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2004 J. Phys.: Condens. Matter 16 6977

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A Mössbauer study of the magnetization of γ -Fe₂O₃ nanoparticles in applied fields: the influence of interaction with CoO

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Received 13 July 2004, in final form 19 August 2004

Published 17 September 2004

Online at stacks.iop.org/JPhysCM/16/6977

doi:10.1088/0953-8984/16/39/030

Abstract

By use of Mössbauer spectroscopy we have followed the gradual alignment of the magnetization of γ -Fe₂O₃ nanoparticles as a function of the applied field. At moderate fields, the magnetization was less aligned with the field if the particles were mixed with CoO nanoparticles. This indicates a strong exchange interaction between the γ -Fe₂O₃ and the CoO nanoparticles. The effect manifests itself in a way which can be difficult to distinguish from localized spin canting.

1. Introduction

Magnetic nanoparticles are interesting because their properties in several ways deviate from those of the corresponding bulk materials. One example is superparamagnetic relaxation, which can be described in terms of fluctuations of the (sublattice) magnetization directions among the easy directions of magnetization. Interactions between magnetic nanoparticles can have a significant influence on their magnetic behaviour. Dipole interaction between ferro- or ferrimagnetic particles can have a large influence on the superparamagnetic relaxation, and can lead to a transition to a spin-glass-like state at low temperatures [1–5]. Interactions between antiferromagnetic particles of α -Fe₂O₃ [6–8] or NiO [9] can also have a strong influence on the relaxation. In this case dipole interactions are insufficient to produce the effect, and it has been concluded that it is due to exchange interaction between surface atoms of neighbouring particles. Recently we have used Mössbauer spectroscopy to study nanocomposites of magnetic materials with two different types of nanoparticles, and found some unexpected results. When nanoparticles of α -Fe₂O₃ [7, 8] or γ -Fe₂O₃ [10] were mixed with NiO nanoparticles it resulted in a faster superparamagnetic relaxation compared to samples of the pure iron oxide nanoparticles. However, when the iron oxide nanoparticles were mixed with CoO nanoparticles the relaxation was to a large extent suppressed. The

difference between nanocomposites with NiO and CoO was explained by the different magnetic anisotropy energies of these particles.

In ^{57}Fe Mössbauer spectra of magnetic materials, the relative areas of the six lines depend on the angle, θ , between the magnetic field at the nucleus and the gamma ray direction and are given by $3:x:1:1:x:3$ with $x = 4 \sin^2 \theta / (1 + \cos^2 \theta)$. Thus the area ratio can give information on, for example, the degree of alignment of the magnetization in a ferro- or ferrimagnetic sample exposed to a magnetic field. This has been utilized in numerous studies of spin canting both in nanoparticles and in bulk materials; see, for example [11–15].

In this paper we report on results of Mössbauer studies of the magnetic structure of both pure $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles and $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles mixed with CoO nanoparticles. We show that in applied fields of the order of 1 T the degree of alignment of the magnetization differ for the two samples. Thus the interaction with CoO has a significant influence on the magnetization of the $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles in moderate applied fields.

2. Experimental details

Samples of $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles were prepared by oxidation of Fe_3O_4 nanoparticles, which were made by co-precipitation of Fe^{2+} and Fe^{3+} in an aqueous solution by adding a solution of NaOH [10]. CoO nanoparticles were prepared by high-energy ball milling of a 1:1 molar ratio mixture of Co_3O_4 and Co in argon for 115 h.

The samples of pure $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles and mixtures of nanoparticles of $\gamma\text{-Fe}_2\text{O}_3$ and CoO (1:1 by weight) were prepared by suspending the particles in distilled water, and exposing them to intense ultrasound to obtain a homogeneous mixture. The samples were left to dry in open Petri dishes in air at room temperature for about two days. Mössbauer absorbers of the two samples were prepared with a thickness of $20 \text{ mg } \gamma\text{-Fe}_2\text{O}_3 \text{ cm}^{-2}$.

