well as polycrystalline bulk. This interpretation resolves the conflict concerning the temperature reversibility of the interconversion between the observed ferrous and ferric valence states, and is consistent with the cation-vacancy stabilization model.

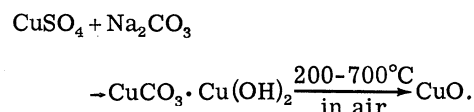
A controversy has recently arisen concerning the origin of ferric ions in CoO doped with ^{57}Co .^{1,2} Mössbauer-effect studies using such samples as sources showed resonances indicating that the iron ions following the K -capture decay of the ^{57}Co existed in both the divalent and the trivalent states.^{3,4} This observation was originally interpreted³⁻⁵ in terms of metastable chemical charge states created by the Auger effects following the decay, and possessing lifetimes comparable with the nuclear lifetime ($\tau_{1/2} = 100$ nsec).³ Triftshäuser and Craig¹ (hereafter denoted by TC) combined the delayed-coincidence technique with Mössbauer-effect measurements. They found no time dependence of the charge states within the lifetime of the nuclear level. However, a reversible interconversion between the Fe^{2+} and the Fe^{3+} states for varying temperatures was observed, but on a time scale much slower than the nuclear lifetime. TC interpreted this interconversion in terms of thermodynamic equilibrium between ferric and ferrous ions, with the relative intensities fixed by the amount of deviation of the samples from perfect stoichiometry. Mullen and Ok² (hereafter denoted by MO) produced two different forms of CoO. One of these, labeled CoO(I), showed only Fe^{2+} resonances, consistent with similar earlier observations by Bearden, Mattern, and Hart.⁶ The other form, labeled CoO(II), showed only Fe^{3+} resonances. When heated above 300°C , CoO(II) goes irreversibly over into a sample labeled CoO(I,II), showing a mixture of Fe^{2+} and Fe^{3+} ions. MO developed a model in which CoO(II) consists of CoO with the normal lattice structure, but with half of both the cobalt and the oxygen lattice sites vacant. This model was based primarily on the low density and large oxygen absorption of their CoO(II) sample. MO consider all CoO samples to consist of various ratios of these two forms. The irreversibility and the interpretation of the data as two distinct coexisting "phases" of CoO appeared to contradict the TC model.

We would like to propose an alternative explanation for the data of MO, which explains the difference between the TC and MO experiments. We suggest that the CoO(II) samples of MO actually consist of microcrystals of CoO, with an average diameter of about 50 \AA , and would like to summarize the evidence supporting this interpretation.

Physical aspects.—The methods of preparation of the CoO(II) samples of MO can be expected to produce small microcrystals. One sample preparation technique involves the reaction in liquid:



Takada and Kawai⁷ carried out a similar reaction with copper, namely



This resulted in microcrystals, with the particle diameter increasing with the reaction temperature: Heating for 40 min at 200°C gave 100-\AA -diam particles, 40 min at 410°C — 230-\AA diam, 70 min at 550°C — 380-\AA diam, and 100 min at 700°C — 1000-\AA diam. The second sample preparation technique for CoO(II) used by MO included the heating of cobaltous nitrate at 200°C to give a higher oxide of cobalt, followed by reduction in a hydrogen atmosphere at about 210°C . Heating iron nitrate at 250°C for several hours gives $\alpha\text{-Fe}_2\text{O}_3$ microcrystals with a diameter of 50 \AA .⁸ MO prepared their CoO(I) sample at $800\text{-}900^\circ\text{C}$, and it therefore is expected to consist of large polycrystals and to exhibit bulk characteristics.

MO found the density of the CoO(II) samples to range down to about half that of their bulk CoO(I) sample. Microcrystals of this small size tend to be spherical, as observed in Au ⁹ and CoFe_2O_4 ,¹⁰ for example. If CoO(II) is made up of small, al-

most spherical microcrystals, and if these are packed in small clumps as is usually observed in such samples, then the fraction of the total sample volume occupied by them will depend on the particular packing arrangement. It may be as low as $V(\text{sphere})/V(\text{cube}) = [\frac{4}{3}\pi(\frac{1}{2}d)^3]/d^3 = \frac{1}{6}\pi = 0.52$. This is in agreement with the lower limit on the density observed by MO. Since the particle size varies with sample preparation, and since larger particles tend to be less spherical, the observed variations in density are reasonable.

The broadening in the x-ray spectra of the CoO(II) samples is consistent with the existence of microcrystals of about 50 Å diam.

MO observed very strong oxygen absorption by their CoO(II) sample. This may be due to the oxygen settling into the many defect lattice sites at the surface of the microcrystals. The splitting into two peaks of the Mössbauer spectrum for their oxygenated sample corresponds possibly to a quadrupole splitting due to a lattice distortion transferred throughout the whole microcrystal volume from the oxygen at the surface.⁸ The CCl₄ liquid used in the density measurements does not necessarily penetrate into these clumps of microcrystals because of surface tension, and because of the much larger molecular size.

