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Stability and magnetic properties of an iron-mercury alloy

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Abstract. Iron amalgams have been studied by Mössbauer spectroscopy and magnetization measurements between 7 and 425 K. The Mössbauer spectra at 12 K show that the iron is present in at least two different sites. After heat treatments the Mössbauer spectra change into the typical spectrum of α -Fe, and the magnetic moment per iron atom, at 275 K, increases. It is suggested that the iron forms a metastable alloy with mercury, which decomposes at about 360 K. The Fe-Hg alloy is found to be ferromagnetically ordered with a corresponding Curie temperature of about 445 K.

1. Introduction

Iron and mercury are only slightly dissolvable in each other—the solubility of iron in mercury has been estimated to be less than 10^{-5} wt % [1]. However, more iron is easily incorporated in mercury [2–5], which results in the formation of a colloid of magnetic particles in the mercury. These iron amalgams are typically produced either by an electrolytic reduction of iron ions at a mercury cathode [3], or by the reduction of iron ions to the metallic state by electron transfer from sodium atoms dissolved in mercury [4]. About 2.5 wt % of iron can be incorporated in mercury before it turns to gel.

The magnetic properties of iron amalgams have been studied extensively (see e.g. the reviews by Luborsky [6] and Charles and Popplewell [7]). The first interest in iron amalgams arose because they were observed to have relatively large coercivities [2–4]. These properties have been optimized by varying the shape and size of the magnetic particles in the amalgams [6, 8, 9]. The iron amalgams are *metallic ferrofluids*, which means that they are excellent conductors of both heat and electricity [7], in contrast to conventional ferrofluids.

From x-ray diffraction studies it has been concluded [5], that the magnetic particles in iron amalgams are α -Fe particles. Cobalt in mercury has, likewise, been quoted to be in the elemental form in mercury, while nickel and mercury seem to form a (non-magnetic) alloy [5]. Apart from the x-ray studies by Lihl [5], structural studies of as-prepared iron amalgams seem not to have been performed. In the analysis of the numerous magnetization studies of iron amalgams, the magnetic particles have been assumed to be elemental iron (α -Fe) particles [6–8].

Recently, Mössbauer spectroscopy has also been employed for the study of iron amalgams [10–13]. In addition to an α -Fe component in the Mössbauer spectra, van Wouterghem *et al* [10] found a component with a magnetic hyperfine field of 39–40 T. In

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studies by Linderoth *et al* [11, 12] on iron amalgams apparently no α -Fe was observed—the magnetic hyperfine fields were significantly larger than that for α -Fe. It has been suggested that iron and mercury can form a metastable alloy [11–13]. In this paper we study, using Mössbauer spectroscopy and magnetization measurements, the transition of the proposed metastable alloy phase to the stable α -Fe and liquid Hg phases upon heat treatment. The temperature dependence of the magnetization of the alloy is studied between 7 and 320 K and a very different temperature dependence than that for α -Fe is found. This is in favour of the idea of the formation of an Fe–Hg alloy.

2. Experimental procedure

The samples used for the present studies were prepared by first dissolving sodium in mercury. The amalgams contained about 2 wt % of Na. The sodium amalgam was then poured into a beaker and an aqueous iron solution was added. The mixture was agitated by a magnetic stirrer during the process time of about one hour. The iron amalgam was formed by the reaction $\text{Fe}^{2+} + 2\text{Na} \rightarrow \text{Fe} + 2\text{Na}^+$. After the end of the reaction the amalgam was washed with acetone.

Three sample preparations were made. For Mössbauer spectroscopy studies two preparations were made with a solution of 90% enriched ^{57}Fe metal dissolved in 10% H_2SO_4 , while another preparation was made by using an aqueous solution of FeSO_4 . One of each type of sample was magnetically concentrated in a strong magnetic field, which resulted in iron amalgams that had iron concentrations of about twice of that of the unconcentrated sample.

