

Oxidation of nanometer-sized iron particles

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The evolution of the oxidation of ultrafine (5 nm diameter) α -iron particles in ambient air has been studied using Mössbauer spectroscopy and electron microscopy. A 1–2 nm thick oxide layer was found to appear almost immediately, whereafter the oxidation proceeded rather slowly. The rate of oxidation can be understood from the Cabrera–Mott model of oxidation of metal surfaces. The oxide formed consists of a mixture of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$, but with the magnetic properties significantly modified due to the finite size of the oxide crystallites, e.g. the magnetic hyperfine fields are somewhat smaller than for the bulk Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$, and a very strong spin-canting was revealed. A Verwey transition was found to occur between 12 and 80 K. The Debye temperature of the oxide layer was found to be about 185 K for the thinnest observed oxide layer, increasing to about 215 K after exposure of the α -iron particles to air for one week.

1. Introduction

Ultrafine magnetic particles are of significant industrial importance. Applications include magnetic recording, ferrofluids, and catalysis. Particles of metallic iron are of increasing interest for use in, for example, magnetic tapes due to their high saturation magnetization and coercivity. However, iron particles are very reactive and do readily oxidize in air, whence some of their advantageous properties may be deteriorated upon exposure to the ambient air. On the other hand, a thin oxide layer reduces the rate of further oxidation. Oxidation, however, will proceed, and one of the aims of the present work was to follow this evolution of the oxidation of ultrasmall iron particles in ambient air.

The oxide phases created on the surfaces of ultrasmall iron particles, or foils, upon exposure to an oxygen-containing atmosphere have been studied by a number of groups [1–11]. There exists some controversy about which oxides are formed, but from Mössbauer spectroscopy and X-ray and electron diffraction studies it is generally concluded that the oxide phases consist of ultrasmall $\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4 crystallites. The oxide phases formed are expected to depend on the oxidation procedure.

In the determination of the degree of oxidation, it is important to realize that the Debye–Waller factor (f -factor) of the oxide phases and that of α -iron are generally different. Thus, it is important to perform studies at low temperatures in order to evaluate properly the amount of oxide formed as a function of oxidation time. We have therefore carried out measurements at temperatures down to 5 K, and also applied external magnetic fields in order to elucidate the magnetic properties of the oxide phases.

2. Experimental procedure

The investigated particles were prepared by evaporation of metallic iron from a tungsten crucible in an atmosphere of 1 mbar He. This procedure is a standard method for producing ultra-fine particles; the mean particle size being dependent on the evaporation temperature, the gas pressure and the type of gas in the chamber. The particles were collected on a vertical cold finger (cooled to liquid nitrogen temperature).

Two sets of samples were prepared; one sample (A) of particles was collected on a cold finger covered with solid octadecane. After termination of the particle production, the cold finger was heated to above the melting point of the octadecane ($T_m = 302$ K). The particles, suspended in molten octadecane, were then collected in a container, and the chamber was opened to the air. A Mössbauer absorber was prepared and studied as a function of temperature, applied magnetic field and oxidation time (up to 75 days). The Mössbauer studies were performed below the melting point of octadecane and with the sample under vacuum conditions.

Another sample set (B) was prepared by first slowly oxidizing (passivating) the particles collected on a clean cold finger, then opening the preparation chamber. Samples for Mössbauer spectroscopy studies were prepared after exposure to air for periods between 0 and 130 weeks. In order to obtain the recoil-free absorption of the Mössbauer γ -rays, these samples were also incorporated in octadecane prior to the Mössbauer spectroscopy studies.

The Mössbauer spectroscopy studies were performed by using a standard constant-acceleration spectrometer with a ^{57}Co source in rhodium. The isomer shifts are given relative to that of α -iron at 295 K.

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Transmission electron micrographs and electron diffraction patterns were obtained by using a Philips EM 430 microscope operated at 300 kV. The particles were placed on a holey carbon film.

3. Results

Transmission electron micrographs showed that the particles were about 5 nm in diameter. Each particle consisted of two phases; a core of α -Fe surrounded by a thin oxide shell. The electron diffraction patterns of freshly prepared samples revealed the presence of spots due to α -Fe. Six diffuse rings corresponding to the lattice spacings of cubic iron oxide (γ - Fe_2O_3 and/or Fe_3O_4) could also be identified. The appearance of diffuse rings instead of spots indicates that the oxide crystallites are much smaller than the metallic crystallites.

