

Moessbauer studies of ultrafine iron-containing particles on a carbon support

Citation for published version (APA):

Boedker, F., Moerup, S., Oxborrow, C. A., Linderoth, S., Madsen, M. B., & Niemantsverdriet, J. W. (1992). Moessbauer studies of ultrafine iron-containing particles on a carbon support. *Journal of Physics: Condensed Matter*, 4(31), 6555-6568. <https://doi.org/10.1088/0953-8984/4/31/008>

DOI:

[10.1088/0953-8984/4/31/008](https://doi.org/10.1088/0953-8984/4/31/008)

Document status and date:

Published: 01/01/1992

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
- The final author version and the galley proof are versions of the publication after peer review.
- The final published version features the final layout of the paper including the volume, issue and page numbers.

[Link to publication](#)

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license above, please follow below link for the End User Agreement:

www.tue.nl/taverne

Take down policy

If you believe that this document breaches copyright please contact us at:

openaccess@tue.nl

providing details and we will investigate your claim.

Mössbauer studies of ultrafine iron-containing particles on a carbon support

F Bødker†‡, S Mørup†, C A Oxborrow†, S Linderoth†, M B Madsen§
and J W Niemantsverdriet¶

† Laboratory of Applied Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark

§ Physics Department, H C Ørsted Institute, Universitetsparken 5, DK-2100 Copenhagen Ø, Denmark

¶ Laboratory of Inorganic Chemistry and Catalysis, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

Received 14 April 1992

Abstract. Carbon-supported metallic iron particles with an average diameter of 3.7 nm have been studied *in situ* by Mössbauer spectroscopy in the temperature range 5–305 K and with external magnetic fields up to 4 T. Depending on the preparation conditions various amounts of amorphous Fe–C particles are also formed. The average magnetic hyperfine fields of the surface atoms of α -Fe particles are significantly larger than that of bulk α -Fe at 5 K, but decrease much faster with increasing temperature than the bulk hyperfine field. The superparamagnetic blocking temperature for the α -Fe particles is about 70 K, but after oxidation it decreases to about 50 K, indicating that the magnetic anisotropy energy constant of the oxidized particles is significantly lower than that of the metallic particles. The temperature dependence of the spectral area is similar in the metallic and the oxidized states. In both cases the vibrational modes are dominated by particle vibrations.

1. Introduction

Ultrafine magnetic particles with dimensions below a certain critical size (of the order of 100 nm) consist of a single domain. For a single-domain particle with uniaxial anisotropy the magnetic energy may be written as

$$E(\theta) = KV \sin^2 \theta \quad (1)$$

where K is the magnetic anisotropy energy constant, V the volume, and θ the angle between the magnetization direction and the easy direction of magnetization. When the particle size is below about 10–20 nm the particles become superparamagnetic at ambient temperature, i.e. the magnetization direction fluctuates between the energy minima at $\theta = 0$ and $\theta = \pi$. The relaxation time is given by [1, 2]

$$\tau = \tau_0 \exp(KV/k_B T) \quad (2)$$

‡ Present address: Department of Chemistry, University College of North Wales, Bangor, Gwynedd LL57 2UW, UK.

where k_B is Boltzmann's constant, T the temperature and τ_0 is of the order of 10^{-11} s.

Mössbauer spectroscopy has been used extensively for studies of ultrafine particles [3–8]. This technique is very sensitive to superparamagnetic relaxation effects when the relaxation time is of the order 10^{-7} – 10^{-10} s, corresponding to values of the parameter $KV/k_B T$ in the range of about 2.5–10. If τ exceeds 10^{-7} s the spectrum consists of six narrow lines, and when $\tau \leq 10^{-10}$ s the spectrum collapses to one or two sharp lines. In the intermediate range the spectrum consists of broadened and partially collapsed components. The blocking temperature, T_B , for an individual particle is defined as the temperature above which the magnetic hyperfine splitting disappears.

In ultrafine particles a large fraction of the atoms are present in the surface layer. If the contribution from these atoms to the Mössbauer spectrum can be identified, Mössbauer spectroscopy can be used to study surface effects in small particles. Moreover, Mössbauer spectroscopy also gives information about the vibrational motion of the atoms in the sample, and in several cases it has been found that vibrations of the individual particles may play a significant role in samples of ultrafine particles [9–13].

Ultrafine particles are often prepared on a support because this prevents them from sintering. Metallic iron particles have been prepared on different oxide supports, carbon supports, and in zeolites. When oxides (e.g. SiO_2 , Al_2O_3 or MgO) are used, the particle size is normally larger than 5 nm.

Carbon is a favourable support for making smaller metallic iron particles [14], and it is possible to obtain particle sizes as small as 2.5 nm [15]. Such particles are superparamagnetic even at 80 K [15, 16].

In this paper we present the results of a Mössbauer spectroscopy study of carbon-supported iron particles in the temperature range 5–305 K and with applied magnetic fields up to 4 T.

2. Experimental procedure

The samples were prepared by incipient wetness impregnation of an activated carbon black support with an aqueous ferric nitrate solution enriched with ^{57}Fe . Different concentrations of iron were used, and therefore different degrees of enrichment were needed to obtain good Mössbauer spectra. Supports were activated by baking in hydrogen at 673 K for 48 hours. The impregnated samples were slowly dried in air, gradually increasing the drying temperature to 398 K. Thin wafers of the dried powders were made in a press and these wafers were mounted in the Mössbauer *in situ* cell.

