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Inter-particle interactions and the magnetocaloric effect in a sample of ultrafine $\text{Fe}_{1-x}\text{Hg}_x$ particles in Hg

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Abstract. Ultrafine magnetic particles consisting of a metastable iron–mercury alloy in Hg have been investigated by Mössbauer spectroscopy and magnetization measurements. It was found that the magnetic particles interact strongly, and around 100 K there is a transition from a superparamagnetic state to a state in which the magnetic moments of the particles are ordered. The magnetic entropy change induced by application of a magnetic field was determined in the temperature range from 70 to 200 K. When the sample was magnetized in 1 T the magnetic entropy change was almost constant in the temperature range from 130 to 200 K. In an applied field of 0.1 T, the entropy change was lower, and decreased with increasing temperature in the same temperature range. A model which takes into account the magnetic interactions between the particles was found to give a better description of the magnetic entropy change than a model for non-interacting superparamagnetic particles.

1. Introduction

Upon application of an external magnetic field, the magnetic spins in a material attempt to align with the field, thereby reducing the magnetic entropy of the spin system. If this process is performed adiabatically, the specimen temperature will rise. Conversely, if the magnetic field is removed adiabatically the specimen temperature will be reduced by the same effect. This temperature change is referred to as the magnetocaloric effect. The magnitude of this effect depends strongly on material-related properties including the size of the magnetic moment and the heat capacity of the system.

The magnetocaloric effect in paramagnetic materials has been widely used for magnetic refrigeration below liquid helium temperature [1]. Due to the potential for applications, extensive studies have been carried out in order to make use of the magnetocaloric effect also at higher temperatures. It has been suggested that ferromagnetic materials with high ordering temperatures [2–5] or magnetic nanometre-size particles [6–10] may be used for this purpose.

The magnetic properties of nanometre-scale materials differ considerably from those of bulk materials, and this will influence the observed magnetocaloric effect. Ultrafine magnetic particles, with particle diameters below approximately 20 nm, are single-domain particles and are superparamagnetic, i.e. the magnetization direction fluctuates with a temperature-dependent relaxation time, τ [11, 12]. The blocking temperature is defined

as the temperature at which τ is equal to the timescale of the experimental technique that is used to study the magnetic properties of the sample. Therefore different experimental techniques may yield different blocking temperatures.

In samples with a strong magnetic inter-particle interaction (dipole interaction and/or exchange interaction) the magnetic moments of the particles may order below a critical temperature [13–17]. Depending on, for example, the geometrical arrangement of the particles, the ordered state may have parallel spins (superferromagnetism) or a spin-glass-like structure. In practice, there will be a distribution in the strength of interactions because of, for example, the particle size distribution and the more or less random distribution of particles in the sample. Thus there will normally not be a uniquely defined transition temperature in a sample containing magnetic nanoparticles. Anyway, we use in this paper the term ‘ordering temperature’, by which we mean the temperature at which approximately half of the nanophase magnetic material is in a state which is ordered due to inter-particle interactions. The term ‘ordered state’ should be understood in a similar way.

In the superparamagnetic state the magnetic moment relaxes quickly, and the system is magnetically disordered, but the application of a magnetic field will lead to a more ordered state with a lower entropy. It has been shown [6–10] that the entropy change, and thus the magnetocaloric effect, in samples of ultrafine magnetic particles may be larger by several orders of magnitude than that of bulk materials. In a system consisting of strongly interacting particles, the entropy change above the ordering temperature is enhanced compared to that of non-interacting particles [6]. In such a system one may find a large magnetocaloric effect even at high temperatures.

The iron–mercury system was one of the first systems in which superparamagnetic relaxation was investigated in detail [18–23], and several studies have been carried out in order to elucidate the properties of this system [24–28]. The samples consist of ultrafine particles of a metastable ferromagnetic Fe–Hg alloy in Hg [27]. As the superparamagnetic relaxation is fast at relatively low temperatures, different experimental techniques may be applied to study the relaxation and yield information about the strength of the magnetic interaction. Here we present results of Mössbauer spectroscopy and magnetization measurements, which show that the magnetic properties of the samples are strongly influenced by magnetic inter-particle interactions. Furthermore, we present results of studies of the entropy change accomplished by applying moderate magnetic fields of 0.1 T and 1 T. It is found that the entropy change is enhanced due to the inter-particle interactions.

2. The magnetocaloric effect in samples of nanoparticles

According to basic thermodynamics and the thermodynamic Maxwell equation, the entropy change dS in a spin system can be calculated [6, 29] from

$$dS = \left(\frac{\delta S}{\delta T} \right)_B dT + \left(\frac{\delta M}{\delta T} \right)_B dB \quad (1)$$

where M is the magnetization, dT the change of the temperature, and dB the change of the applied magnetic field.

For a process at constant B , we have

$$\left(\frac{\delta S}{\delta T} \right)_B = \frac{c_B}{T} \quad (2)$$

where c_B is the heat capacity at constant B .

For a reversible adiabatic process $dS = 0$, in which case

$$dT = -\frac{T}{c_B} \left(\frac{\delta M}{\delta T} \right)_B dB. \quad (3)$$

This is the general expression for the temperature change when the applied field is changed.

For an isothermal magnetization process one can calculate the contribution from the magnetization to the entropy change by the use of equation (1):

$$\Delta S = \int_0^{B_1} \left(\frac{\delta M}{\delta T} \right)_B dB \quad (4)$$

where B_1 is the maximum applied magnetic field. Setting $T = T_i$ and $\Delta T = T_{i+1} - T_i$, one finds for small values of ΔT

$$\Delta S_i \approx \frac{1}{\Delta T} \int_0^{B_1} [M(T_{i+1}, B) - M(T_i, B)] dB \quad (5)$$

where ΔS_i is the entropy change of the spins obtained by isothermal magnetization from zero field to B_1 at the temperature T_i .