Mössbauer spectra of sample A obtained immediately after its preparation are shown in Fig. 1. The fresh sample was protected from exposure to air by keeping it under liquid nitrogen or in a vacuum. Absorption lines due to α -iron and an iron oxide are clearly seen. At 5 K (and at 80 K) a single line, with a relative area of about 2%, is also observed. This line is due to the iron present in the beryllium windows used

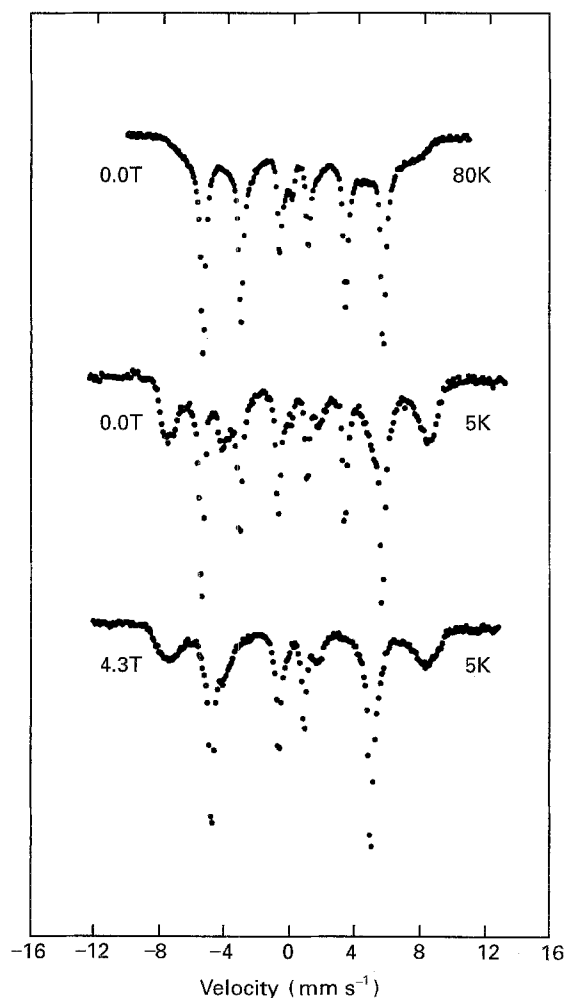


Figure 1 Mössbauer spectra of sample A, without direct exposure to air, at 80 K in zero applied field, and at 5 K in zero field and with 4.3 T applied parallel with the γ -ray direction.

in the cryostats. The spectra are well described by an α -iron sextet, two sextets due to iron oxide in a single line. The relative area of the metallic α -iron component amounts to about 48% at 5 K ($B_{\text{hf}} = 34.2$ T and $\delta = 0.12$ mm s $^{-1}$). At 80 K this relative area has increased to approximately 60%. This shows that the f -factor of the oxide shell decreases faster with increasing temperature than that of α -iron.

In Fig. 1 the Mössbauer spectrum at 5 K with a magnetic field of 4.3 T applied parallel to the γ -ray direction shows the disappearance of lines 2 and 5 of the α -iron spectrum, while these lines remain for the oxide component. Simultaneously, the magnetic hyperfine field of the metallic component decreases to about 30.2 T because the applied field is anti-parallel to the intrinsic magnetic hyperfine field of α -iron. The lines of the oxide component broaden on application of the field, but the average magnetic hyperfine fields (48 and 50 T) and the relative areas (28% and 20%) of the two sextets describing the oxide component remain essentially unaltered by the magnetic field. The isomer shifts of the sextets are about 0.4 mm s $^{-1}$. The relative area of the α -iron component is found to be 48%, in agreement with the value found in zero applied field.

When exposed to air at room temperature, the particles of sample A continue to oxidize slowly. Fig. 2 shows 12 K Mössbauer spectra obtained of sample A when left in air for periods between 0 and 75 days, and in Fig. 3 the relative area of the iron oxide is shown as a function of time for the sample kept in ambient air. After 7 days, or more, of exposure to air the hyperfine parameters of two sextets used to fit the magnetically split oxide spectrum are very similar to those immediately after sample production, possibly with a slightly larger average magnetic hyperfine field.

