Magnetic Properties of Nickel and Zinc Double Hydroxides

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Magnetic properties of nickel and zinc double hydroxides were studied using an axial extraction apparatus and a Faraday balance. Measurements were taken mainly between 4.2 and 40 K for applied fields 50–45 000 Oe.

The results confirm the existence of two types of structure α and β, which were previously determined by X-ray analysis.

The β solids, i.e., with a low zinc concentration, are essentially antiferromagnetic at 4.2 K for fields smaller than 45 kOe. They are compared with the hydroxide β-Ni(OH)$_2$. The α solids are metamagnetic with a low threshold field. The magnetization isotherms obtained for the α solids at 4.2 K show magnetic viscosity phenomena.

This difference in magnetic behaviour is useful for attributing the α or β structure to samples in which the phase containing the double hydroxide is not detected by X-ray analysis.

I. Introduction

Two of the authors have previously described (*1*) a method for preparing highly dispersed zinc and nickel double hydroxides which can be the precursors to hydrogenation catalysts. As noted above, two hydroxide types are found by radio-crystallography and electron microscopy:

(*a*) A β type: it has the same microscopic appearance and the same structure as β Ni(OH)$_2$. However, the "a" parameter of the hexagonal unit cell has its value slightly higher, due to the substitution of zinc for nickel ions.

(b) An α type: its microscopic appearance is completely different from that of pure β hydroxide. The structure is also hexagonal and comes from the structure of β-Ni(OH)$_2$ by "c" axis expansion from 4.6 to 7.9 Å, due to the insertion of zinc hydroxide layers according to Feitknecht (*2*) or more likely of constitution water molecules. Its chemical formula corresponds to (Ni$_{0.68}$Zn$_{0.32}$)(OH)$_2$, 0.14 H$_2$O.

The β nickel hydroxide's magnetic properties were studied by Miyamoto, Takada et al. (*3, 4*). It possesses the characteristic properties of metamagnetic compounds. The crystal is made

of successive Ni^{2+} ions layers, perpendicular to the "c" hexagonal axis and separated by two hydroxyl layers. The metallic ions have magnetic moments, parallel to the "c" axis. They are ferromagnetically coupled in the same layer and antiferromagnetically with the ions of the adjacent metallic layers.

Furthermore, Mollard et al. (*5*) recently described the magnetic properties of α-Ni(OH)$_2$ "turbostratic" hydroxide, i.e., where the interlayer distance is large and of the order of 8 or 9 Å. The sample used in this work was of a dispersed nature and displayed particular magnetic properties at low temperature. These authors considered that they were dealing with "a metamagnet in small particles which has a low threshold field."

In this paper, the magnetic properties of the α type double hydroxides have been studied and compared with the properties of the β-Ni(OH)^2 hydroxide prepared under the same conditions.

II. Experimental

The magnetization measurements were made with an axial extraction apparatus, already described (*6*). The principal components of the

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measurement circuit were an induction double coil and a ballistic galvanometer, the variations of which are recorded by means of a spot detector. The field was produced by a super-conducting coil. This apparatus, although requiring the use of liquid helium, has the advantage of being very convenient, since it gives the possibility of working with (a) high fields (up to 50 kOe), (b) low fields (between 60 and 300 Oe), or (c) nearly no field (earth field). Indeed, the use of a thermal switch offers an excellent field stability, and hence a good sensibility even for a low field. The sample temperature was determined by a separated cryogenic bath. For most of the runs, it was at 4.2 K, but could be lowered to nearly 1.5 K by pumping.

The field values given by the manufacturer were controlled in two ways: for high fields, by measuring at 300 K the magnetization of a Mohr salt sample, of well known susceptibility, and for low fields by means of a Hall effect probe which was previously calibrated on an EPR apparatus. In the two cases, the values agree very well (within approximately 1 %).

The variations with temperature of the magnetic susceptibilities were measured with a Faraday balance. The device for controlling and measuring the sample temperature between 2 and 300 K has already been described (7). The balance was a Setaram MTB 10-8 model, with its maximum load extended to 50 grams. The sensibility was the order of 3 μg for a 20-g load. The electromagnet was fed either by a dc power supply with a stability of 0.1 %, or, for the measurements at low field, by a 12-V battery.

