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Magnetism in Ultra Fine Oxide Particles

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Magnetic susceptibility measurements by the torsion balance have been made in the temperature range 100-300°K for each series of antiferromagnetic oxide samples, such as α-Fe_2O_3, NiO, CuO and V_2O_4 prepared by the calcination of their metallic salts. The particle size of these powders given by the x-ray diffraction method varied from 50 to 1000Å. The magnetic susceptibility curves of α-Fe_2O_3, NiO, CuO resemble those obtained by other investigators for NiO and α-Fe_2O_3. Samples of each oxide particles whose sizes are above 1000Å, exhibit susceptibilities typical of an antiferromagnetic materials, while samples whose particle sizes are less than 300Å exhibit susceptibilities increasing with decreasing temperature even below the Néel point. The value of χ also increases as the particle size decreases. But the maxima of the susceptibility cannot be found in the temperature range.

Introduction

Over last ten years, we have studied the morphological and crystallographic properties of very fine particles obtained by the calcination of metallic salts. Recently we have studied the superparamagnetic properties of γ-Fe_2O_3 and Fe_3O_4. Last autumn (1960), one of the authors visited England and heard from K. M. Creer the results of measurements of magnetic properties of a series of very fine α-Fe_2O_3 particles. Subsequently we have studied the magnetic properties of ultra fine particles of α-Fe_2O_3 and also similar antiferromagnetic substance such as NiO, CuO and V_2O_4. In this report, the results of measurements of the magnetic susceptibilities of series of very fine particles of these antiferromagnetic substances are presented.

Experimental

The test samples of these particles were prepared by the thermal decomposition of metallic salts at various temperatures or by precipitation from aqueous solution of the salts.

Each series of samples was examined by Debye-Scherrer powder x-ray analysis, and the particle sizes of these samples were determined from the half-width of the (113) line for α-Fe_2O_3, the (111) line for NiO, the (111) line for CuO and of the (011) line for V_2O_4 respectively.

Electron microscopic observations were used to observe the shape and size of the particles.

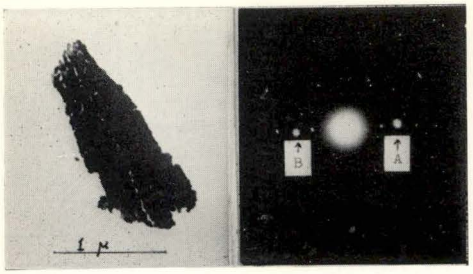
Electron diffraction observations were made in order to clarify the crystallographic structure of each fine particle. The magnetic susceptibilities were measured by the magnetic torsion balance method[1].

Results

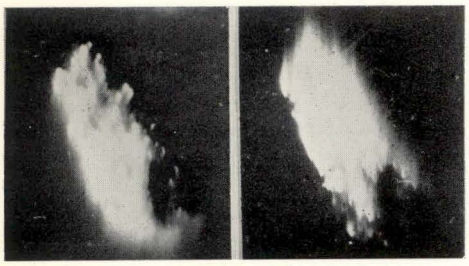
Morphological Properties and Crystal Size of Prepared Particles

Table I. The reactions by which the particles are obtained.

(1)	$Fe(NO_3)_3 \cdot 9H_2O \xrightarrow[\text{in air}]{125°C} \alpha\text{-}FeOOH \xrightarrow[\text{in air}]{250\text{-}900°C} \alpha\text{-}Fe_2O_3$
(2)	$NiSO_4 + NH_4OH \longrightarrow Ni(OH)_2 \xrightarrow[\text{in air}]{310\text{-}900°C} NiO$
(3)	$CuSO_4 + Na_2CO_3 \longrightarrow CuCO_3 \cdot Cu(OH)_2 \xrightarrow[\text{in air}]{200\text{-}700°C} CuO$
(4)	$VOCl_2 + NaOH \longrightarrow VO(OH)_2 \xrightarrow[\text{in vacuum}]{300°C} V_2O_4$ (No. 1)
	$V_2O_5 \xrightarrow[\text{in } NH_3]{370°C} V_2O_4 \xrightarrow[\text{in vacuum}]{500°C} V_2O_4$



(a) (b)



(c) (d)

Fig. 1. (a) Electron microphotograph and (b) diffraction photograph of α-Fe_2O_3 obtained by the calcination of $Fe(NO_3)_3 9H_2O$ at 500°C for 2 hrs. (c), (d) Dark field image photographs of corresponding diffraction patterns of A and B in (b).

