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LETTER TO THE EDITOR

Magnetocaloric effect in Mn₁₂ 2-Cl benzoate**F Torres¹, X Bohigas², J M Hernández¹ and J Tejada¹**¹ Departament de Física Fonamental, Universitat de Barcelona, Diagonal, 647, 08028 Barcelona, Spain² Departamento de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Diagonal, 647, 08028 Barcelona, Spain

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Online at stacks.iop.org/JPhysCM/15/L119**Abstract**

The magnetocaloric effect in high spin Mn₁₂ 2Cl-benzoate clusters was studied. We observed a high entropy change around the blocking temperature of the magnetization. Theoretical simulations indicate the shift of the entropy change with the sweeping rate of the magnetic field.

The magnetocaloric effect is of significant technological importance since magnetic materials with large magnetocaloric effect values could be employed as magnetic refrigerants in magnetic refrigerators. Recently, interest in research into the magnetocaloric effect has been considerably enhanced owing to its potential impact on energy savings and environmental concerns. It is known that the magnetocaloric effect is useful in achieving low temperatures. Materials that may work as refrigerants in the range from 10 K to room temperature take advantage of the entropy change associated with the ferro- and ferrimagnetic to paramagnetic transition near their Curie temperature [1–4]. Below 10 K some paramagnetic salts show enough entropy variation when the magnetic material is subjected to an applied field variation to be used as magnetic refrigerants [5, 6]. In the range of the hydrogen and helium liquefaction temperatures, superparamagnetic materials showing blocking temperatures in this interval compete with the ferro- and ferrimagnetic materials.

In this letter we present results obtained in magnetic nanocomposites, the so-called molecular clusters, in which we have observed a high entropy change in the range of temperatures below 4 K.

The magnetocaloric effect is the temperature change produced when a magnetic field variation is applied to a magnetic material. It can be measured as the adiabatic temperature change or as the isothermal magnetic entropy change ΔS_M , as was demonstrated experimentally [7].

The magnetic entropy change of the system is related to the change of the magnetization M as a function of temperature and magnetic field, and can be calculated from magnetization data [8] using the well known Maxwell relationship

$$\Delta S_M(T, H) = \int_{B_{min}}^{B_{max}} \left(\frac{\partial M}{\partial T} \right)_B dB \quad (1)$$

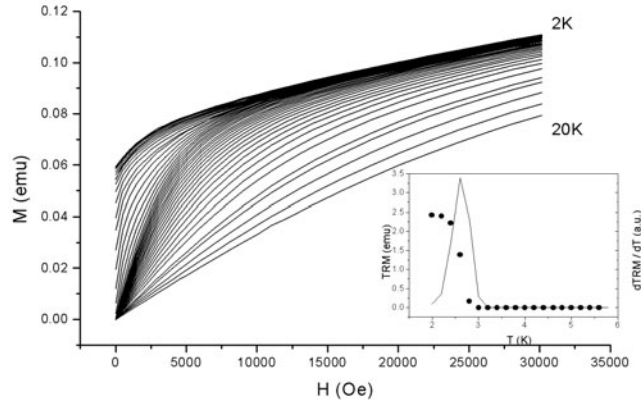


Figure 1. Isothermal $M(H)$ curves measured at different temperatures from 2 to 20 K. The inset shows the temperature dependence of the thermal remanent magnetization measured under a field of 3.0 T. The full curve is the dM/dT curve.

where B_{min} and B_{max} represent the initial and final values of the magnetic induction. It seems clear that a high magnetocaloric effect will be observed when the magnetization varies sharply in a constant field. Thus, a high entropy change can be observed in the ferro- to paramagnetic phase transition when magnetization decays sharply at the Curie temperature.

Magnetic molecular clusters like Mn_{12} 2-Cl benzoate have the advantage over magnetic nanoparticles that a macroscopic sample of molecular magnets consists of a large number of chemically identical entities. The high value of the spin $S = 10$ of these molecules, in addition to their blocking temperature at low K , suggests that these materials should be tested for very low temperature magnetic cooling.