Heat treatments of the iron amalgams used for the Mössbauer spectroscopy studies were performed in the following manner: droplets of the iron amalgam were encapsulated in a small glass container, which was then evacuated and closed. The glass containers were kept at liquid nitrogen temperature until the time of heat treatment. Heat treatments were performed, for a period of one hour, at each of the following temperatures: 325, 350, 375 and 400 K.

Mössbauer absorbers of the samples were made by squeezing droplets of the ferrofluids into films, and then freezing the films to below the melting temperature of mercury. In this manner the absorbers could be made sufficiently thin to allow the Mössbauer γ -rays to penetrate the amalgam.

The Mössbauer measurements were carried out by using conventional constant-acceleration spectrometers with sources of ^{57}Co in rhodium. Measurements at 5 K were performed with the sample in a helium cryostat. 12 K spectra were obtained by attaching the absorber to the cold finger of a closed-cycle He cryostat, while measurements at higher temperatures were made in a liquid nitrogen cryostat. All isomer shifts are given relative to the centroid of the spectrum of a thin foil of α -Fe, measured at 295 K.

Samples for magnetization measurements were made by filling a small Cu tube with iron amalgam, and then closing it tightly. The samples were kept below the melting temperature of mercury when not subject to magnetization studies.

Magnetization measurements from 7–320 K were made in a SQUID magnetometer. Magnetization studies between 275–425 K were performed by using a vibrating-sample magnetometer.

3. Results

Mössbauer spectra of the unconcentrated and concentrated iron amalgams are shown in figure 1. The spectra were obtained at 12, 80 and about 225 K. The absorption was 1–2% in the most intense lines. The spectra for the unconcentrated sample have been discussed in a previous publication [12], but are shown here for the aid of discussion. The 12 K spectra reveal asymmetric sextets, which clearly demonstrates that the spectra consist of more than one sextet. Good fits were obtained when two sextets were used to fit the spectra, but the line widths were well above the experimental resolution of the spectrometer. The fitted line widths were 0.5–0.9 mm s⁻¹, which is 2–4 times larger than the line widths obtained from fits of bulk α -Fe spectra. The best fit with two sextets yields the following hyperfine parameters at 12 K: $B_{\text{hf}} = 39.7 \pm 0.5$ T, $\delta = 0.18 \pm 0.05$ mm s⁻¹ and $B_{\text{hf}} = 36.0 \pm 0.5$ T, $\delta = 0.37 \pm 0.05$ mm s⁻¹. The quadrupole shifts are negligible for both components. Both sextets have a relative area of about 50%. An incorrect statement of the isomer shifts was given in a report prior to this [11]; in that case the values of the isomer shifts were interchanged.

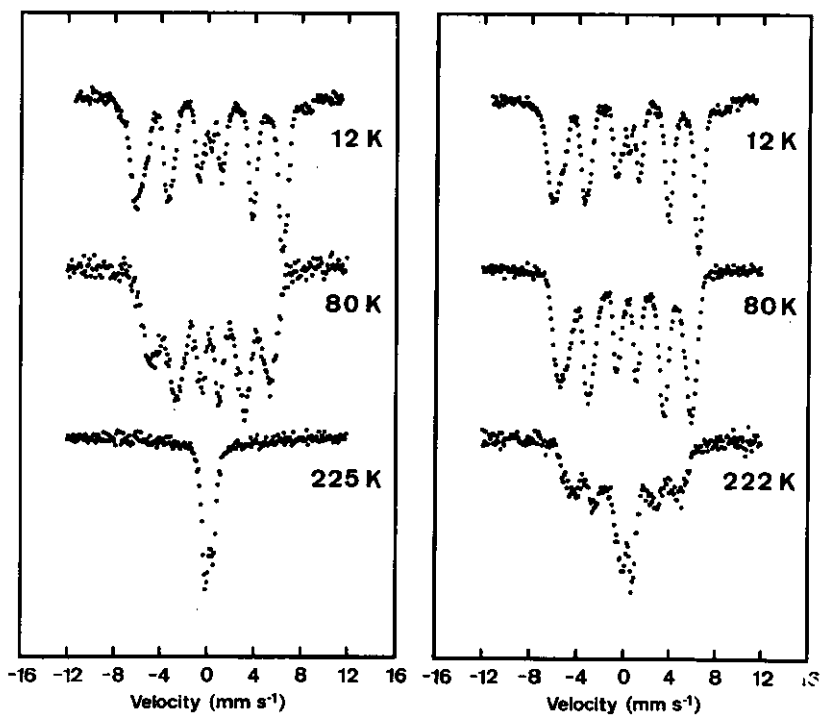


Figure 1. Mössbauer spectra of iron amalgams obtained at the indicated temperatures. The spectra to the right are for a sample concentrated in an inhomogeneous magnetic field.