The evolution of the oxidation of sample B is illustrated in Fig. 4 by Mössbauer spectra obtained at 12 and 80 K for different exposure times (0–130 weeks). As for sample A, the relative amount of iron oxide increases with the time of exposure to ambient air. The initial fraction of iron oxide of sample B is approximately 65% as deduced from the 12 K Mössbauer spectrum. This fraction is found to attain values of approximately 69%, 69% and 75% after 1, 2 and 4 weeks, respectively. The average hyperfine parameters of the oxide component are $B_{\text{hf}} \approx 50.5$ T, $\delta \approx 0.47$ mm s $^{-1}$, and a negligible quadrupole shift for all spectra obtained at 12 K. The same hyperfine parameters were deduced for the sample exposed to air for 130 weeks, but the fractional area of the oxide component has increased to about 96%.

The spectra obtained at 80 K are difficult to fit, even by using several sextets. This may partly be due to relaxation phenomena, e.g. superparamagnetic relaxation, but the application of a magnetic field of 0.6 T did not change the magnetic hyperfine splitting of the oxide component of sample B immediately after the preparation. This result indicates that the magnetic moment of the oxide phase particles is very small. The average magnetic hyperfine field is about 48.5 T for all spectra of sample B at 80 K, and the relative area of

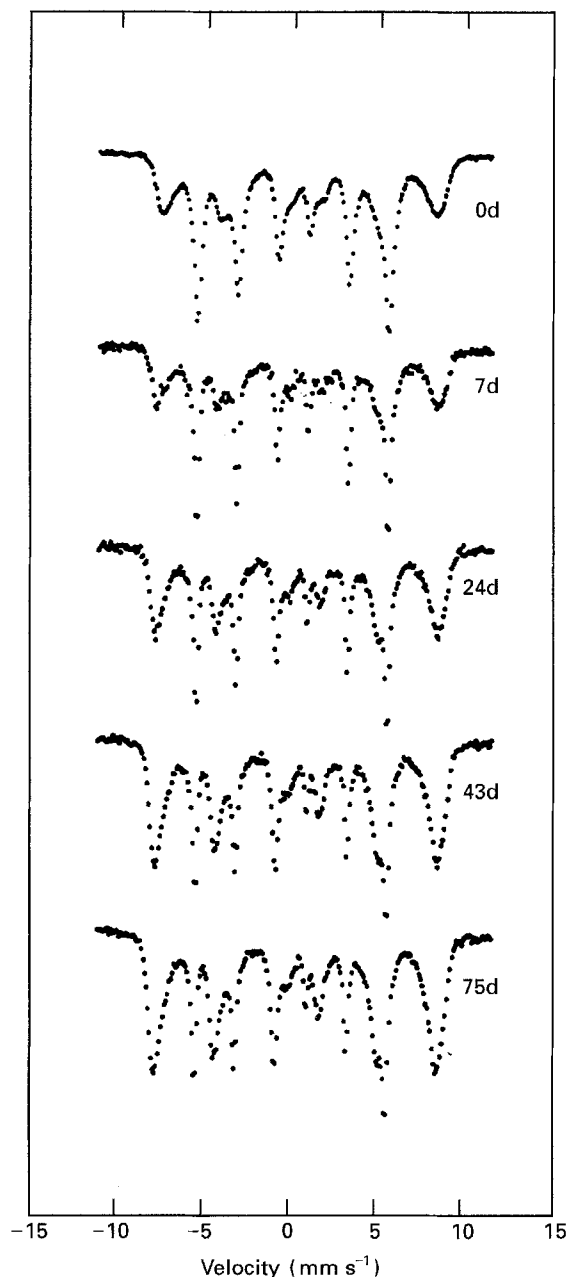


Figure 2 Sample A exposed to air for the periods indicated in the figure. The Mössbauer measurements were performed at 12 K.

the oxide phase is deduced to be 56%, 65%, 65%, 71%, and 93% after 0, 1, 2, 4, and 130 weeks, respectively.

It should be noticed from Fig. 4 that in the spectra obtained at 12 K, the intensity of line 1 of the oxide component is larger than that of line 6 of the same component (situated at approximately $\pm 8 \text{ mm s}^{-1}$), while in the spectra obtained at 80 K, these intensities are reversed.

