Theoretical calculations of the magnetocaloric effect in MnFeP$_{0.45}$As$_{0.55}$: a model of itinerant electrons

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Abstract
In this paper we calculate the magnetocaloric effect in the compound MnFeP$_{0.45}$As$_{0.55}$. We use a microscopical model in the picture of the band theory, including a magnetoelastic interaction. The theoretically calculated isothermal entropy changes upon magnetic field variations are in good agreement with the available experimental data.

The ability of the magnetic materials to heat up or cool down when subjected to a magnetic field variation is known as the magnetocaloric effect [1–5]. The magnetocaloric effect is measured by the isothermal entropy change (ΔS) and by the adiabatic temperature change (ΔT_{ad}) upon magnetic field variation. In the later 1990s [6, 7] it was shown that the isothermal entropy change for a magnetic field variation from 0 to 5 T in the compound Gd$_5$Si$_2$Ge$_2$ reaches a large value around room temperature. This observation was termed the giant magnetocaloric effect. After this discovery, many experimental works have been done in order to get new magnetic materials with a giant magnetocaloric effect. Tegus *et al* [8] have shown that for the same magnetic field variation the isothermal entropy change around room temperature in the compound MnFeP$_{0.45}$As$_{0.55}$ is as large as the one observed in Gd$_5$Si$_2$Ge$_2$. Wada *et al* [9, 10] showed that the compound MnAs also exhibits a giant magnetocaloric effect around room temperature. Very recently [11] it has been reported that the isothermal entropy change in the compound MnAs under hydrostatic pressure is much greater than the one observed in this same compound at ambient pressure. For instance, at a pressure of 2.23 kbar and for a magnetic field variation from 0 to 5 T the isothermal entropy change is around 267 J K^{-1} kg^{-1}. Due to this huge value of the isothermal entropy change, which exceeds the limit expected from the saturation value of the magnetic entropy, i.e., $\Delta S_{\text{mag}} = R \ln(2J + 1)$, this effect was termed the colossal magnetocaloric effect. It is worth mentioning here that all three compounds Gd$_5$Si$_2$Ge$_2$, MnAs and MnFeP$_{0.45}$As$_{0.55}$ undergo a first-order magnetic phase transition together with a sizable change in the lattice parameters. The experimental observations of the giant and the colossal magnetocaloric effect indicate that something other than the alignment of the magnetic moments contributes to the isothermal entropy change in compounds undergoing a first-order magnetic phase transition. Pecharsky *et al* [12] have

experimentally estimated that the isothermal entropy change in the compound Gd_5Ge_4 has a sizable contribution from the crystallographic transformation induced in this compound by the applied magnetic field. More recently, Morellon *et al* [13] have estimated the contribution from the crystallographic transformation to the isothermal entropy change in the compound $Tb_5Si_2Ge_2$ under pressure. All these experimental evidences show that in the theoretical calculations of the magnetocaloric effect in compounds with a first-order magnetic phase transition, it is very important to include the dependence of the crystalline lattice entropy on the applied magnetic field. Bearing this discussion in mind, we use a simple analytical model to estimate the contribution from the crystalline lattice to the isothermal entropy change [14]. In this paper we claim that the colossal magnetocaloric effect comes from the crystalline lattice.

Very recently, we calculated the magnetocaloric effect in the compound $MnFeP_{0.45}As_{0.55}$, by using a Heisenberg-like model including the magnetoelastic effect [15] on the basis of the Bean and Rodbel model [16]. However, the magnetocaloric effect in the compound $MnFeP_{0.45}As_{0.55}$ should be better described by a model Hamiltonian based on the band theory of magnetism which incorporates the itinerant electrons [17]. In the present work, we describe the magnetocaloric effect in the compound $MnFeP_{0.45}As_{0.55}$, by using a Hubbard-like model Hamiltonian, including the magnetoelastic coupling which renormalizes the crystalline lattice vibrations and the electronic structure of the compound. It has been experimentally shown [18] that the compound $MnFeP_{1-x}As_x$ for concentrations $0.15 \leqslant x \leqslant 0.66$ crystallizes in the hexagonal Fe_2P-type structure. Its saturation magnetization is about $3.9\mu_B$/fu and is mainly due to the Mn ions, although there is a small magnetic moment at the Fe sites parallel to Mn ones. It has also been experimentally shown that the compound $MnFeP_{0.45}As_{0.55}$ undergoes a first-order transition from the paramagnetic to the ferromagnetic phase accompanied by a sudden decrease of the lattice parameters. A more rigorous theoretical description of the magnetic properties of the compound $MnFeP_{0.45}As_{0.55}$ should consider the effect of the disorder in its electronic structure and include two coupled sublattices, namely, one sublattice for Mn ions and the other one for Fe ions. However, this kind of calculation is very complex and it is beyond the scope of the present work. So in order to perform the theoretical calculations and get an insight into the physical mechanism involved in the magnetocaloric effect observed in the compound $MnFeP_{0.45}As_{0.55}$, we adopt some approximations:

