

A Mössbauer Study on the Surface Hyperfine Field of Uniform Hematite Particles

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Abstract. A Mössbauer spectroscopic study was performed on uniform spherical hematite particles (99 ± 9 nm, Sample I) and those enriched with ^{57}Fe on the surface (Sample II). A striking difference was found between the spectra of these two samples, in that Sample I showed a spectrum with nearly symmetrical resonant absorption lines, while Sample II showed a spectrum with the lines broadened toward the central peaks asymmetrically. But after the ^{57}Fe -enriched sample was heated to 623 K, the spectral lines became narrower due to the diffusion of the surface ^{57}Fe -ions into the bulk. The above results showed that the centripetal broadening of the spectral lines for small uniform hematite particles resulted from a surface effect. The surface exhibited a hyperfine field about 5.2% lower than that for the bulk. The wider distribution of the surface hyperfine field was explained by structural inhomogeneity of the surface.

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Hematite, $\alpha\text{-Fe}_2\text{O}_3$, is an antiferromagnetic compound. There has been growing experimental and theoretical interest in samples of this material, particularly on the part of Mössbauer investigators, who have placed their stress on the magnetic properties of hematite [1–4]. Mössbauer parameters were found to change with its particle size, including the asymmetric broadening of spectral peaks toward the central peaks. Van der Kraan [5] and Shinjo et al. [6] explained the asymmetric broadening by a smaller hyperfine field for the surface than that of the interior, while Topsøe [7] proposed that the line broadening may be due to collective magnetic excitations of small particles. Because of the non-uniformity of the particle size of samples generally employed in the literature, the surface effect could not be distinguished convincingly from the effect of the particle size distribution on the spectra.

Developments in preparing uniform (also known as monodispersed) colloidal particles [8] provide the possibility of using small uniform particles in Mössbauer spectroscopic studies, so that the interference arising from particle size distribution can be ruled out from the true surface effect. In this way, we prepared small uniform particles of hematite, and employed the method of enrichment of ^{57}Fe on the hematite surface. This made it possible to compare the spectra of these samples. An attempt has been made to explore the true surface effect on Mössbauer spectra by comparing the spectra of ^{57}Fe -coated and uncoated samples. To our knowledge, this is the first time that reliable evidence for a surface effect on the hyperfine field of hematite has been demonstrated.

1. Experimental

Preparation of Hematite Samples

The phrase uniform particles is used to refer to particles with a narrow size distribution, in the literature. Here

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spherical uniform hematite particles were prepared by the forced hydrolysis method first developed by Matijevic and Scheiner [9] and later modified by Zhang et al. [10]. Ferric chloride solution was mixed with hydrochloric acid in the proper proportion, and heated to 378 K. After hydrolysing at this temperature for 24 h, the flask was cooled to room temperature to stop the reaction. Then the precipitate was subjected to repeated centrifugalization and washing until the supernatant was free from chloride ions. The product was finally dried at 353 K under vacuum. The sample so-obtained was labelled as Sample I and had a spherical shape and a diameter $d = 99 \pm 9$ nm as shown by the electron micrograph. The particle size was consistent with the diameter estimated from the specific area measured by the BET method. The x-ray diffraction spectra showed that the sample was α -Fe₂O₃ with a high degree of crystallization and purity. Sample II was prepared by coating the surface of Sample I with ⁵⁷Fe. A commercial ⁵⁷Fe₂O₃ (abundance 82%) was reduced by ultrapure hydrogen at 673 K and the reduced iron was dissolved in nitric acid, and mixed with Sample I, and then aged at 363 K for 20 h. The adsorbed ⁵⁷Fe was analyzed chemically and it was determined that over 98% of the ⁵⁷Fe was coated, probably as a monolayer on the surface of the hematite particles. Sample III was obtained by annealing Sample II at 623 K for 10 h.