The entropy change can thus be calculated from the area enclosed between two isothermal magnetization curves divided by the temperature difference between the isotherms [30]. The corresponding temperature change will be

$$\Delta T = -\Delta S \frac{T}{c_B}. \quad (6)$$

In a sample of non-interacting superparamagnetic particles the magnetization is given by

$$M = n\mu L(a). \quad (7)$$

Here $L(a) = \coth(a) - 1/a$ is the Langevin function, n the number of particles per unit volume, μ the magnetic moment of a particle, and $a = \mu B / (k_B T)$ where k_B is Boltzmann's constant.

By differentiating (7) with respect to temperature, one obtains

$$\left(\frac{\delta M}{\delta T} \right)_B = nk_B \left(\frac{a^2}{B} \operatorname{cosech}^2(a) - \frac{1}{B} \right). \quad (8)$$

Inserting (8) in (4) and performing the integration, one obtains [19]

$$\Delta S = nk_B \left(1 - a \coth(a) + \ln \left(\frac{\sinh(a)}{a} \right) \right). \quad (9)$$

This equation gives the magnetic entropy change for isothermal magnetization of a superparamagnetic material where the magnetic interaction between the particles is negligible.

Above the ordering temperature of a system of strongly interacting particles with negligible anisotropy, $(\delta M / \delta T)_B$ is larger than that for similar non-interacting particles at the same temperatures [6, 30]. This will, according to equation (4), lead to a larger entropy change. Therefore, such a system may show a large magnetocaloric effect even at high temperatures. One can take into account the magnetic interaction between the nanometre-size particles by means of a mean-field model [14, 31–34]. In this model it is assumed that the magnetic field is applied parallel to the mean-field direction, that the

magnetic anisotropy is negligible, and that there is only one particle size. The magnetization of an ensemble of interacting particles may then be given as [14, 31–34]

$$M = \mu n b(T, B) \quad (10)$$

where $b(T, B)$ is an order parameter given [32] by

$$b(T, B) = L\left(\frac{3T_o}{T}b(T, B) + \frac{\mu B}{k_B T}\right) = L(x). \quad (11)$$

Here T_o is the ordering temperature of the system and $L(x)$ is the Langevin function. By differentiating (10) with respect to temperature, one obtains [34]

$$\left(\frac{\delta M}{\delta T}\right)_B = -\mu n \frac{L'(x)(3T_o b(T, B) + \mu B/k_B)}{T(T - 3L'(x)T_o)} dB \quad (12)$$

where

$$L'(x) = \frac{1}{x^2} - \frac{1}{\sinh^2(x)}. \quad (13)$$

Using equation (4) one obtains

$$\Delta S = -\mu n \int_0^{B_1} \frac{L'(x)(3T_o b(T, B) + \mu B/k_B)}{T(T - 3L'(x)T_o)} dB. \quad (14)$$

Equation (14) can be solved numerically.

3. Experimental procedure

A sample of iron–mercury alloy particles in Hg was prepared as described in [25]. The particles were concentrated by use of a weak magnet. The concentrated part of the sample was used for the experimental studies. It is the same sample as was investigated in [35]. For magnetic measurements a sample of the alloy was put into a cylindrical holder with diameter 3 mm and length 4 mm. The sample used for Mössbauer spectroscopy was prepared by squeezing a droplet of the liquid and freezing it in liquid nitrogen.

Mössbauer spectra were obtained using a constant-acceleration spectrometer with a 50 mCi source of ^{57}Co in rhodium. Isomer shifts are given relative to that of $\alpha\text{-Fe}$ at room temperature.

The magnetic measurements were performed with a vibrating-sample magnetometer from Oxford Instruments in which magnetic fields, B , up to 12 T can be applied and the sample temperature, T , varied between 4 K and room temperature. In the magnetometer there are two pairs of pick-up coils with different vertical distances, h , between the coils in each pair, the peak coils with $h = 7.5$ mm and the flat coils with $h = 15.3$ mm. In order to investigate any influence of the sample geometry [36], the magnetic moment of the sample was measured at 200 K with each of the coil pairs. The zero-field-cooled magnetization curve, M_{ZFC} , was measured on the sample that was initially cooled to 5 K in zero field. Then a small field (3–40 mT) was applied, and the magnetization measured in a constant field during heating. To obtain the field-cooled magnetization, M_{FC} , the sample was cooled to 200 K in zero field. This is well below the melting point of the sample, and still in the region where all the particles undergo superparamagnetic relaxation. Then a constant small field was applied, and the magnetization measured during cooling down to 10 K. The cooling and warming rates were 0.05 K s^{-1} . The initial susceptibility, χ_i , was determined from the slope of the isothermal magnetization curves in low fields.

Isothermal magnetization curves were measured in fields up to 1 T at different temperatures, with steps of $\Delta T = 5 \text{ K}$, in the range between 70 and 200 K.

