Calorimetric method for the determination of Curie temperatures of magnetic nanoparticles in dispersion

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Abstract

$Mn_xZn_{1-x}Fe_2O_4$-based magnetic fluids with $x = 0.1$–0.9 are synthesized by coprecipitation. The samples are heated in a radio frequency (rf) magnetic field using an rf generator at different powers, and the temperature is measured as function of time using an optical thermometer. The heating effect of the dispersed magnetic nanoparticles is proportional to the imaginary part of the dynamic magnetic susceptibility of the ferrofluid, a quantity that depends on the temperature through the magnetization of the ferrite nanoparticles and the Néel or Brownian relaxation times, respectively. We propose an extrapolation method to actuate the Curie temperatures of the dispersed magnetic nanoparticles. By means of appropriate fitting functions for (dT/dt) versus T for both the heating and the cooling process, we deduce the Curie temperature of the samples under investigation. For $Mn_xZn_{1-x}Fe_2O_4$-based magnetic nanoparticles the Curie temperatures decrease with increasing Zn content. They turn out to be lower than the literature values for bulk $Mn_xZn_{1-x}Fe_2O_4$, a phenomenon which is generally observed for phase transitions of nanocrystalline materials.

1. Introduction

It is widely known that ferrofluids [1] have an interesting behavior in high frequency magnetic fields. Although they are superparamagnetic, i.e. have no hysteresis losses in the classical sense, they absorb magnetic energy from an applied high frequency magnetic field. This is due to the unique mechanism of magnetic relaxation in soft monodomain magnetic particles like $Mn_xZn_{1-x}Fe_2O_4$ known as the Néel relaxation. Therefore, the magnetism of ferrofluids is partly dependent on the material properties of the particles, i.e. their chemical composition. On the other hand, it depends on the properties of the colloidal dispersion which they form as a ferrofluid. It is still not yet completely understood how the Néel type fluctuations are related to the atomic scale magnetic fluctuations inside the nanoparticle, which have their most prominent effect in the transition from the ferro- or superparamagnetic to the paramagnetic state at the Curie temperature. Moreover, the Curie temperatures (T_C) of magnetic particles in ferrofluids are highly relevant for magnetic fluid hyperthermia [2, 3]. Bio-functionalized magnetic materials are also used in cancer therapy for magnetic drug targeting [4, 5]. It is also possible to heat superparamagnetic particles by irradiation with microwaves utilizing the phenomenon of ferromagnetic resonance [6]. In the present paper we study the rf energy absorption of ferrofluids based on different manganese–zinc ferrites $Mn_xZn_{1-x}Fe_2O_4$ as a function of their chemical composition and of temperature. Using a calorimetric measurement technique we find a clear correlation between the temperature dependence of the magnetization $M(T)$ of the ferrites and the energy absorption in an applied rf field. As we are limited to temperatures below the boiling point of the carrier liquid of our ferrofluids, we apply an extrapolation method to calculate the energy absorption up to the Curie temperatures of the ferrites, which for large Mn content are well above the boiling point of

Table 1. The average particle size (D_{XRD}) and the estimated Curie temperatures (T_C) as a function of the Mn content of the specimens.

x content of Mn	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
D_{XRD}	6.5	7.3	7.8	7.7	7.9	9.3	11.2	13.5	15.4
Estimated T_C (K)					361	397	402	405	463

the ferrofluids. In this way we can give an estimate of the Curie temperature of the magnetic nanoparticles. The new aspect here is that this estimate of the Curie point is completely based on measurements made in a colloidally dispersed system. The disappearance of the rf absorption in the ferrofluid at temperatures close to the nominal Curie temperatures of the respective ferrites demonstrates that the Néel type fluctuations of the particles in the ferrofluid and the fluctuations of the magnetic moments of the ions on their lattice places inside the particle are independent features, and coexist in the considered material.

Other methods of Curie temperature determination are hardly applicable to ferrofluids: magnetization measurements are not possible at temperatures above the boiling point of the dispersion medium (water); optical methods suffer from the extremely high optical absorption (ferrofluids have a deep black color).