III. Results and Discussion

The α type double hydroxide which is called here solid A has been studied in comparison with a sample of β structure nickel hydroxide, called here solid B.

A. Thermomagnetic Analysis of the Solids

1. With High Fields. The Fig. 1 shows the variations with temperature of the susceptibilities of solids A and B, measured in a 6900-Oe field. The curve B is in close agreement to the curve published by Miyamoto for the β nickel hydroxide. Therefore the solid B is an antiferromagnet below 6900 Oe, with a Neel temperature of nearly 23 K.

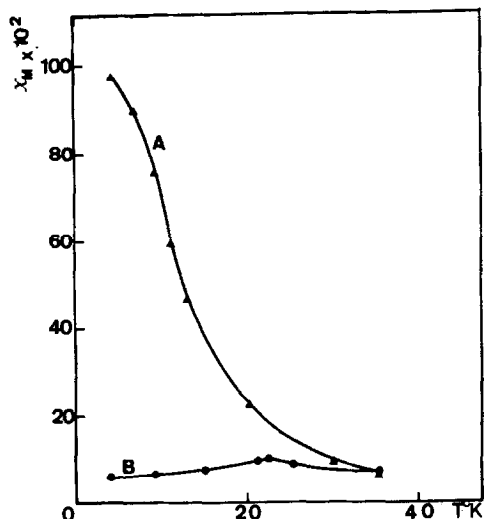For the solid A, the observed curve is typical of a ferromagnet, with a Curie point close to

FIG. 1. Thermomagnetic analysis of solids A and B. $H = 6900$ Oe.

10 K. The gradual ferromagnet–paramagnet transition makes it difficult to determine exactly the order temperature T_c. In this paper, it has been considered that T_c is given by the inflexion point on the curve.

The Fig. 2 shows that in the paramagnetic region, the reciprocal molar susceptibility increases linearly as a function of temperature, according to the law χ_M $(T - 40) = 0.84$. It corresponds to a magnetic moment of 2.6 μ_B per Ni ion. Furthermore the sign of the Weiss constant shows a ferromagnetic interaction between the ions, which indeed favours the hypothesis of the metamagnetism of the solid A.

2. With Low Fields. As above, the solid A is ferromagnetic at 4.2 K below 7 kOe with an order
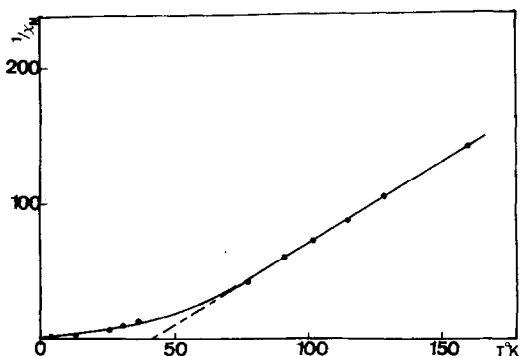

FIG. 2. Reciprocal molar susceptibility of solid A vs temperature. $H = 6900$ Oe.
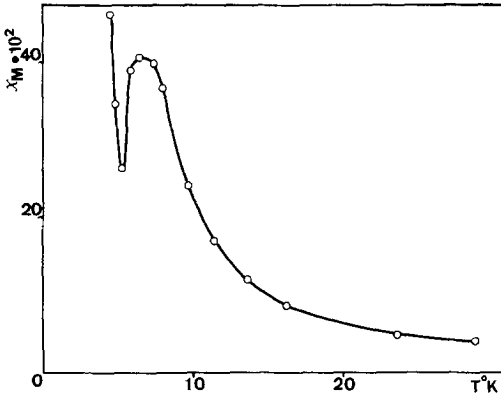
FIG. 3. Thermomagnetic analysis of solid A. $H = 230$ Oe.

temperature close to 10 K. If it is really a meta-magnet, it must be antiferromagnetic at the same temperature for fields lower than the threshold field and its order temperature will be seen as a Neel point on the curve of susceptibility vs. temperature. This variation is clearly seen for neptunium (V) oxalate, for example (8).

The Fig. 3 shows the results obtained with a 230 Oe field. Effectively, the appearance of a susceptibility maximum at 6.5 K demonstrates the existence of an antiferromagnetic phase, stabilized by the weakness of the measurement field. Therefore, if it exists, the threshold field must be lower than 230 Oe.