(i) since the magnetization of the $MnFeP_{0.45}As_{0.55}$ is mainly dominated by the Mn ions, we consider, as our first approximation, only the sublattice of the Mn ions with an effective magnetization renormalized by the magnetic moments from the Fe ions;

(ii) we take, as our second approximation, an effective electron density of states, which incorporates the presence of the disorder in the compound $MnFeP_{0.45}As_{0.55}$.

Within these approximations, we start with the following model Hamiltonian in the mean field approach:

$$H = \sum_{i\sigma}(\varepsilon_0 + U\langle n_{-\sigma}\rangle - \mu_B h^{ext})d_{i\sigma}^+ d_{i\sigma} + \sum_{ij\sigma} T_{ij\sigma} d_{i\sigma}^+ d_{j\sigma}. \tag{1}$$

This Hamiltonian describes a system of itinerant electrons, in the single-band approximation. ε_0 is an atomic energy level, U is the Coulomb interaction parameter for itinerant electrons and h^{ext} is the applied magnetic field. The term $T_{ij\sigma} = \sum \tilde{\varepsilon}_{k\sigma} e^{ik(r_i - r_j)}$ represents the electron energy of hopping between two different sites, where the energy $\tilde{\varepsilon}_{k\sigma}$ is taken as $\tilde{\varepsilon}_{k\sigma} = \varepsilon_{k\sigma}(1 - \gamma_{el}\Omega)$ where $\Omega = (V - V_0)/V_0$ is the unit cell deformation and γ_{el} is the electronic magnetoelastic coupling parameter which renormalizes the width of the energy band. This parametrization is an extension of the Bean and Rodbel approach of the magnetoelastic effect for a model of itinerant electrons. Here, we take the unit cell deformation, associated with the magnetoelastic

coupling, proportional to the square of the total magnetization, i.e., $\Omega \sim M^2$. Using the Green function techniques, the local Green function for the Hamiltonian in equation (1) is given by

$$g_{00\sigma}(\omega) = \int \frac{\rho_0(\varepsilon')\,\mathrm{d}\varepsilon'}{\omega - (1 - \gamma_{\mathrm{el}}M^2)\varepsilon' - \varepsilon_0 - U\langle n_{-\sigma}\rangle + \mu_{\mathrm{B}}h^{\mathrm{ext}}} \tag{2}$$

where $\omega = \varepsilon + \mathrm{i}0$ and $\rho_0(\varepsilon')$ is a standard paramagnetic electron density of states. The spin dependent density of states for 3d electrons is obtained from $\rho_\sigma(\varepsilon) = -(1/\pi)\,\mathrm{Im}\,g_{00\sigma}(\omega)$. The electron occupation number per spin direction is given by $\langle n_\sigma\rangle = \int \rho_\sigma(\varepsilon)f(\varepsilon)\,\mathrm{d}\varepsilon$, where $f(\varepsilon)$ is the Fermi distribution function. The magnetization is calculated from $M = 5(\langle n_\uparrow\rangle - \langle n_\downarrow\rangle)$, where the factor 5 accounts for the degeneracy of the 3d states. The spin dependent electron density of states must be self-consistently determined under the condition that the total electron occupation number should be kept constant. From equation (2) it can be observed that the width of the electron density of states changes as a function of temperature due to the magnetoelastic coupling parameter γ_{el}. Once the magnetic self-consistency is solved, we can calculate the thermodynamic properties. The contribution from the itinerant electrons to the total entropy is given by [17]

