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Magnetocaloric effect. Physics and applications

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The principles of magnetic cooling and the magnetocaloric properties of various magnetic compounds have been presented with a special focus on materials with giant and colossal magnetocaloric parameters. The magnetocaloric properties of manganites and cobaltites have been considered. The maximum entropy change in polycrystalline $La_{0.7}Ca_{0.3}MnO_3$ for the field of 2 T reaches 8 $J \cdot kg^{-1} \cdot K^{-1}$, exceeding that of gadolinium. It is suggested that the manganites with superior magnetocaloric properties and low material costs are attractive magnetic refrigerator materials for technical applications.

Key words: *magnetocaloric effect; entropy; phase transition; magnetic refrigerator*

1. Introduction

The magnetocaloric effect is characterized by an adiabatic change in temperature T (or an isothermal change in entropy, ΔS) arising from the application of external magnetic field H. Recently, one can note an increased interest in this more than 100-year old phenomenon (see review papers [1–7]). The magnetocaloric effect arises due to the presence of two energy reservoirs in magnetic materials: one with phonon and the other with magnon excitations. These two reservoirs are coupled by the spin-lattice (in other words – magnetoelastic) interactions. An external magnetic field affects the spin degrees of freedom resulting in heating or cooling of magnetic materials. This simple description of the magnetocaloric effect indicates that the highest change in temperature is expected for strongly magnetostrictive magnetic materials. The magnetocaloric effect increases with increase of the applied magnetic field and with the change of magnetization $M(T,H)$ during application of magnetic field. This means that the effect reaches its maximum in the vicinity of magnetic phase transition points.

The magnetocaloric effect in various magnetic materials, summarized in the mentioned review papers, will be briefly considered. The present review will be primarily concerned with the recent results of the magnetocaloric studies of manganites and

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cobaltites. The possibility of use of these materials in magnetic refrigerators will also be discussed.

2. Giant and colossal magnetocaloric effects

During isothermal magnetization processes, the total magnetic entropy change ΔS_H of the magnetic system due to the application of a magnetic field H is given by [5, 6]:

$$\Delta S_H(T,H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H dH \tag{1}$$

The adiabatic temperature change $\Delta T_{ad}(T,H)$ can be determined using the experimentally measured heat capacity $C(T,H)$:

$$\Delta T_{ad}(T,H) = \int_0^H \left(\frac{\partial M}{\partial T}\right)_H \frac{T}{C(T,H')} dH' \tag{2}$$

Since $\frac{\partial M}{\partial H}$ has its maximum at the transition point, a large magnetocaloric effect is expected near the transition temperature. It is exceedingly high ("giant" or "colossal") for the first order phase transition. The upper limit for the molar magnetic entropy variation is given by the magnetic contribution [4, 5]:

$$\Delta S_M^{\max} = R\ln(2J+1) \tag{3}$$

where R is the gas constant and J is the total angular momentum of the magnetic ion.

Though the magnetocaloric effect was first discovered in iron [7], research on practical application of this phenomenon has been for years concentrated on gadolinium rare earth metal with a large $|\Delta S_H|$ parameter (5 $J\cdot kg^{-1}\cdot K^{-1}$ for ΔH= 2 T) at room temperature. Unfortunately, this material is very expensive. Therefore, numerous experimental studies have been focused on the search for new magnetic materials that are cheaper but exhibit magnetocaloric effect larger than Gd. In 1997, a giant magnetocaloric effect was discovered in $Gd_2Si_2Ge_2$ [8], a compound with $|\Delta S_H|$ considerably higher (27 $J\cdot kg^{-1}\cdot K^{-1}$ for ΔH = 2 T) than that in Gd. This material exhibits a first order magnetic transition coupled to a martensitic-like, displacive structural transition from an orthorhombic to a monoclinic phase [9].