The Neel temperature, here observed, is much lower than that of the β hydroxyde (6.5 instead of 23 K). This decrease of the Neel temperature is consistent with the spin wave theory (9). Indeed, some reasonings based on this theory show that in the case of an antiferromagnetic substance built with a succession of weakly bound layers, the Neel temperature T_N is given by the equation:

$$T_N = \alpha C (WW')^{2/3},$$

where α is a factor close to unity, C is the Curie constant for one lattice, and $W = -W_{AB}$ is the coefficient of molecular field acting on an atom of the sublattice A and coming from the assembly of atoms in the sublattice B. Similarly, $W' = W_{AA} = W_{BB}$. With the insertion of zinc hydroxide layers or of constitution water which causes the expansion of the "c" axis in the unit cell, the anti-ferromagnetic interactions W decrease. Therefore, the Neel point is lowered.

In other words, the decreasing of the anti-ferromagnetic interactions increases the two-dimensional ferromagnetic character of the

solid. But, according to the spin wave theory and the Bethe-Peierls type approximate theories, a ferromagnetic plane can be stable only at absolute zero. Therefore, with this scheme, order stabilized by the weakness of the interactions between layers will be able to appear only at a very low temperature (9). Hence, this results in a lowering of the Neel point, which agrees well with the experimental results.

In Fig. 3, another peculiarity is observed, i.e., the drop in the susceptibility between 4.2 and 5.3 K. It can be interpreted by assuming that, even at 230 Oe, the uncoupling of the antiferro-magnetic sublattices already occurs for a sizable proportion of the solid.

B. Magnetization Measurements

Figure 4 shows the magnetization curves, measured at 4.2 K. The solid B curve is similar to that published by Miyamoto for powdered β-Ni(OH)$_2$. Indeed, the hydroxide magnetization is proportional to the field up to 20 kOe. It then increases faster up to 45 kOe. The molar suscept-ibility, evaluated in the field-independent domain, is 6.52×10^{-2} emu. It is slightly higher than 5×10^{-2} found by Miyamoto. In fact, if we take into account that the hydroxide used in this work consists of thin layers, the diameters of which were the order of 150–300 Å, and Miyamoto's layers the order of 2–5 μm, it can be concluded that there is no noticeable increase in suscept-ibility due to the presence of small particles. Although the limit of our apparatus is 45 kOe, the similarity of our results with Miyamoto's allows one to consider that solid B is a meta-magnet with a threshold field close to 55 kOe.

The curve obtained for the solid A with α structure (Fig. 4, curve A) is completely different.

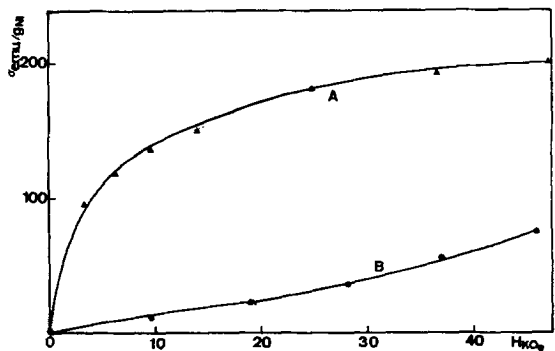

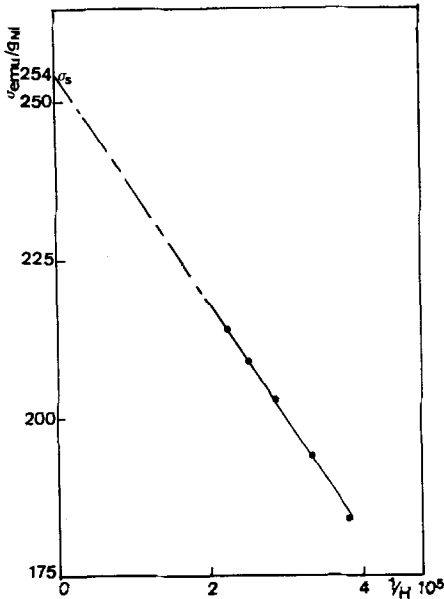FIG. 4. Magnetization isotherm of solids A and B. $T = 4.2$ K.

FIG. 5. Saturation magnetization of solid A obtained by extrapolation vs. $1/H$.

