MÖSSBAUER STUDY OF Fe_3O_4 FINE PARTICLES

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Mössbauer spectroscopy was used to study fine particles of Fe_3O_4 at room temperature. The spectra of coated, uncoated, and annealed samples are all magnetically split in an applied field of 4.4 kOe. The angles between the applied field and the hyperfine field were found to be <30° for all samples.

Introduction

The superparamagnetic behavior of fine magnetic particles has been investigated by several workers [1-4]. It was demonstrated by Berkowitz et al. [2] that the observed decrease of magnetization of $NiFe_2O_4$ and $CoFe_2O_4$ fine particles when coated with an organic surfactant is not associated with a nonmagnetic surface layer, as suggested by Kaiser and Miskolczy [1]. Rather, Berkowitz et al. attributed this decrease to the pinning of the surface spins due to the bonding of the surfactant to the surface layer of the particles, thus producing a high surface anisotropy that prevents saturation of the magnetization even in magnetic fields as high as ~20 T. It was also shown that pinning of the surface spins was much weaker in coated Fe_3O_4 fine particle systems than in $NiFe_2O_4$ and $CoFe_2O_4$, indicating much weaker surfactant—ferrite interactions [2].

Mössbauer studies on coated Fe_3O_4 fine particles [5] indicated that an applied magnetic field of 8 kOe parallel to the direction of incidence of the γ-rays was enough to align the magnetic moments of the particles with the applied field. Xie-long et al. [6] studied coated Fe_3O_4 fine particles using Mössbsuer spectroscopy and reported results consistent with the results previously reported [2, 5].

Mössauer study of coated $NiFe_2O_4$ by Berkowitz et al. [7] showed that it was not possible to align all the magnetic moments with an applied field of 68.5 kOe. In contrast, the uncoated sample showed a virtual alignment of the magnetic moments with the applied field. It was speculated that the surfactant interacts strongly with the ferrite via the Ni^{+2} ion.

In the present work, the effect of coating on the magnetic properties of Fe_3O_4 fine particles is investigated using Mössbauer spectroscopy.

Experimental Techniques

The peptization method of Khalafalla et al. [8] was used to prepare a sample coated with oleic acid and another without coating. Part of the coated sample was separated before centrifuging. The remaining part was suspended in toluene and centrifuged. This sample was placed in a dish and was left at room temperature to dry. Part of the dried powder was annealed at 250°C for 18 h to remove the coating. The uncoated sample was not centrifuged. TEM imaging showed that the mean diameter for the uncoated sample is 125 Å; for the coated centrifuged sample, 70 Å; and for the annealed sample, 100 Å. The Mössbauer spectra were obtained using a standard constant acceleration spectrometer and a 25 mci source of Co^{54}/Pd. A permanent magnet which produces a 4.4 kOe field was used for measurements with a magnetic field.

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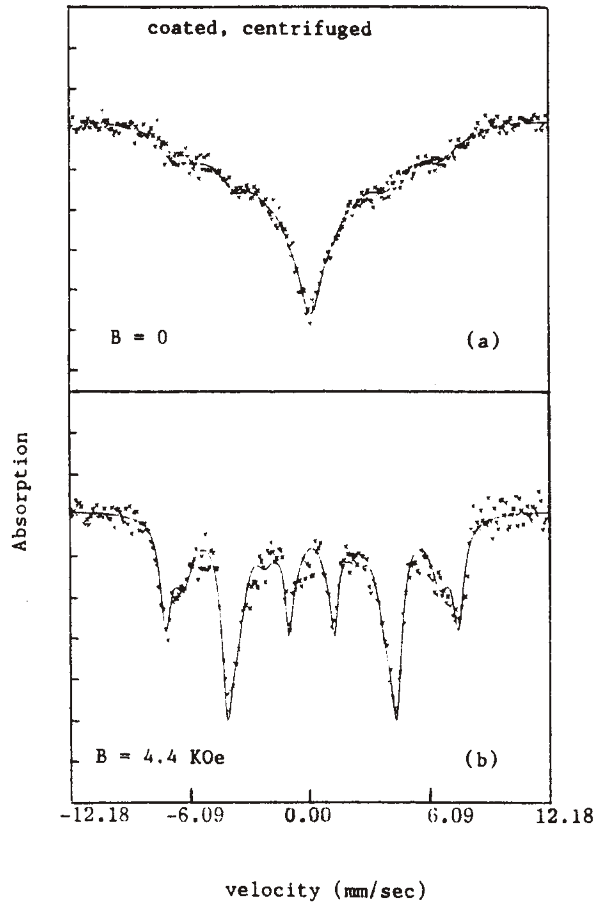

Fig. 1. Room temperature Mössbauer spectra for the coated centrifuged sample with and without an applied magnetic field.