Mössbauer spectra were obtained with a conventional constant acceleration Mössbauer spectrometer with a 100 mCi source of ^{57}Co in rhodium. The measurements were obtained at 6 K in a liquid helium cryostat equipped with a superconducting coil. In-field measurements were made with the magnetic field applied parallel to the gamma ray direction. The spectrometer was calibrated with a $12.5 \mu\text{m}$ foil of metallic iron at room temperature.

3. Results and discussion

The average diameter of the $\gamma\text{-Fe}_2\text{O}_3$ particles, estimated from XRD data, was about 7 nm, whereas the CoO particles were found to have an average diameter of about 10 nm [10]. The results of the XRD analysis were confirmed by transmission electron microscopy studies, which also showed that the $\gamma\text{-Fe}_2\text{O}_3$ and CoO particles were pseudo-spherical in shape [10].

Mössbauer spectra of the two samples, obtained at different fields, are shown in figure 1. In zero field the area ratio of the six lines is close to 3:2:1:1:2:3, as expected for a sample with random orientation of the magnetization directions. With increasing field the relative areas of lines 2 and 5 gradually decrease, indicating an increasing alignment of the magnetization directions. The sample containing CoO nanoparticles shows a slower decrease in the relative intensity of lines 2 and 5 than the sample of the pure $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. This is in particular visible in the spectra obtained with applied magnetic fields in the range 0.5–1.25 T. For smaller and larger applied fields, the spectra of the two samples have almost identical area ratios. Each of the spectra was fitted with a sextet in which the lines pairwise were constrained to have identical areas with the relative areas given by $y:x:1:1:x:y$. The field dependence of the relative areas of lines 2 and 5, x , for the two samples, is shown in figure 2. The value

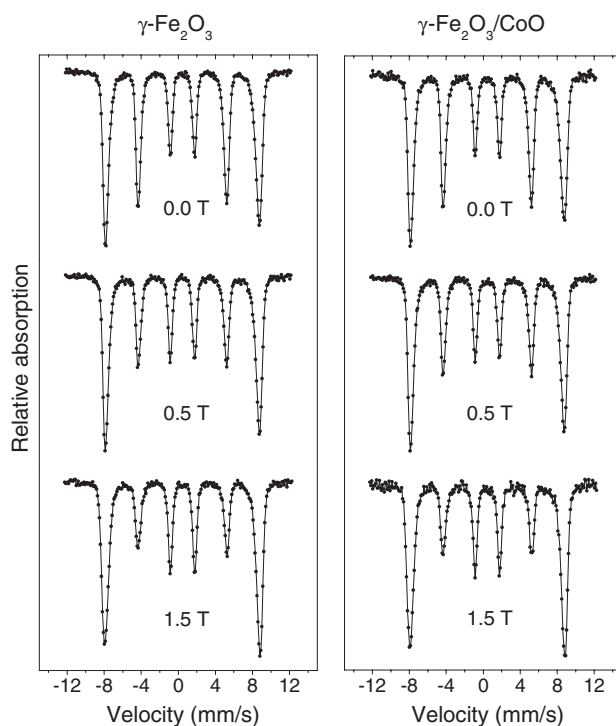


Figure 1. Mössbauer spectra of pure γ -Fe₂O₃ nanoparticles and γ -Fe₂O₃ nanoparticles mixed with CoO nanoparticles. The spectra were obtained at 6 K with the indicated magnetic fields applied parallel to the gamma ray direction.