Particles prepared by the thermal decomposition of mother salts possess the shapes which are very close to the original shape of their mother crystals[2].

Fig. 1(a) is an electron microphotograph of α-Fe_2O_3 prepared from $Fe(NO_3)_3 \cdot 9H_2O$. As shown in this photograph the particle of α-Fe_2O_3 consists of a large number of very fine sub-particles.

Fig. 1(b) is the electron diffraction pattern of the particle, and it is found to be the diffraction pattern of a single crystal of α-Fe_2O_3. The corresponding dark field image photographs obtained from the spots A and B in Fig. 1(b) are shown in Figs. 1(c) and (d). The shape of the dark field images agrees with the shape of the particle. This suggests that the particle is composed of many small single crystals of α-Fe_2O_3 and that the crystals are arranged in a highly oriented manner, that is, the aggregate is also single-crystal-like. Hence we call the small sub-particles "unit particles" and the particle composed of many unit particles "aggregate". The diameter of the unit particle increases with increasing temperature of the heat-treatment as shown in the following tables.

Table II shows the diameter of the unit particle of α-Fe_2O_3 determined by the x-ray method and also by direct measurements on

Table II. Particle diameter of α-Fe_2O_3 powder measured by x-ray method and electron microscope.

Sample Number	No. 1	No. 2	No. 3	No. 4
Calcination	900°C 2 hr.	580°C 2 hr.	400°C 20 min.	250°C 20 min.
Particle Diameter by x-ray Method	>1000Å	770Å	320Å	280Å
Particle Diameter by Electron Microscope	1000–3000Å	400–800Å	300–500Å	—

Table III. Particle diameter of NiO powder measured by x-ray method.

Sample Number	No. 1	No. 2	No. 3	No. 4
Calcination	200°C 40 min.	410°C 40 min.	720°C 100 min.	900°C 120 min.
Particle Diameter by x-ray Method	100Å	230Å	330Å	1200Å

Table IV. Particle diameter of CuO powder measured by x-ray method.

Sample Number	No. 1	No. 2	No. 3	No. 4
Calcination	200°C 40 min.	410°C 40 min.	550°C 70 min.	700°C 100 min.
Particle Diameter by x-ray Method	100Å	230Å	380Å	1000Å

the enlarged electron microphotographs. Tables III and IV show the diameter of the unit particle of NiO and CuO respectively. Figs. 2 and 3 show the electron microphotographs of the aggregates of NiO and CuO respectively.

Magnetic Properties of α-Fe_2O_3

The $\chi-T$ curves of α-Fe_2O_3 prepared from $Fe(NO_3)_3 \cdot 9H_2O$ are shown in Fig. 4.

As shown in Fig. 4, the magnetic susceptibility of the aggregates whose unit particles are greater than 1000 Å in diameter, is almost same as that of the bulk crystals. Whereas the susceptibilities of the aggregate whose unit particles are less than 320 Å in diameter increase with decreasing temperature even below the Néel point.

Likewise, at a constant temperature below $-19°C$ the susceptibility increases as the size of the unit particle decreases. It is also found that the antiferromagnetic transition of α-Fe_2O_3 at $-19°C$ disappears when the diameter of the unit particles of the samples is smaller than about 320 Å.

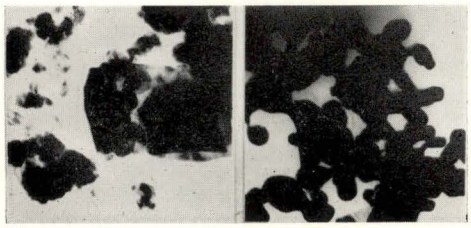
These facts are fairly in agreement with that reported by Creer[3].

Magnetic Properties of NiO

The $\chi-T$ curves of NiO are shown in Fig. 5. The value of χ increases as the diameter of unit particles decreases at a constant temperature.

The aggregates whose unit particles are larger than 1200 Å in diameter exhibit susceptibilities typical of an antiferromagnetic materials, that is, the value of χ decreases with the decreasing temperature below the Néel point. The sample whose unit particles is 330 Å in diameter, exhibits a constant susceptibility at any temperature below the Néel point.