Results

Figure 1a shows a room temperature spectrum for the coated and centrifuged sample with no external magnetic field. The spectrum shows a broad superparamagnetic central line characteristic of Fe_3O_4 fine particles at room temperature. Figure 1b shows the room-temperature spectrum for the same sample with an external magnetic field of 4.4 kOe applied perpendicular to the propagation direction of γ-rays. The spectrum shows that the central superparamagnetic line disappears and becomes magnetically split with lines (2,5) more intense than (1,6).

From the ratio of the intensities of lines (2,5) to those of (1,6), the average canting angle, θ, between the applied field and the magnetic moments of the particles is calculated and found to be $\theta = 18 \pm 3°$. This value is consistent with the estimate of Berkowitz [2] of $0 < 30°$. This angle is, however, smaller than that of $28 \pm 2°$ found by Xie-Long et al. [7].

Figure 2 shows the spectra for the uncentrifuged samples both coated and uncoated as well as the annealed sample, all at room temperature and zero external magnetic field. All spectra are magnetically split, consistent with a mean particle diameter $\gtrsim$10 nm. However, the spectrum for the coated uncentrifuged sample shows a small central superparamagnetic line due to smaller particles. This line was pronounced in the centrifuged sample (Fig. 1a) due to the higher proportion of these smaller particles in the centrifuged sample. The superparamagnetic contribution is absent in the uncoated and annealed samples, indicating a growth of the particle size.

Figure 3 shows the spectra for the samples of Fig. 2 with an applied field of 4.4 kOe perpendicular to the direction of propagation of the γ-rays. This figure shows that the small superparamagnetic component in the coated uncentrifuged sample disappeared as in the case of Fig. 1.