Along the easy axis the magnetic moment can have two possible values, M_+ and M_- . When we apply a magnetic field, the magnetization takes the uncompensated value $M = M_+ - M_-$ and obeys the following differential equation:

$$\frac{dM}{dH} = -\Gamma \frac{M - M_{eq}}{r} \quad (2)$$

where Γ is the total rate of the transitions between the two possible directions of the magnetic moment, r is the sweeping rate of the magnetic field and M_{eq} is the equilibrium magnetic moment. The rate Γ is related to the basic parameters of the magnetic cluster, such as the attempt frequency, ν , the volume and the barrier height between the two possible directions of the moment, U :

$$\Gamma = \nu \exp(-UV/T). \quad (3)$$

Mn_{12} 2Cl-benzoate, or Mn_{12} -benzoate, has a molecular weight of 3502 g mol^{-1} , which forms a molecular crystal of orthorhombic structure with lattice parameters $a = 2.275$, $b = 1.803$ and $c = 1.732 \text{ nm}$ with two molecules per unit cell [9]. The sample studied consist of small crystallites of average length $10 \mu\text{m}$. Due to the super-exchange interactions between eight Mn^{3+} ($s = 2$) and four Mn^{4+} ($s = 3/2$) per unit cell, these molecular clusters have a total spin of $S = 10$. The magnetic easy axes of Mn_{12} -benzoate lie alternatively in the direction (011) or $(0\bar{1}1)$, being nearly perpendicular to their nearest neighbours.

The magnetic measurements were carried out using a SQUID magnetometer. In figure 1, we show the isothermal demagnetization curves in a temperature range from 2 to 20 K. Magnetization was measured under decreasing applied field intensity from 3 to 0 T with 0.2 T

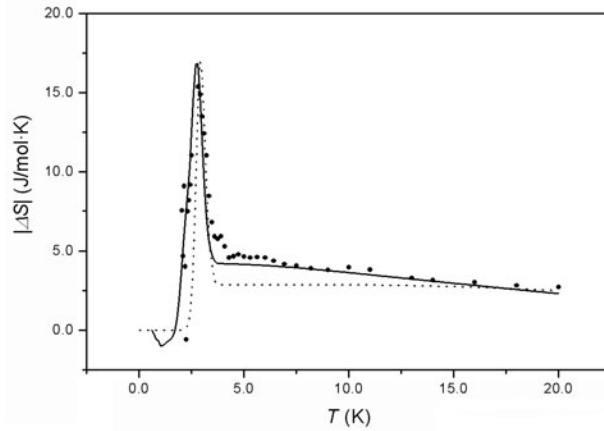


Figure 2. Entropy variation calculated from experimental magnetization curves (dots), and theoretically deduced with two different simulations. See more details in the text.

steps. The remanent magnetization's dependence on temperature is presented in the inset of figure 1. A sharp variation of magnetization at a temperature near the blocking temperature T_B is observed, which suggests a high magnetic entropy change at this temperature; it is clear that above T_B the thermal remanent magnetization goes to zero.

The magnetic entropy change was calculated from these $M(H)$ experimental curves using the numerical formula

$$|\Delta S_B| = \sum_i \frac{M_i - M_{i+1}}{T_i - T_{i+1}} \Delta B_i \quad (4)$$

where M_i and M_{i+1} are the experimental values of magnetization at T_i and T_{i+1} temperatures, respectively, under an applied field of intensity B_i . This expression is a numerical approximation to the integral in equation (1). Figure 2 shows the experimental values of the magnetic entropy change obtained from the experimental isothermal magnetization curves under a magnetic field variation of 3.0 T from saturation to zero field. It is observed that the value of maximum entropy change peaks around the blocking temperature. The dotted curve represents the values of the entropy variation deduced from the simulated isothermal demagnetization curves. This simulation was performed using equation (4) with $\nu = 1 \times 10^{-7}$ s and $U = 66$ K [10]. The values of the sweeping rate, $r = 7 \times 10^{-3}$ Hz, used in this fit corresponds to the time needed to switch off the magnetic field from 3 T. The agreement between theoretical and experimental curves is rather good. However, for temperatures higher than the blocking temperature, there are important differences. In our calculations, the entropy change goes rapidly to the equilibrium value, $2.9 \text{ J mol}^{-1} \text{ K}^{-1}$, but the experimental curve tends much more slowly to this value than the theoretical curve.

