

Evidence of weak ferromagnetism in chromium(III) oxide particles

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Abstract

The low temperature ($4 < T(K) < 350$) magnetic properties of chromium(III) oxide particles have been studied. A clear evidence of the presence of weak ferromagnetism is observed below 250 K. The magnetisation curves as a function of the applied field show coercive fields due to the canted antiferromagnetism of the particles. Around 55 K a maximum is observed in the zero-field-cooled curves; this maximum can be assumed as a blocking temperature, similarly to ultrafine ferromagnetic particles.

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1. Introduction

The study of nanosized systems is a very interesting field due to the change in physical and chemical properties of bulk materials as particle size is reduced. Although the first successful attempt to explain magnetic properties of antiferromagnetic nanoparticles was given by Néel in 1961 [1], the presence of a net magnetic moment in some antiferromagnetic nanosized systems is not always clear [2,3].

Chromium(III) oxide exists in the corundum structure (space group R-3c) and the rhombohedral unit cell have four magnetoactive Cr³⁺ ions placed along the [1 1 1] axis. According to Shull [4], the disposition of the relative spin orientations along the *c* axis are $- + - +$. In this type of antiferromagnetic structure, the presence of ferromagnetism is forbidden by symmetry requirements.

In this paper we report the study of low temperature magnetic properties of chromium(III) oxide nanoparticles.

2. Experimental procedure

Cr₂O₃ nanoparticles were prepared by precipitation with sodium hydroxide, as reported elsewhere [5]. Average crystallite sizes ranged from 20 nm, for samples calcined at 400°C, to 200 nm for those calcined at 1000°C.

Magnetisation measurements were performed by a commercial SQUID magnetometer as a function of temperature ($4 < T(K) < 350$) in zero-field-cooled (ZFC) conditions for an applied field of 1 kOe, and as a function of the magnetic field (up to 50 kOe).

3. Results and discussion

Magnetisation vs. temperature measurements are presented in Fig. 1. For all the crystallite sizes a magnetic transition is observed around 320 K, the corresponding Néel temperature. The samples calcined at higher temperatures exhibit a typical antiferromagnetic behaviour. As the particle size is reduced, a smooth increase of the magnetisation is observed. For the

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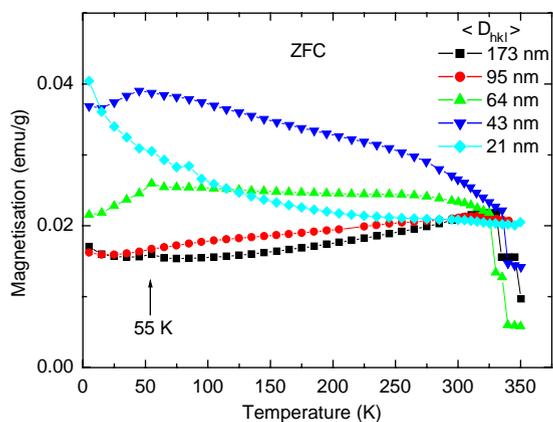


Fig. 1. Temperature dependence of the ZFC magnetisation (applied field of 1 kOe) for samples of different crystallite size.

sample calcined at 400°C, its magnetic behaviour is close to that of a paramagnetic material; however, the magnetisation curve does not match a Curie law. These changes in the magnetisation curves are directly related with the large surface/volume ratio present in nanosized particles and hence the imbalance in the number of spins “up” and “down” that occurs at the surface of the nanoparticles [5].

An anomalous behaviour is observed at 55 K, where a maximum is observed in the magnetisation curve. In order to give some light about the origin of this maximum, we have measured the magnetisation as a function of the applied magnetic field below and above this temperature (Fig. 2).

For temperatures between 55 and 250 K the magnetisation curves show two main contributions: a paramagnetic surface component superimposed to the bulk weak ferromagnetic (WF) behaviour of the nanoparticle core. Taking into account that the structural disorder is more important as the calcination temperature is reduced (and hence the particle size), this WF component can arise from canting of the atomic magnetic moments [6]. This tilting of the magnetic moments toward one another will result in a net magnetic moment.

Below 55 K, the magnetic behaviour in the low-field range changes surprisingly: the magnetisation cycles broaden. This feature can be explained as a “freezing” of the atomic magnetic moments below 55 K. Below this temperature an interfacial exchange anisotropy appears as a result of the surface–core interactions, similarly as it was reported for antiferromagnetic–ferromagnetic systems [7].

Additionally, deviations of the linear behaviour expected for antiferromagnetic materials are observed at high fields (inserted graph in Fig. 2). This feature is related to the spin-flop transition which occurs in

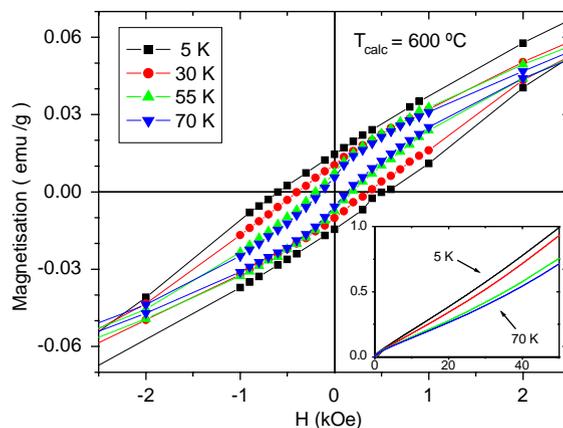


Fig. 2. Magnetisation curves as a function of the applied field at low temperatures for the sample calcined at 600°C. The inserted graph shows a detail of the high-field range.

uniaxial antiferromagnets of the easy-axis type [8]. At sufficiently strong magnetic fields along the *c* axis the directions of the sublattice magnetisations rotate from parallel to this easy axis to directions in the plane normal to this axis.

As far as we know, this evidence of weak ferromagnetism in chromium(III) oxide was not reported before. This WF component is a consequence of the use of nanosized systems and can arise from canting of the structurally disordered atomic magnetic moments.

Acknowledgements

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