Increasing the measuring temperature above 12 K leads to a collapse of the magnetic hyperfine splitting in the Mössbauer spectra of the unconcentrated sample. This collapse in iron amalgams has previously been found to be due to superparamagnetic relaxation [11]. This was demonstrated by the application of magnetic fields during the acquisition of Mössbauer spectra [11], which resulted

in a restoration of the magnetic hyperfine splitting due to blocking of the superparamagnetic relaxation through the interaction between the magnetic moment of the particle and the applied magnetic field. From an analysis of the induced magnetic hyperfine splitting as a function of applied magnetic field, the magnetic moment per particle was found to be of the order of $2 \times 10^4 \mu_B$, which, assuming spherical particles and a magnetic moment per Fe atom of $2\mu_B$, suggests that the particles are at least 6 nm in diameter [11, 12].

At 225 K the collapsed Mössbauer spectra have two clearly resolved absorption lines, positioned at -0.1 mm s^{-1} and $+0.6 \text{ mm s}^{-1}$. None of these have the position for bulk $\alpha\text{-Fe}$ at this temperature (about $+0.03 \text{ mm s}^{-1}$).

The Mössbauer spectra of the concentrated sample at 80 and 222 K are less collapsed than for the unconcentrated sample, which is a result of the magnetic interaction between the particles in the concentrated sample. However, at 12 K the Mössbauer spectra for the two samples resemble each other.

The heat-treated iron amalgam samples were studied by Mössbauer spectroscopy at 12 K. In figure 2 are shown the Mössbauer spectra obtained after heat treatments of the samples at different temperatures. A gradual change is seen, from a very asymmetric spectrum for the as-prepared sample to a symmetric spectrum after annealing at 375 K for one hour. It is also clearly seen that the magnetic hyperfine field of the annealed sample is substantially lower than for the as-prepared sample. The annealed sample can be fitted well with one sextet with $B_{\text{hf}} = 34.2 \pm 0.3 \text{ T}$, $\delta = 0.13 \pm 0.02 \text{ mm s}^{-1}$ and $QS = 0.00 \pm 0.02 \text{ mm s}^{-1}$.

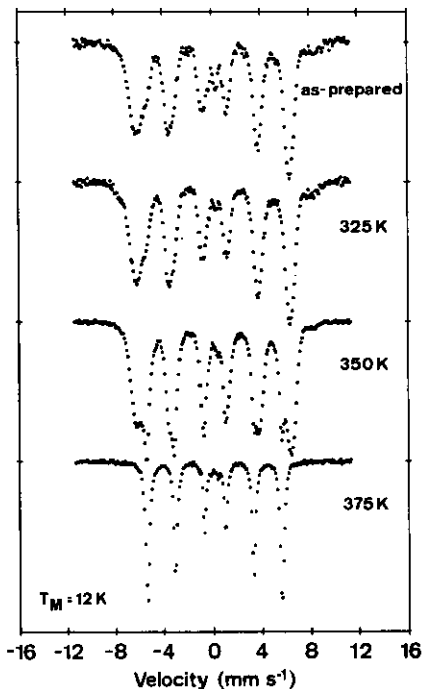


Figure 2. Mössbauer spectra of an iron amalgam after heat treatment at the indicated temperatures for a period of one hour. The measurements were obtained at 12 K.

