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Magnetocaloric properties of compounds with first order phase transition: Hysteresis effect

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ABSTRACT

In this paper we theoretically discuss the magnetocaloric effect in compounds undergoing first order phase transition, taking into account the hysteresis effect. For this purpose we use a microscopical model of localized magnetic moments including the magnetoelastic interaction. Our calculations show that in compounds undergoing first order transition with large magnetoelastic coupling, the magnetocaloric potentials ΔS_{iso} and ΔT_{ad} depend on the direction of the temperature variation. Moreover, our calculations also show that the magnetocaloric potential ΔS_{iso} around a first order phase transition can be calculated using magnetization data via the Maxwell relation only if the hysteresis is negligible.

1. Introduction

The magnetocaloric effect, i.e., the heating or cooling of magnetic materials subjected to magnetic field variation, can be characterized by the entropy change in an isothermal process (ΔS_{iso}) and by the temperature change in an adiabatic process (ΔT_{ad}) under magnetic field variation [1–3]. The magnetocaloric potential ΔT_{ad} can be measured directly by placing a thermometer on the sample. Alternatively, it can be indirectly determined by using either specific heat data or a combination of specific heat and magnetization data. On the other hand, the magnetocaloric potential ΔS_{iso} can only be determined indirectly by using either specific heat or magnetization data.

Due to the fact that magnetization data are usually easier to obtain than specific heat ones, the relation $\Delta S_{iso} = \int_{B_1}^{B_2} (\partial M/\partial T) dB$ is extensively used to determine the isothermal entropy change. In fact, it is well accepted that the use of this relation is valid for compounds with second order phase transition. However, the determination of ΔS_{iso} through the previous relation, in compounds with first order phase transition is a very controversial issue [4–13]. In compounds with first order phase transition, the determination of ΔS_{iso} using the relation $\Delta S_{iso} = \int_{B_1}^{B_2} (\partial M/\partial T) dB$ is only valid in the range of temperatures away from the first order phase transition [8]. Around the range of temperatures of the first order phase transition, the determination of ΔS_{iso} using the relation $\Delta S_{iso} = \int_{B_1}^{B_2} (\partial M/\partial T) dB$ is not reliable [7–12].

In order to determine the magnetocaloric effect around a first order phase transition, where the thermodynamic processes may not be reversible, the thermal and magnetic hysteresis should be taken into account. Although the hysteresis effect has already been discussed in the literature by using phenomenological models, based in the Landau theory of phase transitions [14–17], its physical implication in the magnetocaloric properties of real compounds is not well understood yet. In order to correctly determine the magnetocaloric effect in compounds undergoing first order phase transition and understand the physical mechanisms involved in the magnetocaloric potentials, it is extremely necessary to consider microscopical models in which the real magnetic interactions are taken into account. In this paper, we use for the first time a microscopical model of localized magnetic moments to discuss the hysteresis effect in compounds with first order phase transition and its connection with their magnetocaloric properties.

Our calculations show that depending on the choice of the model parameters, the first order phase transition can occur with or without hysteresis. If the compound exhibits a first order phase transition without visible hysteresis, its magnetization and demagnetization can be considered as reversible thermodynamic processes, despite the discontinuity around the phase transition. In this scenario, the magnetocaloric potentials do not depend on the direction of the temperature variation and the determination of ΔS_{iso} using magnetization data is a very good approximation for the entire range of temperatures. However, if the compound exhibits first order transition with visible thermal or magnetic hysteresis, the magnetization and demagnetization are not reversible processes so that the use of the relation $\Delta S_{iso} = \int_{B_1}^{B_2} (\partial M/\partial T) dB$ to determine ΔS_{iso} around the phase transition is not valid anymore. In this case, the magnetocaloric potential ΔS_{iso} must be determined

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using specific heat data considering the direction of the temperature variation.

