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Ferromagnetic lanthanum manganites

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ABSTRACT

The short overview of the physical properties of the ferromagnetic manganites exhibiting colossal magnetoresistance is given.

1. Introduction

The strong interaction between charge carriers, localized magnetic moments and crystal lattice in ferromagnetic manganites $La_{1-x}D_xMnO_3$ where D is a divalent ion gives rise to many interesting effects observed preferably in a vicinity of the Curie temperature T_C [1–3]. Colossal magnetoresistance (CMR) is, perhaps, most popular but such phenomena as phase separation, giant magnetocaloric effect, etc., are also intensively studied. The aim of this work is to overview results on the physical properties of CMR manganites published mainly during last 5–10 years. We describe the crystal lattice, structural transitions, and magnetic phase diagrams for D=Ca, Sr, Ba. Then we analyze the experimental data on resistivity, magnetoresistance, and Hall effect with special attention to their behavior near T_C. The CMR effect in the materials with the first order transition is considered in close connection with the magnetic inhomogeneity. Optical properties are discussed from the viewpoint of the change of electronic band structure due to change in temperature. Finally we briefly review the magnetocaloric effect.

2. Crystal and magnetic structure

The crystal structure of CMR manganites is called perovskite, which is not completely correct. In the true (cubic) perovskite cell the manganese ions would be located in the environment of six oxygen ions, which form a regular octahedron, and the Mn–O–Mn bond angle would be equal to 180°. In real lanthanum manganites the perovskite structure is always somewhat distorted, so that the symmetry of the lattice is lower than cubic [4–9]. The lattice can be orthorhombic (usually *Pnma* space group but in $La_{0.7}Ba_{0.3}MnO_3$ it is *Imma* [10]), rhombohedral ($R\overline{3}c$), or (in rare cases) monoclinic. It has been established in [11] that two orthorhombic *Pnma* phases can be realized. The first of them (O'), with lattice parameters $\sqrt{b}/2<c<a<b$ is characterized by strong Jahn–Teller distortions of the oxygen octahedra. The second phase, O*, is called pseudocubic. In this phase the distortions of the octahedra are considerably weaker and $\sqrt{b}/2 \approx c \approx a$ but the Mn–O–Mn bond angles, just as in the O* phase, noticeably differ from 180°. In the *Imma* structure the octahedra are not distorted.

A transition between different crystal structures results in significant changes in elastic moduli ([12] and references therein). The resistivity is however weakly affected excepting the case when structural transition temperature coincides with the Curie temperature [13], so in what follows we shall deal preferably with the effects near T_C.

The compounds under consideration are ferromagnets if x lies between 0.1 and 0.5. Fig. 1 shows the Curie temperature as a function of the divalent concentration x for polycrystalline [4,5,13] (open symbols) and single-crystalline [14–18] (solid symbols) samples. One can see that the data for poly- and single-crystalline samples coincide for $La_{1-x}Sr_xMnO_3$ only while in case of La–Ba as well as La–Ca manganites the T_C values for the single crystals are somewhat lower than for the polycrystals. The difference is likely to be due to uncontrolled defects created during the growth of single crystals by floating zone method.

It is necessary to note that the magnetic transition is always smeared. The standard deviation for T_C is the smallest (about 1 K) in $La_{1-x}Sr_xMnO_3$ single crystals, it is significantly greater in $La_{1-x}Ba_xMnO_3$, and in $La_{1-x}Ca_xMnO_3$ the deviation is highest (between 5 and 8 K) [19].

In $La_{1-x}Sr_xMnO_3$ and $La_{1-x}Ba_xMnO_3$ the ferromagnetic-to paramagnetic phase transition is always second order while in $La_{1-x}Ca_xMnO_3$ it is second order only if $x<0.25$, when x is greater, the magnetic transition is first order [16]. In $La_{1-x}Ca_xMnO_3$ with x around 1/3 the Curie temperature is increased with increasing magnetic field: $T_C(H)=T_C(0)+B_MH_{int}$ where H_{int} is an internal field and $B_M \approx 0.8$ K/kOe [20,21].