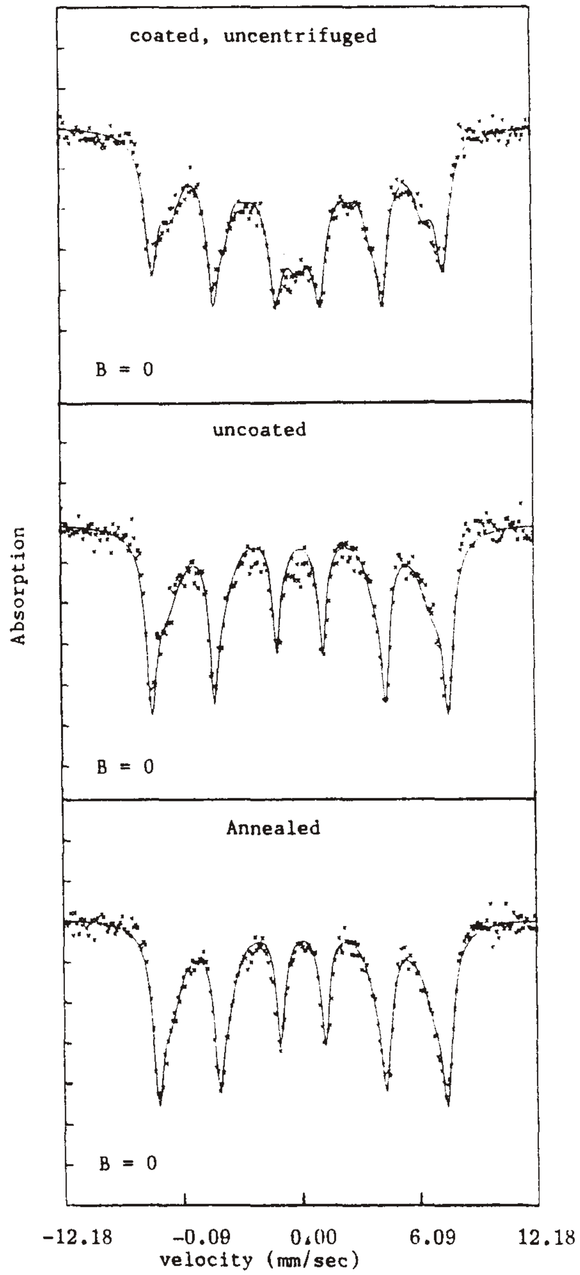

Fig. 2. Room temperature Mössbauer spectra for the coated uncentrifuged, uncoated, and annealed samples in the absence of an applied field.

From the ratio of the intensities of the sixtet lines the canting angle for the coated uncentrifuged sample was 18 ± 3°, for the uncoated sample 22 ± 3°, and for the annealed sample 27 ± 3°. These results are consistent with the results reported by other workers [2, 5, 6].

Discussion and Conclusion

Our results show that a small field (<5 kOe) was enough to remove the effect of superparamagnetic relaxation in Fe_3O_4 fine particles. This indicates that the anisotropy in this system is much weaker than in $NiFe_2O_4$ and $CoFe_2O_4$ [2]. Comparing the canting angles for the centrifuged and uncentrifuged coated samples, we concluded that the magnetic anisotropy is not sensitive to the variation of the particle size in the samples under investigation. The larger angles in the uncoated and the annealed samples indicates that the removal of the coating does not reduce the magnetic anisotropy. The increase in the canting angles in

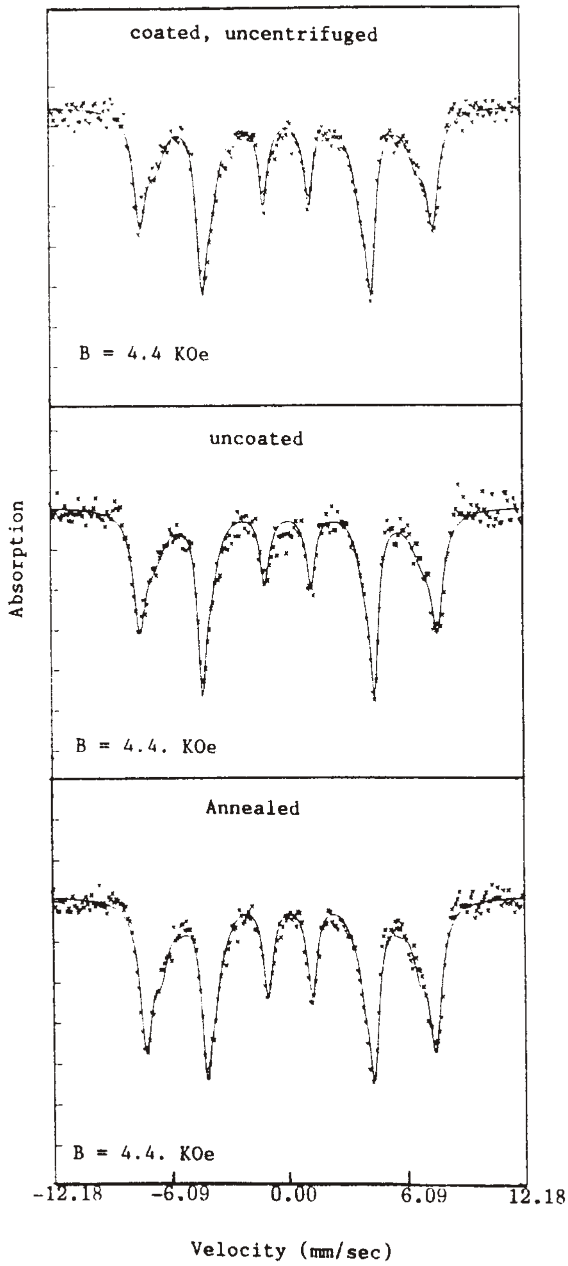

Fig. 3. Room temperature Mössbauer spectra for the samples of Fig. 2, with an applied magnetic field.

these two samples might be attributed to partial oxidation of the particles which is expected to be more significant in the annealed sample. The effect of oxidation on the magnetic anisotropy is under investigation.

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