Zero-field cooled magnetization of amorphous $Fe_{1-x}C_x$ particles-field dependence of the maximum

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Zero-field cooled magnetization of amorphous $Fe_{1-x}C_x$ particles—field dependence of the maximum

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Abstract. We measured the zero-field cooled magnetization, M_{ZFC}, of a frozen magnetic liquid with amorphous $Fe_{1-x}C_x$ particles. M_{ZFC} has a maximum at $T_p \approx 20$ K, which is interpreted as due to blocking of superparamagnetic relaxation in single particles. The maximum shifts towards higher temperatures with increasing measuring field. The shift is explained by the non-linear field dependence of the magnetization of particles with a size distribution. At temperatures below T_p the magnetic particles have a coercivity and remanence in good agreement with those expected for an ensemble of non-interacting uniaxial particles with a random distribution of easy axes.

1. Introduction

The peak observed in the magnetization, M_{ZFC}, measured in a constant field during warming of a sample initially cooled in zero field is archetypal of the blocking of the superparamagnetic relaxation in small magnetic particles [1]. In the Néel model [2] for non-interacting particles with uniaxial anisotropy energy given by $E = KV \sin^2 \Theta$, the thermally activated relaxation occurs between two energy minima at $\Theta = 0$ and π, separated by a barrier $E_B = KV$. Θ is the angle between the magnetization of the particle and its easy axis, K the magnetic anisotropy energy constant and V the volume of the particle. As the temperature is decreased the relaxation becomes blocked at a temperature T_B, given by the relation $\tau_{exp} = \tau_0 \exp(KV/kT_B)$. Here τ_{exp} is the experimental measuring time and k Boltzmann's constant. τ_0 is a characteristic relaxation time of the order of 10^{-10} s, as determined in experiments [3, 4]. The blocking temperature depends strongly on the volume of the particle. In samples with a particle size distribution the position of the peak, at T_p, in M_{ZFC} may be related to the individual blocking temperatures by taking the size distribution into account, as described for instance in [3]. The variation of T_p with the applied field, B, has been observed in experiments on magnetic liquids. It was found that T_p decreases with B for iron oxide particles [5–7] and that T_p increases with B for amorphous iron–carbon particles [4]. The result obtained for the particles of iron–carbon was considered anomalous in comparison with the findings for iron oxide. Luo *et al* [8] studied ferrofluids with different concentrations of iron oxide particles. They interpreted the peak of M_{ZFC} as due to interparticle interactions. In the most concentrated samples T_p decreased with B. In their most dilute liquid T_p increased with B in low fields. They suggested that this could be explained by the applied field causing an increase of the barrier separating the energy minima. In order to study how the applied field affects the position

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of the peak we performed further measurements and numerical calculations for a magnetic liquid with amorphous iron–carbon particles that had been investigated earlier [3, 9]. For this liquid it was shown that the influence of interactions is negligible and that its behaviour is characterized by single-particle effects. In this paper we report on the field dependence of the zero-field cooled magnetization of this liquid. Measurements of the coercivity and remanence at temperatures below the peak are also included.

2. Experimental details

The magnetic liquid, with about 1.5 vol.% of particles consisting of amorphous iron–carbon, $Fe_{1-x}C_x$ with $x \approx 0.25$, in decalin, is the same as described in [3] and [9] and together with other liquids in [10] and [11]. The magnetic properties of this liquid scale with the concentration for dilutions down to 1:20. This ascertains that the particle interactions are negligible. The particles have a log-normal size distribution with median diameter $D_v = 3.2$ nm and standard deviation 0.3 nm [3]. The zero-field cooled magnetization was measured with a vibrating sample magnetometer in a constant field for seven values of B in the range $0.002\ \text{T} \leqslant B \leqslant 0.4\ \text{T}$. The warming rate was 0.05 K s^{-1} in all cases. Hysteresis curves were measured in fields $-2\ \text{T} \leqslant B \leqslant 2\ \text{T}$ at six temperatures between 4 K and 10 K, below T_p, and at 100 K, well above T_p. The coercive field and remanent magnetization were determined from the hysteresis curves.