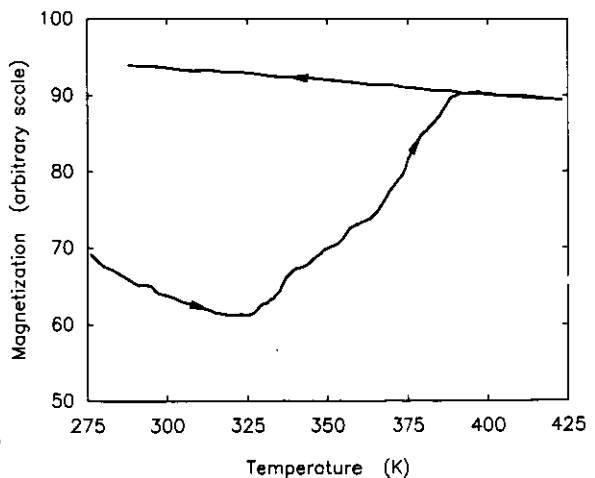


Figure 3. The magnetization of an iron amalgam sample measured as a function of temperature. The arrows show the direction of temperature change. The magnetization was measured in an applied field of 1.0 T.

Thermomagnetization measurements were made on an iron amalgam encapsulated in a Cu tube. Figure 3 shows the magnetization of the sample as a function of temperature, with a magnetic field of 1.0 T applied. The measurements initiated with the sample at 276 K. The temperature was increased at a rate of 1.5 K min^{-1} . After reaching a temperature of 425 K measurements were made at decreasing temperatures down to 285 K. The magnetization, at first, decreased with increasing temperature, but at about 325 K the magnetization started to increase, signifying a transition in the sample. At about 390 K the magnetization reached a maximum, whereafter the magnetization again decreased for increasing temperatures. When again lowering the temperature the magnetization continued to increase down to 285 K. At room temperature the magnetization is about 50% larger for the heat-treated amalgam than for the as-prepared amalgam.

The magnetization of the sample, both prior to the heat treatment and after the heat treatment, was measured as a function of applied field at 275 K. Figure 4 shows the magnetization curves. It is clear from these magnetization curves, that an applied field of 1.0 T, at 275 K, is not sufficient to reach saturation, but it is also clear that an extrapolation of the two magnetization curves to a larger applied field will yield different magnetization values for the two states of the sample. The magnetic moment per Fe atom is larger in the annealed sample than in the as-prepared sample when measured at 275 K. The increase of the magnetic moment per Fe atom, however, is not sufficient to explain the difference in shape of the magnetization curves; the magnetization curve for the heat-treated sample has a more rapid increase of the magnetization with field than the as-prepared sample, and the magnetization curve for the heat-treated sample has a smaller slope upon the approach to saturation magnetization than does the untreated sample. These differences indicate that the particles have grown in size during the heat treatment [14]. A proper estimation of particle size cannot be made from the measurements because the particles are interacting magnetically, as was seen by the Mössbauer spectroscopy studies on a similar concentrated sample (cf figure 1).

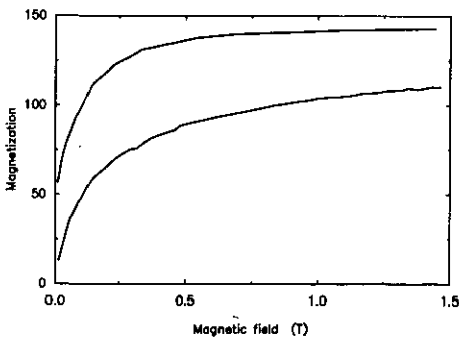


Figure 4. The magnetization as a function of applied magnetic field for the as-prepared sample (lower curve) and after heating to 425 K.

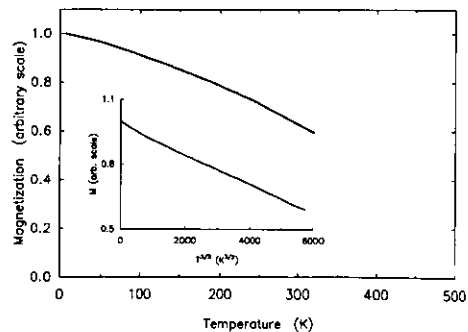


Figure 5. The magnetization as a function of temperature for the as-prepared iron amalgam. The applied magnetic field was 1.0 T. The inset shows the magnetization against $T^{3/2}$.

