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Adiabatic temperature change in perovskite manganites

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The adiabatic temperature change ΔT is studied theoretically in perovskite oxides such as $La_{1-x}Ca_xMnO_3$ crystals. We use a two-parameter phenomenological model which accounts for electron-phonon coupling. The model predicts the linear dependence of ΔT on magnetic field ΔH if only the electronic specific heat is accounted for. In order to determine the peak value of ΔT at T_C it is enough to measure the magnetization vs the magnetic field. The calculated quantities are discussed in the context of various measurements.

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The application of an external magnetic field to magnetic materials such as perovskite manganites causes a change of their internal energy. If the magnetic field is applied adiabatically (thermal isolation of the material) the material changes its temperature. This adiabatic temperature change ΔT upon the application of a magnetic field H is the basic parameter in the thermodynamics of the Carnot cycle. Another important parameter is the magnetic entropy change ΔS_M. The determination of both parameters attracted considerable research interest[1–4] due to application in the refrigeration technology, making it more efficient and ecological. While ΔS_M can simply be derived from a magnetization measurement, the determination of ΔT is associated with considerable difficulties.[2,5–9] Therefore, in publications on the magnetocaloric effect often only the determination of ΔS_M is reported.[10–14] In this paper, we analyze the theoretical aspects of a ΔT calculation. In ferromagnetic materials an adiabatic temperature change ΔT is largest at the critical temperature T_C, where application of a magnetic field influences strongly the electronic configuration change. In this analysis we use the two-level phenomenological model of both abrupt and continuous phase transitions described previously.[15] A starting point in this model is a single pair Mn^{3+}-Mn^{4+} of neighboring ions entering the Mn^{3+}-O^{2-}-Mn^{4+} chain. At $T=0$ K, the e_g electron occupies the bonding state $|b\rangle$. In this state the e_g electron is equally distributed between two $d_{3z^2-r^2}$ orbitals of both Mn ions. With the increase of temperature the ground state admixes the nonbonding (excited) state $|c\rangle$. This is the $d_{x^2-y^2}$ state located on any of two Mn ions. In thermal equilibrium, the electron distribution n is determined by a minimization of the free energy with respect to n, which gives[15]

$$n = \frac{1}{\frac{1}{g}\exp\left(\frac{tR - 2\varepsilon n + 2\mu H}{k_B T}\right) + 1}, \tag{1}$$

where tR is the product of the hopping integral t between Mn ions multiplied by the Huang-Rhys factor R, ε is the Jahn-Teller energy, μ is the magnetic moment, $g=2$ accounts for the configurational degeneracy of state $|c\rangle$ and k_B is the Boltzmann constant. Equation (1) includes electron-phonon interaction and, hence, the energy gap between ground and excited states depends on n itself. Thus, Eq. (1) is a self-consistent equation for the partition function.

The ferromagnetic-to-paramagnetic phase transition is associated with a change of the electron configuration due to a breakdown of the adiabatic approximation. In a narrow temperature range around T_C, the spectrum of valence electron levels is stepwise changed so that the various physical properties of the material are influenced. We assume that the lattice heat capacity and the lattice vibrational entropy are changed much less pronounced than the corresponding electronic quantities and we take them as constants averaged at T_C. The electronic entropy S can be directly obtained from the expression for the free energy and is given as[15]

$$S(H,T) = -k_B[-n \ln g + n \ln n + (1-n)\ln(1-n)]. \tag{2}$$

In Fig. 1 the function $S(H,T)$ is shown. In the two-level scheme, the distribution function is correctly described within the range $0 \leqslant n \leqslant 1/2$. Taking in Eq. (1) $n=1/2$ one obtains the critical temperature T_C expressed in terms of the model parameters. We use the previous values of model parameters $\varepsilon=289$ cm^{-1} and $tR=392$ cm^{-1}. They were adjusted