The magnetization increases, initially quickly. After 25 kOe, a plateau is observed corresponding to a saturation effect. The curve has the appearance of that expected for the saturation of a ferromagnetic solid which confirms the results obtained by thermomagnetic analysis.

For getting the saturation magnetization value, the temperature is lowered down to 1.4 K by pumping on the cryogenic bath. But the magnetization measured at 45 kOe remains nearly

constant and its extrapolation versus $1/H$ (Fig. 5) gives the magnetization value 254 emu/g Ni or nearly 2.66 μ_B, which is slightly lower than the values usually observed for nickel ions, varying between 2.8 and 3.2 μ_B.

The low value observed for the threshold field is a direct result of the "c" axis expansion which gives a decrease of the antiferromagnetic interactions between two adjacent nickel layers. Therefore, the threshold field necessary for uncoupling the two antiferromagnetic sublattices decreases too. These magnetic properties are the same as those observed for compounds of a layered structure, e.g., the basic silicates of nickel (6) or the graphites impregnated with iron chlorides (10), which behave like a metamagnet with very low threshold field. For determining the threshold field, we measured the solid A magnetization in fields between 60 and 1000 Oe. The results are shown in Fig. 6. If the curve A in the Fig. 4 is seen perfectly reversible, the same is not true for the low fields region here investigated. The curves in Fig. 6 are distinct from those published by Mollard et al. (5) for the α nickel hydroxide, (a) by the very low value of the remanent magnetization and (b) by the total lack of reversibility, even between 0 and 150 Oe. However, these drawn cycles cannot be assimilated with the usual hysteresis cycle. Indeed, they may be due, at least partly, to magnetic viscosity phenomena, since in a given field, the magnetization slowly increases with time, as shown in Fig. 7, for $H = 280$ Oe.
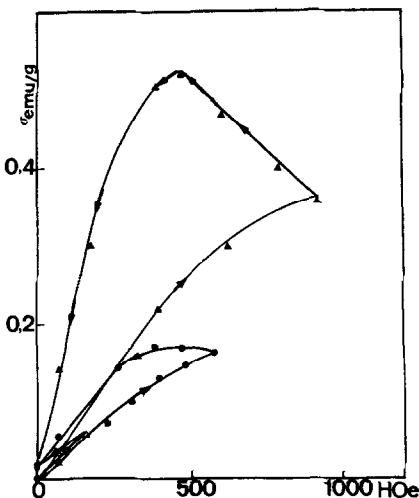
IV. Determination of the Structure of Double Hydroxides from the Magnetic Results

It was previously shown that the double hydroxides are of α or β type, depending on their nickel concentration. Since the magnetic properties are modified by the "c" axis expansion, which characterises the α and β solids, it is possible to use the magnetic curves not only to confirm the structure already identified by X-ray diffraction, but also to permit structure determination not possible by X-ray analysis.

For example, if one considers a double hydroxide, called solid C, its atomic percentage in nickel is 82.6%. The curve of thermomagnetic analysis (Fig. 8, curve C) indicates a Neel point at 19 K, meaning the existence of an antiferromagnetic phase in the order domain. The curve of magnetization vs. field is shown similar to that of

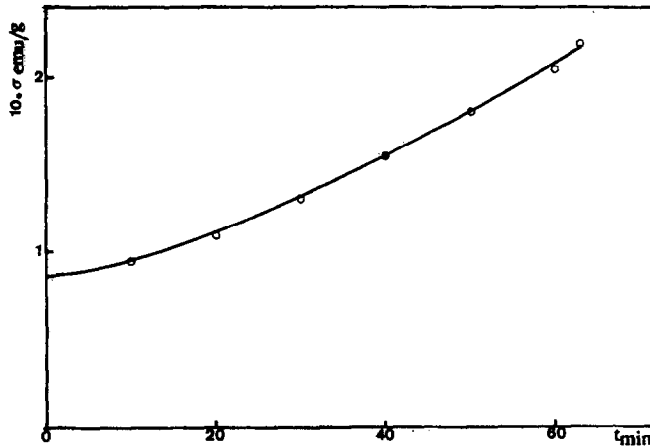FIG. 6. Magnetization isotherm of solid A for low applied fields. $T = 4.2$ K.