Spectra of sample B at 5 K, obtained after 130 weeks in ambient air, are shown in Fig. 5. The application of a magnetic field of 4.3 T applied parallel to the Mössbauer γ -ray direction did not cause lines 2 and 5 to disappear, as would normally be the case for a ferrimagnetic oxide ($\gamma\text{-Fe}_2\text{O}_3$ and Fe_3O_4). Instead, the relative intensities of the two lines increase. However, this is merely a result of the large broadening of the outer lines of the oxide component. In fact, the effect of the large applied magnetic field is solely to

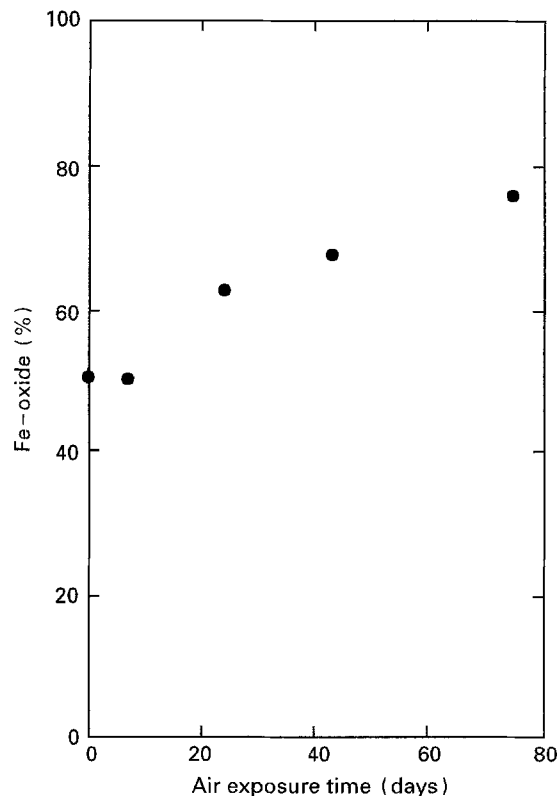


Figure 3 The fraction of iron oxide in sample A as a function of time of exposure to air.

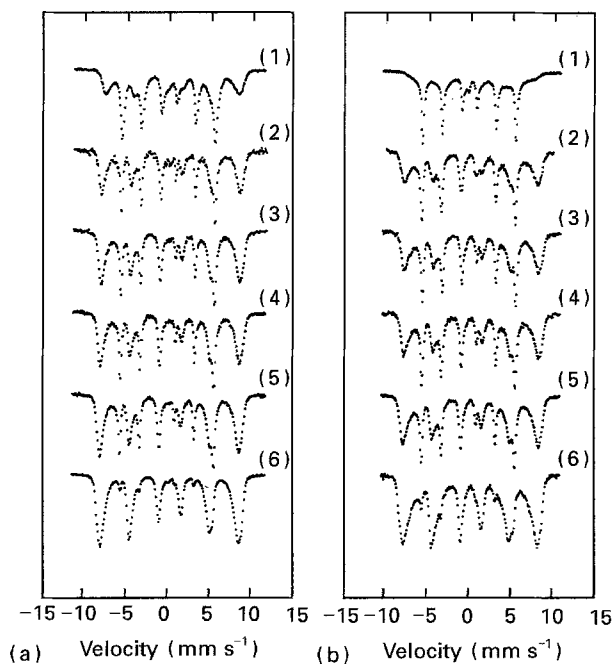


Figure 4 Mössbauer spectra of sample B as a function of air exposure time: (2) 0, (3) 1, (4) 2, (5) 4, and (6) 130 weeks. Spectrum (1) is of sample A without air exposure; (a) spectra obtained at 12 K and (b) spectra obtained at 80 K.

broaden the absorption lines, likewise the behaviour observed for sample A (cf. Fig. 1).