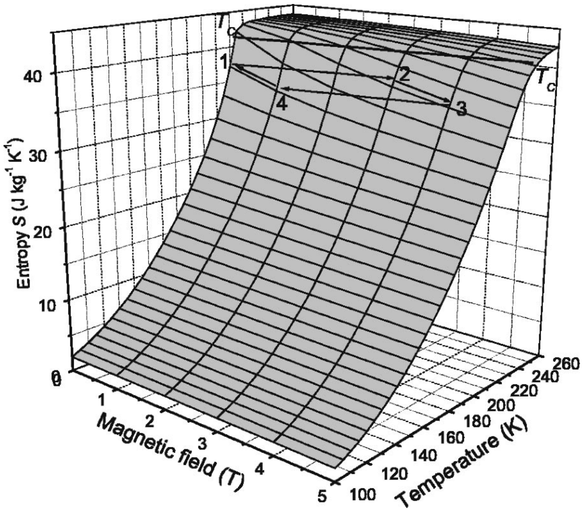

FIG. 1. The entropy S as a function of an applied magnetic field H and temperature T. The critical temperature is marked by the T_C-T_C line. The rectangle 1-2-3-4 containing two isotherms and two isentropic lines represents the Carnot cycle.

to reproduce the critical temperature $T_C \approx 210$ K for a La$_{0.8}$Ca$_{0.2}$MnO$_3$ crystal and to reproduce the value of the specific heat at $H=0$.[16] The adiabatic path for $n=1/2$ is a straight line denoted by $T_C - T_C$ in Fig. 1. Similar straight lines can be drawn for other $n<1/2$ values. The line $T_C - T_C$ projected on the $T-H$ coordinate plane gives directly the temperature change at various critical points T_C vs H.

In classical thermodynamics[1,2] the adiabatic temperature change ΔT is obtained from the condition of zero entropy change as a function of H and T. ΔT is given as

$$\Delta T = -\int_0^H \frac{T}{C_V}\left(\frac{\partial M}{\partial T}\right)_H dH, \tag{3}$$

where $M=\mu(1-2n)$ is the magnetization per ion and $C_V(T)=T(\partial S/\partial T)_V$. In statistical physics the electronic entropy is expressed by means of the electron distribution function. It is seen from Eq. (2) that the adiabatic condition $S(H,T)=$constant can be replaced by $n(H,T)=$const. Therefore, the condition for the adiabatic process can be written as

$$dn = \left(\frac{\partial n}{\partial T}\right)_H dT + \left(\frac{\partial n}{\partial H}\right)_T dH \equiv 0. \tag{4}$$

Taking into account Eq. (1) and calculating the respective derivatives in Eq. (4) one arrives at

$$dT = \frac{2\mu T}{tR - 2\varepsilon n + 2\mu H} dH. \tag{5}$$

It follows from Eq. (1) that

$$-\frac{1}{\ln[n/g(1-n)]} = \frac{k_B T}{tR - 2\varepsilon n + 2\mu H} = -\frac{k_B T}{2\mu C_V}\left(\frac{\partial M}{\partial T}\right)_H. \tag{6}$$

Integrating Eq. (5) and using (6) one obtains

$$\Delta T = -\frac{2\mu}{k_B \ln\left[\dfrac{n}{g(1-n)}\right]}\int_0^H dH. \tag{7}$$

The last equation is equivalent to Eq. (3), provided only the electronic specific heat is accounted for. Figure 2 shows the adiabatic temperature change vs H for various initial temperatures T at $H=0$. As we mentioned after Eq. (2), Fig. 2 can be obtained directly by seeking for the isentropic lines.