Another important type of magnetocaloric materials are MnAs based compounds. The base material MnAs undergoes a combined structural and ferro-paramagnetic transition of the first order with $|\Delta S_H|$= 32 $J\cdot kg^{-1}\cdot K^{-1}$ at ΔH = 2 T near room temperature [10].The colossal magnetocaloric effect was discovered in MnAs under hydrostatic pressure [11]. In this case $|\Delta S_H|$ reaches values up to 267 $J\cdot kg^{-1}\cdot K^{-1}$ for ΔH = 2 T, T = 281 K and p = 2.23 kbar. In molar terms, it results in a value of 34.7 $J\cdot K^{-1}\cdot mol^{-1}$, 1.47 times greater than the theoretical limit $\Delta S^{\max}$ determined according to Eq. (3). The origin of this colossal magnetocaloric effect is the contribution to the entropy variation

coming from strong magnetoelastic interactions. The strong magnetoelastic interaction is the driving force for structural and first order magnetic phase transitions. The phenomenological model of the colossal magnetocaloric effect in MnAs was recently developed by von Ranke et al. [12]. The model confirms the fundamental role of the lattice entropy in the colossal magnetocaloric effect for the MnAs based compounds. In some cases, there exists a full analogy between external pressure and chemical pressure. Because of a small difference in the atomic radii, it is expected that the substitution of Fe for Mn should emulate the pressure effect in MnAs [13]. The colossal magnetocaloric effect at ambient pressure in $Mn_{1-x}Fe_xAs$ for $x = 0.003$ reaches values up to 330 $J \cdot kg^{-1} \cdot K^{-1}$ for $\Delta H = 5$ T. Important point is that Fe doping does not change the density of states at the Fermi level in the host compound.

3. Giant magnetocaloric effect in manganites

In recent years, there has been increasing interest in using manganites not only as materials with a colossal magnetoresistivity but also as materials with interesting magnetocaloric properties. Such a proposition was made more than 10 years ago by Zhang et al. [14] who performed magnetocaloric measurements in $La_{0.67}Ca_{0.33}MnO_3$ and $La_{0.60}Ca_{0.33}Y_{0.07}MnO_3$. In next years, many other manganites have been examined from this point of view (see [5, 6, and 15] for references). A large magnetocaloric effect makes manganites excellent candidates for working materials in magnetic refrigeration units especially because they are less costly than any other materials, particularly those based on Gd.

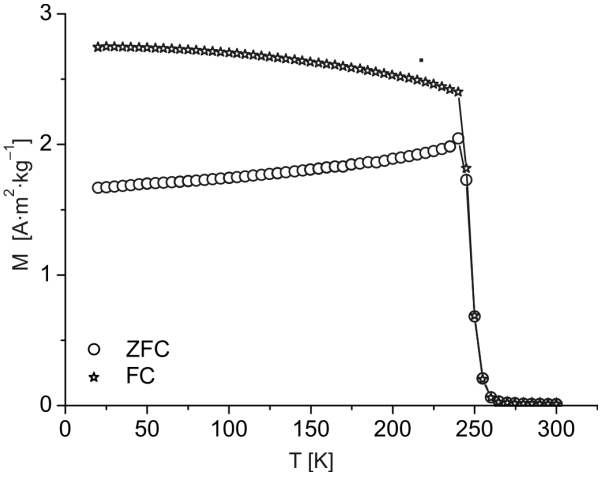

Fig. 1. Temperature dependence of the susceptibility for $La_{0.65}Ca_{0.35}MnO_3$ polycrystals in low field (20 Oe) for field cooling (FC) and zero field cooling (ZFC) regimes

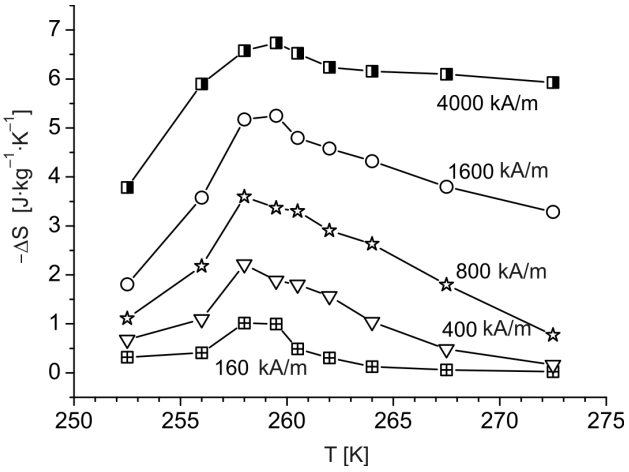

Fig. 2. Change of the magnetic entropy of $La_{0.65}Ca_{0.35}MnO_3$ polycrystals in function of temperature at fixed values of the external magnetic field