Fig. 6 shows Mössbauer spectra of sample B (130 weeks in air) as a function of measurement temperature. The magnetic hyperfine splitting of the oxide component is seen to decrease rapidly at temperatures above 190 K. At 295 K the magnetic splitting of the

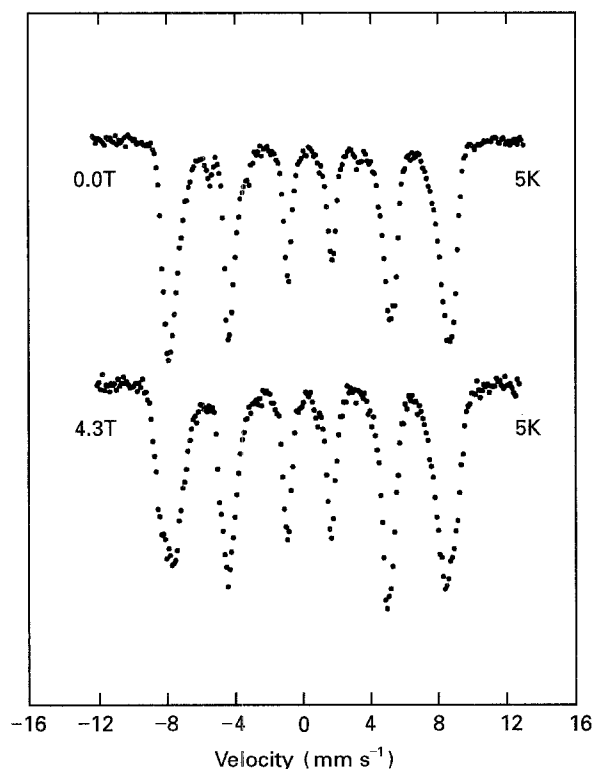


Figure 5 Mössbauer spectra of sample B after exposure to air for 130 weeks. The spectra were collected at 5 K with and without a magnetic field applied parallel to the Mössbauer γ -rays.

Mössbauer spectrum has almost completely collapsed, apart from the α -iron component. Fig. 7 illustrates the effect of applying a magnetic field of 0.6 T perpendicular to the γ -ray direction. At 80 K, the effect of an applied field is unnoticeable, at 190 K the effect is to sharpen the lines, while at 295 K some magnetic splitting of the otherwise relaxed spectrum can be noticed. This indicates that the collapse of the magnetic splitting at around 190 K is not due to a phase transition to a paramagnetic state, but rather due to superparamagnetic relaxation. The rather weak effect of the applied field indicates that the magnetic moment of the oxide particles is small.

4. Discussion

The electron diffraction patterns revealed that the oxide phase had a cubic structure, which indicates that the oxide phase is Fe_3O_4 and/or $\gamma\text{-Fe}_2\text{O}_3$. However, the average magnetic hyperfine field ($B_{\text{hf}} = 48.0\text{--}50.5$ T) of the oxide phase at around liquid helium temperature is clearly smaller than that of bulk $\gamma\text{-Fe}_2\text{O}_3$ ($B_{\text{hf}} \approx 52.0$ T [12]). The Mössbauer spectrum of Fe_3O_4 is rather complicated at these temperatures, but by a comparison of the spectra of Fig. 5 with spectra of a pure Fe_3O_4 bulk sample [13, 14], it is clear that the Mössbauer spectrum of the oxide phase is different from that of a pure bulk Fe_3O_4 spectrum. From the Mössbauer spectroscopy and the electron diffraction studies it therefore seems most likely, as has also been concluded in some other works on oxidation of ultrafine iron particles [1, 3, 5, 10], that the oxide layer is a mixture of Fe_3O_4 - and $\gamma\text{-Fe}_2\text{O}_3$ -like phases, but with the magnetic properties modified due to the

