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Linderoth, Søren; Mørup, Steen

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Ultrasmall iron particles prepared by use of sodium amalgam

S. Linderoth and S. Mørup

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

Ultrasmall magnetic particles containing iron have been prepared by reduction of iron ions by the use of sodium in mercury. Mössbauer studies at 12 K show that the magnetic hyperfine field is significantly larger than in bulk α-Fe, suggesting that an iron mercury alloy rather than α-Fe has been formed. The particles exhibit superparamagnetic relaxation above 120 K.

I. INTRODUCTION

Ferrofluids consisting of transition-metal particles dispersed in a liquid metal have an inherent advantage compared to conventional ferrofluids because they are excellent heat and electrical conductors. The iron-mercury system is such a system and has been studied extensively in the past.[1-3] The standard method for preparation of iron-mercury ferrofluids is by electrolysis of iron in aqueous solution with a mercury cathode under vigorous stirring. It has been assumed that microcrystals of α-Fe are produced by this method, and magnetization measurements have so far been interpreted with this assumption. However, very recent Mössbauer spectroscopy studies on iron-mercury ferrofluids have revealed magnetic hyperfine fields of 39–40 T at 12 K (Refs. 4 and 5), which is significantly larger than the 34.7 T for single domain α-Fe particles.

In this paper we present preliminary Mössbauer spectroscopy studies on an iron-mercury ferrofluid prepared by another method—by reducing the iron ions to the metallic state by sodium amalgam. The results are compared with those for a system prepared by the electrolytic method.

II. EXPERIMENT

A sample of sodium amalgam was prepared by dissolving sodium in mercury. The amalgam used in this work contained about 2 wt. % Na. The sodium amalgam was poured into a beaker on a magnetic stirrer and a solution of 90% enriched ^{57}Fe metal dissolved in 10% H_2SO_4 was added. The iron ions were reduced to the metallic state through the reaction: $Fe^{2+} + 2\ Na \rightarrow Fe + 2\ Na^+$. The process ran for about 1 h. The produced iron amalgam was washed in acetone. A thin film for Mössbauer spectroscopy studies was prepared by squeezing a droplet of the ferrofluid and freezing it to liquid-nitrogen temperature.

A ferrofluid prepared by the electrolysis method has been studied previously.[5] Some of the results are included in this paper for comparison.

The Mössbauer measurements were carried out with a constant acceleration spectrometer using ^{57}Co in rhodium as the source. Isomer shifts are given relative to α-Fe at 295 K. Measurements with the sample held at temperatures at or above 80 K were made with the sample in a liquid nitrogen cryostat. For lower temperatures a closed-cycle helium cryostat was employed. In computer fits the Mössbauer absorption lines were described by Lorentzian lines. A least-squares method was used for the fitting procedure.

III. RESULTS

In Fig. 1 are shown Mössbauer spectra of the iron-sodium-amalgam obtained at different temperatures in zero applied field.

At 80 K the spectrum is clearly magnetically split. The spectrum is asymmetric; line 6 is deeper and narrower than line 1, showing that the spectrum consists of at least two sextets.

At slightly higher temperatures the spectrum collapses and at 120 K two lines around zero velocity constitute about 50% of the total area. At 225 K the Mössbauer spectrum has collapsed completely into two absorption lines positioned at about -0.1 and 0.6 mm s^{-1}. The high temperature spectrum resembles that of a ferrofluid produced by the electrolytical method.[5]

When applying an external magnetic field perpendicular to the γ-ray direction, the magnetic hyperfine splitting at 80 K increases, and the relative intensities of lines 2 and 5 increases (see Fig. 2). The average magnetic hyperfine field at 80 K, without and with a field of 0.7 T applied, is deduced to be 31.4 and 33.6 T, respectively.

The Mössbauer spectrum of an iron-sodium-amalgam sample, obtained at about 12 K, is shown in Fig. 3(a). The 12 K spectrum for an iron-amalgam sample, prepared by electrolysis, is also shown in Fig. 3(b). The two spectra are remarkably similar. The spectra are asymmetric and the lines are broad, showing that at least two magnetically split components are present. The average magnetic hyperfine field and the isomer shift are 38–39 T and about 0.25 mm s^{-1}, respectively, for both samples.

IV. DISCUSSION

The collapse of the magnetically split component when increasing the measuring temperature (see Fig. 1) occurs in a manner typical for superparamagnetic particles. This behavior has also previously been observed for an iron-amalgam.[5] In that case the interpretation was substantiated by
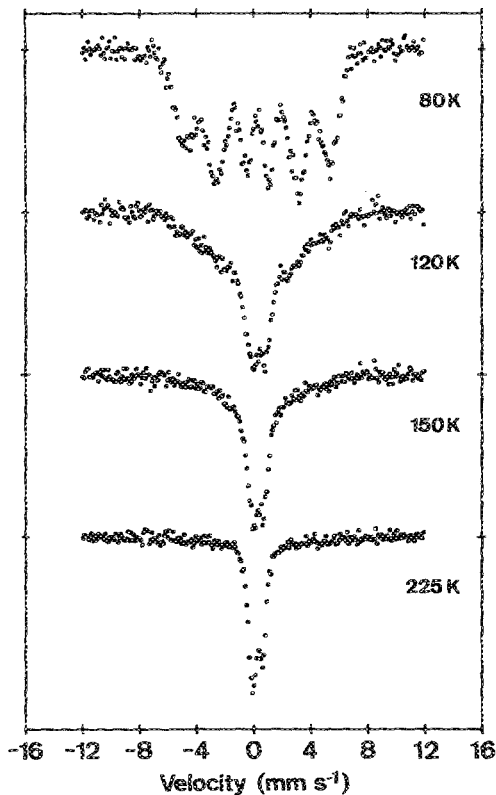
FIG. 1. Mössbauer spectra of the iron-sodium-amalgam obtained at the indicated temperatures in zero applied field.

the application of an external field, which had the effect of restoring the magnetic splitting.

