Proceedings of the European Conference "Physics of Magnetism 96", Poznań 1996

EFFECT OF ALLOYING WITH Ca IN $LaMnO_3$ SYSTEM STUDIED BY KKR-CPA METHOD AND GIANT MAGNETORESISTANCE

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$La_{1-x}Ca_xMnO_3$ perovskites show semiconducting properties in the paramagnetic range. The gap is reduced near $x = 0.33$, where ferromagnetic ordering is observed. The ferromagnetic ordering then induces a semiconductor–metal transition, and gives rise to a giant magnetoresistance effect. The ground state electronic structure calculations were done with KKR-CPA method for hypothetical cubic and ferromagnetic $LaMnO_3$ and $CaMnO_3$ compounds, as well as for disordered $La_{1-x}Ca_xMnO_3$ ($x = 0.33$, 0.4, 0.5) alloys with real crystal data. As a result, we get a magnetic moment per formula $4.00\mu_B$ and $3.00\mu_B$ and half-metallic behaviour for end-compounds, respectively. In the ferromagnetic region a linear decrease in the magnetic moment of $La_{1-x}Ca_xMnO_3$ is observed, together with the decrease in the gap width for spin-down carriers, if doping Ca in $La_{1-x}Ca_xMnO_3$. A simple model is developed, which describes magnetic and transport properties as resulting from an exchange-induced band-crossing semiconductor–metal transition, as for instance in EuO.

PACS numbers: 71.20.Lp, 71.20.–b

1. Introduction

The mixed valence manganites $La_{1-x}M_xMnO_3$ (M = Ca, Sr, Ba) have recently attracted attention due to the huge magnetoresistance (MR) effects observed near the Curie temperature T_c for a composition range around $x = 0.33$. The magnetic and transport properties have been investigated much earlier and explained within the frame of double exchange mechanism [1]. However, the origin of the huge MR effect is still not completely understood, the aim of the present paper is to provide additional information on the electronic structure, and a simple model in order to explain these phenomena. It is well known that stoichiometric $LaMnO_3$ (orthorombic: $a = 7.7362$ Å, $b = 7.8257$ Å, $c = 7.7844$ Å) and $CaMnO_3$ (cubic: $a = 7.465$ Å) are semiconducting phases, which order antiferromagnetically below room temperature. Solid solutions with x close to 0.33 (cubic: $a = 7.6990$ Å) show a reduced energy gap, and the onset of ferromagnetism with T_c in the range

200–240 K, associated with the simultaneous occurrence of Mn^{3+} ($x = 0$) and Mn^{4+} ($x = 1$) and the easier hopping of electrons from site to site. For these solutions, effective gaps measured in the semiconducting paramagnetic state lie then in the range 500 to 2000 K. Ferromagnetic order leads to a sudden decrease in the resistivity, which drops by several orders of magnitude at low temperature. The effect of an applied magnetic field is to lower drastically the zero-field resistivity, especially in the vicinity of the Curie point.

2. Band-structure calculations

The electronic structure studies of $La_{1-x}Ca_xMnO_3$ system were stimulated by the observed giant magnetoresistance (GMR) effect, supposed to result from the band decoupling and the striking different densities of states (DOS) near the Fermi level for spin-up and spin-down electrons. The band structure of ordered $LaMnO_3$ and $CaMnO_3$ were investigated by the charge and spin self-consistent Korringa–Kohn–Rostoker (KKR) method, while for disordered $La_{1-x}Ca_xMnO_3$ ($x = 0.33, 0.4, 0.5$) systems the KKR method with the coherent potential approximation (CPA) [2] was used. The KKR-CPA band structure calculations were done for the measured crystal data, assuming the simple cubic structure in the whole range of Ca content. The hypothetical undistorted parent compounds were found as ferromagnetic half-metals with the integer value of the magnetic moment per formula $4.0\mu_B$ ($\mu_{Mn} = 3.39\mu_B$) for $LaMnO_3$ and $3.00\mu_B$ ($\mu_{Mn} = 2.59\mu_B$) for $CaMnO_3$. For both end compounds, the spin-up electron channel is metallic with small DOS at E_F, while for spin-down electrons a gap occurs. This gap decreases with Ca doping from $\Delta E = 1.9$ eV for $x = 0.0$ to $\Delta E = 0.7$ eV for $x = 1.0$. The first value of gap well corresponds to the experimental $\Delta E = 1.7$ eV [3]. In the antiferromagnetic (AF) state, this fully polarized local DOS will prevent hopping from site to site, and the expected gap will be close to that calculated for the minority band. The half-metallic character, which arises only for integer moment systems, should not occur for intermediate solid solutions. Nevertheless, the large decoupling of spin-projected subbands leads to a strong difference in the up and down DOS at E_F. As we see in Fig. 1 the calculated electronic spectra for $La_{0.67}Ca_{0.33}MnO_3$ system show a gap in the spin-down DOS ($\Delta E = 1.2$ eV), while for spin-up electrons a small DOS at E_F drives the metallic character of system. A large peak of unoccupied La $4f$-states arises just above the Fermi level, which unexpectedly moves towards E_F when calcium concentration increases, which is not supported by previous calculations [4]. As we found in KKR-CPA calculations for $x = 0.33$ and 0.5, a small magnetic moment is induced on La site $\mu_{La} = 0.25\mu_B$ (parallel to μ_{Mn}), since the $4f$ La tail of spin-up DOS peak slightly crosses E_F. When observing the partial DOS for spin-up electrons, we see the $3d$ Mn DOS peak moving towards the Fermi level with increase in Ca content, since the effective potential becomes less attractive. In the ferromagnetic (FM) region the KKR-CPA method gives the following magnetic moments (total and Mn in μ_B): 3.66, 3.17 ($x = 0.33$) and 3.5, 3.13 ($x = 0.5$) in agreement with the magnetization measurements [5]. Due to the drastically different shapes of DOS near the Fermi level for spin-up and down electrons in $La_{1-x}Ca_xMnO_3$ systems, the electrical current (below T_c) strongly depends on polarization of carriers. Since the conducting electrons possess mainly