On the other hand, the susceptibilities of the samples increase with decreasing temperature, when the diameter of unit particles



No. 1 No. 4

Fig. 2. Electron microphotographs of NiO.

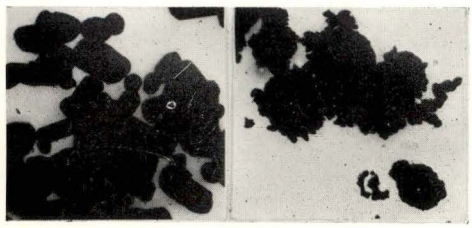


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Fig. 3. Electron microphotographs of CuO.

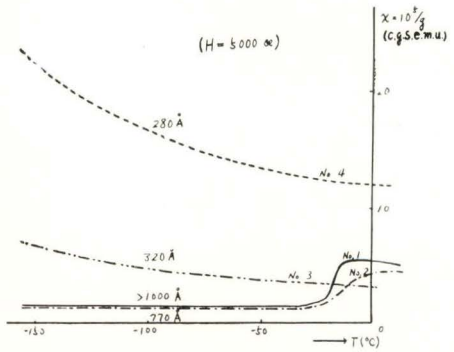

Fig. 4. $\chi-T$ curves of α-Fe_2O_3 prepared from $Fe(NO_3)_3 \cdot 9H_2O$.

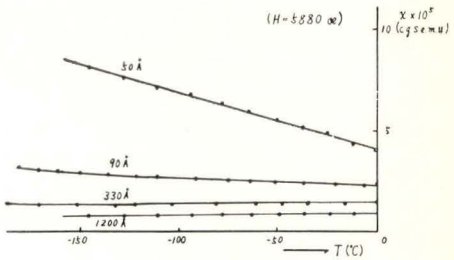

Fig. 5. $\chi-T$ curves of NiO prepared from $Ni(OH)_2$.

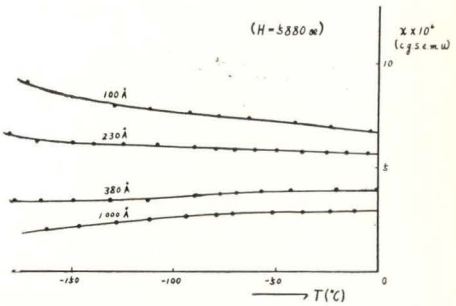

Fig. 6. $\chi-T$ curves of CuO prepared from $Cu(OH)_2 \cdot CuCO_3$.

is smaller than 300 Å.

Magnetic Properties of CuO

Fig. 6 shows the $\chi - T$ curves of CuO.

These curves resemble those of NiO. The Néel point of this material is −50°C. So we can study the behavior of the susceptibility in the temperature range around the Néel point. Above the Néel point, the values of χ of fine unit particle do not agree with those of larger unit particle. This fact is not similar to that of the earlier investigator[4] who reported the value of χ of fine particles of NiO did not vary due to the size of particle above the Néel point.

However, the Néel point of NiO is fairly high and the measurement of the Néel point requires this material to heat up to 250°C. This temperature is high enough for NiO to grow up to larger grain size than the original one. If it is possible for us to measure the χ of NiO at 250°C without increasing its grain size, it is plausible to say that the values of χ should be larger than those mentioned in reference (4).

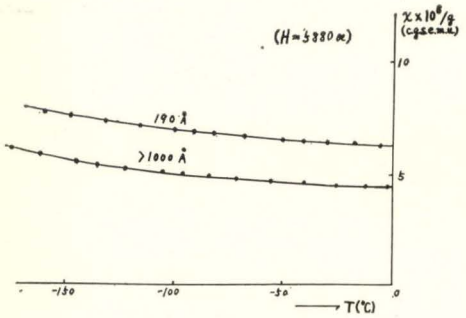

Fig. 7. χ-T curves of V_2O_4.

Magnetic Measurements of V_2O_4

Fig. 7 shows the $\chi - T$ curves of the aggregates of V_2O_4. But it is peculiar that the susceptibility of the aggregate whose unit particle is larger than 1000 Å in diameter increases with decreasing temperature below the Néel point (70°C). Further investigations of this phenomenon are required. As shown in this figure, at a constant temperature the value of the susceptibility increases as the size of unit particle decreases.

Acknowledgment

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