Mössbauer Spectra Measurements

Mössbauer spectra were measured with a constant-acceleration spectrometer [11]. The best Lorentzian fit to the experimental data was found by the method of least squares.

2. Results and Discussion

The electron micrographs for Samples I and II are shown in Figs. 1 and 2 respectively. Comparing the electron micrographs, we found that the size distribution and the shape of the uniform α -Fe₂O₃ particles did not change after coating with ⁵⁷Fe. Figure 3 shows the Mössbauer spectra measured at room temperature for the uniform hematite particles with and without ⁵⁷Fe-coating. The hyperfine field data obtained from computer fitting are given in Table 1. It can be seen clearly that the spectra for Sample II are composed by two different sets of six-line spectra and the computer fitted curves are shown in curve 3d. Curve 3c represents the spectra of Sample III and exhibits much less broadening and an increased symmetry as compared to curve 3b.

Figure 3 indicates that the enrichment of ⁵⁷Fe on the surface caused merely the asymmetric broadening

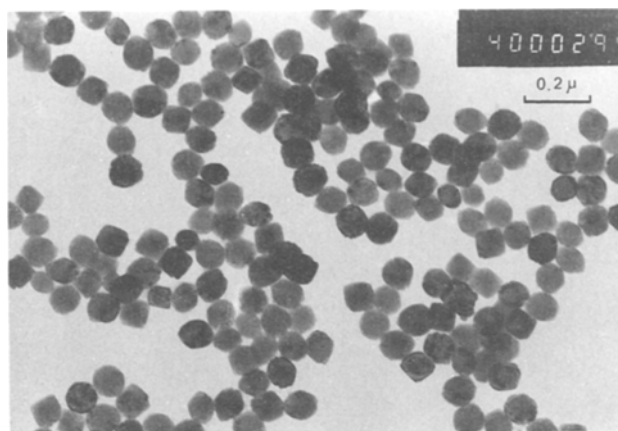


Fig. 1. Electron micrograph of uniform α -Fe₂O₃ particles (Sample I)

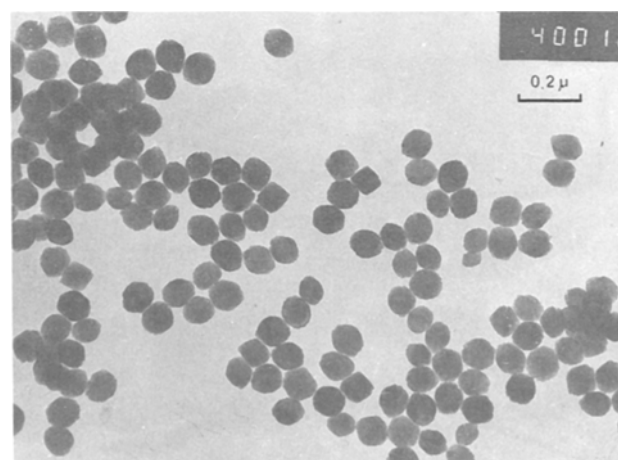


Fig. 2. Electron micrograph of ⁵⁷Fe₂O₃-coated uniform α -Fe₂O₃ particles (Sample II)

toward the central peaks of the spectra without any appearance of other absorption lines in the spectra. Van der Kraan [5], as well as Shinjo et al. [6] attributed this line broadening to a surface effect, whereas Topsøe [7] proposed a collective magnetic excitation model for explaining the line broadening of small particles. In this report we found that uniform α -Fe₂O₃ particles before and after ⁵⁷Fe-coating showed an identical spherical shape and particle size as evidenced by Figs. 1 and 2. Thus the line broadening is not due to the presence of small particles, nor can it be explained by the superparamagnetic relaxation effect. The only reasonable conclusion is that the line broadening resulted from a surface effect.