$$S_{\mathrm{mag}}(T, h^{\mathrm{ext}}) = R\left[\sum_\sigma \int_{-\infty}^{\mu} \ln[1 + \mathrm{e}^{-\beta(\varepsilon-\mu)}]\rho_\sigma(\varepsilon)\,\mathrm{d}\varepsilon + \frac{1}{kT}\sum_\sigma \int_{-\infty}^{\mu}(\varepsilon-\mu)\rho_\sigma(\varepsilon)f(\varepsilon)\,\mathrm{d}\varepsilon\right] \tag{3}$$

where μ is the chemical potential of the itinerant electrons, R is the gas constant and $\beta = 1/kT$, k being the Boltzmann constant. It should be emphasized that, in transition metal based compounds, it is not possible to separate the magnetic and the electronic entropies, since in these compounds the magnetism is due to the itinerant electrons. Thus, the previous expression for S_{mag} contains both the magnetic and the electronic entropies. Notice also that the magnetic entropy given in equation (3) depends on the cell deformation through the electronic magnetoelastic coupling parameter γ_{el}, which modifies the width of the spin dependent electron density of states. Taking into account the magnetoelastic coupling, the contribution from the crystalline lattice to the total entropy, in the Debye approximation, is given by [17]

$$S_{\mathrm{lat}}(T, h^{\mathrm{ext}}) = \left[-3R\ln(1 - \mathrm{e}^{-\frac{\tilde{\Theta}_{\mathrm{D}}}{T}}) + 12R\left(\frac{T}{\tilde{\Theta}_{\mathrm{D}}}\right)^3 \int_0^{\tilde{\Theta}_{\mathrm{D}}/T} \frac{x^3}{\mathrm{e}^x - 1}\,\mathrm{d}x\right]. \tag{4}$$

Here $\tilde{\Theta}_{\mathrm{D}} = \Theta_{\mathrm{D}}(1 - \gamma_{\mathrm{ph}}M^2)$ is the renormalized Debye temperature, where Θ_{D} is the bare value of the Debye temperature and γ_{ph} is the phononic magnetoelastic coupling parameter. Notice that the crystalline lattice entropy depends on the applied magnetic field via the renormalized Debye temperature. The total entropy of the compound is given by $S = S_{\mathrm{lat}} + S_{\mathrm{mag}}$.

In order to calculate the magnetocaloric effect in the compound MnFeP$_{0.45}$As$_{0.55}$ we need to fix a set of model parameters. We use an effective electron density of states and properly choose the Coulomb interaction parameter to reproduce the experimental value of the saturation magnetization at $T = 0$ K. The compound MnFeP$_{0.45}$As$_{0.55}$ undergoes a first-order transition from the paramagnetic to the ferromagnetic phase accompanied by a sudden decrease of the lattice parameters, which modifies the Debye temperature and the electronic structure of the compound. In our model these effects are taken into account by the electronic (γ_{el}) and phononic (γ_{ph}) magnetoelastic parameters. The electronic magnetoelastic coupling parameter γ_{el} was chosen to yield a first-order magnetic phase transition and the parameter γ_{ph} was taken as $0.06\gamma_{\mathrm{el}}$. The bare value of the Debye temperature was taken as $\Theta_{\mathrm{D}} = 400$ K. With these parameters, which are kept fixed during the entire self-consistent process, we calculate the temperature dependence of the magnetization and the temperature dependence of total
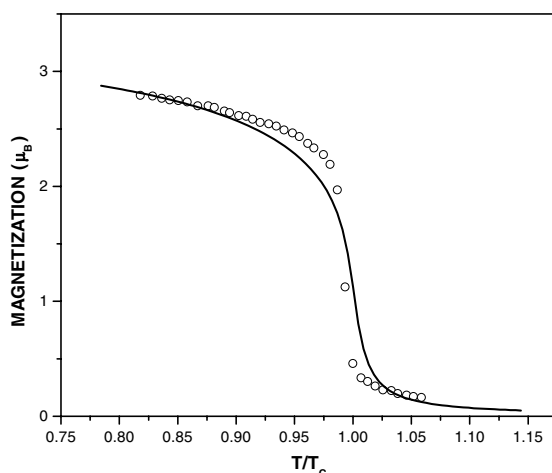
Figure 1. Temperature dependence of the magnetization for MnFeP$_{0.45}$As$_{0.55}$. The solid line corresponds to our calculations whereas circles represent experimental data [8] for an applied magnetic field of 1 T.