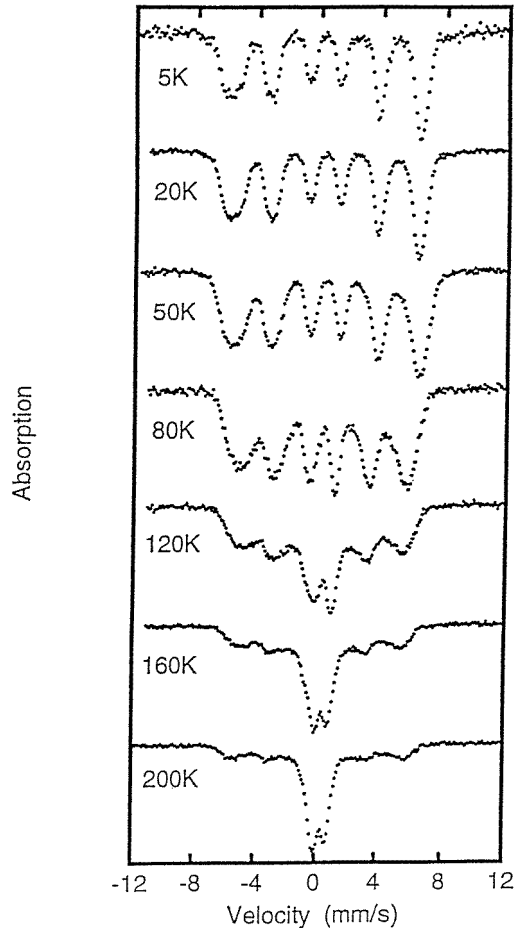


Figure 1. Mössbauer spectra of the Fe–Hg sample obtained in the temperature range from 5 to 200 K in zero applied magnetic field.

4. Results

Figure 1 shows Mössbauer spectra obtained in the temperature range from 5 to 200 K in zero applied magnetic field. The spectrum at 5 K could be fitted with two sextets which gave the following values for the magnetic hyperfine fields and the isomer shifts: $B_{obs} = 39.7 \pm 0.5$ T, $\delta = 0.18 \pm 0.02$ mm s⁻¹ and $B_{obs} = 36.1 \pm 0.5$ T, $\delta = 0.38 \pm 0.02$ mm s⁻¹ [35]. For both components the quadrupole shift was negligible. This suggests two main sites for the iron atoms. However, relatively broad lines are observed in the fit with the two sextets, which indicates a distribution of hyperfine fields, possibly caused by disorder. This is in accordance with previous results [25–28] for similar samples.

The Mössbauer spectra obtained above 80 K are significantly affected by superparamagnetic relaxation. This implies that the iron is present in small particles. The temperature T_B , defined as the temperature at which 50% of the spectrum is affected by superparamagnetic relaxation, is determined to 150 ± 20 K.

In the magnetic measurements we found that the sample position for maximum output

signal was about 3 mm above the position with the sample in the centre of the pick-up coils. There was no significant difference between the magnetic moments obtained with the peak and flat coils respectively. For the actual geometry a calibrated signal from the peak coils is expected to be about 9% lower than that from the flat coils [36]. From the observations we can conclude that the magnetic particles are concentrated in a smaller volume of the sample at its lower end.

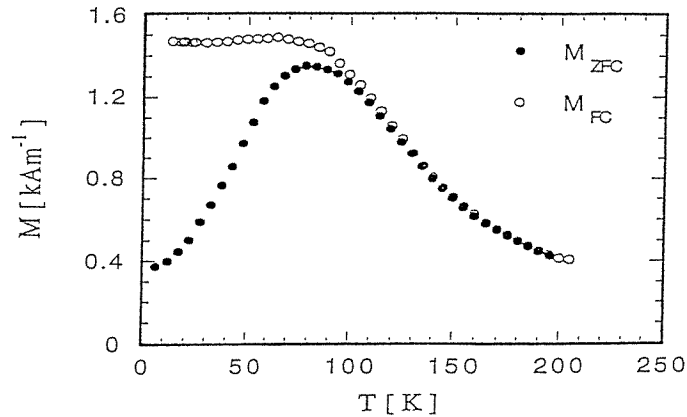


Figure 2. M_{ZFC} - and M_{FC} -curves of the Fe-Hg sample obtained in an applied magnetic field of 3 mT.

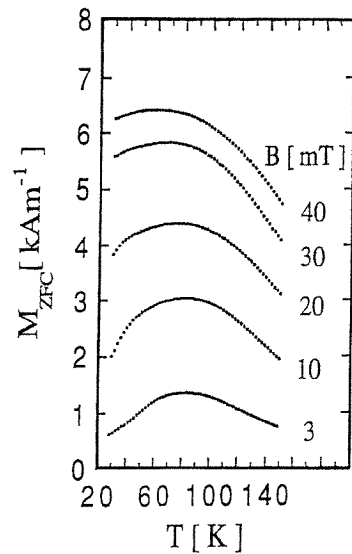


Figure 3. M_{ZFC} -curves of the Fe-Hg sample obtained in the temperature range from 20 to 160 K in applied magnetic fields of 3 mT, 10 mT, 20 mT, 30 mT, and 40 mT.

In figure 2, M_{ZFC} and M_{FC} are shown for a magnetic field of 3 mT. It can be seen that there is a rounded maximum in M_{ZFC} at $T_P = 83$ K. M_{FC} coincides with M_{ZFC} at high temperatures, but as the temperature approaches T_P from above, the curves start to diverge

at a temperature of $T_d = 130$ K. This indicates the temperature at which the relaxation time of the particles with the highest energy barriers (or the strongest interactions) becomes comparable to the experimental measuring time. At temperatures below T_P , M_{FC} flattens out and becomes almost constant.

In figure 3, M_{ZFC} -curves are shown for applied fields of 3 mT, 10 mT, 20 mT, 30 mT, and 40 mT. It can be seen that the value of T_P decreases when the applied field is increased. This field dependence of T_P is shown in figure 4. At low applied magnetic fields the T_P -value becomes almost constant, and the extrapolation to zero applied field yields a T_P -value of approximately 83 K.