2. Model

We start with the following model Hamiltonian of localized magnetic moments: [18,19]

$$H_{mag} = -\sum_{i,l} \Im_0 J_i \cdot J_l - \sum_{i,l} \Im_1 (J_i \cdot J_l)^2 - \sum_i g\mu_B B \cdot J_i. \qquad (1)$$

In this magnetic Hamiltonian, the first term describes the interaction between magnetic moments, where $\Im_0$ is a renormalized exchange interaction parameter and J_i (J_l) is the total angular momentum. It should be mentioned that the exchange interaction term is usually written with a numerical factor 2. In our model this numerical factor 2 is incorporated in the renormalized parameter $\Im_0$. The second term in the previous Hamiltonian, incorporates the effect of the volume change in the exchange interaction energy. The coefficient $\Im_1$ depends basically on the elastic constant of the system and can be calculated through the minimization of the total energy. Alternatively, it can also be calculated by using a microscopical model in which the electron-phonon interaction is considered. However, such calculations are beyond the scope of the present paper. Here, for the sake of simplicity, we consider the coefficient $\Im_1$ as a model parameter. Thus the second term in the previous Hamiltonian somehow describes the magnetoelastic interaction, since it involves the multiplication of a volume change dependent parameter by the magnetic moments. If the volume is kept constant, the parameter $\Im_1$ goes to zero so that the previous Hamiltonian of localized magnetic moments reduces to the usual one found in the literature. The last term represents the Zeeman interaction between the angular momentum and the external magnetic field (B), where g is the Landé factor and μ_B is the Bohr magneton. It should be emphasized that such a model can be applied to rare earth based compounds, whose magnetism has a localized character.

In the mean field approximation, the magnetic Hamiltonian turns out to be $H_{mag} = -\sum_i g\mu_B B^{eff} J_i$, where $B^{eff} = B + (\Im_0 \langle J \rangle + \Im_1 \langle J \rangle^3)/g\mu_B$ is an effective magnetic field. The magnetization is self-consistently determined by $M = g\mu_B J B_J(x)$ where $B_J(x)$ is the Brillouin function and $x = g\mu_B B^{eff}/k_B T$ with k_B being the Boltzmann constant. It should be mentioned that in this model the order of the phase transition is determined by the ratio $\Im_1/\Im_0$. For $\Im_1 = 0$ the magnetization around the critical temperature goes smoothly to zero so that the phase transition is always of second order. For $\Im_1/\Im_0$ greater than a critical value, the magnetization around the critical temperature goes abruptly to zero so that the phase transition becomes of first order. Besides, in this case of first order phase transition, the magnetization self-consistently determined from $M = g\mu_B J B_J(x)$, can exhibit thermal and magnetic hysteresis. In the model, the larger the magnetoelastic coupling parameter $\Im_1$ the wider the hysteresis.

The magnetic entropy is given by [3]:

$$S_{mag}(T, B) = N_m \Re \left[\ln \left(\sum_{m=-J}^{m=J} e^{-\beta E_m} \right) + \frac{1}{k_B T} \frac{\sum_{m=-J}^{m=J} E_m e^{-\beta E_m}}{\sum_{m=-J}^{m=J} e^{-\beta E_m}} \right]. \qquad (2)$$

Here $\beta = 1/k_B T$ and $E_m = g\mu_B B^{eff} m$ is the energy eigenvalues of the magnetic Hamiltonian, where $-J \le m \le J$. The factor N_m represents the number of magnetic ions per unit formula and $\Re$ is the gas constant. The conduction electron entropy is given by $S_{el}(T) = \gamma T$, where γ is the Sommerfeld coefficient. The crystalline lattice entropy is given in the Debye approximation by [3]:

$$S_{lat}(T) = N_i \left[-3\Re \ln(1 - e^{-(\Theta_D/T)}) + 12\Re \left(\frac{T}{\Theta_D} \right)^3 \int_0^{\Theta_D^a/T} \frac{x^3}{e^x - 1} dx \right] \qquad (3)$$

where N_i represents the number of ions per unit formula and Θ_D is the Debye temperature. Once the total entropy ($S = S_{el} + S_{mag} + S_{lat}$) is known the magnetocaloric potentials are calculated by $\Delta S_{iso}(T, \Delta B) = S(T, B_2) - S(T, B_1)$ and $\Delta T_{ad}(T, \Delta B) = T_2 - T_1$ under the adiabatic condition $S(T_2, B_2) = S(T_1, B_1)$, where $\Delta B = B_2 - B_1$.