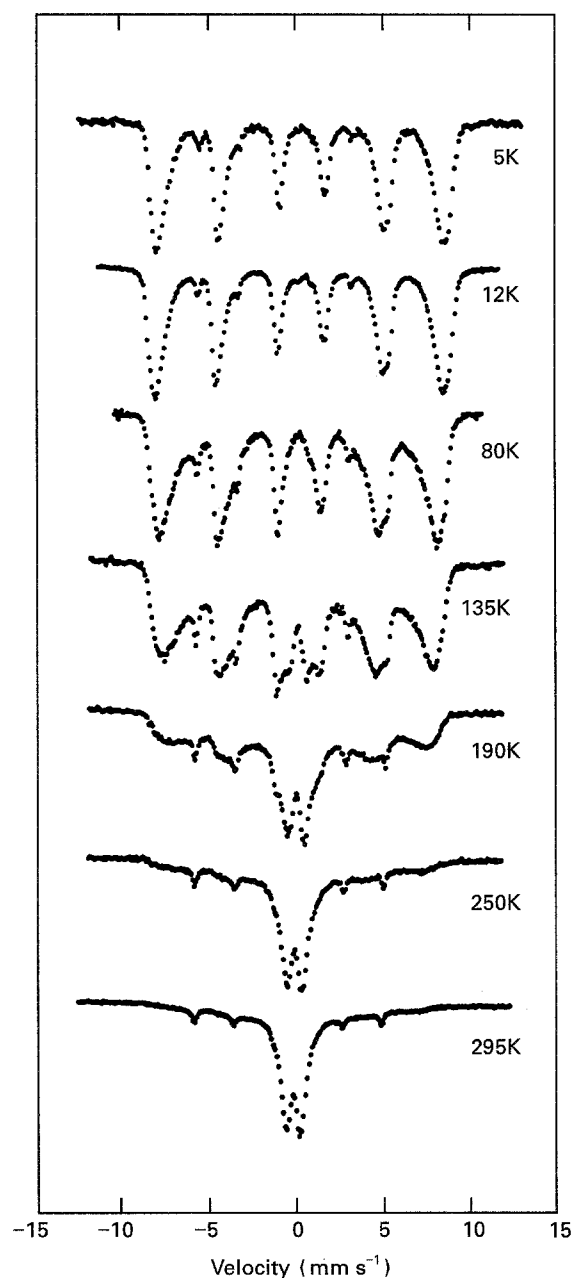


Figure 6 Mössbauer spectra of sample B, exposed to air for 130 weeks, as a function of measurement temperature.

finite size of the crystallites. The Mössbauer spectrum obtained at about 80 K of a one-to-one compositional mixture of bulk Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ [10] is still quite different from that of the oxide component in Fig. 4. However, the small size of the oxide crystallites implies that essentially all iron atoms are at an interface. The magnetic properties should therefore also be expected to be different from bulk properties.

If, as we suggest, part of the oxide phase consists of Fe_3O_4 , the insulator–metal transition (Verwey transition) should be observable as a change of asymmetry of the Mössbauer spectrum of the oxide phase when passing this transition temperature. Such a transition has not been seen in previous works on Mössbauer spectroscopy investigations of corrosion products, although Fe_3O_4 has been argued to make up about 50% of the corrosion product (see, for example, [10]). However, as was pointed out in the context of Fig. 4, the asymmetry changes for sample

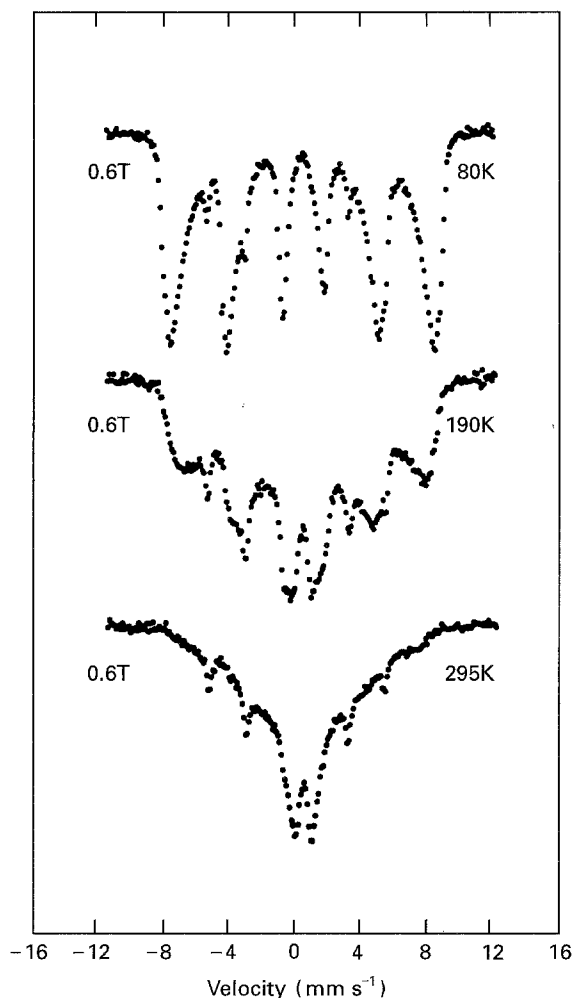


Figure 7 As Fig. 6 but with 0.6 T applied perpendicular to the Mössbauer γ -ray direction.