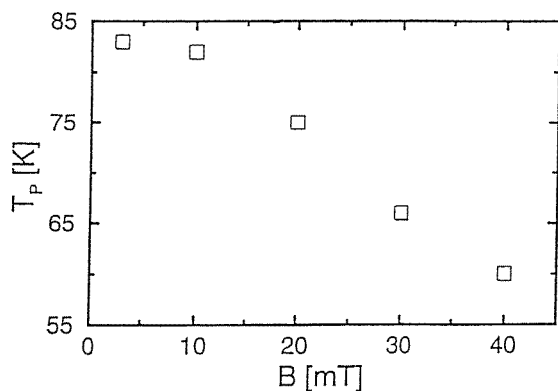


Figure 4. The peak temperature, T_P , as a function of the applied magnetic field.

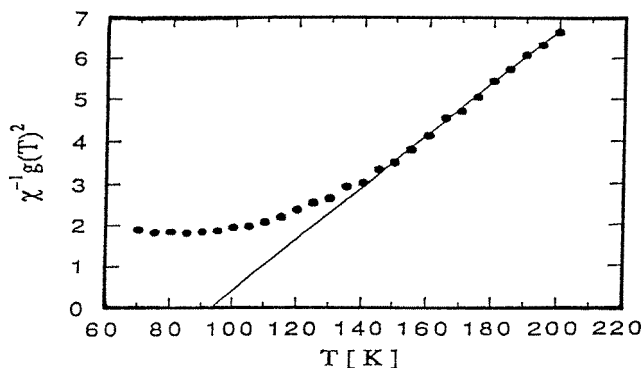


Figure 5. The inverse initial susceptibility, corrected for the temperature dependence of the intrinsic magnetization of the particles, as a function of the temperature. The solid line is the best fit obtained by linear regression to the data in the temperature range from 140 to 200 K.

The initial susceptibility of an ensemble of magnetic particles is proportional to the square of the magnetic moments and thus to the square of the spontaneous saturation magnetization of the particles, $M_0(T)$. $M_0(T)$, which is temperature dependent, is determined from the high-field magnetization extrapolated to zero field [35]. In order to estimate the contribution to the temperature dependence of χ_i , which is not due to the temperature dependence of $M_0(T)$, the susceptibility is multiplied by $[M_0(0)/M_0(T)]^2$. In figure 5, the inverse of this susceptibility is plotted versus temperature. As can be seen, it

obeys a Curie–Weiss law in the temperature range 140 K–200 K, where all of the particles are superparamagnetic. The line in figure 5 was obtained by linear regression. The intercept with the T -axis yields a Curie–Weiss temperature of $T_{CW} = 93 \pm 2$ K. The slope yields a Curie constant, $C = n\mu_0\langle\mu(0)^2\rangle/(3k_B)$, where n is the number of particles per volume unit [35], μ_0 the permeability of vacuum, and $\langle\mu(0)^2\rangle^{1/2}$ the root mean square (RMS) value of the particle moment at 0 K. From the Curie constant we estimate the RMS value of the magnetic moment per particle to be $\langle\mu(0)^2\rangle^{1/2} = 2.0 \times 10^{-20}$ J T $^{-1}$ at 0 K.

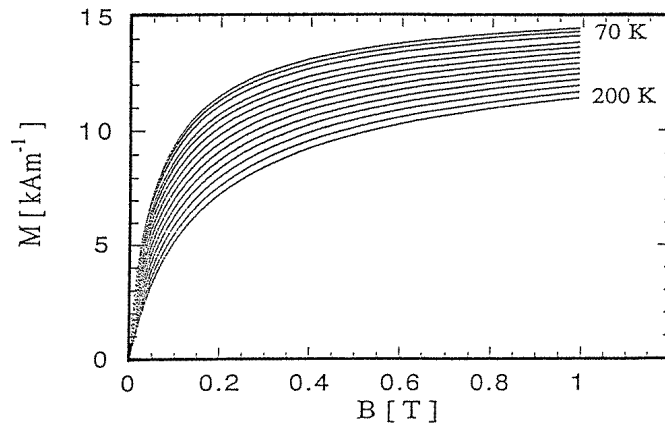


Figure 6. The isothermal magnetization as a function of the applied field between 70 and 200 K, with a temperature difference of 10 K between the magnetization curves.

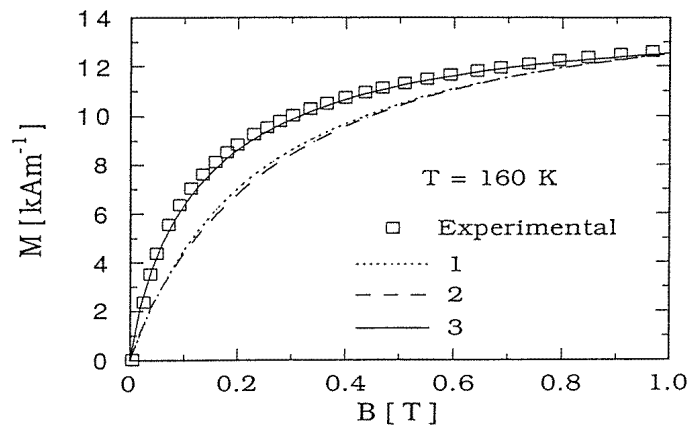


Figure 7. The magnetization as a function of the applied field at 160 K. The simulated curves were obtained from the following models: (1) the Langevin function; (2) a model in which the anisotropy is included [37]; and (3) a model in which both the anisotropy and the magnetic inter-particle interactions are taken into account (see the text). In all three models we have integrated over the particle size distribution.