3. Electronic transport

In the ferromagnetic state well below T_C the temperature dependence of resistivity ρ is of semiconductor type ($d\rho/dT<0$) if $x<x_c$

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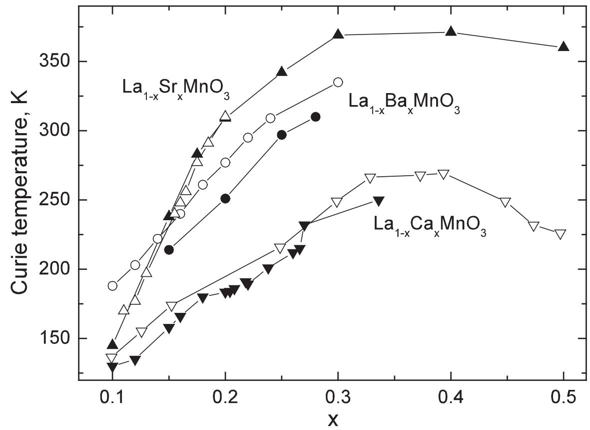

Fig. 1. Dependence of the Curie temperature on divalent element concentration.

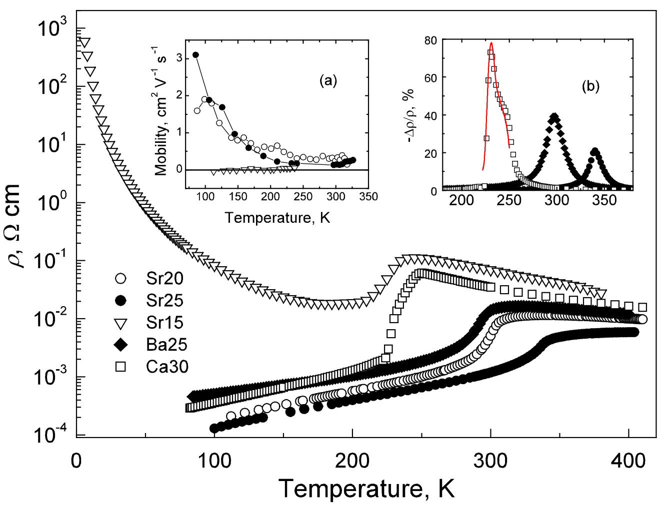

Fig. 2. Temperature dependence of resistivity. Inset (a): Hall mobility versus temperature; Inset (b): Temperature dependence of magnetoresistance.

where x_c is the critical concentration at which metal-semiconductor transition takes place. In $La_{1-x}Sr_xMnO_3$ the value of x_c is 0.17, in $La_{1-x}Ca_xMnO_3$ it is 0.225, and in La–Ba manganites x_c is about 0.22–0.23 [17,22,23]. In the semiconductor state the resistivity is usually dominated by the variable range hopping; for example, in $La_{0.85}Sr_{0.15}MnO_3$ (Sr15 in Fig. 2) the resistivity obeys relation $\rho=\rho_0\exp[(T_o/T)^{1/4}-\delta W/(k_BT)]$ with $\rho_0=1.3\cdot10^{-7}\,\Omega$ cm, $T_0^{1/4}=43$ K$^{1/4}$, $\delta W/k_B=34$ K [24].

If $x>x_c$ the manganites are said to be in metallic state in the sense that $d\rho/dT$ is positive. Below approximately 200 K the temperature dependence of resistivity is described by the relation [17]

$$\rho(T)=\rho(0)+AT^2. \tag{1}$$

The residual resistivity $\rho(0)$ is less than $10^{-4}\,\Omega$ cm in $La_{1-x}Sr_xMnO_3$ when $x=0.3$ or greater [17]; in the $La_{1-x}Ba_xMnO_3$ and $La_{1-x}Ca_xMnO_3$ crystals with the same level of doping $\rho(0)$ is significantly greater [22–24].