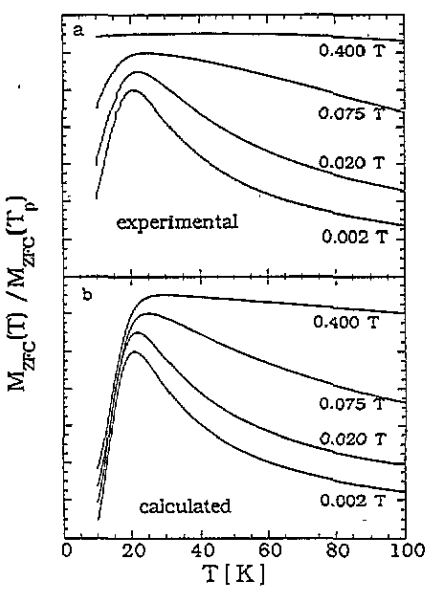

Figure 1. (a) The temperature dependence of the zero-field cooled magnetization for the magnetic liquid and (b) the Langevin contribution for unblocked superparamagnetic particles with a size distribution, calculated as described in the text. The values of the magnetization are normalized with respect to the peak value and the curves are displaced with respect to each other in order to facilitate comparisons. The applied fields, B, are indicated in the figure.

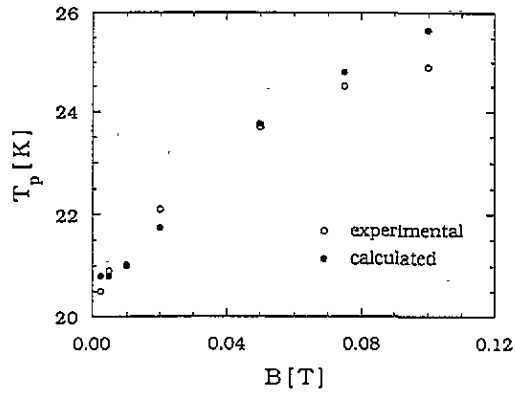

Figure 2. The calculated and measured values of the temperature at the maximum of M_{ZFC} versus measuring field for the magnetic liquid with amorphous iron–carbon particles.

3. Results

3.1. Zero-field cooled magnetization

The zero-field cooled magnetization measured in the lowest field, $B = 0.002$ T, has a maximum at $T_p = 20$ K. This is shown in figure 1(a) where $M_{ZFC}(T)$, normalized to the value at the peak, $M_{ZFC}(T_p)$, is plotted versus the temperature, T. When B is increased T_p increases. At the same time the peak broadens. The shift of T_p is less than 5 K for B up to 0.1 T, as shown in figure 2. In earlier work the linear approximation for the field dependence of the magnetization has been applied to describe the temperature dependence of the zero-field cooled magnetization. We calculated the temperature dependence of M_{ZFC} by integrating the full Langevin function $L(\alpha)$ over the particle size distribution for all the measuring fields, according to the relation

$$M_{ZFC} \propto \varepsilon M_S \int_0^{y_B(T)} y^2 L(\alpha) f_{LN}(y)\,\mathrm{d}y. \tag{1}$$

ε is the volume fraction of particles with spontaneous magnetization M_S and $\alpha = M_S V(y)B/kT$. $V(y)$ is the volume of a particle with diameter $D(y) = yD$. The log-normal distribution is given by the relation [12]

$$f_{LN}(y)\,\mathrm{d}(\ln y) = (1/\sqrt{2\pi}\,\ln\sigma)\exp\left(-\left(\ln^2 y/2\ln^2\sigma\right)\right)\mathrm{d}(\ln y). \tag{2}$$

