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[14] A detailed account of the spectra produced by group IV dopants in GaP has been prepared by P. J. Dean, C. J. Frosh, and C. H. Henry, to be published. Their results are also in complete accord with the conclusions of this analysis. The author wishes to thank Dr. Dean for providing a preprint.

REBUTTAL TO THE ALTERNATIVE SCHROEER-TRIFTSHÄUSER INTERPRETATION OF RECENT MEASUREMENTS ON COBALTOUS OXIDE*

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In a recent Letter Schroeer and Triftshäuser offered a reinterpretation to the extensive data on cobaltous oxide by the present authors. We show herein that a careful examination of the microcrystal model proposed by Schroeer and Triftshäuser does not, in fact, account for the main observation on cobaltous oxide.

Recently much interest has been shown in the origin of the multiple charge states found in Mössbauer spectra of Fe^{57} in CoO.[1-4] After a period, during which much work was done with samples showing both Fe^{2+} and Fe^{3+} lines, we succeeded in isolating two materials showing only Fe^{2+}, or Fe^{3+}, in their respective Mössbauer spectra, with each having the nominal composition CoO. Extensive experimental data on CoO(I), CoO(II), and CoO(I, II), a mixture of forms I and II, were analyzed and explained on the basis of a two-phase model.[2] In this model we postulated that CoO(I) had ideal stoichiometry and translational symmetry, while CoO(II) was a highly vacated lattice with the number of Schottky defects equal to the number of CoO molecules contained in this material. The main reasons for assuming the vacated structure, CoO(II), was the observation that the relative density ρ_{II}/ρ_I was of order 0.5, the relative Debye temperature, θ_{II}/θ_I, was 0.61, and CoO(II) was observed to absorb more than 60% excess oxygen at room temperature. Also, thermal cycling and quenching experiments supported this view. Furthermore, this Schottky defect model for CoO(I, II) could explain the reversible increase[2-4] of Fe^{3+} with increasing temperature on the basis of anion vacancy dissociation.[2]

Recently, however, Schroeer and Triftshäuser (ST) reinterpreted our data for CoO(II) on the basis of a microcrystal model, using vague arguments supplemented by rough numerical estimates. The purpose of this Letter is to point out some weaknesses in the ST arguments, which indicate that their model is not consistent with our observations.

ST propose that CoO(II) is merely microcrystals of CoO, with an average diameter of about 50 Å. As evidence for their microcrystal model they point out that our preparation technique, involving a liquid reaction, can lead to microcrystals, quoting a similar preparation for CuO. The fact that such reactions do not necessarily lead to microcrystals, however, has been strikingly shown by Ikornikova,[6] who has grown large single crystals of $CoCO_3$ in aqueous solutions at 100-500°C.

To explain our observed low density of CoO(II), ST assume a simple cubic packing of spherical microcrystals to show that the density of CoO(II) can be about half of that of CoO(I). There is, however, no reason why spherical microcrystals should be packed in a simple cubic arrangement. A close-packed structure, such as fcc or hcp, gives 0.74 as the relative density.

ST suggest that the very strong oxygen absorption by CoO(II) is due to surface adsorption, and that the collapse of the six-line hyperfine pattern to a doublet is due to a lattice distortion transferred throughout the entire microcrystal volume from the surface oxygen. If the O_2 absorption is a surface adsorption, we would expect to observe similar effects for other gases such as N_2. But our experiments[7] show that a CoO(II) sample of mass 2181.75 mg increased in mass by only 0.45 mg after $\frac{1}{2}$ h, while the quantity of O_2 absorbed after $\frac{1}{2}$ h was 101.30 mg. Also, the Mössbauer pattern after exposure to pure N_2 gas was unchanged for CoO(II), in marked contrast to the radically changed pattern after exposure to O_2. The failure to pick up N_2 gas indicates that the surface area of the sample used is much less than that required by the assumption of 50-Å microcrystals. The coexistence[7] of a six-line hyperfine pattern and a doublet in the Mössbauer spectra of O_2-absorbed CoO(II), at 77°K, rules out the possibility of a uniform lattice distortion transferred throughout the whole microcrystal volume from the oxygen at the surface, as suggested by ST. The proportional increase of the doublet area with the increase in the amount of oxygen absorbed by CoO(II) indicates that the oxygen pick-up is a volume effect, as required by our vacated model of CoO(II).

One of the most unsatisfactory parts of the ST interpretation is their attempted explanation of the much lower Debye temperature for CoO(II) (320°K) relative to that of CoO(I) (510°K). Assuming a hypothetical lattice expansion for CoO(II) microcrystals, which was not observed in our actual x-ray data,[8] they calculated a 9% decrease in θ from Hank's formula,[9]

