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Physical Properties of Cobaltous Oxide Prepared at Low Temperature—A Reply*

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The results of Mollard *et al.* are shown not to conflict with our results or our model of low-temperature oxide preparations. Given in detail are our earlier published results which reveal superparamagnetism and "blocking-temperature" effects. These nonstoichiometric samples are similar to those described by Mollard *et al.*, but are not the same as the stoichiometric material which we have designated as form II.

Mollard *et al.*[1] have studied susceptibilities and "blocking temperatures" for microcrystals prepared from cobaltous hydroxide. In one of these recent papers they state,[2] "The specimen is prepared and preserved . . . under argon; in spite of this the oxide CoO retains some water formed in the course of the decomposition of the hydride." They indicate that spectrographic analysis in the infrared indicates the presence of free hydroxides and bound surfaces of molecular water. Our samples by contrast were prepared from nitrates and carbonates. We found that nitrate and carbonate contamination (analogous to this water contamination) occurred only for samples annealed for insufficient time intervals. We referred[3,4] to these samples as CoO* and NiO*, because they are not stoichiometric and well characterized as our form-II samples, referred to as CoO (II) and NiO (II). These samples, in contrast to our form-II materials, did show clear evidence of superparamagnetism, and even "blocking-temperature" effects of the type described by Mollard *et al.*[1] We illustrate this in Figs. 1(a) and 1(b), where we find a marked effect on the hyperfine structure due to a magnetic field of 51 kG applied to a sample of NiO*. The very low temperature (282 °K), where no hyperfine pattern was found is consistent with the ideas of Néel[5] on "blocking temperature." We do not think this has any bearing on the slight reduction in Néel temperature which we ascribed[3,6,7] to point defects in CoO (II) and NiO (II). When we prepared CoO (II) and searched for superparamagnetism, we found no evidence for it as we discussed in an earlier paper.[6] Figures 1(c) and 1(d) show the marked contrast of stoichiometric samples of about the same size. In this case our sample was prepared at a relatively high temperature in silica gel and did not show evidence of superparamagnetism. This is analogous to our findings for form II and indicates that our stoichiometric samples have already sintered and do not reveal the typical superparamagnetic behavior discussed by Néel.[5] It is noteworthy that Mollard and co-workers do not give any indication of having made direct measurements of the stoichiometry of their samples, and their observations of excess water and the presence of hydroxide is proof that they did not have materials anything like our well-characterized CoO (II) and NiO (II). Although one of their papers[8] discusses specimen preparation, they are apparently

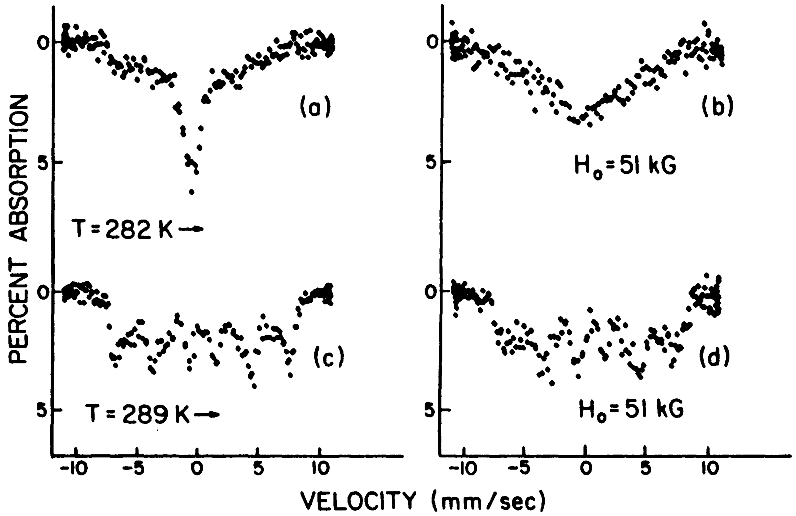

FIG. 1. Effect of an external magnetic field on the Mössbauer spectra of NiO* prepared at 300 °C, (a) $H=0$, and (b) $H=51$ kG, and on a sample of NiO prepared at 600 °C in 140-Å silica gel, (c) $H=0$, and (d) $H=51$ kG.

unaware of the significance of annealing-time interval or stoichiometry, which our studies have shown to be of paramount importance.

We agree with Mollard *et al.* that purity of samples is important in these studies. For these reasons we took special precautions, using only 99.999 %-purity starting materials. Also, we found no evidence for inclusions like Co_3O_4 in our samples, from either x-ray, Mössbauer, or stoichiometric measurements. We could produce such inclusions by rapid exposure of CoO (II) to air, since the oxygen uptake that we have described in our earlier papers is exothermic, and rapid exposure to oxygen produces a reaction leading to Co_3O_4. Thus, much care was taken in our experiments on CoO (II) not to permit exposure of the sample to oxygen.

Density measurements of samples having extremely complicated topology is difficult and such measurements are not in themselves subject to unambiguous interpretation as Mollard *et al.*[1] point out. It was our purpose in these studies, however, to bring to bear as many measuring techniques as were available to us on the same samples, instead of following the traditional pattern in this field of performing one-shot measurements and then making speculative correlations with other data on samples which are later shown to be of different defect composition. It is noteworthy, however, that our density measurements on form-II samples were reproducible and that they basically correlate well with our observation of large oxygen uptake for CoO (II) exposed to air at room temperature.

To summarize, we believe that Néel's[5] analysis of superparamagnetism is useful for describing microcrystals like NiO* and CoO*, but it does not appear to apply to our defect saturated, stoichiometric samples NiO (II) and CoO (II).

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Conduction-Electron Enhancement of Exchange Interactions in SmS

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La doping of SmS is found to greatly increase both the Sm^{2+}-Sm^{2+} exchange interaction (as measured by the Van Vleck susceptibility) and the Sm^{2+}-Eu^{2+} (impurity) exchange interaction (as measured by the EPR *g* shift). It is shown that this enhancement is primarly due to the indirect exchange caused by the conduction electrons donated by the La. Furthermore, these two exchange interactions have different dependences on La doping.

Exchange interactions in the samarium monochalcogenides have recently been a subject of both experimental and theoretical interest.[1-6] In this note we report on the enhancement of these interactions in samarium sulfide caused by the introduction of electrons into the conduction band.

The Sm-Sm and Sm-impurity exchange interactions in SmS, SmSe, and SmTe can readily be measured owing to the fact that the Sm^{2+} ions are Van Vleck ions,[7] with a nonmagnetic $^7F_0$ ground state. However, the first excited state ($^7F_1$) is very close in energy (~ 300 cm^{-1}) and can be admixed into the ground state either (i) by an external magnetic field or (ii) by exchange interactions with a paramagnetic impurity. This admixture gives rise (i) to a Van Vleck temperature-independent susceptibility, which can be used to determine the Sm-Sm exchange[1,4,6] or (ii) to deviations of the *g* values of impurity ions from their values in diamagnetic hosts[8,9] which can be used to determine the impurity-Sm exchange.[1,2,4,5]

Both of these large exchange interactions have been explained theoretically in terms of second-order interactions through the virtual excitation of bound 4*f* electrons to the 5*d* states,[1-3] which are quite close in energy in these narrow-gap