Here σ is the geometrical standard deviation, which is 1.1 in our case. The upper limit of integration, $y_B(T)$, is obtained from the volume $V_B(T) = (\pi/6)y_B^3(T)D_V^3$ of the particle that becomes blocked at the actual temperature, according to the relation $\tau_{exp} = \tau_0 \exp(KV_B(T)/kT)$. The calculations were made with the assumption that only particles with a blocking temperature below the measuring temperature contribute to the magnetization. In low fields the influence of the anisotropy on the magnetization is small [9]. Therefore it was neglected in the calculations. The blocking temperatures were determined using the values $K = 2.9 \times 10^5$ J m^{-3}, $\tau_0 = 2.8 \times 10^{-11}$ s and $\tau_{exp} = 10$ s [3]. The results of the calculations are shown in figure 1(b). As can be seen, the temperature at the peak is shifted towards higher temperatures with increasing values of the magnetic field,

and the character of the curves is changed in a way similar to the experimental behaviour, cf. figure 1(a). In figure 2 the position of the maximum is plotted as a function of the measuring field. In low fields there is good agreement between the experimental and the calculated data. In higher magnetic fields, approaching the anisotropy field, the experimental values of T_p are lower and those of $M_{ZFC}(T)/M_{ZFC}(T_p)$ significantly higher than the calculated ones. This can be explained by the fact that in this range the magnetic energy $M_S V(y)B$ is of the same order of magnitude as the energy barrier, $KV(y)$. The spontaneous saturation magnetization of the amorphous magnetic particles is $M_S = 1.4 \times 10^6$ A m^{-1} [3]. The magnetic dipolar energy of such a particle becomes equal to its anisotropy energy in a field $B = K/M_S \approx 0.2$ T. Therefore a significant magnetization can be induced within the experimental measuring time even below T_p in applied fields of this magnitude. The influence of the magnetic field on the superparamagnetic relaxation was neglected in the calculations which can explain the difference between the calculated and measured magnetizations. Thus we conclude that the shift of T_p should be interpreted not as an affect of the applied field on the relaxation time, but mainly as a consequence of the non-linear field dependence of the magnetization of the unblocked particles. For iron oxide particles in a hydrocarbon carrier El-Hilo *et al* observed that in a corresponding range of fields T_p decreased with increasing field [7]. We believe that the main reasons for the difference in behaviour is that in our system the interactions are negligible, whereas El-Hilo *et al* are studying a system with interactions. In the work of Luo *et al* [8] one can see that the liquids change behaviour with respect to the field dependence of the peak when the liquids are diluted. The field dependence of the zero-field cooled magnetization has also been included in the theoretical calculations by Pfeiffer and Chantrell [13].

3.2. Coercivity and remanence

Figure 3 shows the hysteresis curves for the magnetic liquid measured at 100 K, 10 K and 4.2 K. At 100 K, well above the peak in M_{ZFC}, there is no hysteresis and the magnetic liquid is superparamagnetic. At 10 K the hysteresis is significant with a coercive field, B_C, of about 0.037 T and a remanence to saturation magnetization ratio, M_r/M_0, of about 0.3. Here the magnetization measured in a field of 2 T was taken as the saturation magnetization, M_0. As the temperature is decreased the coercive field and the remanence increase (see figure 4), and at 4.2 K the values are $B_C \approx 0.11$ T and $M_r/M_0 \approx 0.45$. The value of the remanence is very close to the value of 0.5 that is expected at 0 K for an ensemble of non-interacting, uniaxial single-domain particles with randomly oriented easy axes [14]. It is reasonable to assume that it will become even closer when the temperature is decreased. The coercivity for particles with the easy axis oriented along the applied field has been shown to follow a $T^{1/2}$ temperature dependence [1], but to our knowledge the detailed temperature dependence for a random orientation of the easy axis has not been theoretically investigated. The temperature interval is too narrow to admit any reliable data fit, but a simple estimate of the coercivity at 0 K may be obtained by extrapolating the values for the two lowest temperatures. This yields $B_C(0) \approx 0.16$ T, in good agreement with the value $B_C(0) = 0.958K/M_S \approx 0.20$ T deduced for the ensemble of randomly oriented particles [14]. The fact that the values of remanence and coercivity are very close to the values for non-interacting particles supports our interpretation that the peak in the zero-field cooled magnetization is due to superparamagnetic relaxation and blocking in single magnetic particles.