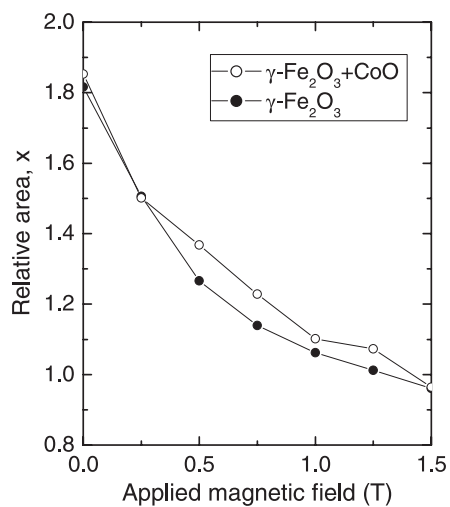


Figure 2. The relative area, x , of line 2 and 5 in the Mössbauer spectra obtained at 6 K as a function of the applied magnetic field.

of y is constant (≈ 2.72) in all spectra with a scatter of the values of about ± 0.01 , indicating that we can measure the relative areas with this accuracy. The deviation from $y = 3.0$ can be explained by the influence of absorber thickness.

For applied fields in the range 0.5–1.25 T the relative areas of lines 2 and 5 for the two samples are clearly different, and it appears that the magnetization in the sample containing CoO is consistently less aligned with the applied field than the magnetization in the sample without CoO at the same applied fields. In the sample without CoO the magnetization direction is mainly determined by a competition between the applied field and the magnetic anisotropy. The smaller degree of alignment in the sample with CoO indicates that in this sample the applied field also has to overcome an interaction field due to interactions between γ -Fe₂O₃ and CoO nanoparticles. As we have shown earlier [10], the interaction between CoO and γ -Fe₂O₃ nanoparticles can lead to a significant suppression of the superparamagnetic relaxation of the γ -Fe₂O₃ nanoparticles and to an enhanced coercivity. Similar observations have been made for α -Fe₂O₃ nanoparticles mixed with CoO nanoparticles [8]. The effect was explained by a strong exchange interaction between the nanoparticles of iron oxide and cobalt oxide, which have a relatively large anisotropy. The present measurements support this interpretation.

In several previous Mössbauer studies of incomplete spin alignment in nanoparticles in external magnetic fields, the data were interpreted in terms of localized spin canting of surface spins due to the different magnetic environment of surface ions compared to the bulk environments; see, for example, [11, 13, 16]. Magnetization data for magnetic nanoparticles have been explained by a similar model [17, 18]. Another source of localized spin canting can be defects in the interior of the particles [16, 19]. This mechanism can also be important in bulk materials, such as, for example, diamagnetically substituted ferrites [14–16]. The present study shows that still another mechanism, namely exchange coupling between nanoparticles, can give rise to a smaller degree of spin alignment in an external magnetic field, even in samples prepared just by drying aqueous suspensions of nanoparticles of γ -Fe₂O₃ and CoO at room temperature. The interface regions of neighbouring γ -Fe₂O₃ and CoO nanoparticles presumably involve only a small fraction of the atoms because of the rounded shape of the particles. Therefore, it is unlikely that the data can be explained by a localized spin canting in the interface regions. The results rather indicate that rotation of the magnetization direction of each γ -Fe₂O₃ particle as a whole gives the main contribution to the effect. It is likely that the effect can be larger in nanocomposites prepared in other ways such that the exchange interaction is larger. The mechanism may also be effective in samples consisting solely of one type of nanoparticles, e.g. γ -Fe₂O₃, but in this case it will presumably be smaller, because the exchange coupling between γ -Fe₂O₃ particles is much smaller than that between γ -Fe₂O₃ and CoO nanoparticles [10].

4. Summary

By use of Mössbauer spectroscopy at low temperatures and with applied magnetic fields we have studied the magnetic properties of samples of nanoparticles of pure γ -Fe₂O₃ and γ -Fe₂O₃ nanoparticles mixed with CoO nanoparticles. Both samples were prepared by drying aqueous suspensions at room temperature. The studies show that the alignment of the magnetization of γ -Fe₂O₃ nanoparticles in applied magnetic fields of the order of 1 T is reduced if the particles are mixed with CoO nanoparticles. This indicates that there is a significant exchange interaction between γ -Fe₂O₃ and CoO nanoparticles in samples. The results are in accordance with previous studies of superparamagnetic relaxation in similar samples at higher temperatures.

Acknowledgments

We thank Lis Lilleballe for help with sample preparations. The work was supported by the Danish Technical Research Council.

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