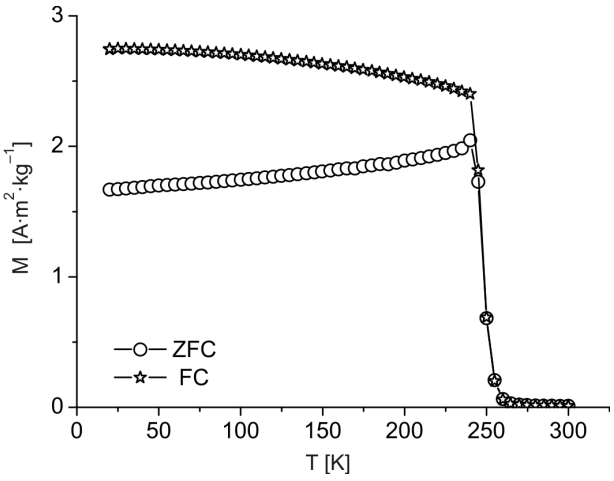

Fig. 3. Temperature dependence of susceptibility for $La_{0.7}Ca_{0.3}MnO_3$ polycrystals in low field (20 Oe) for field cooling (FC) and zero field cooling (ZFC) regimes

Recently, we have shown [16] that the changes in entropy near T_C depend strongly on various extrinsic factors. These dependences suggest that the magnitude of the magnetocaloric effect should depend strongly on methods of sample preparation. We have performed detailed studies of the magnetocaloric effect for $La_{1-x}Ca_xMnO_3$ with $x = 0.3$, 0.35 and 0.4 prepared by a nonstandard ceramic method. It was shown that the sharpness of the paramagnetic to ferromagnetic transition increases with Ca doping. It is seen in Fig. 1 that this transition is very sharp in $La_{0.65}Ca_{0.35}MnO_3$ polycrystals. Although the sharp transition indicates a first-order phase transition, the M vs. H dependences exhibit no anomalies characteristic of this type of transition. It is interesting that for almost the same level of doping in $La_{0.67}Ca_{0.33}MnO_3$, the paramagnetic-ferro-

magnetic transition was shown to be of the first-order (see [17] and discussion therein). Thermally driven first-order transitions may be rounded by quenched disorder [17]. This mechanism, related to the method of sample preparation, may be responsible for the second-order transition observed in our samples. Such samples demonstrate large values of the magnetocaloric effect reaching 6.5 J·kg·K^{-1} for 5 T (Fig. 2). A similar situation was observed for $La_{0.7}Ca_{0.3}MnO_3$, in which the paramagnetic-ferromagnetic transition (Fig. 3) is extremely sharp suggesting the first-order phase transition. Nevertheless we have shown that $La_{0.7}Ca_{0.3}MnO_3$ manganite is characterized by a second-order transition near to the first-order one. In this system, the magnetocaloric effect is very high (Fig. 4) and reaches 8 J·kg^{-1}·K^{-1}) for ΔH = 2 T. It is the highest value ever observed for doped $LaMnO_3$ manganites, considerably larger than that known for gadolinium.

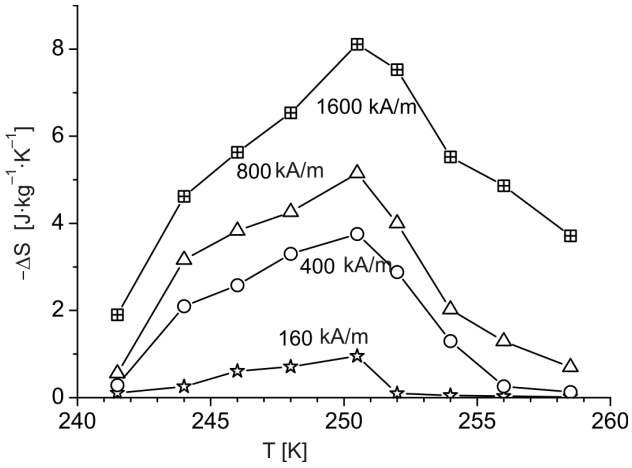

Fig. 4. Change of the magnetic entropy of $La_{0.7}Ca_{0.3}MnO_3$ polycrystals in function of temperature at fixed values of the external magnetic field

It has to be added that for manganites an interesting relation has been established [18] between magnetic entropy change ΔS_H and resistivity r:

$$\Delta S_H\left(T,\ H\right) = -\ \alpha \int_0^H \left[\frac{\partial \ln(r)}{\partial T}\right]_H dH \tag{4}$$

with α = 21.27 emu/g. The dependence may be used to determine $\Delta S_H(T,H)$ from resistivity measurements.