Some of the measured isothermal magnetization curves are shown in figure 6. The curves cannot be described by a Langevin function nor by a superposition of Langevin functions, even above T_d where all particles are superparamagnetic. This is illustrated in figure 7. Such a deviation from Langevin behaviour may be explained by magnetic

anisotropy [37] and/or magnetic interactions between the particles. In section 4 we will discuss how these effects can be taken into account in a simple model.

5. Discussion

5.1. Inter-particle interactions

The influence of inter-particle interactions on the magnetic properties of nanoparticles has been the subject of numerous theoretical and experimental studies [12–17, 31–34, 38–51]. The inter-particle interactions will affect the energy barriers separating the energy minima of superparamagnetic particles, and thereby have an influence on the relaxation time. As discussed in the introduction, strong magnetic interaction may also result in ordering of the magnetic moments of the particles below a critical temperature. The presence of strong interactions between the FeHg particles may be inferred from several experimental features; the comparison between the blocking temperatures in experiments with different timescales, the field dependence of T_P , the temperature dependence of χ_i above T_P , and the shape of the magnetization curves.

The peak temperature, T_P , in M_{ZFC} , and the temperature, T_B , obtained from the Mössbauer spectroscopy measurements, may either be due to thermal blocking of the magnetic moments of non-interacting or weakly interacting particles (in which case one considers a blocking temperature), or to ordering of the magnetic moments of strongly interacting particles (in which case one may use the term ‘ordering temperature’) [16, 17, 38]. One may distinguish between these two cases by considering the ratio between the two temperatures T_P and T_B . For systems of non-interacting particles, one would expect a ratio between the blocking temperature determined from the Mössbauer spectroscopy measurement (with the experimental timescale of about 5×10^{-9} s) and T_P determined from magnetization measurements (with the experimental timescale of about 10 s) to be in the range 4–6 [16, 17, 52, 53]. For strongly interacting particles, where the transition to the superparamagnetic state occurs at an ordering temperature, the ratio should be close to 1 [16, 17, 32]. In our case the ratio is approximately 1.8. This indicates the presence of magnetic interactions between the particles.

The decrease of T_P as a function of the applied field (figure 4) is a further indication of the importance of interactions between the particles. An increase of T_P when B increases has been observed in experiments on dilute ferrofluids [38, 54]. In [54] the effect was explained by means of the non-linear relation between the magnetization and field in a system with negligible interactions. In samples with significant inter-particle interaction, T_P decreases with increasing values of B [17, 38]. The large value of T_{CW} , obtained from the Curie–Weiss analysis, supports the conclusion that there is a strong magnetic interaction between the particles in the sample [15, 32, 52].

A detailed interpretation of experimental results for the magnetic properties of small particle systems is, in general, not straightforward. The distribution in particle size and magnetic anisotropy energies may not be known in detail. Moreover, if inter-particle interactions are significant, there will be a distribution in the strength of the interactions. If the magnetic interaction is solely due to dipole coupling and the distance between the particles is known, one can make at least rough estimates of the strength of the interactions [43, 52]. In the present system it is likely that exchange interactions via the conduction electrons in the mercury also play a significant role, and in this case there is no simple model which can predict the interaction strength. In the following we include the interactions in a simple model, in which the strength of the interaction is treated as a single parameter in

the numerical calculation of the magnetization. As will be shown, the model gives a good agreement between the calculated and experimental values.

In order to make the model calculations, we first have to estimate the size of the different contributions to the energy of the system. At temperatures below T_B , the Mössbauer spectra are affected by collective magnetic excitations, i.e. fluctuations of the direction of the magnetization in directions close to the easy direction of magnetization [31, 55]. These fluctuations are fast compared to the timescale of Mössbauer spectroscopy, and they lead to a reduction of the magnetic hyperfine splitting in the Mössbauer spectra. In the Fe–Hg system the magnetic inter-particle interaction is strong, and this will affect the collective magnetic excitations. If we assume uniaxial anisotropy and that the interaction field is in the same direction as the easy axis of magnetization, the energy of a particle in zero field may be expressed as [31, 56]

$$E(\theta) = -KV \cos^2\theta - K_m \langle M \rangle M \cos\theta. \quad (15)$$

Here K_m is a coupling constant for the interaction between the magnetic particles, K the magnetic anisotropy energy constant, and V the volume of a particle. θ is the angle between the magnetization direction and the direction of the easy axis of magnetization, M the magnetization of a particle, and $\langle M \rangle$ is the average magnetization of the surrounding particles. If the temperature dependence of the intrinsic magnetization of the particles is neglected, $K_m M^2 \approx 3k_B T^*$ [31, 56], where T^* is the ordering temperature for $K = 0$.

For $KV \gg k_B T$, the observed hyperfine field in zero applied field, $B_{obs}(T)$, may be approximated [31] by

$$\frac{B_{obs}(T)}{B_0(T)} = 1 - \frac{k_B T}{2KV + 3k_B T^*}. \quad (16)$$

$B_0(T)$ is the saturation hyperfine field at the temperature T . The collective magnetic excitations may be suppressed by the application of a magnetic field. The value of the average saturation hyperfine field for the two magnetically split components in the iron–mercury alloy has been obtained by applying a magnetic field of 4 T to the sample at 5 K [35]. The temperature dependence of the saturation hyperfine field has also been measured earlier [26]. By use of equation (16) at 5 K, 20 K, 50 K, and 80 K we could estimate the value of $E_1 = KV + 3k_B T^*/2$ to be $(5.2 \pm 1.5) \times 10^{-21}$ J. This value is of the same order as those observed previously for similar samples, $E_1 = (4.2 \pm 0.7) \times 10^{-21}$ J [57] and $E_1 = 6.5 \times 10^{-21}$ J [25].