The conversion change from CoO(II) to CoO(I, II) above 300°C indicates fusing inside the sample. This is typical of microcrystals, and is indeed irreversible.⁷ The fact that in MO's CoO(I, II) samples at 614°K some Fe³⁺ goes irreversibly to Fe²⁺ indicates the presence of some fraction of small particles in those samples as well.

Effects of the particle size.—The Debye temperature in the CoO(II) sample of MO is $\Theta_{\text{II}} = 320^\circ\text{K}$, much lower than that of $\Theta_{\text{I}} = 510^\circ\text{K}$ for the bulk CoO(I) sample. The apparent Debye temperature in microcrystals is expected to differ from the bulk value through modifications in the lattice vibrational spectrum due to the surface, through the lattice spacing changes observed in such microcrystals,^{8,11-13} through incomplete transfer of the recoil to the neighboring microcrystals,¹⁴ etc. The observed reduction in Θ_{II} is probably due to a combination of these effects. Considering only possible lattice-spacing modifications, the Debye temperature can be approximated by¹⁵

$$\Theta_{\text{II}} \approx (1 - \gamma \Delta V/V) \Theta_{\text{I}}$$

where γ is the Grüneisen constant and $\Delta V/V$ is the fractional change in the volume of the unit

cell of CoO from state I to II. Assuming $\gamma \approx 3$, an increase of $\Delta V/V \approx 0.03$ (corresponding to a 1% increase in the lattice spacing) would already decrease the Debye temperature by 9%. The x-ray data of MO appear to indicate shifts of this order of magnitude. Changes in the Debye temperature of microcrystals from the bulk value have been observed.^{11,14,16,17} In $\alpha\text{-Fe}_2\text{O}_3$ microcrystals with a diameter of 50 Å, the unit cell has expanded by 0.06.^{8,13} Van Wieringen¹⁴ has found the recoilless fraction in 20- to 30-Å iron-oxide particles to be less than half that of the bulk value and dependent on the packing of the powder sample. Suzdalev et al.¹⁶ found the Debye temperature in tin microcrystals to be lower than in bulk. Extrapolating their data to 50-Å-diam particles indicates $\Theta(50 \text{ Å})/\Theta(\text{bulk}) \approx 0.5$.

These microcrystals may be expected to exhibit the phenomenon of superparamagnetism.¹⁸ The magnetic hfs spectrum of the MO bulk CoO(I) sample goes very abruptly from the single line above the Néel temperature of 288°K to a definite six-line spectrum at 283°K. The transition of the MO CoO(II) (microcrystals), on the other hand, extends over a much larger temperature range. It begins below 242°K, goes through spectra in which the peaks are very much broadened and the central peaks are much larger than the outer ones, until the transition is finally completed below 135°K. This same behavior has been observed in NiO microcrystals¹⁹ for example (see also Van der Kraan and Van Loef²⁰ and Schuele, Shtrickman, and Treves²¹). Such relaxation spectra are observed when the Larmor precession time T_{L} becomes comparable with or larger than the superparamagnetic relaxation time τ (cf. Ref. 18). τ can be written as $\tau = (1/f) \times \exp(KV/kT)$, where K is the anisotropy energy density, V the average particle volume, and kT the thermal energy, and f is about 10^9 Hz. We can quantitatively evaluate the anisotropy energy constant K for the CoO(II) sample of MO from their spectra, just as Ando et al.¹⁹ analyzed the data for NiO. The magnetic hfs spectra of CoO(II) near 200°K very closely resemble those of 102-Å NiO particles at 300°K. Since for NiO $K \approx 5 \times 10^4$ erg/cm³, this means that for CoO $K \approx 3 \times 10^5$ erg/cm³.

The Néel transition temperature T_{N} in CoO rises under direct pressure by 0.6°K/kbar.²² If we assume the compressibility of CoO to be similar to that of Fe, namely $K \approx 17 \times 10^5$ kg/cm²,²³ then an expansion of the lattice on the order of 1% would lead to a decrease in the Néel temperature of about 30°K. MO found that the Néel tem-

perature in the CoO(II) (microcrystals) is about 20°K lower than in bulk. From the Curie-Weiss law the Weiss temperature T_W is defined through $T_W = [2S(S+1)/3k] \sum_k Z_k J_k$, where S is the spin per atom, Z_k the number of k th-nearest neighbors of a given atom, and J_k the exchange interaction between a pair of k th-nearest neighbors.²⁴ From this expression, taking into account only nearest-neighbor interactions, a transition temperature T_W of 330°K is derived for CoO, in relatively good agreement with the actually observed Néel temperature T_N of 291°K. Assuming that the exchange interaction J_k remains the same, the Néel temperature is directly proportional to the number of nearest neighbors.²⁵ If CoO(II) has half of its lattice sites vacant, it should have a T_N about half that of the CoO(I) with the perfect lattice; the decrease observed by MO for their CoO(II) sample is only about 6%.