$$\theta_{\mathrm{II}} = [1-\gamma(\Delta V/V)]\theta_{\mathrm{I}}.$$

Not only is the application of this formula to hypothetical microcrystals invalid, because 50-Å microcrystals of dielectric CoO would have a much different vibration spectrum from the bulk material with the long-wavelength phonons excluded, but the calculated characteristic temperature of 464°K is much greater than our experimental value of 320°K for CoO(II). If one were to use the more accurate limit to the lattice expansion indicated by our data,[8] the disagreement is even greater. ST make reference to other possibilities, and they cite the work of Marshall and Wilenzick,[10] who do take into account the low-frequency cutoff in the phonon frequency distribution. This effect, however, increases the θ value calculated instead of decreasing it. We used the explicit formula derived by Marshall et al.,[10] to calculate f values as a function of temperature. Our results are shown in Fig. 1, curve c. To further support their interpretation, ST extrapolate Sn data obtained by Suzdalev et al.[11] to the 50-Å region,[12] ignoring the crucial difference between Sn and CoO. In fact, data for Sn have no relevance to CoO, because of the large differences in the characteristic temperatures between CoO and Sn (510°K compared with 140°K). In using Sn data for CoO, ST considered only geometrical particle size, but neglected the gross difference in binding for these two materials. Applying the same formula used by Suzdalev et al.,[11] originally derived by Rich,[13] we calculated f values as a function of temperature, and we obtained the results shown in Fig. 1, curve d. From these calculations, summarized in Fig. 1, it is evident that none of the three attempts of ST, nor any combination thereof, can explain the experimental results.

ST also suggest that the gradual transition from a six-line pattern to a single one as T increases from 200 to 270°K was evidence for superparamagnetism by microcrystals. To test this point we applied a strong magnetic field (~50 kG) to a CoO(II) sample at 250°K, which is an intermediate temperature between the six-line resolved pattern and the sharp single line. A strong mag-

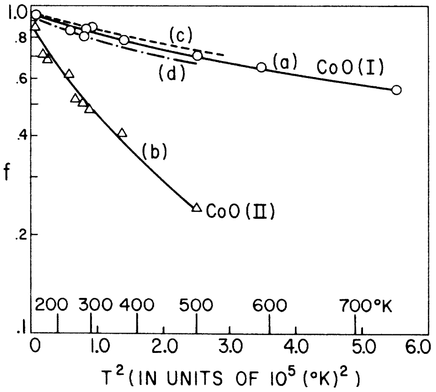

FIG. 1. The experimental and calculated f values of CoO as a function of temperature. Experimental values of f for CoO(I) are shown by curve a and for CoO(II) by curve b. The calculated values of f for 50-Å particles of CoO using the formula of Marshall et al. (Ref. 11) are given by curve c, and using the formula derived by Rich [Phys. Letters 4, 153 (1963)], by curve d.

netic field should increase the "superparamagnetic" relaxation time, and, consequently, we should observe a more nearly resolved hyperfine pattern. Our experimental results, however, show no change in the Mössbauer spectra before and after applying a 50-kG magnetic field, except for a slight broadening due to direct interaction between the nuclear spin and the external field. (The full details of these experiments will be published in a separate article.)

In order to explain our observed Néel temperature for CoO(II), ST use the formula $T_N = [2S(S+1)/3k]\sum_k Z_k J_k$. This formula, however, is not the correct formula for the Néel temperature (T_N), but rather obtains for the paramagnetic Néel temperature (referred to as θ usually). The actual Néel temperature is given by[14]

$$T_N = \frac{2S(S+1)}{3k} \sum_{j \neq i} Y_{ij} Z_{ij} J_{ij} ,$$

where $Y_{ij} = 0$ or ± 1, Z_{ij} is the number of neighbors to the ith ion, and J_{ij} is the exchange interaction between the ions i and j. This formula shows that T_N is not necessarily proportional to the number of nearest neighbors. The difference between the paramagnetic Néel temperature and the Néel temperature is usually tremendous, e.g., $T_N = 116°\mathrm{K}$ and $\theta = -610°\mathrm{K}$ for MnO, while $T_N = 523°\mathrm{K}$ and $\theta = -3000°\mathrm{K}$ for NiO.[14]

In addition to the above rebuttal we must add some additional facts which were overlooked by ST, and which are inconsistant with their model. First, the recoil energy of 50-Å microcrystals of CoO is two orders of magnitude greater than the Mössbauer linewidth. Thus, the actual observation of well-defined Mössbauer spectra for our powder samples of CoO(II) is not in harmony with the microcrystal model. Although ST make a reference to "incomplete transfer of recoil to the neighboring microcrystals," such an "incomplete transfer" is not compatible with the essential requirement for the observation of the Mössbauer effect that there be no local excitation to take up the recoil momentum accompanying the emission of the Mössbauer γ ray. Secondly, ST did not explain why the Fe^{3+} line intensity increases reversibly with increasing temperature for CoO(I, II). If CoO(I, II) contained a certain fixed number of cation vacancies, we should see the same ratio of $\mathrm{Fe}^{3+}/\mathrm{Fe}^{2+}$ intensities throughout the temperature interval, because the jump time of the cation[15] is much greater than 10^{-7} sec, the lifetime of the first excited state of Fe^{57}.

In conclusion, ST attempted to explain our experimental results with qualitative arguments, which a more careful analysis does not support. By contrast with the ST microcrystal model, our two phase model explains every phenomenon observed, thus far, for CoO(I), CoO(II), and CoO(I, II).

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