In numerical calculations of the magnetization we must separate the contributions from the anisotropy and the interactions to the energy. The influence of KV on the value of the ordering temperature, T_o , was investigated in [56]. For $A = KV/(k_B T^*) = 0$, T_o is equal to T^* , and for $A \rightarrow \infty$, $T_o/T^* \rightarrow 3$ [56]. If we assume that A is of the order of 5–10, then $T_o/T^* \approx 1.8$. Assuming that $T_o = T_p$ (extrapolated to zero field), we find that $T^* \approx 50$ K and $KV \approx 4.2 \times 10^{-21}$ J. The values should be considered as rough estimates because the calculation is based on assumptions and approximations which may not be correct in detail. For non-interacting particles, the value of $KV = 4.2 \times 10^{-21}$ J would yield a blocking temperature in magnetization measurements of about 12 K. This means that when the sample is cooled the ordering occurs at a temperature higher than the blocking temperature in a sample with similar, but non-interacting particles.

From the mean and the root mean square values of the magnetic moment, we may estimate the width of the distribution of moments. Small particles are often obtained with a log–normal distribution; thus we apply this in our case. A log–normal distribution of magnetic moments with a mean value of 1.2×10^{-20} A m² [35] and a root mean square value of 2.0×10^{-20} A m², obtained above, yields a median moment $\mu_{\text{median}} = 0.84 \times 10^{-20}$ A m²,

and a geometrical standard deviation $\sigma = 2.5$. Any mono-modal distribution would yield similar results. The magnetic moment of a particle is $\mu = MV$, and the anisotropy energy is given by KV . If we assume that K and M are independent of the particle size, then μ and KV both have the same distribution, determined by the distribution of particle sizes.

The shape of the magnetization curves (figure 6) can also be explained by the influence of interactions. We made a detailed analysis of the experimental magnetization curve obtained at 160 K, i.e. well above T_d . The magnetization curve was compared with three different models: (1) the Langevin function; (2) a model in which the anisotropy is included as described in reference [37]; and (3) a model in which both the anisotropy and the magnetic interaction are taken into account. In all three cases we integrated over the size distribution.

In the third model the energy of a particle in an external field is given [32] by

$$E \approx -KV \cos^2 \alpha - \left(\mu B + 3k_B T^* b(T, B) \left(\frac{M(T)}{M(T^*)} \right)^2 \right) \cos \theta. \quad (17)$$

Here α is the angle between the magnetic moment of a particle and its easy axis. $b(T, B) = \langle M(T) \rangle / M(T)$ is the reduced magnetization, and θ is the angle between the magnetic moment and the applied external field. The interaction field is assumed to be parallel to the applied field, but the easy directions are assumed to be randomly oriented. The expectation value of the magnetization for a given value of α can be calculated from

$$\langle M \rangle = M \left(\int \cos \theta \exp(-E/k_B T) d\Omega \right) / \left(\int \exp(-E/k_B T) d\Omega \right). \quad (18)$$

The calculation was carried out for each magnetic moment assuming $T^* = 50$ K and a root mean square value $KV = 4.2 \times 10^{-21}$ J. Finally, the total magnetization was obtained by superposition of the contributions from particles with different orientations of easy axes and magnetic moments using the log-normal distribution described above. The experimental and calculated magnetizations at 160 K are shown in figure 7. It is obvious that the first two models cannot explain the experimental results, but the third model gives results in excellent agreement with the experimental data. This strongly supports the conclusions drawn above that interactions between the particles play an important role, and that the value of the interaction parameter, T^* , is of the order of 50 K.

In an earlier study of a similar sample [25] it was found that exposure to a magnetic field gradient at room temperature leads to irreversible agglomeration of the magnetic particles. Thus the particles in the present sample are also expected to be inhomogeneously distributed in the mercury, and the inter-particle interaction may be essentially independent of the overall concentration of particles in mercury. The magnetization measurements show in fact that the magnetic particles are inhomogeneously distributed even at a macroscopic scale (see section 3).

5.2. The magnetocaloric effect

The isothermal magnetization curves were used to calculate the entropy change as described by equation (5). The entropy changes calculated in the range 70 to 200 K for two different values of the maximal applied field are shown in figure 8. Strictly speaking, one can only use magnetization values obtained above T_d , since some of the particles may not reach thermodynamic equilibrium below this temperature within the timescale of the measurement, and equation (5) was derived from equilibrium thermodynamics. However, for temperatures down to $T \approx 90$ K, the difference between M_{ZFC} and M_{FC} is small, indicating that only few particles are blocked above 90 K. Therefore the model should be a good approximation

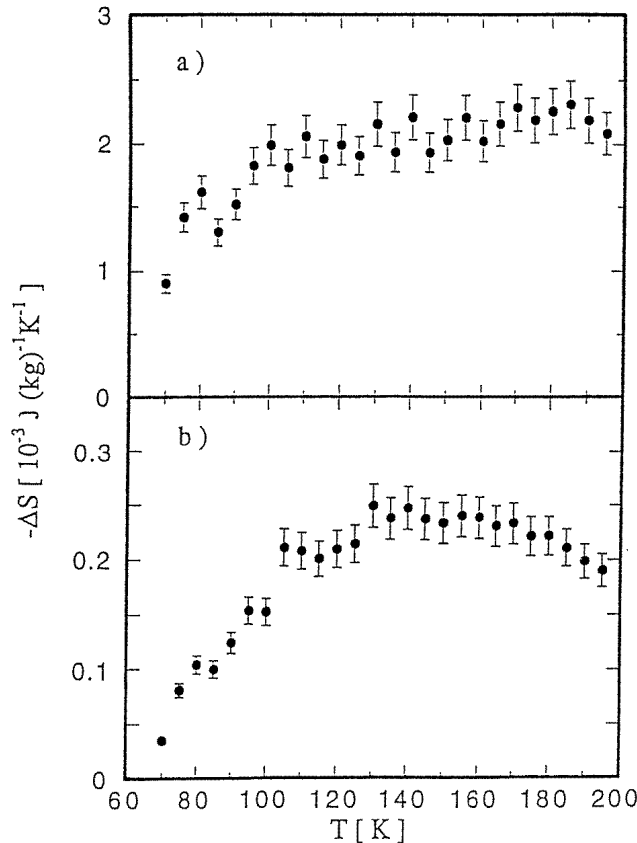


Figure 8. The entropy change, estimated from the magnetization curves (figure 6) by using equation (5) at various temperatures, (a) for a magnetic field change from 0 to 1 T, and (b) for a magnetic field change from 0 to 0.1 T.

