# Magnetic properties of chromium (III) oxide nanoparticles

# Manuel Bañobre-López, Carlos Vázquez-Vázquez, José Rivas and M Arturo López-Quintela

Facultade de Química, Departamento de Química Física, Universidade de Santiago de Compostela, Avenida das Ciencias, s/n, 15782 Santiago de Compostela, Spain

Received 17 September 2002, in final form 18 December 2002 Published 28 January 2003 Online at stacks.iop.org/Nano/14/318

#### Abstract

 $Cr_2O_3$  nanoparticles of controlled particle size were prepared by calcination of a precursor,  $Cr(OH)_3$ , obtained by precipitation with sodium hydroxide. Samples were characterized by transmission electron microscopy and x-ray diffraction. Average particle sizes ranged from 20 to 200 nm. The magnetic properties of  $Cr_2O_3$  nanoparticles show the presence of a net magnetic moment at the surface due to the large surface/volume ratio. This fact modifies the classical behaviour expected for bulk antiferromagnetic particles. Below the Néel temperature, magnetization curves as a function of the applied magnetic field show the presence of coercive forces in the low-field range.

## 1. Introduction

The study of fine and ultrafine particles has become of increasing interest due to new properties that materials may show when the grain size is reduced. Recently, antiferromagnetic nanoparticles have also received much attention due to their potential for showing reversal of magnetization by quantum tunnelling [1, 2]. In 1961, Néel suggested that a net magnetic moment could appear in antiferromagnetic nanoparticles due to an imbalance of spins 'up' and 'down' at and near the surface [3]. Although net magnetic moments have been reported in antiferromagnetic nanoparticles, their origin is not always very clear [4–6]. Recent works have studied in detail the magnetic properties of antiferromagnetic nanoparticles, such as NiO [7] or  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> [8] in trying to clarify this problem.

In this paper we report on the preparation and study of the magnetic properties of  $Cr_2O_3$  nanoparticles. Bulk chromium (III) oxide is an antiferromagnetic material with a Néel temperature  $T_N \sim 307$  K [9]; however, a rather different magnetic behaviour is observed when the particle size is reduced.

#### 2. Experimental procedure

 $Cr_2O_3$  nanoparticles of various sizes were obtained by calcining portions of a dried gel of precipitated  $Cr(OH)_3$  in air for 3 h at various temperatures. The chromium hydroxide used as a precursor was prepared by precipitation from a solution of

the corresponding metallic nitrate  $(Cr(NO_3)_3 \cdot 9H_2O)$  using a slight molar excess of NaOH with respect to the stoichiometric reaction. The resulting gel was filtered, washed several times with deionized water and finally dried at 65 °C for 1 day. Thermal analysis, infrared spectroscopy and x-ray diffraction indicate that, in effect, the amorphous precipitate obtained corresponds to the formula  $Cr(OH)_3 \cdot xH_2O$  [10].

This precursor was separated in several portions and calcined in air for 3 h at several temperatures, ranging from 200 to 1000 °C, in order to decompose the hydrous chromium (III) oxide and crystallize it to the rhombohedral chromium (III) oxide.

The structural characterization was carried out by x-ray powder diffraction, using a Philips PW-1710 diffractometer with a Cu anode (radiation K $\alpha$  of  $\lambda = 1.54186$  Å). The morphology and the average particle size were determined by transmission electron microscopy using a Philips CM-12 microscope (with a W filament) working at acceleration voltages of 100 kV. The magnetic measurements were carried out in a vibrating sample magnetometer (VSM) in the temperature range from 100 to 700 K and in magnetic fields up to 10 kOe.

#### 3. Results and discussion

Chromium (III) oxide is isostructural with corundum  $(\alpha$ -Al<sub>2</sub>O<sub>3</sub>), with a rhombohedral structure (space group 167,  $R\bar{3}c$ ). The lattice parameters of the bulk material for a



**Figure 1.** X-ray diffraction evolution of the precursor as a function of the calcination temperature.

hexagonal setting are: a = b = 4.9588 Å and c = 13.5942 Å [9].

X-ray diffraction patterns show that all samples heated below 300 °C are amorphous. Annealing of the samples for 3 h at 300 °C is necessary to crystallize them into the rhombohedral  $Cr_2O_3$  phase (JPCDS-ICDD card 38-1479). At higher calcination temperatures the degree of crystallinity of the samples increases, and narrower peaks are obtained in the x-ray diffraction patterns (figure 1).