MO's CoO(II) sample exhibits both the magnetic hfs splittings and the isomer shift corresponding to trivalent iron, whereas the normal CoO(I) bulk sample shows the divalent iron splittings and isomer shift. In the case of the very analogous compound NiO, the Mössbauer studies of Ando *et al.*¹⁹ indicate that the iron following the ⁵⁷Co K -capture decay in 102-Å NiO particles also shows exclusively Fe³⁺ properties. In bulk NiO on the other hand, both Fe²⁺ and Fe³⁺ coexist, with complete reversibility of interconversion between them as a function of temperature.^{1,26}

Discussion.—As shown above, the properties observed by MO for their pure CoO(II) sample can be explained quite well on the basis that they consist of CoO microcrystals with a diameter of about 50 Å. The complete stabilization of the Fe³⁺ ions in both CoO and NiO microcrystals is presumably due to the additional cation defects and excess oxygen ions introduced by the surface of the microcrystals.²⁷ Richardson and Milligan²⁷ find an oxygen excess of about 0.4% in NiO microcrystals with a diameter of 80 Å, for example; deviations of this magnitude from stoichiometry are not large enough to be detected by MO.

In our interpretation, the CoO(I, II) samples of MO are not just mixtures of separate CoO(I) and CoO(II) phases. When prepared at low temperatures they initially contain CoO particles of various sizes, including some small enough so that they exhibit the pure CoO(II) behavior. As the samples are heated above 300°C, there will be fusion of these microcrystals into larger perfect crystals, so that some of the Fe³⁺ ions are

no longer stabilized. This fusion process represents the irreversible conversion observed by MO. The sample ultimately reaches thermodynamic equilibrium, and becomes bulk CoO with enough cation vacancies to stabilize a certain fraction of the Fe³⁺ at the various temperatures. Once this thermodynamic equilibrium is reached, interconversion between ferrous and ferric ions as the temperature is varied does become reversible as reported in Refs. 1 and 4 for samples prepared at high temperatures where no microcrystals are produced. The relative intensities of these lines is then fixed by the amount of deviation of the equilibrium samples from perfect stoichiometry.

Experiments are in progress to produce CoO microcrystals of various size, and to study the ratios of ferrous and ferric ions as a function of particle size and temperature. These measurements should further clarify the nature and range of the interaction of the cation vacancies with the iron ions in CoO and similar oxides.

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OBSERVATION OF LOCALIZED VIBRATIONS IN Cu-4% Al BY COHERENT INELASTIC NEUTRON SCATTERING*

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The localized vibrations of Al in a Cu host lattice have been observed in a Cu-4% Al crystal by coherent inelastic neutron scattering. Both the local-mode frequency and the \vec{q} dependence of the neutron scattering cross sections are in good agreement with a calculation based on a mass-defect theory.

In this Letter we report some preliminary results of coherent inelastic neutron scattering measurements of the localized vibrational modes in a Cu single crystal containing 4.1 at.% Al as a substitutional impurity. The experiments were performed on a triple-axis neutron spectrometer at the High Flux Isotope Reactor (HFIR). All the measurements were obtained with the spectrometer operating in the constant- \vec{Q} mode¹ and with the scattered neutron energy E' held fixed at 18.9 meV (4.5×10^{12} cps). Inelastic-neutron-scattering studies of localized vibrations have been reported previously,²⁻⁴ but to our knowledge there have been no previous coherent-inelastic-scattering measurements of local vibrational mode in single crystals.

The cross section for the coherent inelastic neutron scattering from a concentration c of isolated light-mass substitutional impurities in a cubic lattice, provided there is no change in the interatomic force constants, is given by Elliott and Maradudin⁵ as

$$\frac{d^2\sigma}{dE d\Omega} = \frac{k_0}{2k'} (n_l + 1) \delta(\nu - \nu_l) \frac{cb^2 \nu_l}{MB(\nu_l^2)} e^{-2W} \sum_j [\vec{Q} \cdot \vec{e}_j(q)]^2 \left[\frac{b'/b - 1}{\nu_l^2 \epsilon} + \frac{1}{\nu_l^2 - \nu_j^2(q)} \right]. \quad (1)$$

Only energy loss of the neutron is considered. n_l is the equilibrium number of phonons with frequency ν_l , e^{-2W} is the Debye-Waller factor, and b' and b are the scattering lengths of the impurity and host, respectively. \vec{Q} is the wave-vector transfer of the neutron, $\vec{e}_j(\vec{q})$ and $\nu_j(\vec{q})$ are the polarization vector and frequency of the normal mode in the pure crystal with wave vector \vec{q} and branch index j , and $\epsilon = 1 - (M'/M)$, where M' is the impurity mass and M is the host mass. ν_l is given by the solution of

$$\nu_l^2 \int \frac{g(\nu) d\nu}{\nu_l^2 - \nu^2} = \frac{1}{\epsilon}, \quad (2)$$

where $g(\nu)$ is the frequency distribution function (normalized to unity) of the unperturbed host lattice, and

$$B(\nu_l^2) = \int \frac{\nu^2 g(\nu) d\nu}{(\nu_l^2 - \nu^2)^2}. \quad (3)$$

The concentration of impurities in the sample studied in the present work may not be sufficiently small for each impurity to be considered isolated. In addition, one might expect changes in the interatomic force constants, since there is a tendency toward short-range order in the more