2. Power dissipation in alternating magnetic fields

In general, the magnetic complex susceptibility of a ferrofluid can be written as

$$\chi(\omega, T) = \frac{M^2(T)V_p\phi}{3\mu_0 k_B(T - T_B)} \frac{1}{1 + i\omega\tau_s(T)} \qquad (1)$$

where τ_s is the Néel relaxation time of the ferrofluid, T_B the blocking temperature (well below room temperature here) and ϕ is the volume fraction of magnetic particles. The magnetic loss factor is the imaginary part of $\chi = \chi' - i\chi''$ in an alternating magnetic field of strength H_{rf}; the power dissipation per unit volume is

$$\frac{P}{V} = \frac{1}{2}\mu_0\omega\chi''(\omega, T)H_{rf}^2 = \frac{M^2(T)V_p\phi}{6\mu_0 k_B(T - T_B)}$$
$$\times \frac{\omega^2\tau_s(T)}{1 + \omega^2\tau_s^2(T)}H_{rf}^2. \qquad (2)$$

In the high frequency regime where $\omega\tau_s \gg 1$, this reduces to a frequency independent result

$$\frac{P}{V} \propto \frac{M^2(T)V_p\phi}{6\mu_0 k_B\tau_s(T)(T - T_B)}H_{rf}^2. \qquad (3)$$

As is known from magnetic fluctuation theory, close to the Curie point the magnetization $M(T)$ behaves as $M(T) \propto \sqrt{T_C - T}$ for $T < T_C$. Inserting this in (3) shows that the rf absorption P behaves as

$$\frac{P(T)}{V} \propto \frac{T_C - T}{T_C}\left(1 + \frac{T_C - T}{T_C} + \frac{T_B}{T_C}\right.$$
$$\left. + \mathcal{O}\left(\frac{T_C - T}{T_C}\right)^2 + \mathcal{O}\left(\frac{T_B}{T_C}\right)^2\right) \qquad (4)$$

close to the Curie point. For this reason we apply a linear extrapolation method as an estimate of the power absorption as a function of temperature when approaching T_C, neglecting nonleading terms in $(T_C - T)/T_C \ll 1$ and $T_B/T_C \ll 1$ in the above formula. Considering the positive signs of the neglected correction terms, we may further state that the linear extrapolation yields a lower bound for the Curie temperature of the particles.

The heating and the cooling branches in the diagram displaying the temperature increase and decrease rates dT/dt versus temperature T are connected to the power P per volume V which is absorbed by the ferrofluid from the rf field, where ρ_f is the fluid density and C_p is the specific heat, by

$$\frac{P}{V} = \rho_f C_p\left[\left(\frac{dT}{dt}\right)_{heating} - \left(\frac{dT}{dt}\right)_{cooling}\right]. \qquad (5)$$

It is thus evident that the distance between the two branches at a given temperature T should be proportional to $T_C - T$. At $T = T_C$ the branches should finally intersect. As we do not know the Curie temperatures of our ferrites in advance, we construct this intersection point of the heating and cooling branch and take the respective temperature as an estimate for T_C.

3. Sample preparation and characterization

The colloidal $Mn_xZn_{1-x}Fe_2O_4$ samples have been prepared by the coprecipitation technique with x varying from 0.1 to 0.9. The metal precursors used during the synthesis in aqueous solutions were $MnCl_2$, $ZnCl_2$ and $FeCl_3$. Aqueous ammonia was added to stoichiometric reagent solutions to precipitate under intensive stirring at 95 °C. A 2 M HNO_3 solution was used to disperse the magnetic nanoparticles in water. The reaction time of the synthesis was 1 h. The details of the preparation conditions for all the samples are reported elsewhere [7]. The structural properties of magnetic particles were studied using x-ray powder diffraction (Siemens D500, Cu Kα radiation) and transmission electron microscopy (JEOL LEM-100CXII). The XRD patterns for all the powder samples are illustrated in figure 1.