Further processing of the samples was carried out in the *in situ* cell to avoid contamination and oxidation. The reduced samples were made by passing high-purity hydrogen (better than 9.9995% pure) through the cell while slowly increasing the temperature of the sample. Temperatures up to 670 K can be reached with this equipment.

The construction of the *in situ* cell allows us to take Mössbauer spectra of the samples in the same vessel in which they were reduced, hence reducing the possibility of oxidation. This cell can be inserted into a helium cryostat with a superconducting magnet, so that we can obtain spectra over a range of temperatures from 5 to 570 K and with an external magnetic field up to 5 T. After the measurements of the reduced

samples were made, the samples were slowly oxidized in regular grade argon at room temperature. Spectra were then taken of the oxidized samples. In this paper we will report results for two of the most interesting samples, designated A and B in the reduced state and AO and BO in the oxidized state. Details of their preparation are given in table 1. A constant-acceleration Mössbauer spectrometer was used with a 50 mCi source of ^{57}Co in rhodium. The spectrometer was calibrated with a $12.5\ \mu\text{m}$ thick α -iron foil at room temperature. All isomer shifts are given relative to that of α -Fe at room temperature.

Table 1. Preparation conditions for samples A and B.

	Sample A	Sample B
Support	Kejtenblack ED-600JD $1250\ \text{m}^2\ \text{g}^{-1}$	Cabot Black Pearl 2000 $1475\ \text{m}^2\ \text{g}^{-1}$
% weight Iron	2.3%	0.8%
% ^{57}Fe	20%	95%
Drying	295 K for 7 days; 323 K, 24 h; 343 K, 48 h; 363 K, 72 h and 398 K for 56 h	as sample A
Initial reduction	348 K, 1 h; 393 K, 1 h and 523 K for 0.5 h	as sample A
Final reduction	603 K for 45 h	603 K for 36 h

The Mössbauer spectra were fitted with a modified version of the program described by Wivel and Mørup [17]. This program can fit one or two distributions of hyperfine fields to spectral data, as well as determine the quadrupole splitting and isomer shift of each distribution.

The relative line intensity ratios were allowed to vary as $3:x:1:1:x:3$, where the best values of x were determined by the program. This is necessary when full or partial alignment of magnetic moments is achieved with an external magnetic field.

3. Results

3.1. Sample A

Figure 1 shows Mössbauer spectra of sample A at temperatures between 5 and 305 K. At 5 K the spectrum is magnetically split. The relatively sharp lines in the spectra correspond to an α -Fe component with a magnetic hyperfine field of about 34 T, and an isomer shift of $0.13\ \text{mm}\ \text{s}^{-1}$. Besides the α -Fe component, components with broad lines are also present. At 35 K the relative area of the broad components has grown, and further increase of the temperature leads to a gradual reduction in the relative spectral areas of the magnetically split component, indicating the presence of superparamagnetic relaxation. At 305 K the spectrum has collapsed completely. This shows that all the particles are above their blocking temperature at 305 K.

This interpretation is verified by Mössbauer studies which show that the magnetic splitting can be restored above T_B by application of a small external magnetic field.

If the magnetic anisotropy energy is negligible compared to the Zeeman energy, the observed magnetic hyperfine field is given by [4, 5, 7]

$$B_{\text{obs}} = B_0 L(\mu B/k_B T) - B \quad (3)$$

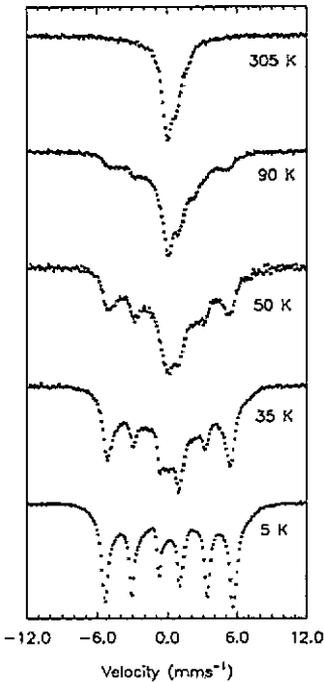


Figure 1. Mössbauer spectra of sample A, consisting of 2.3 wt % Fe on carbon, at different temperatures.

where $L(\mu B/k_B T)$ represents the Langevin function, B_0 is the magnetic hyperfine field in the absence of relaxation and μ is the magnetic moment of one particle. When $\mu B/k_B T > 2$ one may use the approximation

$$B_{\text{obs}} + B = B_0(1 - k_B T/\mu B). \quad (4)$$

If the easy directions of magnetization of the particles in a sample are distributed randomly, this expression is a good approximation even if the magnetic anisotropy is large [18]. Thus a plot of $B_{\text{obs}} + B$ as a function of B^{-1} should give a straight line with slope $B_0 k_B T/\mu$. We have measured the magnetic field dependence of the spectra at 150 K and, using equation (4), have estimated an average magnetic moment of $\mu = (4.6 \pm 1.1) \times 10^{-20} \text{ J T}^{-1}$ [19]. If the magnetization is assumed to be equal to that of bulk α -Fe, this value of μ corresponds to about 2250 iron atoms, a volume of $27 \pm 7 \text{ nm}^3$, giving an average particle diameter of $3.7 \pm 0.3 \text{ nm}$, assuming spherical particle shape.

