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Colossal magnetoresistance at room temperature in manganites and chromium chalkospinels

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A colossal magnetoresistance (CMR) has been found near room temperature in manganite $La_{1/3}Nd_{1/3}Sr_{1/3}MnO_3$ and in chromium chalkogenide spinels xCuCr$_2$S$_4$–(1–x)Cu$_{0.5}$Al$_{0.5}$Cr$_2$S$_4$ at $0.05 \le x \le 0.20$. It attains 27 % and 9 % for the manganite in 8.4 and 2.2 kOe magnetic fields, respectively, and 12.5 to 1.5 for thiochromites in 84.4 kOe field. The CMR in these materials is supposed to be of the same nature and is associated with an inhomogeneous magnetic state caused by an intense *s–d* exchange.

Обнаружено колоссальное магнитосопротивление (КМС) в районе комнатной температуры в манганите $La_{1/3}Nd_{1/3}Sr_{1/3}MnO_3$ и хромовых халькогенидных шпинелях xCuCr$_2$S$_4$–(1–x)Cu$_{0.5}$Al$_{0.5}$Cr$_2$S$_4$ с $0.05 \le x \le 0.20$. В манганите оно достигает 27 % и 9 % в магнитных полях 8.4 и 2.2 кЭ соответственно, а в тиохромитах 12.5–1.5 % в поле 8.4 кЭ. Предполагается, что КМС в этих материалах имеет одинаковую природу и связано с неоднородным магнитным состоянием, обусловленным сильным *s–d* обменом.

The interest in magnetic semiconductors is caused by the unique physical properties thereof, first of all, by the colossal magnetoresistance (CMR) that was found both in europium monoxide and monochalkogenides and in chromium chalkospinels as well as in manganites. Those materials show a wide variety of chemical, structure and electron properties. That is why the theoretical and experimental studies thereof and comparison of the results so obtained provides an unique chance to understand the CMR nature in more detail.

For practical applications of CMR materials, the Curie point thereof is required to excess the room temperature and the CMR effect should be attainable in low magnetic fields. In manganites, however, the CMR is obtainable as a rule in high fields of 60 to 130 kOe. A record CMR amounting 96 % in a low (7.6 kOe) field has been found in $La_{1/3}Nd_{1/3}Ca_{1/3}MnO_3$ ceramics at 90 K [1]. In this work, Sr was substituted for Ca in the above composition to increase the T_c value and the $La_{1/3}Nd_{1/3}Sr_{1/3}MnO_3$ single crystal so obtained was studied. Furthermore, studied was the solid solution system of copper thiochromite: xCuCr$_2$S$_4$–(1–x)Cu$_{0.5}$Al$_{0.5}$Cr$_2$S$_4$, since the copper thiochromites are known to show the highest magnetic ordering temperatures among the chromium chalkogenide spinels [2, 3]. Before, the CMR near T_c was revealed in xCuCr$_2$S$_4$–(1–x)Cu$_{0.5}$Me$_{0.5}$Cr$_2$S$_4$ compositions of related structure but having T_c values much lower than the room temperature [4, 5]. Note that a high negative magnetoresistance was found recently for ferromagnetic semiconductors $Fe_{1-x}Cu_xCr_2S_4$ (x = 0 and 0.5) [6, 7]; for x = 0.5, it amounted 7 % in 60 kOe field near T_c = 340 K.

In this work, studied have been the temperature and field dependences of electric conductivity and longitudinal magnetoresistance (MR) for $La_{1/3}Nd_{1/3}Sr_{1/3}MnO_3$ manganite and xCuCr$_2$S$_4$–(1–x)Cu$_{0.5}$Al$_{0.5}$Cr$_2$S$_4$ chromium chalkospinels at $0 \le x \le 0.20$. The measurements were carried out using the

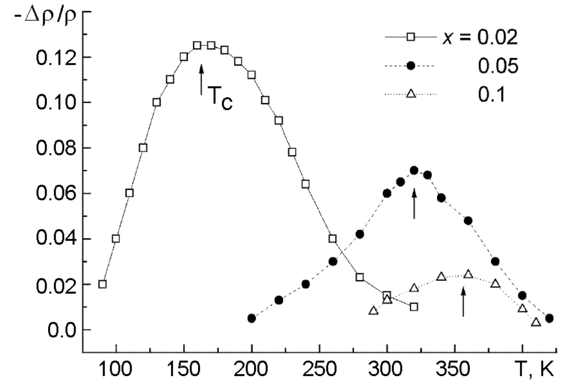

Fig. 1. Temperature dependences of magnetoresistance for $La_{1/3}Nd_{1/3}Sr_{1/3}MnO_3$ in various magnetic fields.