The Bragg reflections show the pattern characteristic of the cubic spinel structure. The patterns with $x = 0.2, 0.4, 0.6$ and 0.8 fully respect the reported values (Powder Diffraction Files, cards no 74-2399, 74-2400, 74-2401 and 74-2402, respectively). The sample with $x = 0.1$ content of manganese suggests the incomplete formation of the ferrite structure due to the partial substitution of Mn^{2+} and Fe^{3+} with Zn^{2+} ions. The average size of particles for each sample was calculated by means of academic software using a Lorentzian convolution from the XRD data and is listed in table 1. We notice that the average particle size increases with content of manganese,
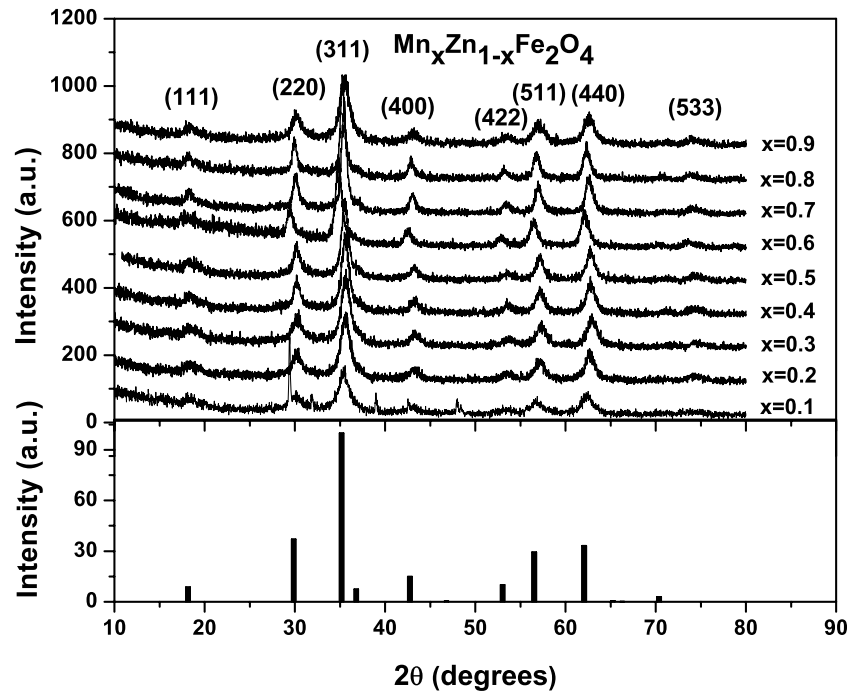
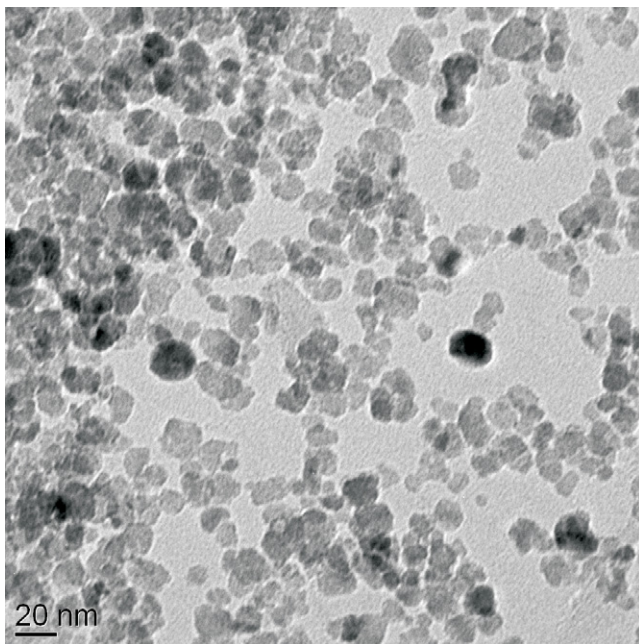**Figure 1.** XRD patterns of $Mn_xZn_{1-x}Fe_2O_4$.

Figure 2. TEM micrograph of $Mn_{0.8}Zn_{0.2}Fe_2O_4$ dispersion.

Figure 3. Hysteresis loops for different *x* contents of manganese at 5 K. The inset shows the field scan from −0.08 to 0.08 T with the corresponding specific magnetization values.

x [8]. The morphology of the samples has been studied by transmission electron microscopy. Direct observations of the shape and size of dispersed nanoparticles for one sample can be provided from figure 2.

The particle diameters from TEM measurement are slightly larger than the observed crystal sizes from XRD, due to the presence of noncrystalline surface layers. Magnetization measurements were made using a Physical Properties Measurement System (Quantum Design, model 6000) in high
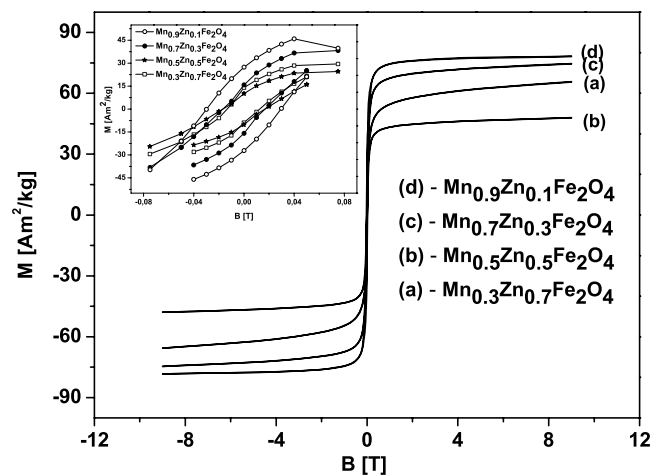
magnetic field at 5 K. Hysteresis loops of several samples are shown in figure 3 and exhibit a superparamagnetic behavior. All particles are single domain particles and the magnetization contribution is determined by the crystal structure, particle shape and surface [9, 10].