Below the blocking temperature and in zero external magnetic field, the observed magnetic field is reduced relative to B_0 because of the influence of collective magnetic excitations [4, 5, 7, 20, 21]

$$B_{\text{obs}} = B_0(1 - k_B T/2KV). \quad (5)$$

An analysis of the low-temperature spectra in figure 1 shows that the magnetic hyperfine splitting of the α -Fe component decreases faster with increasing temperature than the bulk hyperfine field, in accordance with equation (5). Using the value of V , derived above, we obtain a magnetic anisotropy energy constant $K = (2.0 \pm 0.5) \times 10^5 \text{ J m}^{-3}$. This value falls between those obtained earlier for α -Fe particles

with average diameters of 2.5 nm [15] and 6.3 nm [7]. The size dependence of K is presumably related to the increasing importance of the surface anisotropy when the particle size decreases [7, 19].

For α -Fe particles with a diameter of 3.7 nm, 25–35% of the atoms are present in the surface layer. Therefore, it should be possible to study the properties of the surface atoms in sample A if the hyperfine parameters are different from those of the atoms in the core of the particles. However, when the spectra are smeared because of superparamagnetic relaxation, it may not be possible to distinguish the surface and core components. The superparamagnetic relaxation can, however, be suppressed by application of a large external magnetic field, and it may then be possible to study surface effects even above T_B . We have obtained spectra of sample A at temperatures up to 150 K with a magnetic field of 4 T applied parallel to the gamma ray direction.

For α -Fe particles with a magnetic moment of 4.6×10^{-20} J T $^{-1}$, the reduction in the magnetic hyperfine splitting due to relaxation effects is, according to equation (4), less than about 1% at temperatures below 150 K. Therefore the spectra reflect the temperature dependence of the magnetic hyperfine fields of the core and surface components [22]. Figure 2 shows the spectra together with the distributions of the magnetic hyperfine fields. The distributions for the narrow core component and the broad component are shown separately. The separation of the two components is possible because the broad component has an isomer shift which is about 0.40 mm s $^{-1}$ larger than that of the narrow component. At all temperatures lines 2 and 5 have, within the experimental uncertainty, zero intensity, indicating that all atomic magnetic moments are aligned parallel to the applied magnetic field. The broad distribution seems to contain two broad maxima, one in the range of 5–20 T, and the other in the range of 25–45 T. The tail of this distribution, extending above 35 T at 5 K, gradually disappears when the temperature increases. Thus the atoms with the largest magnetic hyperfine fields at 5 K exhibit a faster decrease of the magnetization with increasing temperature than bulk α -Fe.

After slow oxidation of sample A a series of Mössbauer spectra were obtained at temperatures between 5 and 295 K. The spectra are shown in figure 3. As was also observed for the non-oxidized sample (cf figure 1) the spectra obtained at the lowest measuring temperatures are magnetically split. The absorption lines are rather broad, which shows the presence of a distribution of magnetic hyperfine fields. At 5 K the average hyperfine field is 48.0 ± 0.5 T and the isomer shift is 0.47 ± 0.02 mm s $^{-1}$. The value of the magnetic hyperfine field is smaller than those of pure, crystalline iron oxides, but is close to that of amorphous Fe $_2$ O $_3$ prepared by sputtering [23]. At higher temperatures the magnetic hyperfine splitting gradually disappears because of superparamagnetic relaxation. The average blocking temperature, defined as the temperature at which 50% of the area has collapsed, is of the order of 50 K.

Spectra of sample AO, obtained in an external magnetic field of 4 T, are shown in figure 4. At 5 K the spectrum is little affected by the external magnetic field. However, application of the external field at 80 K results in a substantial broadening, indicating that the particles possess a small magnetic moment. Similar results have been found in a study of supermagnetic ferrihydrite [24].

Figure 5 shows the temperature dependence of the logarithm of the area of the Mössbauer spectra of sample A and sample AO. In both cases the data are normalized such that the area is equal to one at 0 K. It is seen that the data can be fitted well with a linear temperature dependence in both cases. The slopes are $-(5.52 \pm 0.2) \times 10^{-3}$ K $^{-1}$ and $-(5.22 \pm 0.2) \times 10^{-3}$ K $^{-1}$ for samples A and AO, respectively.