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FIG. 7. Viscosity phenomena observed for the solid A. Magnetization isotherm vs. time. $T = 4.2$ K. $H = 280$ Oe.
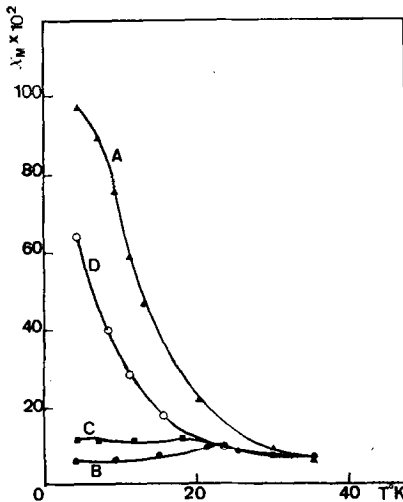

FIG. 8. Comparison of thermomagnetic curves, for the solids A, B, C and D. $H = 6900$ Oe.
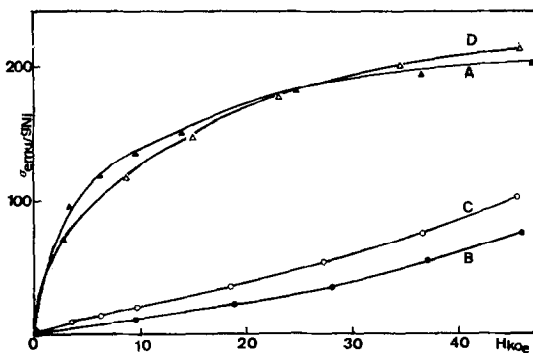

FIG. 9. Comparison of magnetization isotherms, for the solids A, B, C and D. $T = 4.2$ K.

β-Ni(OH)$_2$ (Fig. 9, curve C). Therefore the solid C is essentially β type, as previously shown by X-ray analysis.

By contrast, if one considers a hydroxide of composition 13.6% in nickel, or solid D, the phase containing the nickel is not detected by X-ray analysis. However, the magnetization curve (Fig. 9, curve D) is very close to the curve of the solid A, and the thermomagnetic behaviour is very similar (Fig. 8, curve D). Thus, it can be concluded that its structure is probably α type.

Conclusion

The study of the magnetic properties of nickel and zinc double hydroxides confirms the existence of two types of structures, α and β, which were previously determined by X-ray analysis.

The β solids are essentially antiferromagnetic at 4.2 K for the values of the field smaller than 45 kOe. They can be compared to the β nickel hydroxide studied by Miyamoto. The α solids are metamagnetic with a low threshold field. The determination of the threshold field is difficult because of magnetic viscosity phenomena.

By studying their magnetic properties, one can take advantage of this difference in behaviour to attribute the α or β structure to other samples containing various percentages in nickel. This is particularly useful when the phase containing the nickel is not detected by X-ray analysis because of an insufficient concentration or a poor crystallization.

References

1. M. HOUALLA, P. TURLIER, R. FRETY, R. BARDET, H. URBAIN, AND Y. TRAMBOUZE, to be published *Ann. Chim.*
2. W. FEITKNECHT AND W. LOTMAR, *Helv. chim. Acta* **18**, 1369 (1935).
3. H. MIYAMOTO, *Bull. Inst. Chem. Res. Kyoto Univ.* **44**, 420 (1966).
4. T. TAKADA, Y. BANDO, M. KIYAMA, AND H. MIYAMOTO, *J. Phys. Soc. Japan* **21**, 2745 (1966).
5. J. DEPORTES, P. MOLLARD, J. PENELON, S. LE BIHAN, AND M. FIGLARZ, *C.R. Acad. Sci. Paris* **272**, 449 (1971).
6. G. A. MARTIN, J. A. DALMON, R. DUTARTRE, P. TURLIER, AND J. C. VOLTA, *J. Chim. phys.* **69**, 277 (1972).
7. R. SPITZ AND P. TURLIER, *J. Chim. phys.* **66**, 1256 (1969).
8. E. R. JONES AND J. A. STONE, *J. Chem. phys.* **56**, 1343 (1972).
9. A. HERPIN, "Théorie du Magnétisme," Bibliothèque des Sciences et Techniques Nucléaires, Chapter 13, Presses Universitaires de France, Paris (1968).
10. Y. S. KARIMOV, A. V. ZVARYKINA, AND Y. N. NOVIKOV, *Soviet Phys. Solid State* **13**, 2388 (1972).