Lattice parameters were calculated after indexing all the reflections to the rhombohedral space group  $R\bar{3}c$  using a least-squares minimization program. An increase in the lattice parameters was observed with increasing calcination temperature until an almost constant value was reached for the higher calcination temperatures. Except for slight deviations, the values obtained for the samples calcined at high temperatures agree with the theoretical ones corresponding to bulk Cr<sub>2</sub>O<sub>3</sub>, while higher differences are observed in the sample calcined at 400 °C, which indicates that major structural disorder exists in this sample.

An average crystallite size,  $D_{hkl}$ , was estimated using the Debye–Scherrer equation for all x-ray diffraction peaks [11]:

$$D_{hkl}(\text{\AA}) = \frac{k\lambda}{\beta(\text{size})\cos\Theta}$$

where k is a shape factor which normally ranges between 0.9 and 1.0 (in our case k = 0.9),  $\lambda$  is the x-ray wavelength, and  $\Theta$ is the Bragg angle.  $\beta$  (size) is the difference in profile widths of broadened and standard samples (in our case, a silicon standard was used):  $\beta$  (size) =  $\beta_{sample} - \beta_{standard}$ ,  $\beta$  being the integral breadth defined as:

$$\beta = \frac{\operatorname{Area}(\operatorname{Cu} \operatorname{K} \alpha 1)}{\operatorname{Intensity}(\operatorname{Cu} \operatorname{K} \alpha 1)}$$



**Figure 2.** Comparison between the TEM and x-ray sizes as a function of the calcination temperature. The full lines are guides to eye.

Individual fitting of the diffraction peaks was carried out using the Philips APD program, which fits the sample-dependent variables (angle position, intensity and line broadening) to the experimental diffraction profile using a Marquardt nonlinear least-squares algorithm.

The variation in the average crystallite is shown in figure 2 ( $\blacksquare$ ) as a function of the calcination temperature. The average crystallite size increases from ~24 nm at 400 °C to ~173 nm at 1000 °C due to the coalescence of the smaller Cr<sub>2</sub>O<sub>3</sub> particles.

Figure 3 shows some micrographs of samples calcined at different temperatures. The average particle size was also determined from TEM micrographs assuming the particles to be spherical. For the sample calcined at 400 °C (micrograph (a)) we can observe some crystallized particles coexisting with amorphous regions or a large number of aggregates not fully crystallized. The histogram shows a bimodal particle size distribution. Fitting to Gaussian distributions we obtained an average size of  $D_{TEM} = 51 \pm 18$  nm for the smaller particles and  $D_{TEM} = 116 \pm 18$  nm for the larger ones. For the sample calcined at 800 °C (micrograph (b)) an increase in the degree of crystallinity and the average particle size is observed. In this case the particle size distribution, fitted to a Gaussian distribution, gives an average particle size of  $D_{TEM} = 85 \pm 24$  nm.

Figure 2 shows a comparison between the results obtained with x-rays and those with TEM. The values agree at 800 °C but not at 400 °C. This indicates that at low calcination temperatures even the smaller particles observed by TEM are composed of several nanocrystallites.

Zero-field cooling (ZFC) magnetization curves are shown in figure 4. A magnetic transition is observed around 320 K, corresponding to the Néel temperature ( $T_N$ ), although a very different behaviour is observed for several samples in the lowtemperature range.

Above this transition temperature, a small magnetization is induced by the applied field. The magnetization curve follows a Curie–Weiss law,

$$\chi = \frac{M}{H} = \frac{C}{T - \theta}$$



Figure 3. Transmission electron micrographs and histograms of samples calcined at 400 °C (a) and 800 °C (b). In both cases the bar length = 100 nm.



Figure 4. ZFC magnetization curves under an applied field of 1000 Oe for several calcination temperatures.

where *C* is the Curie constant and  $\theta$  is the paramagnetic Curie point. An effective magnetic moment per atom of 3.7–3.8  $\mu_B$  was observed in all cases. This value agrees with that found in the literature for Cr<sup>3+</sup> ions [12].

Samples calcined at 1000 and 800 °C exhibit a typical antiferromagnetic behaviour. As the temperature decreases,

the magnetization increases and goes through a maximum at the Néel temperature. However, important differences are observed for the samples calcined at 600 and 400 °C. For the sample calcined at 600 °C, a rather large increase in the magnetization is observed at the transition temperature. Below this temperature a smooth increase in the magnetization continues. For the sample prepared at 400 °C only a shoulder is observed at the Néel temperature and the magnetization curve continuously increases as the temperature decreases.