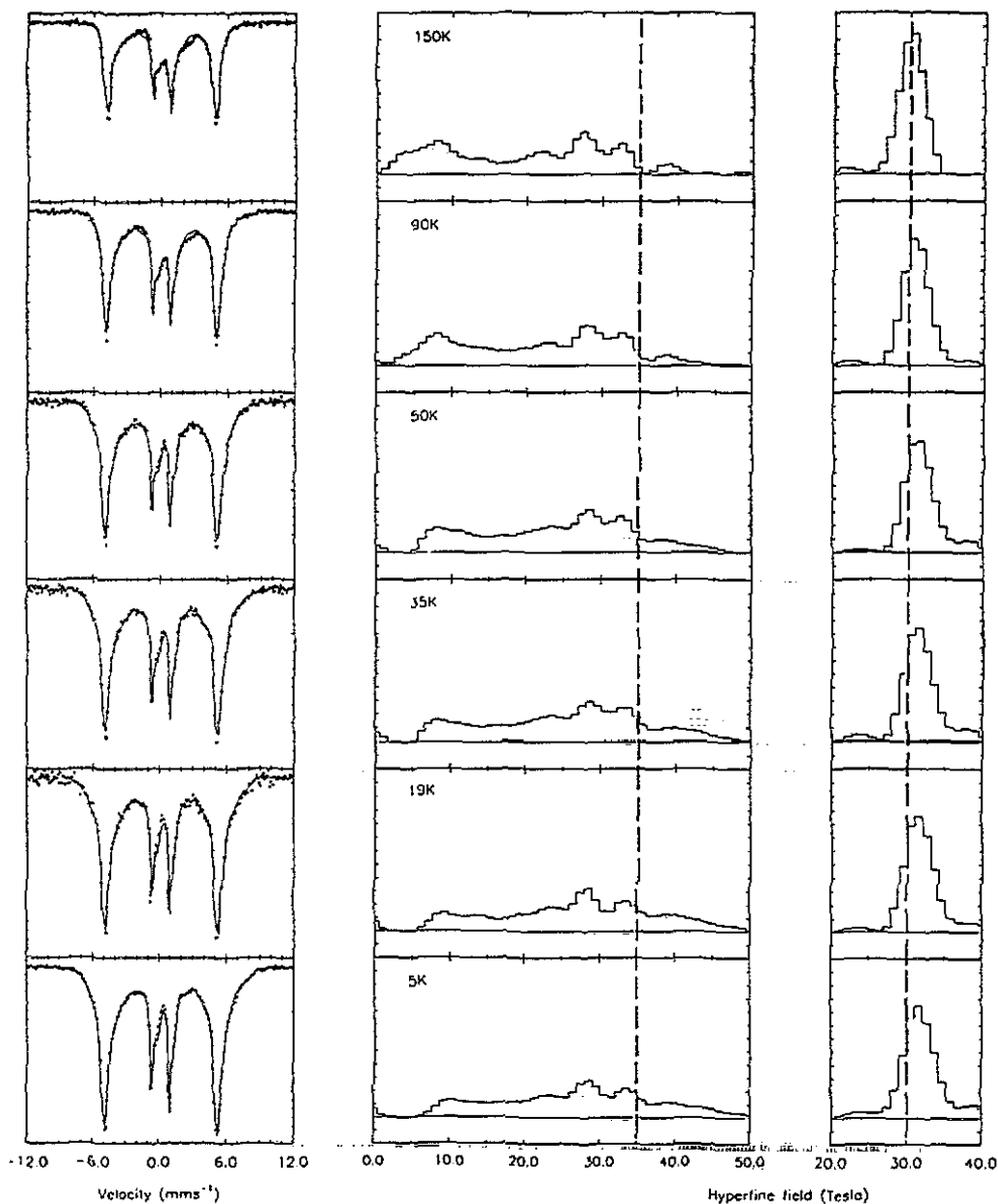


Figure 2. Mössbauer spectra of sample A, consisting of 2.3 wt % Fe on carbon, in the reduced state at different temperatures and with an applied magnetic field of 4.0 T. The distributions of magnetic hyperfine fields for the two components with different isomer shifts are also shown. The dashed lines at 35 and 30 T are guides for the eye.

Mössbauer spectra of sample B, which has a much lower concentration of iron than sample A, are shown in figure 6. Between room temperature and 20 K no magnetically split components can be seen in the spectra, and even at 5 K the spectrum is only partially magnetically split. However, application of a magnetic field of 4 T at 5 K leads to the disappearance of the central absorption lines and the spectrum then consists of a sextet with very broad absorption lines corresponding

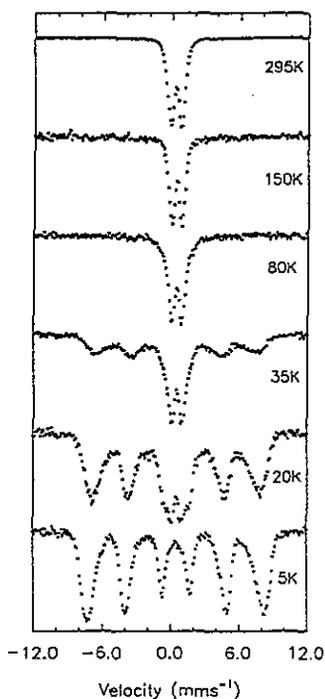


Figure 3. Mössbauer spectra of sample AO, consisting of 2.3 wt % oxidized Fe on carbon, at different temperatures.

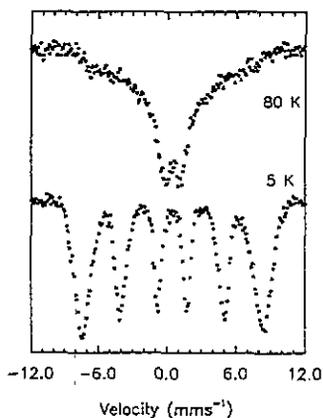


Figure 4. Mössbauer spectra of sample AO, consisting of 2.3 wt % Fe on carbon, in an applied magnetic field of 4.0 T at 5 and 80 K.