Recently, Pecharsky *et al.*[3,4] proposed an approximation

$$\Delta T = -\frac{T}{C_V}\int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH. \tag{8}$$

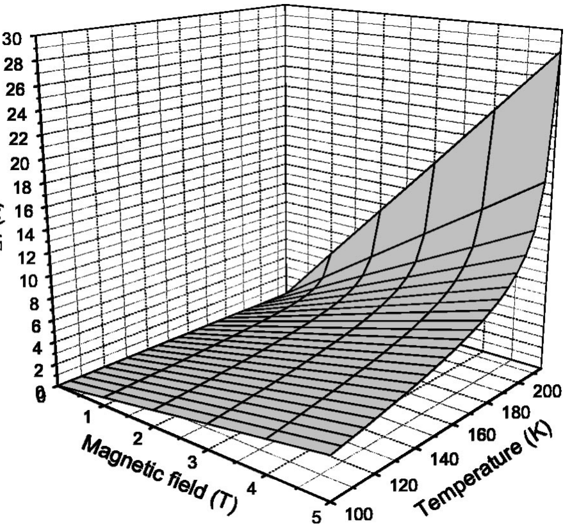

FIG. 2. The isentropic temperature change $\Delta T(H,T)$ vs H for various initial temperatures T at $H=0$ for La$_{0.8}$Ca$_{0.2}$MnO$_3$s crystal.

ΔT was determined following this approximation in Refs. 6 and 7 for La$_{2/3}$(Ca,Pb)$_{1/3}$MnO$_3$ and La$_{1-x}$Sr$_x$MnO$_3$ (with $x=0.1$, 0.125, 0.175, and 0.3) crystals, respectively. In fact, the approximation (8) can be obtained directly from Eq. (3) by averaging the ratio T/C_V and taking it off the integral. Indeed, when the transition is not steep, the heat capacity is well approximated by the lattice capacity alone and the ratio T/C_V can be averaged over a fairly large temperature range (see Fig. 2 in Ref. 4 and Fig. 4 in Ref. 6). However, such transitions are of minor interest because they possess but a small magnetocaloric effect. The magnetocaloric effect is pronounced for steep or abrupt transitions. Then, in the region around T_C the electronic heat capacity is comparable to or larger than the lattice heat capacity (for example, see Fig. 3 in Ref. 9). Taking into account the explicit expression for the entropy S, one can calculate the electronic contribution to the heat capacity C_V

$$C_V(T) = T\left(\frac{\partial S}{\partial T}\right)_V = (tR - 2\varepsilon n + 2\mu H)\frac{dn}{dT}, \tag{9}$$

Fig. 3 shows a hill of the electronic heat capacity around T_C, calculated with the parameters for the La$_{0.8}$Ca$_{0.2}$MnO$_3$ crystal. Indeed, around T_C the heat is used to change the electronic configuration and this produces the large peak in the total heat capacity. In this case approximation (8) is not applicable. Moreover, this approximation suggests that the form of ΔT is the same as that of ΔS_M. On the other hand, the relation (7) indicates that the shape of ΔT is given by the function $k_B \ln[n/(g(1-n)]$. This function is the derivative of

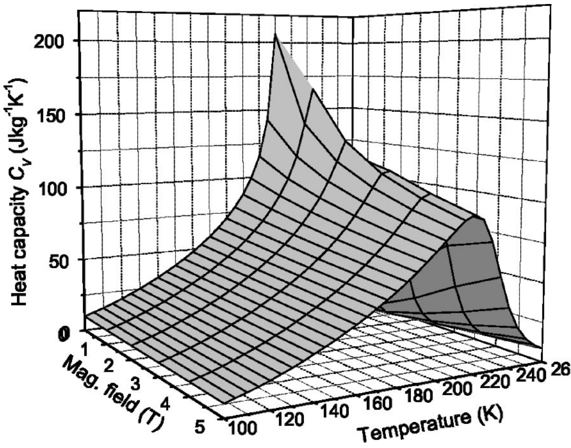

FIG. 3. The electronic specific heat C_V for the La$_{0.8}$Ca$_{0.2}$MnO$_3$ crystal.