These differences could be explained by the different surface/volume ratio of the samples. As particle size is reduced, the surface/volume ratio increases and hence the role of the surface in the magnetic behaviour becomes more and more important. Néel proposed a model for antiferromagnetic nanoparticles based on the presence of two sublattices, one with spins 'up' and another with spins 'down' [3]. The imbalance in the number of spins 'up' and 'down' that occurs at the surface is the origin of a net magnetic moment in antiferromagnetic nanoparticles below the Néel temperature. This paramagnetic susceptibility due to the non-compensation of the two magnetic sublattices can easily dominate over the antiferromagnetic contribution itself [3]. Because of the structural disorder, the surface spin can be more easily deviated from the antiferromagnetic alignment by a magnetic field. In addition, the fact that a surface spin has a smaller number of



Figure 5. Magnetization as a function of the applied field at 100 K. Inset: detail of the low-field range.



**Figure 6.** Variation of the coercive field,  $H_c$ , as a function of the temperature for several samples. The particle size indicated in the graph was obtained by x-ray diffraction.

neighbours than it would have in bulk implies a change in the magnetization near the surface of the particle. If the particle size is very small the proportion of surface spins is such that they will make a major contribution to the magnetization [3].

These features are well observed in the sample calcined at 600 °C, where a paramagnetic surface component is superimposed on the antiferromagnetic behaviour of the bulk nanoparticle. So, there are two main contributions to the magnetization:

$$M = M_u + \chi_{AF} H.$$

The first term,  $M_u$ , is responsible for the large magnetization value observed at low temperature due to the noncompensation of the surface spins. This contribution is superimposed on the common antiferromagnetic contribution,  $\chi_{AF} H$ .

As the particle size is reduced, the paramagnetic surface contribution becomes more important while the contribution of the antiferromagnetic core diminishes. The magnetization decrease above the Néel temperature can be explained by this decrease in the antiferromagnetic core size.

In the sample calcined at 400 °C the surface effects are very large: the structural disorder at the surface determines the almost paramagnetic behaviour observed in the magnetization curve: only a weak shoulder can be observed in the magnetization curve at the Néel temperature. However, the sample does not match the paramagnetic Curie law,  $\chi = \frac{M}{H} = \frac{C}{T}$ ; so, a small antiferromagnetic contribution is still present.

Magnetization measurements were performed as a function of the magnetic field at different temperatures after cooling the samples in zero field (figure 5).

All the samples show a similar behaviour below  $T_N$ . A deviation is observed from the linear dependence expected for an antiferromagnetic sample:  $M_{AF} = \chi_{AF} H$ . These deviations from linearity are also observed for the samples prepared at higher calcination temperatures. The inset of figure 5 shows these deviations clearly. The first term in the previous magnetization equation,  $M_u$ , is responsible for the rapid increase in the magnetization at low field; whereas the second one,  $\chi_{AF} H$ , is responsible for the non-saturation of the

magnetization at high field values. As expected, the increase in magnetization at low fields is larger for the samples prepared at lower calcination temperatures.

The inset of figure 5 also shows the presence of coercive forces at low fields in all the samples. Figure 6 shows the variation of the coercive field with temperature for several calcination temperatures. For all the samples it is observed that the coercive field has its largest value at low temperatures and decreases as the temperature approaches the Néel temperature, where a paramagnetic behaviour is expected. This can be explained by the thermal disorder at higher temperatures.

The presence of a coercive field is also an indication of the extent of imbalance of 'up' and 'down' spins that occurs at the surface. As the particle size decreases, the total number of atomic moments that may be uncompensated is not negligible. The result is the appearance of a canted antiferromagnetic component at the surface that increases as the particle size decreases. This effect has been observed experimentally in fine particles of NiO [6]. In these NiO nanoparticles the canting of the magnetic moments is in the origin of a weak ferromagnetic behaviour. However, in our samples we have obtained no clear evidence of weak ferromagnetism.

The coercive forces of polycrystalline ferromagnetic samples are expected to increase as the particle size decreases, at least until very small sizes are reached [12]. It is observed that the sample calcined at 800 °C shows the largest coercive field at all the measured temperatures. So, compared with the case of ferromagnetic materials, this average particle size  $(D_{TEM} \approx 90 \text{ nm})$  could be considered to be close to the size where the rotation modes of the atomic magnetic moments change from coherent (smaller sizes) to incoherent (larger sizes) [12].