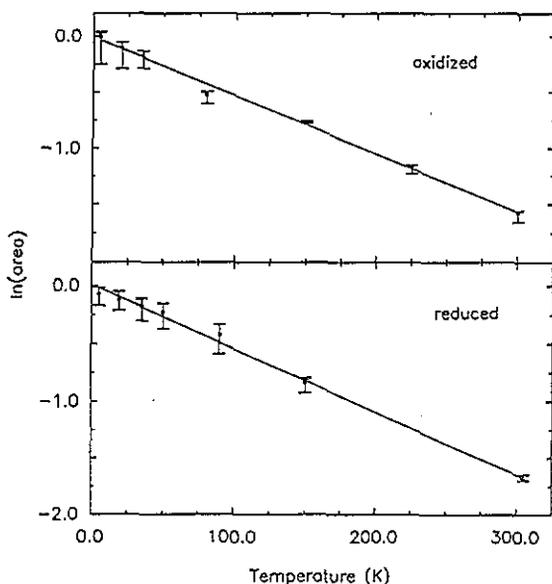


Figure 5. Temperature dependence of the logarithm of the area of the Mössbauer spectra of samples A and AO.

to an average hyperfine field of about 21 T. The results indicate that the particles

are superparamagnetic with an average blocking temperature of about 5 K. This indicates that the particles in sample B are extremely small. The very broad absorption lines indicate the presence of a broad distribution of magnetic hyperfine fields which suggests an amorphous structure of the particles. A fit to the spectrum with a distribution of magnetic hyperfine fields shows that lines 2 and 5 have very low intensities, indicating that the phase is ferromagnetic.

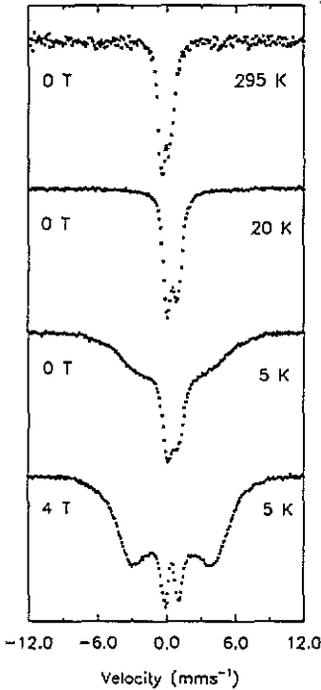


Figure 6. Mössbauer spectra of sample B, consisting of 0.8 wt % Fe on carbon. The temperatures and the values of applied magnetic fields are indicated.

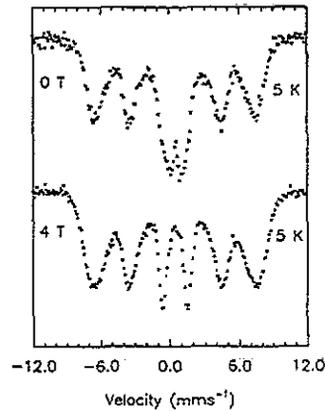


Figure 7. Mössbauer spectra of sample BO, consisting of 0.8 wt % Fe on carbon at 5 K without and with an applied magnetic field of 4 T.

Fe and C are the obvious candidates as the elements in this amorphous phase. We have therefore compared the spectrum with those of amorphous Fe-C films prepared by sputtering [25]. For a proper comparison it should be remembered that we applied a magnetic field of 4 T when recording the Mössbauer spectrum. Because the magnetic structure of the particles in sample B is ferromagnetic, a field of 4 T should be added to the hyperfine field. By comparing the magnetic hyperfine field distribution of our particles with those of amorphous Fe-C films of different compositions we estimate that the particles in sample B have an average carbon content of about 25 at.%. The isomer shift at 5 K for sample B is about 0.5 mm s^{-1} , while the isomer shifts of amorphous films with 25 at.% C are about 0.35 mm s^{-1} at 4.2 K.

Sample B like sample A, was studied by Mössbauer spectroscopy after slow oxidation. Figure 7 shows Mössbauer spectra of sample BO obtained at 5 K in zero and 4 T magnetic field applied parallel to the gamma rays. The measurements reveal superparamagnetic relaxation even at 5 K. This supports the conclusion that the par-

ticles in sample B are very small. The absorption lines are somewhat broader than for sample AO and the average hyperfine field is smaller (about 43.0 T). The lower value for the hyperfine field is possibly due to the presence of larger amounts of carbon in the particles compared to sample AO.

4. Discussion

4.1. Superparamagnetic relaxation

Samples A and AO both exhibit superparamagnetic relaxation effects. If the particles are non-interacting, the relaxation time is expected to vary in accordance with equation (2). Because the concentration of iron in the sample is low it is a good approximation to assume that the magnetic interaction between the particles is negligible. The oxidation of the reduced sample was performed slowly, and it therefore seems unlikely that the particles sintered during oxidation. Hence the particles in samples A and AO are expected to contain the same number of iron atoms. If it is assumed that the oxidized particles have the same density as crystalline α -Fe₂O₃ we find that the average diameter of the oxidized particles is about 4.8 nm.

By comparing figures 1 and 3 it is clear that the oxide particles have a lower blocking temperature than the metallic particles. The blocking temperatures are approximately 50 ± 10 K and 70 ± 10 K for samples AO and A, respectively. Therefore, the oxide particles seem to have a lower magnetic anisotropy constant than the metallic particles. If we use the value $K = (2.0 \pm 0.5) \times 10^5$ J m⁻³ for the metallic particles, a value estimated from the influence of collective magnetic excitations, and if we assume that τ_0 has the same value for the metallic and the oxidized samples we find that $K = (0.65 \pm 0.3) \times 10^5$ J m⁻³ for the oxidized particles. It is, however, possible that the values of τ_0 may be different for the two samples.