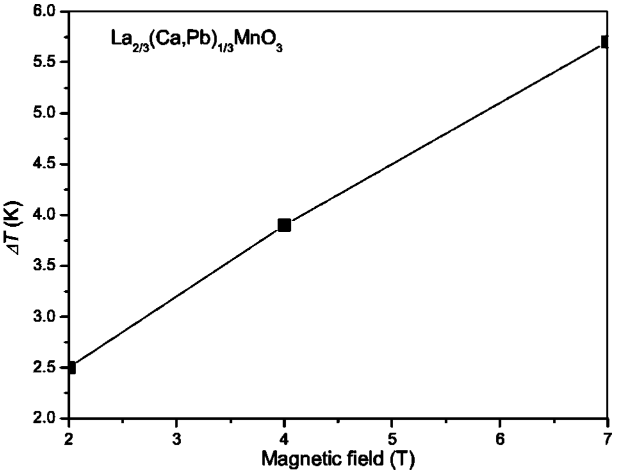

FIG. 4. The linear dependence of ΔT vs H drawn from data in Ref. 6.

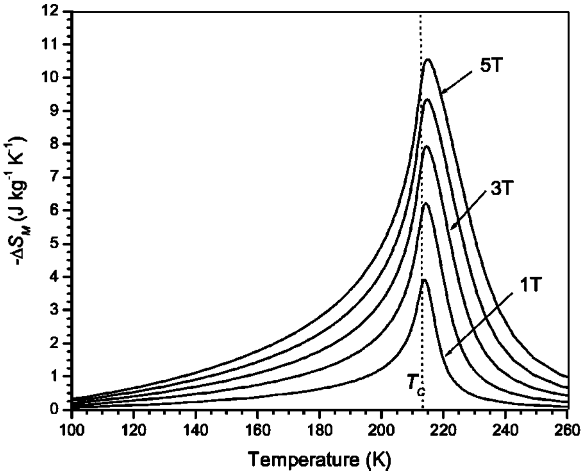

FIG. 5. The magnetic entropy change $\Delta S_M = S(T,H) - S(T,H=0)$ vs T for $H=1$, 2, 3, 4, 5 T.

S over n. Therefore, Eq. (7) can be written in an equivalent form

$$\frac{dS}{dn}\Delta T = 2\mu\Delta H. \qquad (10)$$

Assuming that at T_C, $C_{V,\text{electronic}} \geqslant C_{V,\text{lattice}}$, the effect of the lattice on ΔT can be roughly accounted for by the correction factor $f = 1/[1 + C_{V,\text{lattice}}/C_{V,\text{electronic}}]$. This factor was omitted from the consideration presented in Fig. 2. The result is similar to ultralow-temperature cooling in paramagnets,[17] where $\Delta T/\Delta H = \text{const}$ (see Fig. 4). In drawing Figs. 1–3 and 5 , we set spin $S=2$. In fact, at very low temperatures some ferromagnetic materials exhibit a magnetic moment which is smaller than that following from the theoretical estimation. These findings are related to various imperfections of the materials. Therefore, an effective value of spin S should be estimated from the magnitude of the magnetization for the particular material.

Applying Eq. (7) for two critical points (where $n=1/2$) one obtains $\Delta T = T_{C,H} - T_{C,H=0} = 2\mu H/k_B \ln g$. This gives the possibility to estimate the upper limit of ΔT from the magnetization measurements only because the second-order phase transition takes place at $n=1/2$, independent of the value of the magnetic field. The first-order phase transitions occur at $n \leqslant 1/2$.[15] Our model does not account for the concentration dependence of ΔT. Equation (7) indicates a linear dependence of ΔT vs ΔH. This is simply a consequence of Eq. (1) which predicts a linear relationship between T_C and H. Such linear dependence was observed for MnAs in Ref. 18 and a nearly linear dependence for $La_{0.65}Ca_{0.35}MnO_3$ in Ref. 19. Using the data from Ref. 6, we plot ΔT vs H for $La_{2/3}(Ca,Pb)_{1/3}MnO_3$, where a linear dependence is approximately reproduced. To determine ΔT, magnetic and calorimetric measurements are required. Bohigas *et al.*[5] determined the peak value of ΔT to be 2.1 K at $H=3$ T in a $La_{0.6}Ca_{0.4}MnO_3$ crystal with $T_C=260$ K. Assuming a linear scaling of ΔT with H, this gives $\Delta T=0.49$ K in the field 0.7 T. This is in good agreement with the maximum temperature change of 0.5 K for the field 0.7 T as obtained in Ref. 9 for direct temperature measurements in a $La_{0.6}Ca_{0.4}MnO_3$ crystal. For the $La_{0.8}Ca_{0.2}MnO_3$ crystal with $T_C=213$ K, we obtained $\Delta T=7.5$ K at $H=3$ T, using $f=1/2$. When comparing the theoretical estimation with experimental data one should also take into account an inhomogeneity of crystals which remarkably decreases the peak value of ΔT.