4. Magnetocaloric effect in cobaltites

Although perovskite cobaltites have received less attention than manganites, these materials have been the subject of considerable interest due to prospects of their use as magnetic media, cathode materials, etc. Cobaltites have quite unusual physical proper-

ties. Co^{3+} ions can occur in three different spin configurations: low-spin ($S = 0$), intermediate-spin ($S = 1$) or high-spin ($S = 2$) states. It is generally agreed upon that thermal excitation in cobaltites may induce spin-state transitions. In addition to these spin -state phenomena, magnetoelectronic phase separation occurs in cobaltites upon doping. All these features make the magnetocaloric effect in cobaltites completely different from that in manganites.

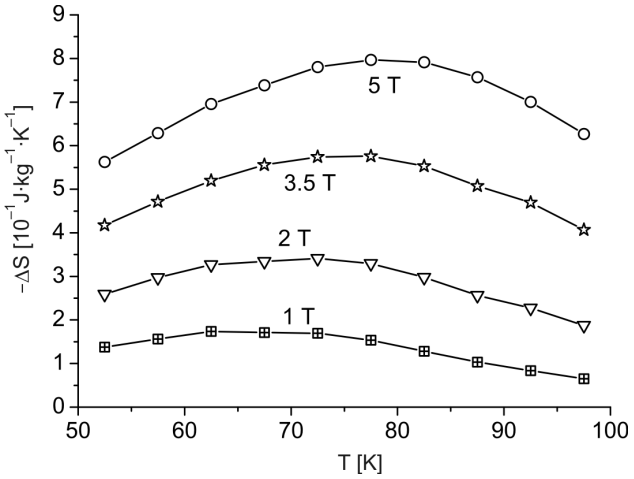

Fig. 5. Change of the magnetic entropy of a $La_{0.8}Ca_{0.2}CoO_3$ single crystal in function of temperature at fixed values of the external magnetic field

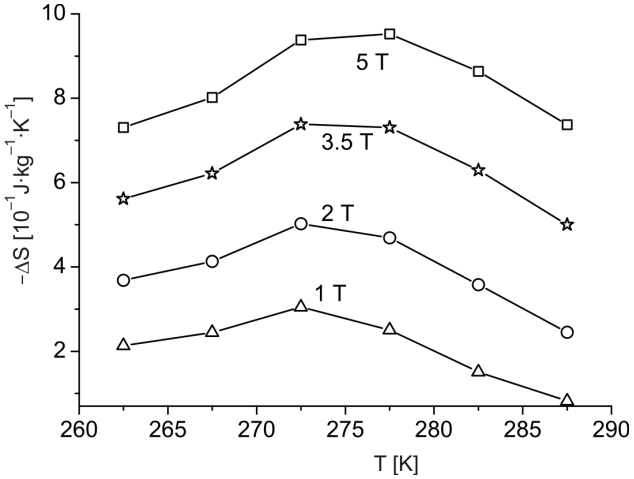

Fig. 6. Change of the magnetic entropy of a $Tb_{0.9}Dy_{0.1}BaCo_2O_{5.5}$ single crystal in function of temperature at fixed values of the external magnetic field

Figure 5 displays the changes of the magnetic entropy of a $La_{0.8}Ca_{0.2}CoO_3$ single crystal in function of temperature at fixed values of the external magnetic field. The ground

state of this cobaltite is a cluster glass [19] arising due to phase separation. It results from Fig. 5 that the observed magnetocaloric effect in cobaltite is weak, considerably weaker than that observed in manganites. Similar magnetocaloric properties have been observed in oxygen deficient $Tb_{0.9}Dy_{0.1}BaCo_2O_{5.5}$ single crystals. This cobaltite is a strongly anisotropic Ising type magnet [20]. Figure 6 presents the magnetocaloric effect in this compound measured near the Curie temperature. Also in this case, the observed magnetocaloric effect is weak.

5. Applications

The development of a new magnetic refrigeration technology, based upon the magnetocaloric effect, has brought an alternative to the conventional gas compression technique. As a result, many new materials with large magnetocaloric effect have been discovered, and a much better understanding of this magneto-thermal property has resulted. The magnetic refrigeration has several advantages compared to conventional techniques. First of all, the cooling efficiency in magnetic refrigerators is very high and there are no harmful gases involved. The refrigerators may be built more compactly and generate much less noise. They are expected to be applied as large-scale air conditioners and heat pumps.