The magnetic remanence and coercivity exhibit very small values (inset of figure 3), corroborated with superparamagnetic behavior and the nanoscale dimensions of the particles.

4. Results and discussion

The $Mn_xZn_{1-x}Fe_2O_4$ water-based fluid samples with a solid content of 2 wt% were introduced into a circular double wall
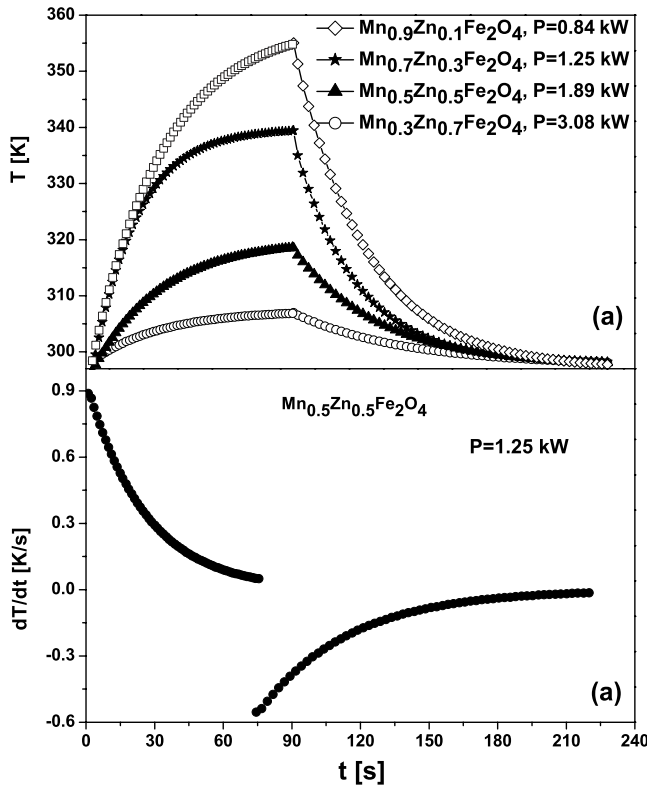
Figure 4. Upper panel: temperature curves of $Mn_xZn_{1-x}Fe_2O_4$ over time for different samples; lower panel: temperature variation rate in unit time (dT/dt) with exposure time for one sample.

Figure 5. Temperature change rate in unit time (dT/dt) versus time of $Mn_{0.8}Zn_{0.2}Fe_2O_4$. The upper rf branch displays the heating, the lower branch the cooling phase.

vessel and inserted into the center of a copper coil. The volume of the sample was 5 ml. An rf generator (Huettinger Elektronik, type IG5) which provides a maximum power of 4.3 kW and 1.95 MHz was used to create an rf magnetic field. The generator power is calculated from the voltage and current readings displayed at the generator panels. In order to provide a well defined heat flux from the ferrofluid into the environment at any given temperature of the ferrofluid, and in order to prevent the inhomogeneous heating we employed a high-precision refrigerating circulating bath (Lauda RM 6, precision 0.1 °C) controlled at 25 °C. In this way we achieved a strict proportionality between the temperature difference of the ferrofluid specimens and the environment, and the heat flux leaving the sample. This feature is essential for accurate measurements of the rf absorption of the ferrofluid.

The specimens were heated from 25 °C up to temperatures as high as 90 °C at different output powers of the rf generator. The temperatures were measured by means of a Fotemp1 optical thermosensor from Optocon, Dresden (Germany), with an accuracy of ±1 K. The sensor head was placed in the center of the specimen. The glass fiber thermosensor with a diameter of 1.3 mm is attached to an analog–digital converter. The temperatures were listed on a display and via interface adapter delivered to a computer. Simple software allows us to set measurement conditions, save data and display plots of temperature versus time. We analyzed the change of the temperature over time with inductive heating for 90 s with the rf power supply turned on, and subsequent cooling with the
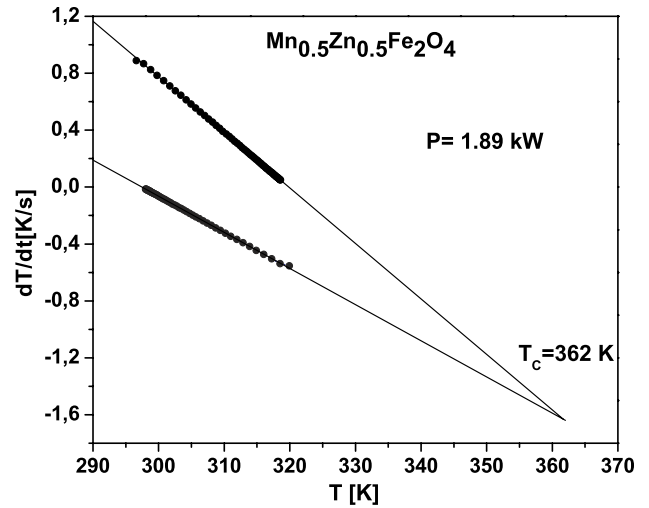
power supply turned off. In this way we have obtained two branches for heating and cooling processes, as is shown in figure 4 (upper panel).