From the value of the average blocking temperature of sample B one can make a rough estimate of the particle size. The magnetic anisotropy energy constant of amorphous 3.3 nm Fe_{0.75}C_{0.25} particles, coated with oleic acid, is $(1.0 \pm 0.3) \times 10^5$ J m⁻³ and these particles have an average blocking temperature of about 50 K [26]. If we assume that the particles in sample B have similar values of both magnetic anisotropy energy constant and τ_0 we find by use of equation (2) that the average diameter is about 1.5 nm. The value of K may, however, depend on the particle size, as was seen for α -Fe particles, and it may also depend on the kind of molecules that are chemisorbed on the particles [7]. Therefore, this calculation of the particle size only gives an estimate of the order of magnitude of the particle diameter.

4.2. Surface magnetism

Surface effects play an important role in many applications of ultrafine particles and are therefore of great interest. The magnetic properties of smooth surfaces of single crystals and films have been studied by several authors [27-29]. The magnetic properties of surface atoms of ultrafine, supported particles may, however, for several reasons be different from those of flat surfaces. For example, atoms at edges, corners and planes may all behave differently, and atoms that interact with the support may exhibit properties which are different from those of atoms on free surfaces or with chemisorbed molecules.

The distributions of magnetic hyperfine fields for sample A (figure 2) contain information about the magnetic properties of the surface atoms, since about 25–35% of the atoms are in the surface layer. At all temperatures there is a tendency for the broad distributions to contain two maxima, one near 30 T and one in the range 5–15 T. The former component is absent in the spectrum of sample B at 5 K. The results therefore suggest that sample A contains iron atoms in three different types of environments. The sharp distribution with low isomer shift is ascribed to iron atoms in the interior of α -Fe particles, the low-field component with the larger isomer shift may primarily be attributed to amorphous Fe–C, and the high field component to metallic surface atoms. The presence of an amorphous Fe–C alloy is in fact not surprising. Nakayama *et al* [30] found that such alloys were formed at the interface between metallic iron and carbon in Fe/C multilayer films. The Fe–C alloy in sample A is possibly present at the interface between the iron particles and the carbon support, but the results for sample B show that Fe–C alloys can also be formed as separate particles when the iron concentration is sufficiently low.

It is of interest to find the distribution of hyperfine fields for the surface atoms alone. In order to obtain this we have fitted the 5 K spectrum at 4 T of sample B with a distribution of hyperfine fields and subtracted this Fe–C distribution function from the distribution function for sample A, as illustrated in figure 8. The upper distribution is that obtained for sample B, normalized to a total area of 100%. The middle distribution is that of the broad component with large isomer shift of sample A. The narrow distribution with the low isomer shift is not shown here. Together these two distributions add up to 100%. Consequently the broad distribution by itself is normalized to 55%—the narrow distribution accounting for 45%. The lower distribution was calculated by subtracting the upper one, multiplied by a factor of 0.3, from the middle one. The value 0.3 was chosen such that the difference spectrum is roughly zero between 15 and 20 T. The difference spectrum should therefore represent the distribution of surface hyperfine fields. The negative intensities in the difference spectrum at low hyperfine fields are probably due to artifacts in the fitting procedure. These effects will not concern us here. According to this analysis 70% of the iron atoms of sample A are present in α -Fe particles, and about 35% of these atoms are present in the surface layer. This is the order of magnitude expected for 3.7 nm particles. The difference spectrum shows that the surface hyperfine fields at 5 K are in the range from about 20–45 T. This range of values of magnetic hyperfine fields is in accordance with those found by Furubayashi *et al* [31,32] in studies of 2 nm α -Fe particles in organic liquids.

The distribution functions for sample A obtained at various temperatures (figure 2) give information about the temperature dependence of the surface hyperfine field. It is clearly seen that the tail in the broad distribution extending above 35 T at 5 K gradually disappears when the temperature is increased. At 150 K essentially all hyperfine fields are less than 35 T. This result shows that the surface hyperfine field of α -Fe decreases much more rapidly with increasing temperature than the bulk hyperfine field. Similar results have been obtained in studies of nanocrystalline iron [33] and in studies of thin films [29]. The results are also in qualitative accordance with recent calculations of the temperature dependence of the magnetization of atoms in small clusters [34].