The presence of small amounts of ferromagnetic  $CrO_2$ nanoparticles has been ignored. The samples were prepared in a static air atmosphere while the formation of chromium (IV) oxide requires high oxygen pressure. This dioxide is only stable in air below ~250 °C; conversion to chromium (III) oxide takes place at higher temperatures [13].

The magnetization as a function of the magnetic field was measured at different temperatures below  $T_N$ . The



**Figure 7.** Reduced magnetization as a function of the reduced variable  $M_s H/T$  for the sample prepared at 400 °C. The linear antiferromagnetic component has been previously subtracted.

antiferromagnetic contribution,  $M = \chi_{AF} H$ , was linearly fitted in the large magnetic field region and it was subtracted from the whole graph. In this way, the magnetic behaviour associated with the uncompensated surface spins can be shown.

Néel predicted that small enough antiferromagnetic particles should exhibit the presence of superparamagnetism [3] and this effect was observed in NiO nanoparticles [6]. For superparamagnetic samples, the magnetization should be given by the Langevin equation [12]. In this case, the magnetization scales with H/T. So, if the magnetization is plotted as a function of H/T, the curves taken at different temperatures should be superimposed. Figure 7 shows this plot for the sample prepared at 400 °C. It is observed that the reduced magnetization curves do not superimpose when plotted as a function of the reduced variable  $M_s H/T$ , where  $M_s$  is the extrapolated saturation magnetization. The same behaviour is observed for the other samples prepared at higher calcination temperatures. The presence of a particle size distribution could be the reason for the non-scaling. Another explanation could be that the samples show spin-glass behaviour. However, more measurements at low temperatures are required to clarify this point.

### 4. Conclusions

 $Cr_2O_3$  nanoparticles of various sizes were synthesized by calcining portions of a dried gel of chemically precipitated  $Cr(OH)_3$  in air for 3 h at various temperatures.

 $Cr_2O_3$  nanoparticles show an antiferromagnetic behaviour, but the presence of a net magnetic moment at the surface is observed due to the large surface/volume ratio present when particle size is reduced. This magnetic moment disappears as the temperature approaches the Néel temperature. On the other hand, the magnetization does not scale with H/T, as expected for superparamagnetic samples.

#### Acknowledgment

The authors want to acknowledge financial support from the MCyT of Spain under project FEDER-MAT 2001-3749.

#### References

- Chudnovsky E M and Tejada J 1994 Macroscopic Quantum Tunneling of the Magnetic Moment (Cambridge: Cambridge University Press)
- [2] Gider S, Awschalom K K, Mann S and Chaparala M 1995 Science 268 77
- [3] Néel L 1961 C. R. Acad. Sci., Paris 252 4075
  Néel L 1961 C. R. Acad. Sci., Paris 253 9
  Néel L 1961 C. R. Acad. Sci., Paris 253 1286
- [4] Richardson J T and Milligan W O 1956 Phys. Rev. 102 1289
- [5] Cohen J, Creer K M, Pauthenet R and Srivastava K 1962 J. Phys. Soc. Japan (Suppl B-I) 17 685
- [6] Schuele W J and Deetscreek V D 1962 J. Appl. Phys. 33 1136
- [7] Makhlouf Salah A, Parker F T, Spada F E and Berkowitz A E 1997 J. Appl. Phys. 81 8
- [8] Zysler R D, Fiorani D and Testa A M 2001 J. Magn. Magn. Mater. 224 5
- [9] 1970 Numerical Data and Functional Relationships in Science and Technology. Crystal and Solid State Physics. Crystal Structure Data of Inorganic Materials. Part b: Key Elements O, S, Se and Te (Landolt–Börnstein New Series) Group III, vol 7 (Berlin: Springer)
- [10] Bañobre-López M, Vázquez-Vázquez C, Rivas J and López-Quintela M A 2002 3rd Int. Conf. on Inorganic Materials (Konstanz, Germany, Sept. 2002) (Int. J. Inorg. Mater.)
- [11] Scherrer P 1918 Nachr. Göttinger Gesell. 98
- [12] Morrish A H 2001 *The Physical Principles of Magnetism* (New York: IEEE)
- [13] Roy R 1965 Bull. Soc. Chem.