6. Conclusions

This review presents new magnetocaloric materials with special focus on manganites. It is shown that manganites are good candidates to work as magnetic refrigerants. Although for all studied manganites paramagnetic-ferromagnetic transition is very narrow, no hysteresis was observed near T_C and the transitions are identified as second-order ones. The magnetic entropy change in $La_{0.7}Ca_{0.3}MnO_3$ is shown to be larger than that exhibited by metallic gadolinium. Moreover, their materials-processing cost is low.

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References

[1] PECHARSKY V.K., GSCHNEIDER K.A. Jr., J. Magn. Magn. Mater., 200 (1999), 44.
[2] TISHIN A.M., [in:] *Handbook of Magnetic Materials*, K.H.J. Buschow (Ed.), Elsevier, Amsterdam, 1999, vol.12, p. 395 .
[3] GSCHNEIDER K.A. Jr., PECHARSKY V.K., PECHARSKY A.O., ZIMM C.B., Rare Earth' 98, 315-3 (1999), 69.

[4] TISHIN A.M., SPICHKIN Y.I., *The Magnetocaloric Effect and its Applications*, Inst. Phys. Publ., Bristol, 2003.
[5] GSCHNEIDER K.A. Jr., PECHARSKY V.K, TSOKOL A.O., Rep. Prog. Phys., 68 (2005), 1479.
[6] PHAN M.-H, YU S.-C., J. Magn. Magn. Mater., 306 (2007), 325.
[7] BRUCK E., J.Phys. D: Appl.Phys., 38 (2005), R381.
[8] PECHARSKY V.K., GSCHNEIDER K.A. Jr., Phys. Rev. Letters 78 (1997), 4494.
[9] PAUDYAL D., PECHARSKY V.K., GSCHNEIDER K.A. Jr., HARMON B.N., Phys. Rev., B 73 (2006), 144406.
[10] WADA H., TANABE Y., Appl. Phys. Lett., 79 (2001), 3302.
[11] GAMA S., COELHO A.A., DE CAMPOS A., CARVALHO M.G., GANDRA F.C.G., VON RANKE P.J., DE OLIVEIRA N.A., Phys. Rev. Lett., 93 (2004), 237202.
[12] RANKE P.J., GAMA S., COELHO A.A., DE CAMPOS A., CARVALHO M.G., GANDRA F.C.G., DE OLIVEIRA N.A., Phys.Rev,. B 73 (2006), 014415.
[13] DE CAMPOS A.,.ROCCO D.L, CARVALHO M.G., CARON L., COELHO A.A., GAMA S., DA SILVA L.M., GANDRA F.C.G., DOS SANTOS A.O., CARDOSO L.P., RANKE P.J., DE OLIVEIRA N.A., Nature Mater., 5 (2006), 802.
[14] ZHANG X.X., TEJADA J., XIN Y., SUN G.F., WONG K.W., BOHIGAS X., Appl. Phys. Lett., 69 (1996), 3596.
[15] SZEWCZYK A., SZYMCZAK H., WISNIEWSKI A., PIOTROWSKI K., KARTASZYNSKI R., DABROWSKI B., KOLESNIK S., BUKOWSKI Z., Appl. Phys. Lett., 77 (2000), 1026.
[16] SZYMCZAK R., CZEPELAK M., KOLANO R., KOLANO-BURIAN A., KRZYMANSKA B., SZYMCZAK H., J. Mater. Sci., 43 (2008), 1734.
[17] ROSSLER S. , ROSSLER U.K., NENKOV K., ECKERT D., YUSUF S.M., DORR K., MULLER K.-H., Phys. Rev., B 70 (2004) 104417.
[18] XIONG C.M., SUN J.R., CHEN Y.F., SHEN B.G., DU J., LI Y.X., IEEE Trans. Magn., 41 (2005), 122.
[19] SZYMCZAK H.,BARAN M., BABONA G.J., DIDUSZKO R., FINK-FINOWICKI J.AND SZYMCZAK R., J. Magn. Magn. Mater., 285 (2005), 386.
[20] BARAN M., GATALSKAYA V.I., SZYMCZAK R., SHIRYAEV S.V., BARILO S.N., BYCHKOV G.L., SZYMCZAK H., J.Phys.: Condens. Matter, 17 (2005), 5613.

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