COMMENTS AND ADDENDA

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Physical Properties of Cobaltous Oxide Prepared at Low Temperature

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The authors summarize, here, their main results concerning the magnetic properties of cobaltous oxide in microcrystals. Those results are interpreted within the limits of Néel's theories of antiferromagnetic fine grains. Their conclusions are in contradiction with those of Helm, Ok, and Mullen, who interpret their observations with a model based on the existence of a second form of CoO.

Mullen and co-workers[1-3] have proposed the existence of two forms, I and II of cobalt oxide CoO to account for physicochemical properties of CoO samples prepared at low temperature. Schroer and Triftshäuser[4] have reinterpreted these results with different models.

In a series of preceding publications[5-11] we described the preparation and some properties of fine grains of cobalt oxide CoO. All of our experimental results lead us to conclusions which are different from those of Mullen; as far as magnetic properties are concerned these conclusions agree with the prediction of Néel's theory of superparamagnetism of antiferromagnetic fine grains.[12] We shortly summarize here the whole of our results and conclusions.

Dehydration of the hydroxide $Co(OH)_2$ under purified argon gives elementary grains of CoO which are mosaic single crystals in shape of porous hexagonal slabs of mean size $2000\times2000\times400$ Å which lie on their (001) plane. The size of the coherent crystallites of CoO increases with the preparation temperature from a minimum value of about 40 Å. Information on the size and shape of the crystallites and pores was obtained from a precise analysis of x-ray diffraction line profiles.[13]

Néel's theory of antiferromagnetic fine grains predicts the existence of a blocking temperature, T_B; the smaller the grain is, the lower is its T_B. We have characterized this phenomenon by a study of the thermoremanent magnetization and have obtained a picture of the blocking-temperature distribution by a study of the partial thermoremanent magnetization. The mean blocking temperature T_B varies as the third power of the crystallite size and tends to the Néel temperature for a crystallite size of about 80 Å. The variation of the apparent Néel temperature (which is, in fact, the blocking temperature of the Néel model) observed by Mullen and co-workers when they heat their samples is easily interpreted by an increase of mean crystallite size with the heating temperature.

Schroer and Triftshäuser propose an interpretation based on a decrease of the Néel temperature due to an expansion of the lattice (which has not been experimentally tested). Contrarily to this, we observed on our CoO samples a slight contraction of the lattice, associated with stress, which, following Schroer, should give rise to an increase of the Néel temperature.

The quoted authors also proposed a model in which the oxide CoO (II) would be distinguished by a high density of Schottky defects which would involve a decrease of the Néel temperature. This model is essentially founded on density measurements. We think that these measurements are not significant. The oxide CoO (II) is highly divided and probably characterized by the existence of pores and intergrain gaps, inaccessible to the densitometric liquid. The problem is still more complicated by the fact that these solids have great specific area and retain great quantities of adsorbed gases and water. Finally, this model is hardly consistent with the rather small increase of the magnetic susceptibility observed at low temperature on our samples; it cannot account for the observed thermoremanent magnetization.

Another fact can make still more complex the interpretation of experimental results, namely, the presence of impurities. For example, traces of the substance used to prepare CoO. We could detect to the accuracy of 100 ppm the completeness of the transformation $Co(OH)_2 \rightarrow CoO$ from the peak of the magnetic susceptibility at 12 K. Other magnetic anomalies may come from a superficial oxidation to Co_3O_4, which cannot be detected by x-ray diffraction, due to either the high division of Co_3O_4, or the mechanism of the oxidation of CoO (oxidation into the same phase).[14] The measurement of the magnetic susceptibility here again appears as a rapid and sensitive method for characterization of Co_3O_4 by the occurrence of high susceptibility at low temperature and, mainly, occurence of thermoremanent magnetizations below 50 K (the Néel temperature of Co_3O_4).

As a conclusion, our results show that it is necessary to take into account the Néel theories of antiferromagnetic fine grains to understand the properties of CoO prepared at low temperature. This had been suggested by Schroer and Triftshäuser[4]; by a Mössbauer experiment, made in a 50-kOe magnetic field and at a temperature higher than the blocking temperature, Ok, Helms, and Mullen[15] rule out the hypothesis of superparamagnetism by verifying that there is no perceptible modification of the spectrum and by interpreting this result on the basis of Cohen and Srivastava's results on small grain NiO. The uncompensated magnetic moment observed on CoO microcrystals of 9×10^{-2} emu/g at 77 K for 50-Å microcrystals is much smaller than that for NiO microcrystals of the same size.

Moreover, the very high blocking energy (3×10^{6} erg/cm^3) calculated from our experimental data on the basis of the Néel theory explains why the Mössbauer spectrum is so little modified by the 50-kOe field in the cited experiment. It is not possible to prove by such a way that there is no shift of the Néel temperature, even if this is actually true for the samples used by these authors.

The occurrence of defects, whose type and density depend on the method of preparation, probably bring some disturbance into the main phenomenon; the evaluation of their influence is nevertheless difficult.[16]

[1]H. N. Ok and J. G. Mullen, Phys. Rev. **168**, 550 (1968).
[2]H. N. Ok and J. G. Mullen, Phys. Rev. Lett. **21**, 823 (1968).
[3]W. R. Helms and J. G. Mullen, Phys. Rev. B **4**, 750 (1971).
[4]D. Schroeer and W. Triftshäuser, Phys. Rev. Lett. **20**, 1242 (1968).
[5]J. Amiel, M. Figlarz, and G. Bugeac, C.R. Acad. Sci. (Paris) **259**, 3512 (1964).
[6]M. Figlarz and F. Vincent, C.R. Acad. Sci. C **266**, 376 (1968).
[7]M. Figlarz and F. Vincent, *Les Solides Finement Divisés* (Documentation Francaise, Paris, 1969), p. 71.
[8]F. Vincent, M. Figlarz, and J. Amiel, *Reactivity of Solids* (Wiley, New York, 1969), p. 181.
[9]P. Mollard, M. Figlarz, and F. Vincent, C.R. Acad. Sci. B **268**, 448 (1969).
[10]P. Mollard, F. de Bergevin, P. Germi, F. Vincent, and M. Figlarz, J. Phys. (Paris) Suppl. **32**, 1041 (1971).
[11]P. Mollard, thèse d'etat (Université de Grenoble, 1970) (unpublished).
[12]L. Néel, C.R. Acad. Sci. (Paris) **252**, 4075 (1961); C.R. Acad. Sci. (Paris) **253**, 9 (1961); C.R. Acad. Sci. (Paris) **253**, 203 (1961); C.R. Acad. Sci. (Paris) **254**, 598 (1962); Cours de Physique Théorique, les Houches, 1961, P.U.F., Paris (unpublished).
[13]F. de Bergevin and P. Germi, J. Appl. Cryst. **5**, 416 (1972).
[14]D. Colaïtis, F. Fievet-Vincent, J. Guenot, and M. Figlarz, Mater. Res. Bull. **6**, 1211 (1971).
[15]H. N. Ok, W. R. Helms, and J. Mullen, Phys. Rev. **187**, 704 (1969).
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