at $T \geq 90$ K. In applied fields that are larger than the anisotropy field, the particles will be in thermal equilibrium at all temperatures. The model for non-interacting superparamagnetic particles therefore has shortcomings only at low temperatures in small applied fields.

The magnetocaloric effect is larger for an applied field of 1 T than for 0.1 T, because the change in the spin order, and thereby the entropy change, will be larger the larger the applied field, until a limit is reached at which the spin system is fully aligned with the applied magnetic field. The entropy change obtained for a magnetic field change from 0 to 1 T (figure 8(a)) is approximately $-2.1 \times 10^{-3} \text{ J kg}^{-1} \text{ K}^{-1}$, almost independently of temperature in the range from 130 to 200 K. This is a relatively large entropy change compared to the values given in [30], where a maximum entropy change for a sample containing 11 wt% Fe on silica was found to be approximately $-1.7 \times 10^{-3} \text{ J kg}^{-1} \text{ K}^{-1}$, when integrating up to 0.9 T at 100 K. In our case, a larger value for the entropy change is obtained for a sample containing only 0.5 wt% Fe. When applying magnetic fields up to 0.1 T (figure 8(b)), $-\Delta S$ reaches a maximum of $2.5 \times 10^{-4} \text{ J kg}^{-1} \text{ K}^{-1}$ at about 140 K, which is close to the temperatures T_d and T_B . The relatively low entropy change reflects the lower degree of overall spin ordering in this field range.

These experimental values of entropy changes are strongly enhanced compared to

those which would be obtained for a sample with the same amount of non-interacting paramagnetic Fe^0 atoms with the same magnetic moment as those in the $\text{Fe}_{1-x}\text{Hg}_x$ alloy, $\mu \approx 2.2\mu_B$ [35]. According to equation (4), such paramagnetic Fe^0 atoms would yield $\Delta S = -1.0 \times 10^{-5} \text{ J kg}^{-1} \text{ K}^{-1}$ for $B_1 = 1 \text{ T}$ and $\Delta S = -1.0 \times 10^{-7} \text{ J kg}^{-1} \text{ K}^{-1}$ for $B_1 = 0.1 \text{ T}$ at 130 K. These values are two orders of magnitude lower than those obtained for our particles.

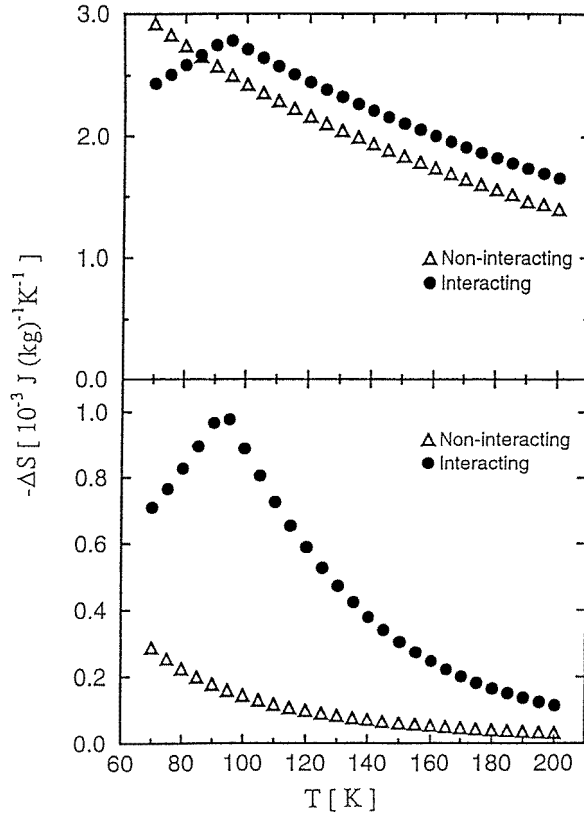


Figure 9. The entropy change, calculated from the mean-field model (equation (14)) in the temperature range 70–200 K with an ordering temperature of 93 K (filled circles). The upper graph is for a magnetic field change from 0 to 1 T, and the lower graph is for a magnetic field change from 0 to 0.1 T. The corresponding values calculated from the model for non-interacting superparamagnetic particles (equation (9)) are shown in the same temperature range (triangles).