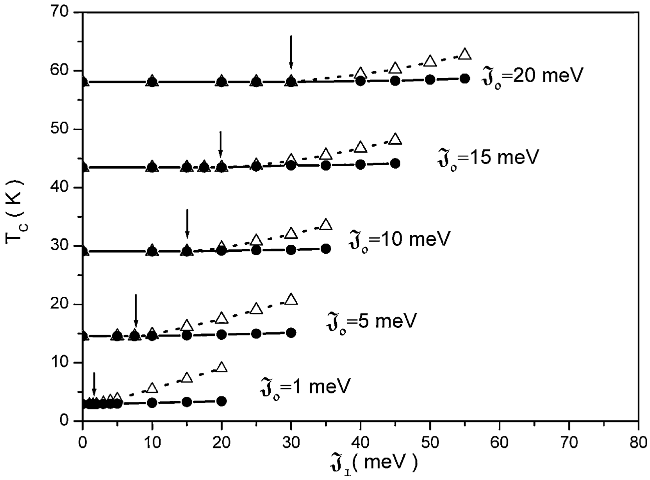

Fig. 1. Critical temperature as a function of $\Im_1$ for some values of $\Im_0$. The solid lines plus closed symbols (dotted lines plus open symbols) represent the calculations when the temperature is decreased (increased).

3. Discussion

For the sake of simplicity, we consider the case of two energy levels by taking the angular momentum as $J = 1/2$. The Landé factor, the Debye temperature and the Sommerfeld coefficient were taken as $g = 2$, $\Theta_D = 200$ K and $\gamma = 5.4$ (mJ/mol K^2) respectively.

In order to understand the appearance of the first order phase transition in the present model of localized magnetic moments, we self-consistently calculate the temperature dependence of the magnetization for some values of the model parameters $\Im_0$ and $\Im_1$. From the magnetization curves obtained by increasing and decreasing temperature, we determine the critical temperatures for the appearance of the magnetic order. In Fig. 1, we plot the critical temperature as a function of the magnetoelastic coupling parameter $\Im_1$ for some fixed values of the exchange interaction parameter $\Im_0$, when the temperature is increased (open symbols plus dotted lines) and decreased (closed symbols plus solid lines). This figure shows that for $\Im_1$ from 0 to a given critical value, the critical temperature does not depend on the direction of the temperature variation. However, above the critical value of the parameter $\Im_1$, the critical temperature obtained by increasing temperature is larger than the corresponding one obtained by decreasing temperature. This dependence of the critical temperature with the direction of the temperature variation characterizes the thermal hysteresis which is inherent to the first order phase transition.

Using the critical value of $\Im_1$ (indicated in Fig. 1 by the arrows), we construct a phase transition diagram shown in Fig. 2. From this figure, we observe that the second order phase transition occurs below the solid line, while the first order phase transition occur above it. It should be emphasized that on the solid line or somewhat above it, the phase transition is of first order but the hysteresis is very narrow and can be neglected. The hysteresis gets larger as

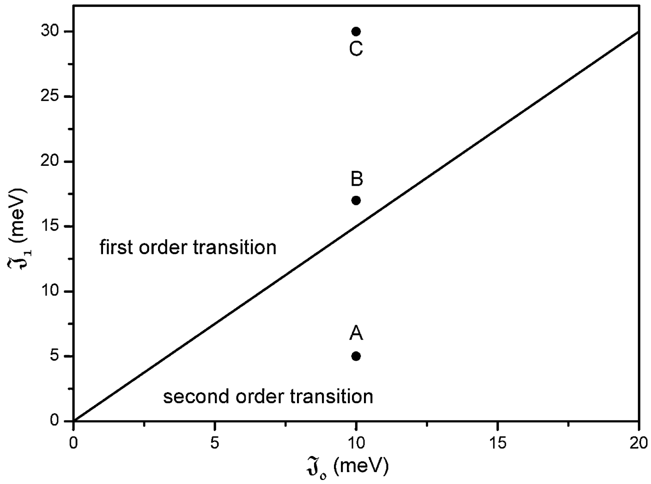

Fig. 2. Phase transition diagram for the model of localized magnetic moments. The solid line separates the regions of first and second order phase transition.

we go upwards from the solid line that separates the region of the second and first order phase transition.