In order to obtain a further verification for the surface effect, Sample II was subjected to annealing at a higher temperature, 637 K, to facilitate the possible diffusion process (or the exchange process) between the surface ⁵⁷Fe and the bulk ⁵⁶Fe. Sample III exhibited

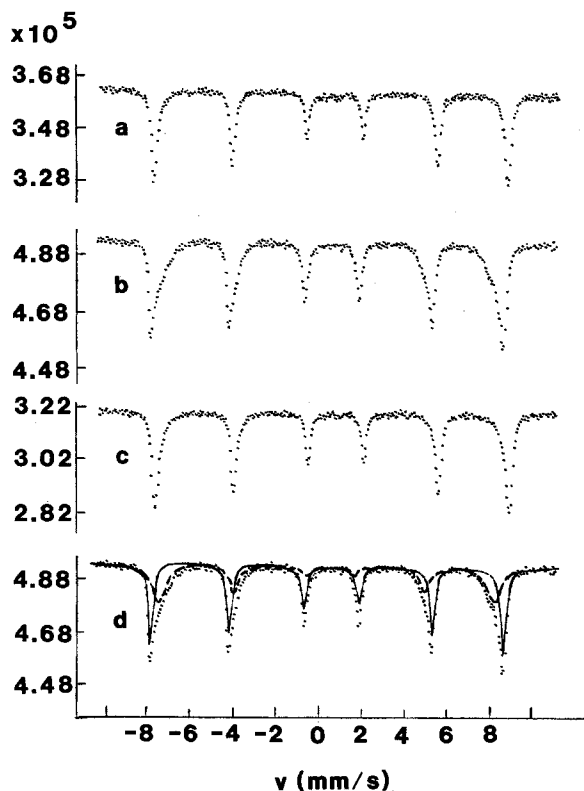


Fig. 3. Mössbauer spectra for uniform α -Fe₂O₃ particles at room temperature: *a* Sample I; *b* Sample II; *c* Sample III; *d* Computer fitted curves of Sample II

Table 1. Mössbauer parameters of uniform hematite particles at room temperature

| Sample | Hyperfine field (kOe) | Area fraction | Width of 6th-line (mm/s) |
|---------------|-----------------------|---------------|--------------------------|
| I | 506.4 | — | 0.17 |
| II (bulk) | 509.4 | 0.57 | 0.16 |
| II (surface) | 482.9 | 0.43 | 0.39 |
| III (bulk) | 509.0 | — | — |
| III (surface) | 482.9 | — | — |

an apparent decrease in linewidth and asymmetry compared to Sample II. Because of the identical ratio of ^{57}Fe to ^{56}Fe in both Samples II and III, the diffusion (or the exchange) of ^{57}Fe into the bulk should be responsible for the line-sharpening of the spectra lines. As pointed out by Morrish and Haneda [12], although small particles can be used for the study of the surface

hyperfine field, it is still difficult to rule out other very complicated factors, and thus reliable conclusions cannot often be obtained. In this work, owing to the uniform samples used and the enrichment technique of ^{57}Fe employed, the effect of particle size distribution was successfully eliminated and the spectra of the surface were satisfactorily separated from the bulk phase as shown in curve 3d (Fig. 3). Reasonable features appeared in that the Mössbauer parameters for the bulk phase obtained by separating the spectral component from the surface effect are very close to those for Sample I (see also Table 1), and the area fraction (0.43) is close to the weight percent of ^{57}Fe analysed in coating experiment (0.39). These facts provide additional evidence for the complete coating of ^{57}Fe on the surface of hematite particles.

It can be concluded from Table 1 that the hyperfine field of the surface of hematite particles is 5.2% lower than the bulk, while the linewidth is over twice that of the bulk. Furthermore, the outer linewidth of the surface spectra (see curve 3d) is significantly larger than the interior. This shows that there exists a wider distribution of the hyperfine field at the surface of the uniform hematite particles. These facts indicate that the surface layer of hematite is neither uniform nor saturated. A similar proposal of Pope [13] is consistent with the findings in this work.

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