entropy of the compound MnFeP$_{0.45}$As$_{0.55}$. Our calculations show that, as we go from low temperature to high temperature, the electron density of states suddenly becomes broader around the magnetic ordering temperature. As a result the magnetization goes abruptly to zero yielding a first-order magnetic phase transition.

It is important to mention that for the Hamiltonian given in equation (1), in which the electron–electron interaction is treated in the mean field approximation, the magnetic ordering temperature (T_C) is overestimated. For the model parameters used in the present work the calculated magnetic ordering temperature is approximately one and a half times higher than the one found experimentally. In order to get a better value of T_C it is necessary to go beyond the mean field approximation used in this work. This kind of calculation is much more complex and it is not within the scope of the present paper. Although the mean field approximation overestimates the magnetic ordering temperature, it provides a good trend of experimental data for the magnetic and thermodynamics properties. So in order to compare our theoretical calculations with the available experimental data, we make plots using the renormalized temperature T/T_C. In figure 1, we plot the temperature dependence of the magnetization calculated by $M = 5(\langle n_\uparrow \rangle - \langle n_\downarrow \rangle)$ for an applied magnetic field of 1 T. In this figure we can observe a good agreement between our theoretical calculations and the experimental data [8]. In figure 2, we plot the total entropy in the absence of a magnetic field (full line), for an applied magnetic field of 2 T (dotted line) and for an applied magnetic field of 5 T (dashed line). From the entropy versus temperature diagram shown in figure 2, we calculated the isothermal entropy change upon magnetic field variation as $-\Delta S(T) = S(T, h^{ext} \neq 0) - S(T, h^{ext} = 0)$. From the entropy versus temperature diagram shown in figure 2 we also calculated the adiabatic temperature change upon magnetic field variation, i.e., $\Delta T_{ad}(T) = T_2 - T_1$ determined under the adiabatic condition $S(T_1, h^{ext} \neq 0) = S(T_2, h^{ext} = 0)$. The theoretically calculated isothermal entropy changes shown in figure 3, for a magnetic field variation from 0 to 2 T (solid line) and one from 0 to 5 T (dashed line), are in good agreement with experimental data [8]. The large value of the isothermal entropy change in the compound MnFeP$_{0.45}$As$_{0.55}$ is associated with the first-order magnetic phase transition, which is due to the strong magnetoelastic coupling. With the model parameters used in this work, we found that the contribution from
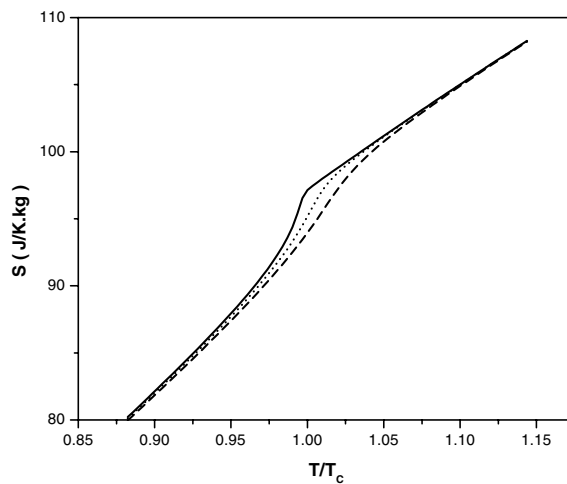
Figure 2. Temperature dependence of the total entropy ($S = S_{lat} + S_{mag}$) for MnFeP$_{0.45}$As$_{0.55}$. The solid line represents the calculations in the absence of an external magnetic field whereas the dotted and dashed lines represent the calculations for 2 and 5 T respectively.
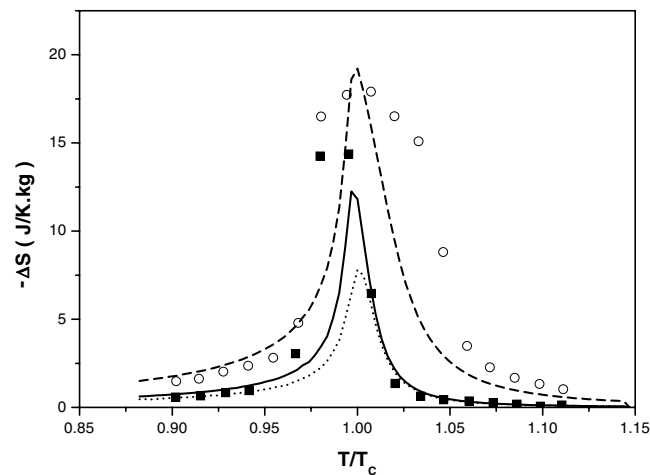