Important information on conductivity mechanism can be obtained from the Hall effect data. Inset (a) in Fig. 2 shows temperature dependence of the Hall mobility $\mu_H=R_0/\rho$ with R_0 being normal Hall coefficient. In $La_{0.85}Sr_{0.15}MnO_3$ ($T_C=232$ K) the variable range hopping dominates conductivity in the ferromagnetic state. The $La_{0.80}Sr_{0.20}MnO_3$ ($T_C=308$ K) and $La_{0.75}Sr_{0.25}MnO_3$ ($T_C=341$ K) crystals behave as ordinary bad metals in which charge carriers are holes and the mobility decreases with increasing T. Above 200–250 K, however, μ_H practically does not depend on T and μ_H is between 0.15 and 0.3 cm^2/(Vs). This means that the main contribution to the conductivity is given by charge carriers whose energy is near the mobility edge; in other words, when T becomes higher than 200–250 K, the growth of the resistivity is caused by the reduction of the concentration of charge carriers in extended states rather than the decrease of their mobility. It follows that the metal–semiconductor transition takes place in a wide temperature interval below the Curie temperature [25].

The experimental data for $La_{1-x}Ba_xMnO_3$ and $La_{1-x}Ca_xMnO_3$ single crystals were summarized in [23] and [26], respectively. Here it is sufficient to say that the mobility of the $La_{0.7}Ca_{0.3}MnO_3$ crystal ($T_C(H=0)=227$ K) behaves as in a "bad" metal and that $La_{0.7}Ca_{0.3}MnO_3$ is at the threshold of localization at $T=220$ K when the rapid rise in resistivity begins.

Now let us consider the resistivity in a vicinity of the Curie point. In the Inset (b) in Fig. 2 we show the temperature dependence of magnetoresistance $\Delta\rho$ $\rho(H)-\rho(0)$ measured in the magnetic field of 10 kOe [20,24,25]. The origin of the CMR effect depends on whether the magnetic transition is second or first order. If the first alternative is realized, i.e., in La–Sr and La–Ba manganites, the resistivity is determined by the dependence of activation energy on magnetization:

$$\rho=\rho_0\exp\left(\frac{E_0-E_1m^2}{k_BT}\right) \tag{2}$$

where $\rho_0=$const, $m=M/M_s$, $M(T,H)$ is magnetization, M_s stands for its saturation value, E_0 and E_1 weakly depend on temperature. If m is small we get

$$\frac{\Delta\rho(H)}{\rho}=-\frac{E_1}{k_BT}\left(m^2(H)-m^2(0)\right).$$

It is worth noting that relation (2) was found to be valid not only in perovskite manganites but also in layered antiferromagnetic $La_{0.5}Sr_{1.5}MnO_4$ [27].

The formula (2) means that just below T_C the change of resistivity arises from change of the activation energy and therefore for the CMR effect in the manganites with the second order magnetic phase transition consists in the change of activation energy under application of a magnetic field.

When the magnetic transition is first order as in $La_{0.7}Ca_{0.3}MnO_3$ the CMR effect arises due to shift of the Curie temperature in a magnetic field [20]. The temperature dependence of magnetoresistance is then described by the relation:

$$\frac{\Delta\rho(T,H)}{\rho}=\frac{\rho(T-\Delta T_C(H))-\rho((T)}{\rho(T)} \tag{3}$$

where $\Delta T_C=B_MH_{\rm int}$ and $\rho(T)=\rho(T,H=0)$. Using (3) we calculated $\Delta\rho/\rho$ for $La_{0.7}Ca_{0.3}MnO_3$; the result is shown in the Inset (b) in Fig. 2as solid line. One can see that in the transition region $\Delta\rho/\rho$ is well described by relation (3).

4. Optical properties

The optical and magnetooptical properties of the CMR manganites were recently reviewed by Gan'shina et al. [28] so in this section the focus is on the relation between optical and transport effects.

The spectra of optical conductivity $\sigma_{\rm opt}(E)$ where E is photon energy are similar in all $LaMnO_3$-based materials. In Fig. 3 we show the spectra for $La_{0.75}Ba_{0.25}MnO_3$ ($T_C=300$ K) as an example [29]. One can see two broad absorption bands, which are typical for the $LaMnO_3$-based compounds. At $T=300$ and 400 K, i.e., at $T\geq T_C$, the low-energy band (band 1) has maxima at $E\approx1.3$ eV. The high-energy band (band 2) occupies the region above 2.5 eV