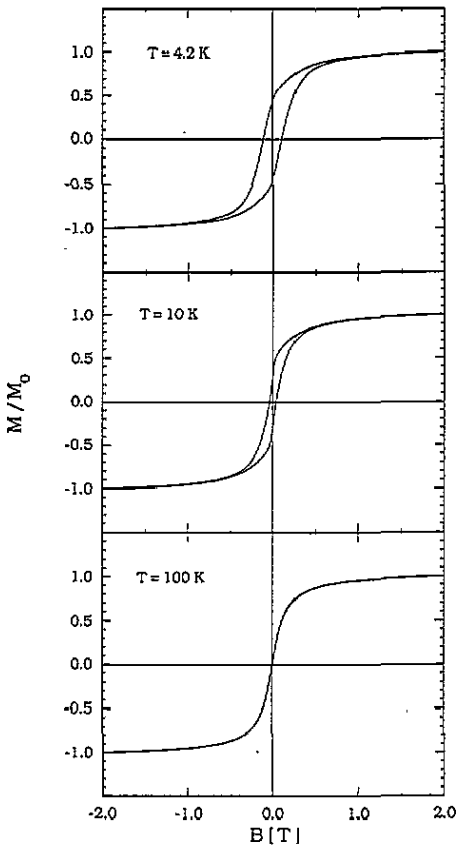

Figure 3. Hysteresis curves at 100 K, 10.0 K and 4.2 K for the magnetic liquid with amorphous iron–carbon particles. The curves are normalized to the magnetization measured in $B = 2$ T.

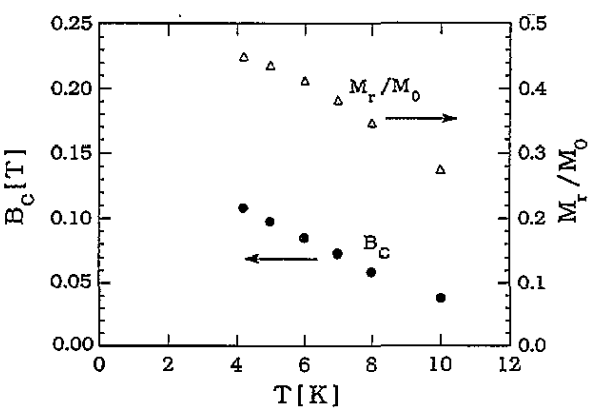

Figure 4. The temperature dependence of the coercivity and remanence to saturation ratio of the magnetic liquid.

4. Conclusions

Our measurements of the zero-field cooled magnetization yield results similar to those obtained by Linderoth *et al* [4] for the same kind of particles as ours, and by Luo *et al* [8] for their most dilute liquid with iron oxide particles. All these results imply that in weakly interacting particle systems the relaxation time is little affected by an applied field, provided a particle's magnetic energy is small compared to its anisotropy energy. The apparent increase of the blocking temperature with the applied field, as observed in experiments, is an artefact due to the non-linear field dependence of the magnetization of particles with a size distribution.

A blocking temperature, as inferred from the temperature at the peak of the zero-field cooled magnetization, that decreases with the applied field is observed in particle systems where interparticle interactions are prevailing. This is often the case in the commonly used magnetic liquids with iron oxide particles in kerosene or oils [5–7, 15]. We are at present performing further experiments on such liquids in order to understand the influence of interactions on their magnetic properties.

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