Figure 3. Isothermal entropy change (ΔS) for MnFeP$_{0.45}$As$_{0.55}$. The dotted, solid and dashed lines correspond to our calculations for a magnetic field variation from 0 to 1.45 T, from 0 to 2 T and from 0 to 5 T respectively. Squares and circles represent experimental data [8].

the crystalline lattice to the isothermal entropy change is less than 10%. In figure 4, we plot the adiabatic temperature changes for the magnetic field variation from 0 to 1.45 T (dotted line), from 0 to 2 T (solid line) and from 0 to 5 T (dashed line). From this figure we can note that the value of the peak in the calculated curve for the magnetic field variation from 0 to 1.45 T is somewhat smaller than the experimental data [19]. This fact could be an indication that the model should be improved to go beyond the Debye approximation in order to better describe the crystalline lattice entropy. Besides, we need further experimental data for other magnetic field variations, in order to check our theoretical calculations and get an insight into the physical mechanism involved in the magnetocaloric effect observed in the compound MnFeP$_{0.45}$As$_{0.55}$.
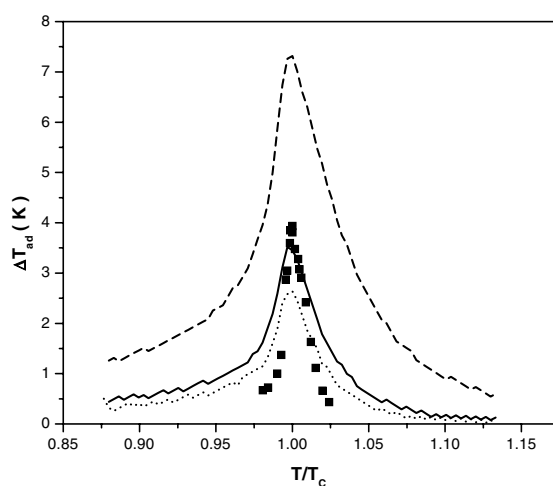
Figure 4. Calculated adiabatic temperature change (ΔT_{ad}) for MnFeP$_{0.45}$As$_{0.55}$ for a magnetic field variation from 0 to 1.45 T (dotted line), from 0 to 2 T (solid line) and from 0 to 5 T (dashed line). Squares are experimental data [19] for a magnetic field variation from 0 to 1.45 T.
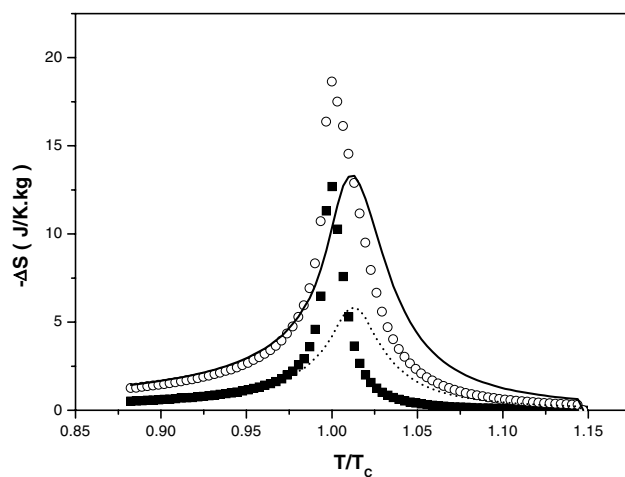