Using a linear extrapolation for the cooling and heating branches in accordance with equation (4), we can estimate the Curie temperatures as the intersection point of temperature change over time with temperature (see figure 5). We expect to have Curie temperatures below those of bulk material.

The estimated Curie temperatures by calorimetric measurements for $Mn_xZn_{1-x}Fe_2O_4$ samples are compiled in table 1. Of course, our method does not work for Curie temperatures at or below room temperature; we would then, above the Curie temperatures, exploit the fluctuation tail of the magnetization above the Curie temperature and would not work in the validity range of equation (4). A real advantage of the experiments is the low temperature measurements of T_C. We can avoid thermal effects in thermo-magnetization curves [11] and particle growth effects.

We note that the Curie temperature rises with increasing x of Mn content. We have compared our results with the values reported in literature relative to the bulk [12, 13] and nanostructured [10, 14] ferrites (see figure 6).

Xuan *et al* [14] claim to have determined T_C values for Mn–Zn ferrites by thermal gravimetry, presumably having determined the force of an applied magnetic gradient field to the ferrite samples as a function of temperature. This method possibly tends to overestimate the Curie temperature as there are still considerable magnetic forces in the paramagnetic range above T_C. Thus these results should be considered as an estimate of the upper limit for T_C rather than as exact values. Arulmurugan *et al* [10] estimate Curie temperatures of Mn–Zn ferrites from magnetization curves using a small linear section of the temperature dependence of the magnetization (M versus T) and obtain T_C values also larger for nanoparticles than for bulk material. With a square route extrapolation $M(T) \propto \sqrt{T_C - T}$, as would be theoretically required, their resulting Curie temperatures would be lower. Compared to the Curie
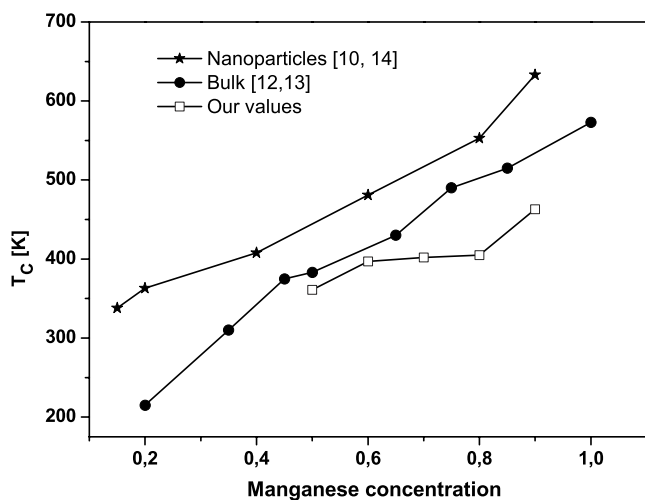
Figure 6. Curie temperatures relative to our samples, bulk and nanostructured MnZn ferrite, against manganese concentration.

temperatures of bulk Mn–Zn ferrites [12, 13] our values are lower, and this appears reasonable in view of the well known feature of nanoparticles that phase transitions in general are lower than in the bulk material [15].

5. Conclusions

We propose a simple and reasonable method for Curie temperature measurement of magnetic colloids. As the calorimetric measurements have been made at low temperatures we prevented undesired effects like particle growth, inhomogeneous radiative heat transfer and phase conversion to another ferrimagnetic phase. Also, we have the advantages of short time measurements, accurate temperature uniformity, high power measurements and direct determination of the losses. The method allows for an accurate measurement of the temperature absorption of magnetic fluids in high frequency magnetic fields, a feature which is of outstanding importance for medical applications of ferrofluids in hyperthermia as well as for process design of ferrite-based industrial heating applications [16].

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