In order to better simulate the experimental data, we performed calculations for $M(T, H)$ by considering the spin Hamiltonian

$$H = -D \cdot S_z^2 - g\mu_B \vec{S} \cdot \vec{h} \quad (5)$$

where D is the so-called anisotropy barrier (0.66 K in Mn_{12} 2Cl-benzoate) and $\vec{S} \cdot \vec{h}$ is the Zeeman term due to the interaction of the spin of the molecules with the external magnetic field. With the help of this Hamiltonian, we can calculate M_{eq} precisely, and then by putting it into equations (2) and (1) we obtain the entropy change of the adiabatic demagnetization

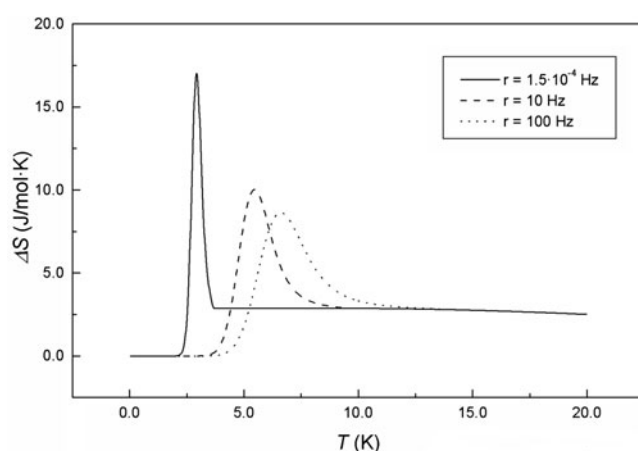


Figure 3. Simulated entropy change for different sweeping rates when the applied magnetic field intensity varies from 3 to 0 T.

process. The use of Mn_{12}Cl powder in our measurements forces us to take into account a spatial distribution of magnetic moments.

The curve in figure 2 represents the entropy change calculated taking into account this Hamiltonian; we can observe the good agreement between our measurements and the new theoretical fit. By comparing the dotted curve and full curve in figure 2, we can see the great importance of the transitions between the spin levels of the system, which contribute to entropy change, especially at temperatures above the blocking temperature.

The entropy change values are greater than those of previously published results calculated in the same range of temperatures [5, 6, 11, 12]. The maximum value of the entropy change detected in our material is $15 \text{ J mol}^{-1} \text{ K}^{-1}$ for a magnetic change of 3 T. This value is half of the entropy change reported in similar material [13], in accordance with the fact that in Mn_{12} -benzoate half of the total spin of the system is aligned in the easy axis direction and the other half in the perpendicular direction. This gives the middle effective magnetic moments than Mn_{12} -acetate where all spins are aligned in the same direction.

Figure 3 shows the entropy change under an applied field of 3 T calculated using the simulation described above for different sweeping rates r of the applied magnetic field. The temperature dependence of the maximum entropy change curve on the sweeping rate parameter is clear. The temperature of the entropy change shows a maximum increase when the sweeping rate of the applied magnetic field increases. Consequently, the entropy change is time-dependent and the shift in the maximum entropy change suggests that it is possible to use this material as a magnetic refrigerant over a broad range of temperatures by varying the sweeping rate of the applied magnetic field.

In conclusion, these data clearly indicate that the magnetocaloric effect in these materials is high and tunable. These materials are, therefore, good candidates to work as magnetic refrigerants in a wide temperature interval in the helium liquid regime.

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