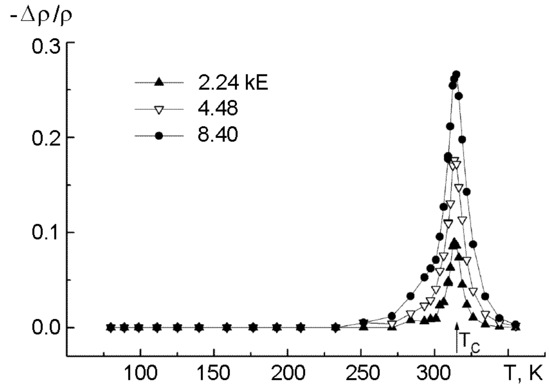

Fig. 2. Temperature dependences of magnetoresistance for $xCuCr_2S_4$–$(1-x)Cu_{0.5}Al_{0.5}Cr_2S_4$ system samples in 8.4 kOe magnetic field.

four-probe technique, the single crystal resistance being measured along the *c* axis. The T_c values for the compounds were determined as the minimum temperatures in the $\partial\chi/\partial T(T)$ curves where χ is the initial magnetic susceptibility measured in alternating magnetic field at 8 kHz using a F5063 ferrometer. For $La_{1/3}Nd_{1/3}Sr_{1/3}MnO_3$, T_c has been found to be of 315 K (for that compound, χ was measured along the *c* axis). Near to that temperature, the electric resistivity ρ has been found to increase sharply from 10^{-4} Ω·cm at 80 K to $3.5\cdot10^{-3}$ Ω·cm at 350 K. Application of an external magnetic field results in decreasing ρ, i.e., causes a negative MR. Temperature dependences of MR for that compound in various magnetic fields are presented in Fig. 1. At T_c, a sharp maximum of the MR absolute value is observed that is typical of single crystals. The negative MR $(\rho_H - \rho_0)/\rho_0$ attains 27 %, 18 %, and 9 % in 8.4, 4.5, and 2.2 kOe fields, respectively.

The magnetic properties of the $xCuCr_2S_4$–$(1-x)Cu_{0.5}Al_{0.5}Cr_2S_4$ solid solution system ($0\le x\le0.20$) have been studied in [8]. The $0.05\le x\le0.20$ compositions of that system have been found to be semiconductors having T_c above room temperature (within 320 to 362 K range). In this work, temperature and field dependences of MR for all the samples of that system have been studied. A negative CMR has been revealed therein with absolute value having a maximum near T_c (Fig. 2). As x increases, that maximum becomes smoothened and lowered. At $x = 0.01$, the MR value attains 48 % in 40 kOe magnetic field near $T_c = 33$ K while for compositions with $0.05\le x\le0.20$, it attains 12.5–1.5 % in 8.4 kOe field near room temperature.

Thus, in the studied manganite and chromium chalkospinels, a maximum absolute value of negative magnetoresistance is observed near T_c. The temperature and field dependences of MR are of the same shape. The MR in the studied manganite and chromium chalkospinels can be supposed to be of the same nature and to be associated with the existence of a magnetically biphase state (MBPS) caused by an intense *s–d* exchange [9]. In [8], the *s–d* exchange integral in $xCuCr_2S_4$–$(1-x)Cu_{0.5}Al_{0.5}Cr_2S_4$ was estimated basing on the paramagnetic Curie point change due to introduction of a dopant. It has been found to be of the order of 0.6 eV, thus, in fact, an intense *s–d* exchange takes place in the system. In it known that in magnetic semiconductors, the charge carrier energy is minimum at the complete ferromagnetic (FM) ordering in the crystal and increases at its deterioration or substitution by another kind of magnetic ordering. That is why the charge carriers are localized in FM droplets situated within an antiferromagnetic (AFM) semiconductor (insulating MBPS). As the impurity concentration rises, the FM droplets increase in size and at a sufficiently high doping level, the percolation thereof takes place and the conductive MBPS is formed, where the insulating AFM droplets are situated within the FM matrix.

The compounds studied in this work are obtained by doping the AFM semiconductors $ReMnO_3$ (Re = La–Nd) or $Cu_{0.5}Al_{0.5}Cr_2S_4$ and the MBPS are realized therein, namely, the insulating one in thiochromites and conductive in manganite. Application of a magnetic field to the sample being in the insulating MBPS results in an increase of the FM droplet volume and the orientation of their magnetic moments along the field, thus favoring the tunneling of charge carriers between the droplets. Moreover, the magnetic field increases the kinetic energy of electrons inside the FM droplets and thus favors the tunneling thereof and the droplet destruction. It is just the factors that cause the CMR. As to the conductive MBPS, there are two mechanisms causing the influence of the impurity-magnet interaction on the resistance. Those are the charge carrier scatter that reduces their mobility and causes the formation of a tail in the band thereof consisting of localized states. Near T_c, the charge carrier mobility drops sharply and those become localized in part within the band tail. In a magnetic field, the impurity-magnetic scattering of the charge carriers becomes reduced (the carrier mobility increases) and those are delocalized from the band tail (the charge carrier number increases), thus resulting in a CMR [9].

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Колосальний магнітоопір при кімнатній температурі у манганітах та хромових халькошпінелях

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Виявлено колосальний магнітоопір (КМО) поблизу кімнатної температури у манганіті $La_{1/3}Nd_{1/3}Sr_{1/3}MnO_3$ та хромових халькогенідних шпінелях $xCuCr_2S_4-(1-x)Cu_{0.5}Al_{0.5}Cr_2S_4$ при $0{,}05 \le x \le 0{,}20$. У манганіті він досягає 27 % та 9 % у магнітних полях відповідно 8,4 та 2,2 кЕ, а у тіохромітах — 12,5–1,5 % у полі 8,4 кЕ. Припускається, що КМО у цих матеріалах має однакову природу та пов'язаний неоднорідним магнітним станом, обумовленим сильним $s-d$ обміном.