The magnetization of the as-prepared iron amalgam was measured down to 7 K in a field of 1.0 T. Figure 5 shows the magnetization between 7 and 320 K. An extrapolation of the magnetization curve reaches zero magnetization at a temperature of $445 \pm 40 \text{ K}$.

The inset in figure 5 shows the magnetization as a function of $T^{3/2}$. The magnetization is seen to depend almost linearly on $T^{3/2}$; a small deviation from the straight line at the lowest temperatures may be due to small amounts of paramagnetic atoms. A fit with a straight line yields a slope of $7.0 \times 10^{-5} \text{ K}^{-3/2}$.

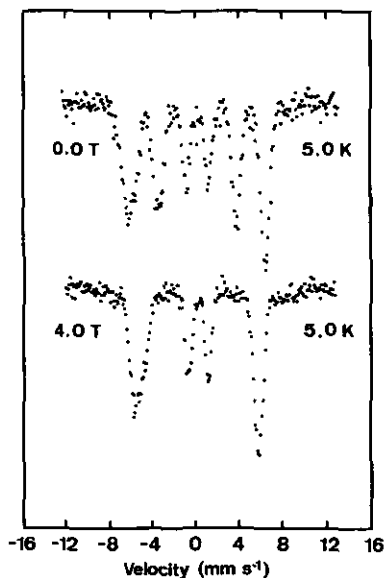


Figure 6. Mössbauer spectra of an as-prepared iron amalgam obtained at 5 K with zero (upper spectrum) and 4 T applied parallel to the direction of the recorded Mössbauer γ -rays.

Figure 6 shows Mössbauer spectra of an iron amalgam at 5 K with zero field applied and with 4.0 T applied parallel to the direction of the measured Mössbauer γ -rays. The magnetic field applied parallel to the γ -ray direction is seen to cause lines 2 and 5 in the Mössbauer spectrum to disappear and to move the positions of the remaining lines inwards. The widths of the absorption lines are unaffected by the applied field.

4. Discussion

The Mössbauer spectra obtained at 12 K show that iron atoms are present in the iron amalgams in at least two different sites. The magnetic hyperfine fields (36.0 T and 39.7 T) for the iron atoms in the as-prepared iron amalgam are different from that of bulk α -Fe at 12 K ($B_{\text{hf}} = 34.0$ T). However, for single-domain particles the demagnetization field is added to the bulk magnetic hyperfine field; for spherical α -Fe particles the hyperfine field then becomes about 34.7 T [15]. A maximum hyperfine field for α -Fe particles is achieved for plate-shaped particles, which can have hyperfine fields of about 36 T when magnetized along the normal to the plates. It could therefore be suggested that the 36 T component in the 12 K spectra is due to the presence of plate-shaped single-domain α -Fe particles, and that the 40 T component corresponds to iron atoms at the interface between the iron particles and the mercury matrix. On the other hand, the isomer shift corresponding to the 36 T component is very different from that of α -Fe iron, and the 225 K spectrum do not indicate the presence of α -Fe. These obvious differences between bulk α -Fe Mössbauer data and

the data for the iron amalgam may be argued to be due to the nearness of all iron atoms to the particle surface. The two components in the Mössbauer spectra both constituted about 50% which, in the picture of plate-shaped particles, means that all iron atoms must be nearby a surface/interface. Electron exchange between the iron and the mercury atoms may result in the observed changes of the isomer shifts with respect to bulk α -Fe. The changes of the Mössbauer spectra upon heat-treatment can, in this model, be understood as being due to particle growth, whereby the influence of the iron-mercury interface is reduced. However, the mercury was strongly agitated during the reaction, which should prevent the formation of e.g. dendrites [16]. The employed preparation procedure should lead to the formation of spherical particles.

Another model for explaining the differences between the Mössbauer parameters of the iron amalgams and those of α -Fe is that the iron is not present as α -Fe, but rather is in the form of an Fe-Hg alloy. Such an alloy will be metastable since, according to Hansen [1], iron and mercury do not form a stable alloy.