B between 12 and 80 K, i.e. a Verwey transition, seems to occur in this temperature interval. For bulk γ - Fe_2O_3 , or any other iron oxide or oxyhydroxide, such a change of asymmetry does not occur [13]. For bulk Fe_3O_4 the Verwey transition takes place at about 119 K, but in Mössbauer studies of ultrafine Fe_3O_4 particles it has been found [14] that the Verwey transition of 6 nm Fe_3O_4 particles takes place between 4.2 and 80 K. Non-stoichiometry of magnetite also results in a decrease of the Verwey transition temperature [15]. The change of asymmetry of the Mössbauer spectra in Fig. 3 thus clearly indicates that a significant part of the oxide phase consists of an Fe_3O_4 -like phase. In the case of bulk Fe_3O_4 and γ - Fe_2O_3 being mixed in the compositional ratio of one-to-one, a change of asymmetry due to the Verwey transition is seen [10].

Bulk and large particles of Fe_3O_4 and γ - Fe_2O_3 are ferrimagnetic materials, which in a moderate magnetic field arrange their magnetic moments parallel to the applied field. This results in the disappearance of lines 2 and 5 in the Mössbauer spectrum when the field is applied parallel or anti-parallel to the γ -ray direction. Clearly, this is not the case for the spectra obtained of the oxide phase grown on ultrafine iron particles (cf. Figs 1 and 5). Indeed, the spectra were almost unaffected by a field of 4.3 T; only a broadening of the

lines was seen. This effect has also been observed in previous studies of oxide layers on particles [1] and films [4] and may be ascribed to spin-canting within the small oxide crystallites [1, 16]. Non-collinear spin structures have been observed in studies of small γ - Fe_2O_3 particles [16–18], in which case the amount of canted spins is found to increase with decreasing particle size [16]. This may be explained by the presence of an about 1.0 nm thick spin-canted surface layer [16, 17]. If the present oxide crystallites are smaller than about 2 nm this surface canting may affect all the atoms in the crystallites. The spin-canting effect has also been argued to be a volume and finite size phenomenon [19]. In either case, the spin-canting of the oxidized layer of the α -iron particles may be regarded as a surface/interface phenomenon due to the small dimensions.

If the spin-canting is isotropic the magnetic structure is termed a speromagnetic structure [20]. The resulting moment is then close to zero and an external magnetic field will primarily have the effect of line broadening. This seems to be the situation at low temperatures for the particles studied in the present work (cf. Figs 1 and 5). At temperatures at which the particles are superparamagnetic, the interaction between an applied field and the small magnetic moment of the particles results in a small magnetic hyperfine splitting (see Fig. 7). Similar results have been found in a study of speromagnetic ferrihydrite [21].

Non-interacting γ - Fe_2O_3 particles with diameters below 5 nm have superparamagnetic blocking temperatures below 80 K [22]. The present results show that the magnetic hyperfine splitting of the oxide components collapses at temperatures above 150 K (see Fig. 6). It is likely that this is because of a strong magnetic coupling between the α -Fe core and the oxide layer [23].

As discussed in the previous section, the relative area, $R(T)$, of the oxide components in the Mössbauer spectra decreases with increasing temperature. This area fraction is given by

$$R(T) = \frac{A_o}{A_o + A_\alpha} = \frac{f_o(T)N_o}{f_o(T)N_o + f_\alpha(T)N_\alpha} \quad (1)$$

where the subscriptions o and α denote the oxide and the α -Fe phases, respectively. In Equation 1, A is the area of the component in the Mössbauer spectrum, f is the f -factor, and N is the number of atoms in the phase.

Solving Equation 1 with respect to f_o yields

$$f_o(T) = \frac{N_\alpha}{N_o} \frac{R(T)}{1 - R(T)} f_\alpha(T) \quad (2)$$

The fraction N_α/N_o can be found from low-temperature measurements

$$\frac{N_\alpha}{N_o} \simeq \lim_{T \rightarrow 0} \left[\frac{1 - R(T)}{R(T)} \right] \quad (3)$$

We will assume $N_\alpha/N_0 = [1 - R(12K)]/R(12K)$. Combining Equations 2 and 3 then yields

$$f_o(80 \text{ K}) = \frac{1 - R(12 \text{ K})}{R(12 \text{ K})} \frac{R(80 \text{ K})}{1 - R(80 \text{ K})} f_\alpha(80 \text{ K}) \quad (4)$$