In order to show the thermal hysteresis in the magnetization curves, we self-consistently calculate the temperature dependence of the magnetization for the following sets of model parameters [$\Im_0$ = 10 meV $\Im_1$ = 5 meV], [$\Im_0$ = 10 meV $\Im_1$ = 17 meV] and [$\Im_0$ = 10 meV $\Im_1$ = 30 meV]. These sets of parameters are represented in Fig. 2 by the letters *A* (below the line), *B* (somewhat above the line), and *C* (well above the line) respectively. The magnetization curves for the first set of parameters calculated by increasing and decreasing temperature are shown in Fig. 3 by the solid line and open squares respectively. Note that in this case, the magnetization curves go smoothly to zero. Besides, there is no difference between the magnetization curves when the temperature is increased or decreased. These both features characterize a second order magnetic phase transition. The obtained magnetization curves for the second set of model parameters are shown in Fig. 3 by the solid line (increasing temperature) and open triangles plus doted line (decreasing temperature). In this case, we can observe a big jump in the magnetization curves around the critical temperature, which is an indication of a first order phase transition. However, the magnetization curves when we increase or decrease temperature are almost coincident, so that the thermal hysteresis is very narrow and can be neglected. The obtained magnetization curves for the third set of model parameters are shown in Fig. 3 by solid line (increasing temperature) and by the open circles plus dotted line (decreasing temperature). In this case, there are both the discontinuity in the magnetization curves and the thermal hysteresis around the critical temperature, which are clear indications of the first order magnetic phase transition. A similar behavior is observed in the entropy curves, not shown in this paper.

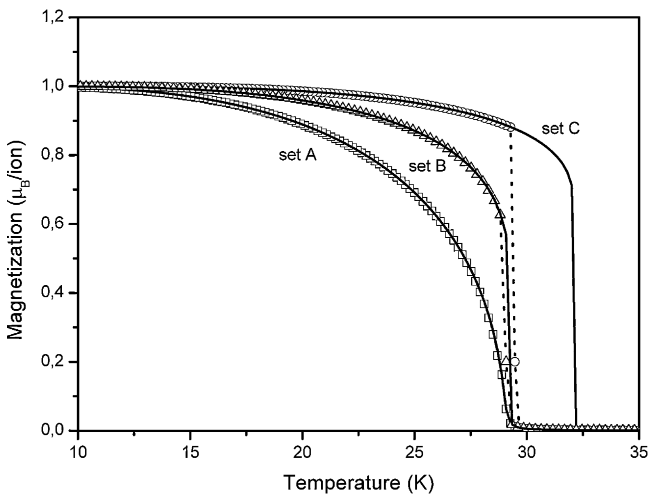

Fig. 3. Magnetization as a function of temperature in the absence of magnetic field for the sets of parameters represented by the letters *A*, *B* and *C* in Fig. 2. Solid lines correspond the calculations with increasing temperature while symbols plus dotted lines represent the calculations with decreasing temperature.

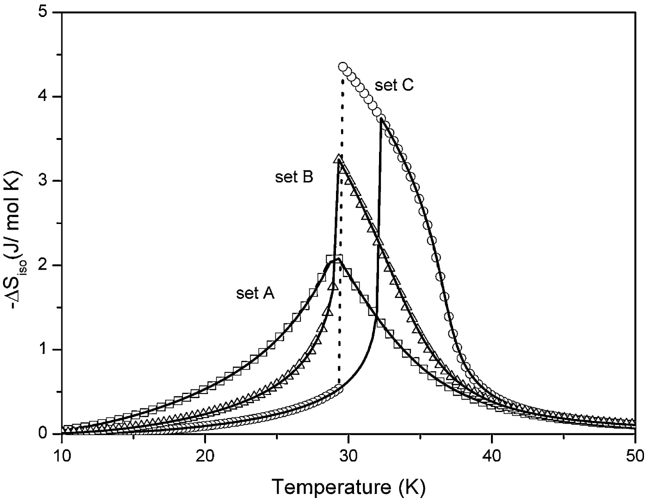

Fig. 4. ΔS_{iso} upon magnetic field variation from 0 to 5 T for the sets of parameters represented by the letters *A*, *B* and *C* in Fig. 2. Solid lines correspond the calculations increasing temperature while symbols plus dotted lines represent the calculations with decreasing temperature.

