Surface magnetism in ultrafine α-Fe particles

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Ultrafine particles of α-Fe have been studied by use of Mössbauer spectroscopy. The spectra contain a magnetically split component with broad lines which can be attributed to surface atoms. The average magnetic hyperfine field of this component decreases much more rapidly with temperature than that of the α-Fe core.

Experimental studies of surface and interface magnetism are in general performed on ultrathin films, and in this way investigations of relatively well-defined surfaces can be carried out [1-2]. However, the electronic and magnetic properties of surface atoms in ultrafine particles are also of great interest because the environments of these atoms may be different from those of surface atoms in thin films. Studies of surface magnetism in small α-Fe particles by use of Mössbauer spectroscopy form the subject of this paper.

The sample was prepared by impregnating a carbon support (Ketjenblack ED-600 JD AKZO Chem. Division, 1250 m²/g) with an aqueous solution of Fe(NO₃)₃·9H₂O (Merck, p.a.) followed by drying in air at temperatures up to 400 K. The sample was then reduced in a flow of purified hydrogen at 600 K in an in situ cell, designed for Mössbauer spectroscopy measurements in a helium cryostat with a superconducting coil. The reduced sample, which was kept in hydrogen during the measurements, contained 2.3 wt% Fe, 20%

Fig. 1. Mössbauer spectra of the α-Fe particles obtained at 5, 35 and 150 K, in a magnetic field of 4.0 T applied parallel to the gamma ray direction. For each spectrum is shown the distributions in magnetic hyperfine fields P(B) for the broad and the narrow components.
of which was $^{57}\text{Fe}$. The preparation procedure is similar to that described in detail in ref. [3].

At temperatures below 50 K the Mössbauer spectra of the iron particles were magnetically split, but at 150 K the magnetic hyperfine splitting had collapsed because of superparamagnetic relaxation. From the dependence of the induced magnetic hyperfine splitting on the applied magnetic field at 150 K we determined an average particle diameter of $(3.7 \pm 0.3) \text{ nm}$, using the procedure described elsewhere [4]. For spherical particles of this size 25–30% of the atoms are in the outermost surface layer.

A series of spectra was obtained at different temperatures in a magnetic field of 4.0 T applied parallel to the gamma ray direction. In a field of this magnitude the sample is essentially magnetically saturated and thus the superparamagnetic relaxation is suppressed. Figure 1 shows some of the spectra. At all temperatures, lines 2 and 5 have zero intensity, indicating that all atoms in the particles are ferromagnetically coupled. Thus there is no indication of spin-pinning in the surface, as has been observed in iron oxide particles [5].

At 5 K the spectrum consists of four narrow lines superimposed on a component with broader lines which is shifted to positive velocities relative to the component with narrow lines. The narrow lines are due to a component with Mössbauer parameters identical to those of bulk $\alpha$-Fe. The spectra obtained at higher temperatures are similar to the 5 K-spectrum, but the splitting of the component with broad lines decreases much more rapidly than that of the $\alpha$-Fe component.

The spectra were fitted with two distributions of magnetically split components with different isomer shifts using a modified version of the computer programme described by Wivel and Morup [6]. The distributions in the hyperfine fields of the two components are also shown in fig. 1. The sharp distribution between 29 and 34 T has an isomer shift identical to that of bulk $\alpha$-Fe at 5 K, and the average magnetic hyperfine field exhibits the temperature dependence expected for $\alpha$-Fe (after correction for the applied field). The broad distribution accounts for about 55% of the total absorption area and has an isomer shift of about 0.5 mm s$^{-1}$ at 5 K relative to $\alpha$-Fe at 295 K. There is a tendency for the broad distribution to contain two broad peaks, one in the range of 5–20 T and the other in the range of 25–45 T. Samples prepared in a similar way, but with less iron, were found not to contain $\alpha$-Fe, but yielded Mössbauer spectra similar to those of amorphous Fe–C alloy particles [7] with a hyperfine field distribution similar to the low-field peak of the present sample. Therefore we attribute this peak to amorphous Fe–C.

We believe that the high-field part of the distribution (between 25 and 45 T) can be attributed to the surface atoms of the $\alpha$-Fe particles. The range of hyperfine fields, although broader, is similar to that found in thin film studies [1,2]. The broader range is presumably due to the fact that surface atoms in small particles are found in a number of different types of environments (in planes, edges, corners etc.). Moreover, some of the surface atoms may be affected by chemisorbed hydrogen whereas others are in contact with the carbon support.

It is remarkable that the average value of the hyperfine fields of the surface component decreases much more rapidly with increasing temperature than that of the bulk $\alpha$-Fe. At 5 K there is a significant number of atoms with hyperfine fields between 35 and 45 T, but at 150 K almost all atoms have hyperfine fields below 35 T. This strong temperature dependence of the surface hyperfine field can be explained by the lower number of nearest neighbour iron atoms which leads to a faster decrease in the surface magnetization with increasing temperature. The results are qualitatively in agreement with theoretical results [8].

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References