The blocking temperature T_B is the temperature below which the Mössbauer spectrum is magnetically split, i.e., the temperature at which the superparamagnetic relaxation time is of the order of 5×10^{-9} s. At temperatures below T_B the spectrum is influenced by collective magnetic excitations, i.e., fluctuations of the direction of magnetization in directions close to the easy direction of magnetization.[6] These fluctuations lead to a reduction of the magnetic hyperfine splitting in the Mössbauer spectra, which for noninteracting particles with uniaxial anisotropy and with $kT \ll KV$ may be approximated by[6,7]
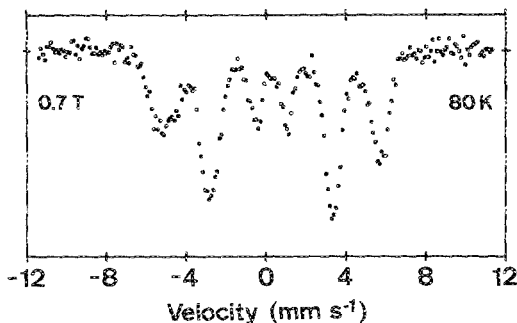
$$B_{obs} \approx B_0 (1 - kT/2KV), \qquad (1)$$

FIG. 2. Mössbauer spectra of the iron-sodium-amalgam, obtained at 80 K, with an external field applied perpendicular to the γ-ray direction.
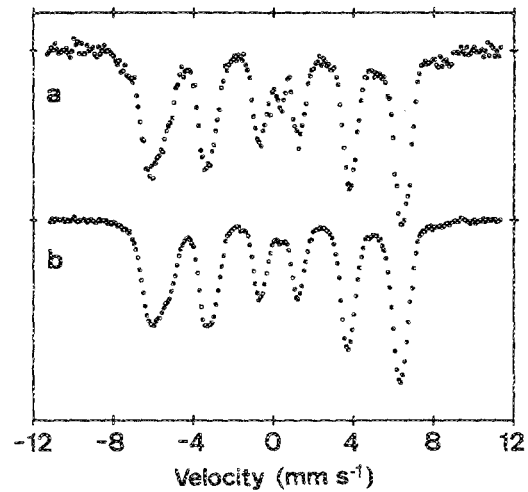

FIG. 3. Mössbauer spectra obtained at 12 K for (a) the iron-sodium-amalgam system and (b) an iron-mercury system prepared by electrolysis (see Ref. 5).

where B_0 is the saturation hyperfine field at temperature T, k is Boltzmann's constant, K is the magnetic anisotropy energy constant, and V is the volume of the individual particles.

The collective magnetic excitations can be partly suppressed by the application of an external field. As the magnetic hyperfine field will be directed opposite an external magnetic field, the true hyperfine field at 80 K, with 0.7 T applied, is about 34.3 T for the particles studied here. Taking this value to be B_0 at 80 K, the product KV can be evaluated to be about 6.5×10^{-21} J.

The superparamagnetic relaxation time of an isolated particle may be expressed by[8]

$$\tau = \tau_0 \exp(KV/kT), \qquad (2)$$

where τ_0 is in the order of 10^{-10}–10^{-12} s. At 120 K the relaxation time is about 5×10^{-9} from which $KV \approx 7.0 \times 10^{-21}$ J is deduced. It is, however, likely that the magnetic interaction between the particles is not negligible. Therefore, the estimated values of KV may be considered as an upper limit.[7]

The temperature dependence of the spectrum is very similar to that found for the sample prepared by electrolysis.[5] Considering the similarity of the Mössbauer spectra for the two samples produced by the two different methods, the volume, as deduced from a series of field dependence measurements on the sample prepared by electrolysis,[5] may be taken to be similar, i.e., $V \approx 10^{-25}$ m³ when the lattice constant is taken to be as for α-Fe. If the particles are spherical they are about 6 nm in diameter.

For spherical α-Fe particles with diameters of 6 nm, about 20% of the iron atoms are at the outer surface layer and their hyperfine parameters will be influenced by the neighbouring mercury. The second surface layer could also be influenced but it is not likely that the magnetic hyperfine fields at most iron nuclei in a 6 nm α-Fe particle would be considerably larger than for the bulk of single domain α-Fe particles at 12 K (= 34.7 T) and it is therefore not likely that the results can be explained solely by surface effects in α-Fe particles.

Iron and mercury do not form any stable alloys.[9] The solubility of iron has been estimated to be less than 10^{-5} wt. %.[9] However, the present Mössbauer results clearly show that the iron is present in a magnetic phase which is different from α-Fe. The isomer shift and the magnetic hyperfine field indicate that the iron is in the metallic state, i.e., in an alloy. The similarity of the spectra prepared using sodium amalgam and electrolysis show that the presence of sodium cannot explain the alloy formation in the samples. The results therefore indicate that the iron atoms interact with mercury and probably form a metastable iron-mercury alloy.

V. CONCLUSIONS

Mössbauer spectroscopy studies of ferrofluids based on iron in mercury have revealed that at 12 K the magnetic hyperfine fields at the iron atoms are considerably larger than in α-Fe. It is proposed that the iron is present in metastable iron-amalgam alloy particles. The particles possess superparamagnetic relaxation with a blocking temperature around 100 K. The Mössbauer spectra of iron amalgams prepared by two quite different methods, i.e., by chemical reduction by sodium and by electrolysis, are remarkably similar.

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