4.3. The recoil-free fraction

The temperature dependence of the logarithm of the normalized spectral areas of

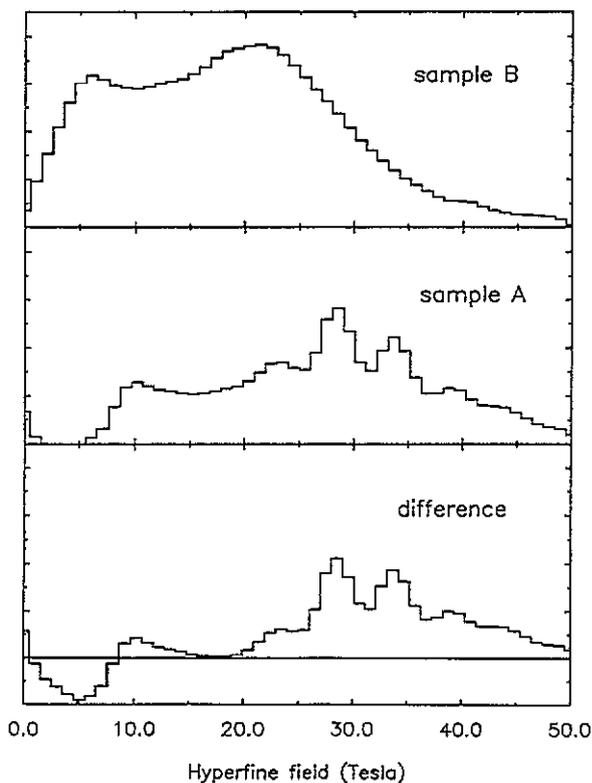


Figure 8. The upper part shows the distribution of magnetic hyperfine fields of sample B at 5 K with an applied magnetic field of 4 T. The middle part shows the equivalent results for sample A (only the broad component is shown). The lower part shows the difference between the two upper distributions after multiplying the distribution function for sample B by a factor of 0.3.

sample A and AO (figure 5) are well fitted with straight lines. Moreover, the slopes of the straight lines are quite similar. This behaviour is different from that normally observed for larger crystals, for which a linear temperature dependence is found only for $T \geq \frac{1}{2}\theta_D$ where θ_D is the Debye temperature. When using the Debye model for the phonon spectrum the recoil-free fraction at $T \geq \frac{1}{2}\theta_D$ can be written

$$f \simeq \exp\left\{-\left(6E_R/k_B\theta_D^2\right)T\right\} \quad (6)$$

where E_R is the recoil energy of a free atom ($E_R = 1.95 \times 10^{-3}$ eV for ^{57}Fe). If we use equation (6) to analyse the results shown in figure 5, we find that the Debye temperatures are 159 ± 10 K and 163 ± 10 K for samples A and AO, respectively. These values are much lower than those typical of macroscopic crystals. For example, for bulk $\alpha\text{-Fe}$, $\theta_D = 470$ K [11], and for $\alpha\text{-FeOOH}$ and $\alpha\text{-Fe}_2\text{O}_3$, $\theta_D \approx 500$ K [12].

In several earlier studies of small particles, similar results for the temperature dependence of the area were found, and it has been shown that the results can be explained by vibrations of the particles as a whole [11–13]. Thus the total mean square amplitude of the atoms is given by

$$\langle x^2 \rangle_{\text{tot}} = \langle x^2 \rangle_{\text{part}} + \langle x^2 \rangle_{\text{latt}} \quad (7)$$

where $\langle x^2 \rangle_{\text{part}}$ and $\langle x^2 \rangle_{\text{latt}}$ are the contributions from the particle vibrations and the phonons within the particles, respectively.

The f -factor can then be expressed as [9–12]

$$f_{\text{tot}} = \exp\{-k_\gamma^2 \langle x^2 \rangle_{\text{tot}}\} = \exp\{-k_\gamma^2 \langle x^2 \rangle_{\text{part}}\} \exp\{-k_\gamma^2 \langle x^2 \rangle_{\text{latt}}\} = f_{\text{part}} \times f_{\text{latt}} \quad (8)$$

where k_γ is the wave number of the gamma radiation.

The motion of carbon-supported iron particles may not be described by a simple model. It is possible that the particles can move more or less freely inside the pores of the carbon support or they may be bonded to the carbon, e.g. by an amorphous Fe–C interlayer. However, in both cases the porous carbon support cannot be considered as a rigid support. In the following we assume that the particle vibrations can be described formally as a harmonic oscillator with an angular frequency given by [9, 11]

$$\omega = (q/M)^{1/2} \quad (9)$$

where q is the force constant and M is the particle mass. The mean square amplitude is given by

$$\langle x^2 \rangle_{\text{part}} = (\hbar/2M\omega) \left\{ 2 / [\exp(\hbar\omega/k_B T) - 1] + 1 \right\} \quad (10)$$

At temperatures above the Einstein temperature, $\theta_E = \hbar\omega/k_B$ one finds

$$\langle x^2 \rangle_{\text{part}} = k_B T / q \quad (11)$$

i.e. the mean square amplitude is independent of the particle mass. We then find

$$\ln(f_{\text{part}}) = -k_\gamma^2 k_B T / q \quad (12)$$

If we analyse the results, shown in figure 5, on the basis of equations (12) and (9), we obtain the parameters given in table 2. The very low values of the angular frequencies and the Einstein temperatures are due to the large mass of the vibrating particles. It is seen that the condition $T > \theta_E$ is fulfilled at $T \geq 5$ K and this explains the linear temperature dependence of $\ln(A)$ down to 5 K. The low vibrational frequencies of particles and the corresponding low velocities also explains why particle motion does not contribute to the second-order Doppler shift [12]. The phonon contribution to $\langle x^2 \rangle_{\text{tot}}$ is expected to result in a curvature in the temperature dependence of $\ln(f_{\text{tot}})$ at $T \approx \frac{1}{2}\theta_D$, where θ_D is the Debye temperature corresponding to the lattice vibrations. However, within the experimental uncertainty there is no indication of such a curvature in figure 5. The results therefore suggest that $\langle x^2 \rangle_{\text{latt}}$ is negligible compared to $\langle x^2 \rangle_{\text{part}}$ for $T < 305$ K for the present samples.

Table 2. Parameters describing the particle vibrations of sample A.