In the Debye model, the recoil-less fraction (f -factor) is given by

$$f = \exp\left(-\frac{3E_R}{2k_B\theta_D} \left[1 + 4\left(\frac{T}{\theta_D}\right)^2 \times \int_0^{\theta_D/T} \left\{x/[\exp(x) - 1]\right\} dx\right]\right) \quad (5)$$

where E_R is the recoil energy, k_B the Boltzmann constant, and T and θ_D the actual and the Debye temperature, respectively. Debye temperatures of α -iron foils have been reported [24, 25] to be in the range 310–421 K. Let us assume θ_D (α -Fe) = 425 K, which yields $f_o(80 \text{ K}) = 0.91$. From the analyses of the Mössbauer spectra shown in Fig. 4, and by the use of Equation 4, $f_o(80 \text{ K})$ is found to be about 0.69 at day zero of oxidation, which increases to about 0.75 upon further oxidation. These values correspond to Debye temperatures of the oxide of about 185 and 215 K, respectively. These values are in very good accord with other recent evaluations of the Debye temperature of the oxide component (189–206 K [6] and 192 K [9]). If, instead, we assume a θ_D (α -Fe) of 310 K, the same treatment as above yields values of θ_D (oxide) of about 145 and 190 K, respectively. Bulk magnetite has been found to have $\theta_D \approx 320 \text{ K}$ [26]. The present results indicate that the effective Debye temperature is lowest for the smallest oxide crystallites and increases with increasing thickness of the oxide overlayer. This may be explained by an enhanced vibrational amplitude of surface atoms, but it is likely that particle vibrations also make a significant contribution to the lowering of the estimated Debye temperature [27].

The Mössbauer studies show that the oxide layer grows very quickly at the very beginning of the oxidation (cf. Fig. 3), but the oxidation process slows down extensively after the first oxidation. In the Caberra–Mott model of oxidation [28, 29] the rate of oxide layer growth is given by

$$dx/dt = Ae^{-x_0/x} \quad (6)$$

where, at 295 K, $A \approx 5.4 \times 10^{-30} \text{ m s}^{-1}$ and $x_0 \approx 8 \times 10^{-8} \text{ m}^{-1}$ [30] and x is the thickness of the grown oxide layer. Integration of Equation 6 gives an expression for the time, t , required to grow an oxide film of thickness, x [30]

$$t = A^{-1}(x^2/x_0)e^{-x_0/x} \quad (7)$$

The time needed, at 295 K, to grow an oxide layer of thicknesses 1, 2, 3, and 4 nm is, from Equation 7 and using the values given by Ruckman *et al.* [30], found to be 0.2 fs, 40 s, 40 weeks, and 600 years, respectively. These values show that an oxide layer of about 2 nm is grown very quickly, within seconds after the exposure to air, while further oxidation proceeds very slowly.

The oxidation process of the metallic iron particles studied in this work thus seems to be well understood in the context of the Caberra–Mott model.

5. Conclusions

Mössbauer spectroscopy studies of the evolution of the oxidation of 5 nm α -iron particles, when exposed to ambient air at room temperature, shows that the oxidation of the outer 1–2 nm layer of the iron particles proceeds very rapidly. Thereafter, the oxidation proceeds rather slowly, in agreement with the Caberra–Mott model for the oxidation of metal surfaces. The oxide layer is concluded to consist of a mixture of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$. The magnetic hyperfine fields differ from that of the bulk constituents, which is considered to be an effect of the finite size of the oxide crystallites. In contrast to previous studies, a Verwey transition is observed for the oxide layer. Although the oxide components are considered to consist of ferrimagnetic crystallites, they do not respond to an applied field in the normal way for ferrimagnetic materials. This is explained as being due to strong spin canting of all the spins in the ultrasmall iron oxide crystallites. At elevated temperatures the fraction of the oxide component in the Mössbauer spectra was found to decrease. An analysis of this decrease in the view of the Debye model of the temperature dependence of the recoil-less fraction of Mössbauer γ -rays, the Debye temperature of the oxide crystallites was found to be about 215 K. The initial oxide layer seems to have a slightly lower Debye temperature ($\approx 185 \text{ K}$).

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