The experimental values of the entropy changes can also be compared to the theoretical values for a sample consisting of non-interacting superparamagnetic particles. From the high-field magnetization data [35] we found an extrapolated average magnetic moment of the particles $\langle \mu(0) \rangle = 1.2 \times 10^{-20} \text{ J T}^{-1}$ at 0 K. This value differs from the RMS value due to the particle size distribution. By comparing this value to the saturation magnetization, one finds that there are $n = 1.4 \times 10^{24}$ particles per m^3 [35]. Inserting these values into equation (9), which was derived assuming non-interacting superparamagnetic particles, and taking into account the temperature dependence of the particle moment, the entropy change can be calculated. Results for $B_1 = 0.1 \text{ T}$ and $B_1 = 1 \text{ T}$ are shown in figure 9. At 130 K we find $-\Delta S = 2.1 \times 10^{-3} \text{ J kg}^{-1} \text{ K}^{-1}$ and $-\Delta S = 8.5 \times 10^{-5} \text{ J kg}^{-1} \text{ K}^{-1}$, when

integrating to 1 T and 0.1 T, respectively. At 200 K the corresponding entropy changes are $-\Delta S = 1.4 \times 10^{-3} \text{ J kg}^{-1} \text{ K}^{-1}$ and $-\Delta S = 3.3 \times 10^{-5} \text{ J kg}^{-1} \text{ K}^{-1}$. These values are lower than the experimental values. For the integration up to 0.1 T, the values are significantly lower than the experimental values in the whole temperature range. The magnetic interaction between the particles may be taken into account by using the mean-field model [34]. Using equation (14) with an ordering temperature of $T_0 = 93 \text{ K}$ and an average magnetic moment per particle of $\langle \mu(0) \rangle = 1.2 \times 10^{-20} \text{ J T}^{-1}$ at 0 K, we obtain the results shown in figure 9 for $B_1 = 0.1 \text{ T}$ and 1 T, respectively. Comparing with figure 8 it can be seen that the mean-field model gives a qualitatively better description of the temperature dependence of the entropy change than the model for non-interacting particles (e.g. we get a maximum in the entropy change at the ordering temperature). The mean-field model also gives values for the entropy change that are close to the experimental values, especially for the integration up to 1 T. For the integration up to 0.1 T the model yields values for the entropy change that are larger than the experimental ones near the ordering temperature, but at higher temperatures the model gives a good description of the entropy change.

In our mean-field model, we assumed that the anisotropy energy is negligible, that the mean field is parallel to the applied field, that all particles have the same volume, and that the magnetic moments of all particles order at the same temperature. These conditions are not fulfilled in a real system. Distributions in the particle size and the ordering temperature will lead to broadening of the peaks in ΔS . The assumption that the mean field is parallel to the applied field will lead to an overestimate of the entropy change, especially in low applied magnetic fields where the influence of the mean field is relatively large. However, even with these simplifications we conclude that the model that takes into account the magnetic interaction between the particles gives a much better description of the experimental values of the entropy change than the model for non-interacting particles.

The fact that the entropy change for large values of B_1 is almost constant over a large temperature range is also consistent with theoretical results obtained by the Monte Carlo method [7], for a particle system consisting of ultrafine strongly interacting particles. Bennet *et al* [7] found that above the ordering temperature of the system the entropy change for $B_1 = 1 \text{ T}$ is slightly decreasing with increasing temperature for very small particles (10–30 atoms/particle), and almost constant over a wide temperature range for larger particles.

The results presented here were obtained on a kind of magnetic material that might be useful for refrigeration at high temperature because of the favourable particle size, magnetization, and strength of inter-particle interactions. Moreover, the good heat conductivity of this system may be an advantage. However, the fraction of magnetic material is very small. The change in temperature corresponding to a given change in entropy can be calculated by use of equation (6). Using the value of c_B for Hg [58], the magnetocaloric effect for the iron–mercury sample is found to be $\Delta T \approx 3 \times 10^{-3} \text{ K}$ at 200 K for magnetization in an applied field of 1 T. If one could make a concentrated sample of interacting magnetic particles in the Hg matrix, the entropy change per unit mass would increase drastically, ultimately up to about $-4.0 \times 10^{-1} \text{ J kg}^{-1} \text{ K}^{-1}$. The corresponding temperature change is $\Delta T \approx 0.2 \text{ K}$ in the temperature range 130 to 200 K. In this calculation we assumed that the particles consist of pure α -Fe with a Debye temperature $\theta_D = 420 \text{ K}$ [59] and that c_B can be derived from the Debye model.

6. Conclusions

It has been shown that the magnetic properties of the system consisting of ultrafine particles of an iron–mercury alloy in Hg are strongly influenced by magnetic interactions. The initial

susceptibility was found to follow a Curie–Weiss law. The ratio between the blocking temperature, estimated from Mössbauer spectra, and the peak temperature of the zero-field-cooled magnetization curves is much smaller than expected for a system of non-interacting particles. Furthermore, the magnetization curve at 160 K, where all particles are superparamagnetic, could only be fitted by using a model in which the influence of magnetic interactions is included.

Magnetization measurements have been utilized to estimate the magnetic entropy change as a function of temperature and applied magnetic fields. The magnetic entropy change is found to have an almost constant value, $-\Delta S = 2.1 \times 10^{-3} \text{ J kg}^{-1} \text{ K}^{-1}$, in the temperature range from 130 to 200 K, for a magnetic field change from 0 to 1 T. For a magnetic field change from 0 to 0.1 T, the magnetic entropy change was found to have a stronger temperature dependence, reaching a maximum of $-\Delta S = 2.5 \times 10^{-4} \text{ J kg}^{-1} \text{ K}^{-1}$ at approximately 140 K. These values are much larger than those calculated for a paramagnetic system with the same number of magnetic atoms. A model which takes into account the interaction between the particles is found to give a better description of the entropy change than that of non-interacting particles, especially at high temperatures.

If the interacting particles could be further concentrated in the mercury, the effect might increase by a factor of up to 200, and the corresponding magnetocaloric effect would be approximately 0.2 K for each magnetization cycle in the temperature range from 130 to 200 K. The present results indicate that it might be possible to engineer a material, based on a nanostructured system, for magnetocaloric refrigeration at high temperatures.

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