Conventionally the total entropy is considered as a sum of separate entropies: magnetic (spin), electronic, and lattice contributions.[2] According to the used model the correlation between spins in the $Mn^{3+}-O^{2+}-Mn^{4+}$ chain is entirely due to Coulomb interaction (the energies tR and ε). We do not assume direct coupling between the total spins on the neighboring Mn ions. We treat the spins as the local entities. Since the value of observed magnetization can be expressed in terms of the total local spins, we use the effective spin ($S=2$ or $3/2$) in the final numerical calculations. Equation (2) represents both the spin and electron entropies which are not separable.

In Fig. 5 we show the magnetic entropy change calculated using Eq. (2) without involving any additional parameters. We note a resonable agreement with measurements presented in Fig. 2 of Ref. 12.

The change of the e_g electron states during the phase transition results in a small modification of the phonon spectrum. This modification influences the lattice heat capacity and entropy. We assume that the lattice free energy of each pure phase can be described by the Debye model separately. The estimation of the phonon modification $\Delta\omega$ with volume ΔV is based on the Grűneisen assumption $\Delta\omega/\omega = -\gamma\Delta V/V$, where $\gamma \approx 1-2$ is a coefficient independent of the frequency ω. Since the Grűneisen assumption also concerns the Debye cutoff frequency ω_D and $\hbar\omega_D = k_B\Theta$, one has

$$\frac{\Delta\Theta}{\Theta} = -\gamma\frac{\Delta V}{V}, \qquad (11)$$

where Θ is the Debye temperature. To compare the calculations and measurements it is necessary to calculate the lattice entropy S_D and lattice heat capacity C_{VD}[20] weighted by the electron distribution function, i.e.,

$$S_{\rm av} = (1-n)S_D(\Theta_F) + nS_D(\Theta_P),$$

$$C_{V\rm av} = (1-n)C_{VD}(\Theta_F) + nC_{VD}(\Theta_P), \tag{12}$$

where Θ_F and Θ_P are the Debye temperature for the ferromagnetic and paramagnetic spin phase, respectively. Equation (12) couples the electronic and lattice subsystems. For the $La_{2/3}Ca_{1/3}MnO_3$ crystal the volume change was determined to be around $\Delta V/V = 1.5\times 10^{-3}$ (see Figs. 2 and 6 in Ref. 21). Assuming $\Theta_F = 528$ K [as for the $La_{0.8}Ca_{0.2}MnO_3$ (Ref. 16)] one finds $\Theta_P \approx 526$ K. Then the direct calculations show that the dS_{av}/dT and dC_{VD}/dT possess the negligible change at $n=1/2$. This result is in agreement with observation of the total heat capacity shown in Fig. 1 of Ref. 16, where was used approximation $\Theta_F = \Theta_P$.

To summarize, we calculated the adiabatic temperature change ΔT directly from Eq. (7). We thus propose a simple method for an estimation of the maximum ΔT at the critical points, solely based on magnetic measurements. This procedure should be helpful in searching for new materials applicable for refrigeration technology.

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