We use the entropy curves calculated for $B = 0$ and $B = 5\ T$ to calculate the magnetocaloric potentials ΔS_{iso} and ΔT_{ad} for the three sets of model parameters [$\Im_0$ = 10 meV $\Im_1$ = 5 meV], [$\Im_0$ = 10 meV $\Im_1$ = 17 meV] and [$\Im_0$ = 10 meV $\Im_1$ = 30 meV] represented in Fig. 2 by the letters *A*, *B* and *C* respectively. The calculated magnetocaloric potentials ΔS_{iso} and ΔT_{ad} are shown in Figs. 4 and 5 respectively. In these figures, the solid lines represent the calculations with increasing temperature while symbols (squares, triangles and circles) represent the calculations with decreasing temperature. From these figures, we can observe that for the first set of

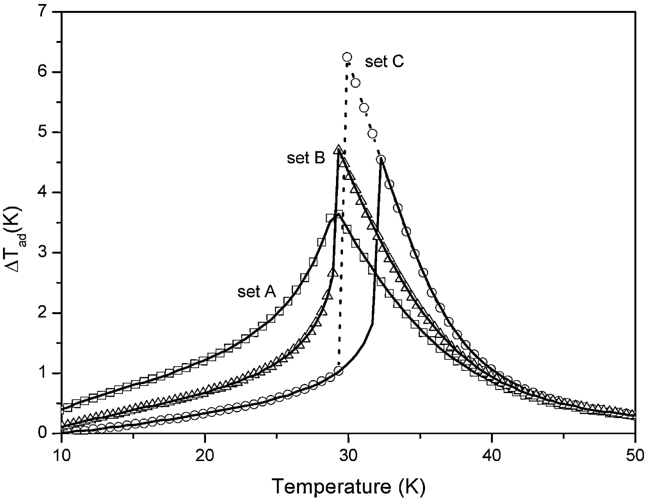

Fig. 5. ΔT_{ad} upon magnetic field variation from 0 to 5 T for the sets of parameters represented by the letters *A*, *B* and *C* in Fig. 2. Solid lines correspond the calculations increasing temperature while symbols plus dotted lines represent the calculations with decreasing temperature.

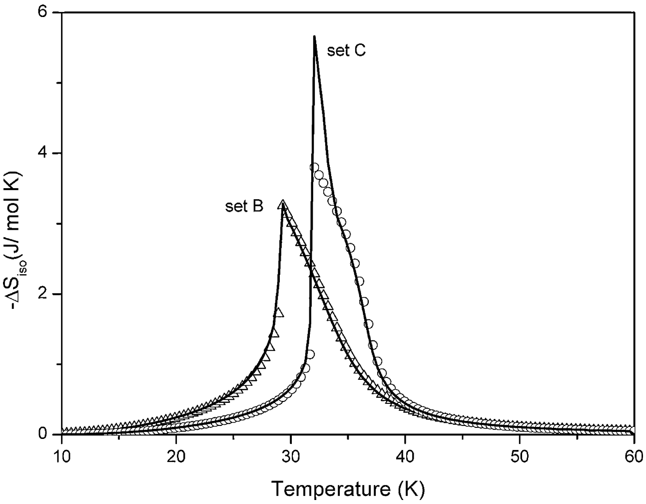

Fig. 6. ΔS_{iso} upon magnetic field variation from 0 to 5 *T* for the sets of parameters represented by the letters *B* and *C* in Fig. 2. The solid lines represent the calculations using magnetization, while symbols represent the calculation using specific heat.