Sample	q (J m ⁻²)	ω (s ⁻¹)	θ_E (K)
A	13.3	2.52×10^{11}	1.93
AO	14.0	2.16×10^{11}	1.65

The slopes of the straight lines in figure 5 are only slightly different. Because the slopes are independent of the mass this result shows that the effective force constants are nearly identical in the reduced and the oxidized states of the sample.

5. Conclusions

Small metallic iron particles with a diameter of approximately 3.7 nm have been studied with Mössbauer spectroscopy, at temperatures down to 5 K and in external magnetic fields of 4 T, with the sample under carefully controlled atmosphere in order to preserve the state of the reduced iron surface.

It is found that the superparamagnetic blocking temperature of metallic iron particles is significantly higher than that of the larger oxidized particles. This can be explained by a difference in magnetic anisotropy energy constants or by different pre-exponential factors in the Néel formula for superparamagnetic relaxation. The surface hyperfine fields for α -Fe particles are found to have a broad distribution in the range 25–45 T at 5 K. The surface hyperfine field decreases much more quickly with increasing temperature than the core hyperfine field. The areas of the spectra decrease much more quickly with temperature than that of bulk material. This is explained by particle vibrations. The strengths of the bondings between the particles and the carbon support are nearly identical for the metallic and the oxidized particles.

Acknowledgments

The work was supported by The Danish Council for Technical Research, The EEC (science programme) and the Haldor Topsøe Research Laboratories.

References

- [1] Néel L 1949 *Ann. Geophys.* **5** 99
- [2] Brown W F Jr 1963 *Phys. Rev.* **130** 1677
- [3] Kündig W, Bömmel H, Constabaris G and Lindquist R H 1966 *Phys. Rev.* **142** 327
- [4] Mørup S, Dumesic J A and Topsøe H 1980 *Applications of Mössbauer Spectroscopy* vol II, ed R L Cohen (New York: Academic) p 1
- [5] Mørup S 1987 *Mössbauer Spectroscopy Applied to Inorganic Chemistry* vol 2, ed G J Long (New York: Plenum) p 89
- [6] Dormann J L 1981 *Rev. Phys. Appl.* **16** 275
- [7] Mørup S, Topsøe H and Clausen B S 1982 *Phys. Scr.* **25** 713
- [8] Morrish A H and Haneda K 1983 *J. Magn. Magn. Mater.* **35** 105
- [9] Viegars M P A and Trooster J M 1977 *Phys. Rev. B* **15** 72
- [10] Hayashi M, Tamura I, Fukano Y and Kanemaki N 1981 *Surf. Sci.* **106** 453
- [11] Picone P J, Haneda K and Morrish A H 1982 *J. Phys. C: Solid State Phys.* **15** 317
- [12] Niemantsverdriet J W, Flipse C F J, Selman B, van Loef J J and van der Kraan A M 1984 *Phys. Lett.* **100A** 445
- [13] Hendriksen P V, Mørup S and Linderoth S 1992 *J. Phys.: Condens. Matter* **4** 3109
- [14] Jung H J, Vannice M A, Mulay L N, Stanfield R M and Delgass W N 1982 *J. Catal.* **76** 208
- [15] Christensen P H, Mørup S and Niemantsverdriet N W 1985 *J. Phys. Chem.* **89** 4898
- [16] Niemantsverdriet J W, van der Kraan A M, Delgass W N and Vannice M A 1985 *J. Phys. Chem.* **89** 67
- [17] Wivel C and Mørup S 1981 *J. Phys. E: Sci. Instrum.* **14** 605
- [18] Mørup S, Christensen P H and Clausen B S 1987 *J. Magn. Magn. Mater.* **68** 160
- [19] Bødker F, Mørup S and Niemantsverdriet J W 1992 *Catal. Lett.* **13** 195
- [20] Mørup S and Topsøe H 1976 *Appl. Phys.* **11** 63
- [21] Mørup S 1983 *J. Magn. Magn. Mater.* **37** 39
- [22] Bødker F, Mørup S, Oxborrow C A, Madsen M B and Niemantsverdriet J W 1992 *J. Magn. Magn. Mater.* **104–7** 1695
- [23] van Diepen A M and Popma Th J A 1978 *Solid State Commun.* **27** 121

- [24] Madsen M B, Mørup S and Koch C J W 1986 *Hyperfine Interact.* 27 329
- [25] Bauer-Grosse E and Le Caër G 1987 *Phil. Mag.* 56 485
- [26] Mørup S, Bødker F, van Wonerghem J, Madsen M B and Bentzon M D 1989 *Hyperfine Interact.* 51 1071
- [27] Shinjo T 1991 *Surf. Sci. Rev.* 12 51
- [28] Przybylski M, Korecki J and Gradman U 1991 *Appl. Phys. A* 52 33
- [29] Gradman U 1991 *J. Magn. Magn. Mater.* 100 481
- [30] Nakayama N, Katamoto T, Shinjo T and Takada T 1988 *J. Phys. F: Met. Phys.* 18 443
- [31] Furubayashi T, Nakatani I and Saegusa N 1987 *J. Phys. Soc. Japan* 56 1855
- [32] Furubayashi T and Nakatani I 1990 *IEEE Trans. Magn.* MAG-26 1855
- [33] Herr U, Jing J, Birringer R, Gonser U and Gleiter H 1987 *Appl. Phys. Lett.* 50 472
- [34] Hendriksen P V, Linderroth S and Lindgaard P-A 1992 *J. Magn. Magn. Mater.* 104-7 1577