The idea that iron and mercury forms an alloy is reinforced by time-differential perturbed- γ -ray distribution studies of iron atoms implanted into solid mercury [17]. In those studies the Fe dose was sufficiently low that the Fe atoms were isolated from each other in the mercury matrix. Mishra *et al* [17] found that the isolated Fe atoms in Hg had strong magnetic moments. They also found that the Fe atoms occupied two different sites. Those sites may be the same two sites that are observed for iron in our Mössbauer spectroscopy studies.

The results of the annealing studies (cf figures 2 and 3 can, in the picture of alloy formation, be understood as being due to the decomposition of the metastable Fe-Hg alloy into liquid mercury and α -Fe particles. At the same time as the alloy decomposes into α -Fe and Hg, the iron may agglomerate to form larger particles. The occurrence of particle growth upon heat treatment was indicated by the magnetization-against-field studies of the iron amalgam sample in the untreated and the heat-treated states. Indeed, Luborsky [16] has found a rapid increase of the diameter of the spherical particles in iron amalgams occurring for temperatures above about 360 K. It is around this same temperature that the Mössbauer spectra show the appearance of α -Fe (cf figure 2), and it is also around 360 K that we observe the transition in the magnetization measurements (cf figure 3).

The measure of the temperature dependence of the magnetization of the as-prepared iron amalgam strengthen the belief that the iron and the mercury forms a metastable alloy. The magnetization decreases much faster with increasing temperature than it does for α -Fe. When the magnetization is plotted as a function of $T^{3/2}$ the dependence is almost linear (cf figure 4). Such a $T^{3/2}$ dependence follows from the spin-wave description of the temperature dependence of the magnetization [18], which has been found to be an appropriate model for bulk as well as for particle systems of ferromagnetically ordered crystalline and amorphous alloys [18, 19]. The slope in the $T^{3/2}$ plot for the as-prepared iron amalgams is about a factor of 20 larger than for bulk α -Fe ($3.3 \times 10^{-6} \text{ K}^{-3/2}$). In a Mössbauer study of the temperature dependence of the magnetic hyperfine fields of the two sextets a $T^{3/2}$ dependence was also found [13], with both slopes about a factor of ten larger than that for bulk α -Fe. The faster decrease of the magnetization with temperature for the iron amalgam compared to α -Fe also implies that the magnetic component in the iron amalgam will have a lower Curie temperature than α -Fe. The Curie temperature for the Fe-Hg particles is estimated to be about 445 K, which should be compared with the 1044 K for α -Fe.

The magnetic structure of the particles can be discussed from the Mössbauer spectroscopy studies at 5 K in 0 T and 4 T applied magnetic field (see figure 6). The measurements showed a decrease (by 4 T) of the magnetic hyperfine splitting when 4 T was applied, without an increase in the width of the absorption lines. This, together with the observation that lines 2 and 5 disappeared with the magnetic field applied parallel to the γ -ray direction, show that the proposed Fe–Hg alloy has a magnetic structure that is ferromagnetically ordered. The decrease of the magnetic hyperfine splitting as the magnetic field is applied shows that the hyperfine field is directed opposite to the magnetic moment, i.e. the hyperfine field is negative. This is in accord with the sign of the magnetic hyperfine fields found by Mishra *et al* [17] for isolated Fe atoms in solid mercury.

5. Conclusions

The Mössbauer spectra of as-prepared iron amalgams are significantly different from that of α -Fe. Heat treatments of the iron amalgams show a transition to α -Fe at about 360 K. The saturation magnetization of the iron amalgam sample at 275 K is clearly higher after the transition of the particles into α -Fe. The magnetization for the as-prepared iron amalgam decreases faster with temperature than it does for α -Fe; an extrapolation yields a Curie temperature of about 445 K for the magnetic particles in the as-prepared iron amalgam. The observations indicate that the particles in the as-prepared iron amalgam consist of an iron–mercury alloy, which decomposes at about 360 K into α -Fe and liquid mercury.

Acknowledgments

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