parameters, represented by the letter *A* in Fig. 2, where the compound undergoes a second order phase transition, the curves of the magnetocaloric potentials calculated increasing or decreasing temperature are coincident. This coincidence occurs because the magnetization and demagnetization are reversible processes. For the second set of model parameters, represented by the letter *B* in Fig. 2, it can be observed that there is also a coincidence between the curves of the magnetocaloric potentials calculated with increasing or decreasing temperature. This coincidence occurs in this case, because the system undergoes a first order phase transition without visible thermal hysteresis, so that the magnetization and the demagnetization can be considered as reversible processes, despite the discontinuity in the magnetization curves. However, for the third set of model parameters, represented by the letter *C* in Fig. 2, where the system undergoes a first order phase transition with a visible thermal hysteresis, the magnetocaloric potentials calculated with increasing or decreasing temperature are quite different. This is because the magnetization and the demagnetization of the system are not reversible processes.

Now we turn our attention to the controversial issue of the determination of ΔS_{iso} in compounds undergoing first order phase transition, by using magnetization data. In order to further discuss this subject, we also calculate the magnetocaloric potential ΔS_{iso} using the Maxwell relation for the two sets of model parameters, namely [$\Im_0 = 10$ meV $\Im_1 = 17$ meV] and [$\Im_0 = 10$ meV $\Im_1 = 30$ meV]. For these sets of parameters, represented in Fig. 2 by the letters *B* and *C*, the system undergoes first order phase transition without and with a visible thermal hysteresis respectively. In Fig. 6, we plot ΔS_{iso} calculated via the relation $\Delta S_{iso} = \int_{B_1}^{B_2} (\partial M/\partial T) dB$ under magnetic field variation from 0 to 5 *T* and increasing temperature (solid lines). For the sake of comparison, we also plot in this figure the corresponding ΔS_{iso} obtained from specific heat (symbols). From this figure we clearly observe that for the model parameters [$\Im_0 = 10$ meV $\Im_1 = 17$ meV], where the system undergoes a first order phase transition without visible thermal hysteresis, the values of ΔS_{iso} calculated using both specific heat and magnetization data are coincident. This coincidence is due to the fact that the thermal hysteresis is very small so that the magnetization process may be considered as a reversible one. However, for the set of model parameters [$\Im_0 = 10$ meV $\Im_1 = 30$ meV], where the system undergoes a first order phase transition with a visible thermal hysteresis, the calculation of ΔS_{iso} by using the relation $\Delta S_{iso} = \int_{B_1}^{B_2} (\partial M/\partial T) dB$ provides overestimated values. This means that this relation must not be used to calculate ΔS_{iso} in compounds undergoing a first order phase transition with a visible thermal hysteresis. In this case, the magnetocaloric potential ΔS_{iso} should be determined by using specific heat data considering the direction of the temperature variation.

In summary, in this paper we discuss the magnetocaloric effect in compounds undergoing a first order phase transition by using a microscopical model of localized magnetic moments. Our main conclusions are: (1) in compounds undergoing a first order phase transition with negligible thermal hysteresis, the magnetocaloric potentials ΔS_{iso} and ΔT_{ad} do not depend on the direction of the temperature variation. Besides, in this case the magnetocaloric potential ΔS_{iso} may be also calculated using magnetization data via the relation $\Delta S_{iso} = \int_{B_1}^{B_2} (\partial M/\partial T) dB$. (2) in compounds undergoing a first order phase transition with visible thermal hysteresis, the magnetocaloric potentials depend on the direction of the temperature variation. Moreover, in this case the values of ΔS_{iso} obtained by using the relation $\Delta S_{iso} = \int_{B_1}^{B_2} (\partial M/\partial T) dB$ are not reliable around the first order phase transition. To conclude this paper, it is worth mentioning that the best materials to be used as magnetic refrigerant should be those in the verge of the first order phase transition, because it can exhibit large magnetocaloric potentials without hysteresis losses. Many magnetic materials can be driven to the condition of first order transition with no visible hysteresis by doping or by applying external pressure.

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