Figure 5. Isothermal entropy change (ΔS) for MnFeP$_{0.45}$As$_{0.55}$ for a magnetic field variation from 3 to 5 T (dotted line) and one from 2 to 7 T (solid line). Squares and circles represent our theoretical calculations for a magnetic field variation from 0 to 2 T and one from 0 to 5 T respectively.

We also calculate the magnetocaloric quantities ΔS and ΔT_{ad} for the magnetic field variations $\Delta h^{ext} = 2$ and 5 T starting from an applied magnetic field different from zero. Our theoretical predictions for the isothermal entropy changes for the magnetic field variations from 2 to 7 T and from 3 to 5 T are shown respectively by the solid and dotted lines in figure 5. For the sake of comparison, we also plot in this figure the isothermal entropy changes calculated for the magnetic field variation from 0 to 5 T (open circles) and that from 0 to 2 T (squares). From figure 5, we can note that the isothermal entropy changes in the compound MnFeP$_{0.45}$As$_{0.55}$ depend not only on the magnetic field variation but also on the starting and final values of the applied magnetic field. We can observe that for the same magnetic field variation, the higher the initial magnetic field, the smaller the peak in the ΔS curve and the
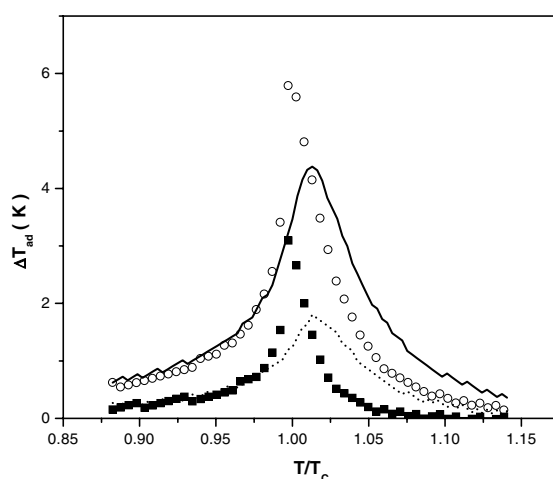
Figure 6. Adiabatic temperature change (ΔT_{ad}) for MnFeP$_{0.45}$As$_{0.55}$ for a magnetic field variation from 3 to 5 T (dotted line) and one from 2 to 7 T (solid line). Squares and circles represent our theoretical calculations for a magnetic field variation from 0 to 2 T and one from 0 to 5 T respectively.

higher the temperature of its location. This occurs because the applied magnetic field shifts the magnetic ordering temperature of the compound MnFeP$_{0.45}$As$_{0.55}$ to higher temperature and tends to change its magnetic phase transition from first to second order. As the compound MnFeP$_{0.45}$As$_{0.55}$ undergoes a first-order magnetic phase transition, its isothermal entropy change for a magnetic field variation from 2 to 7 T is still large. Similar behaviours are observed in the curves for the adiabatic temperature changes shown in figure 6. This kind of behaviour is expected for any material with a first-order magnetic phase transition. These results show that, if we make a magnetic field variation starting with an initial magnetic field different from zero, we can use a given magnetic material with a first-order magnetic phase transition as a magnetic refrigerant in different ranges of temperature.

In conclusion, in this paper we have used a microscopical model to calculate the magnetocaloric effect in the compound MnFeP$_{0.45}$As$_{0.55}$. The model is based in the picture of the band theory and includes the magnetoelastic coupling. Our theoretical calculations for the isothermal entropy change upon magnetic field variation show a good agreement with the available experimental data. The present calculations may be improved by using an approach beyond the mean field approximation and by including a more rigorous treatment of the chemical disorder. However this procedure makes the numerical calculations much more complex and it is beyond the scope of this paper. Besides, it is expected that these improvements would not change the main conclusions of this work.

Acknowledgments

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