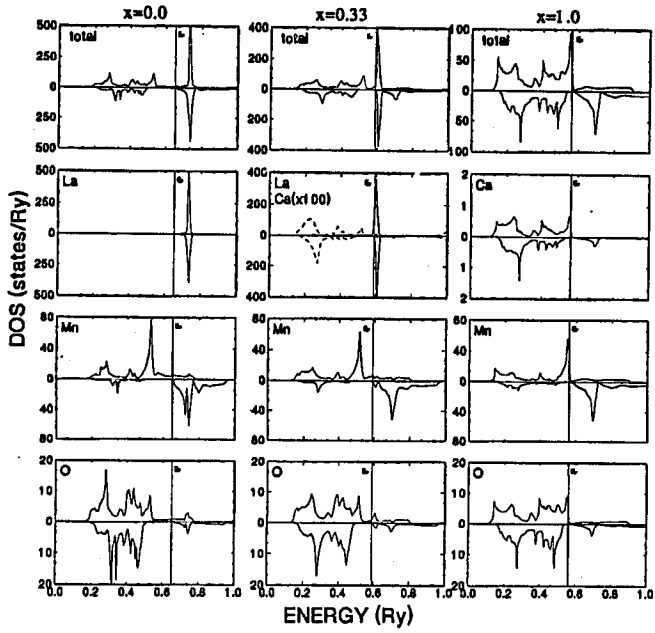

Fig. 1. The spin-projected total and component DOS for $La_{1-x}Ca_xMnO_3$ ($x = 0.0$, 0.33, 1.0). A gap only for spin-down bands is observed.

one spin direction (along magnetization vector), they strongly scatter on borders of magnetic domains. The external magnetic field, which orders the magnetic domains, lowers the energy required for electrons to pass from one domain to another (to continue propagation they do not need invert the spin). This may be related to the strong dropping of resistivity under magnetic field. For the temperatures $T > T_c$, when the polarised current disappears, we observe semiconductor-like (SC-like) behaviour $R(T)$, which may indicate preserving of the gap.

3. Simple phenomenological model

A simple model of the SC–metal transition was previously developed [5]. It is described as an exchange-induced band-crossing transition, similar to that occurring in the ferromagnetic semiconductor EuO [6]. The effect on the transport properties results from the following factors: (i) Band crossing between the former valence and conduction bands occurs if the ratio J/Δ of the exchange interaction to the SC gap is large enough. It suddenly increases the number of carriers and in turn modifies the interactions between magnetic moments. In some cases it can lead to a first-order transition, but more generally to a peculiar temperature dependence of the magnetization. (ii) The increase in the spin correlation function between moments modifies the hopping integral between sites: this hopping is related, within double exchange theory, to the mean angle between moments. This gives rise to a further reduction of the spin disorder resistivity in the ferromagnetic metallic range. From this model (Fig. 2), the MR varies initially as H^2 in the paramagnetic range, and more or less as $\mathrm{arctg}(H/\Delta)$ in the ordered range, as

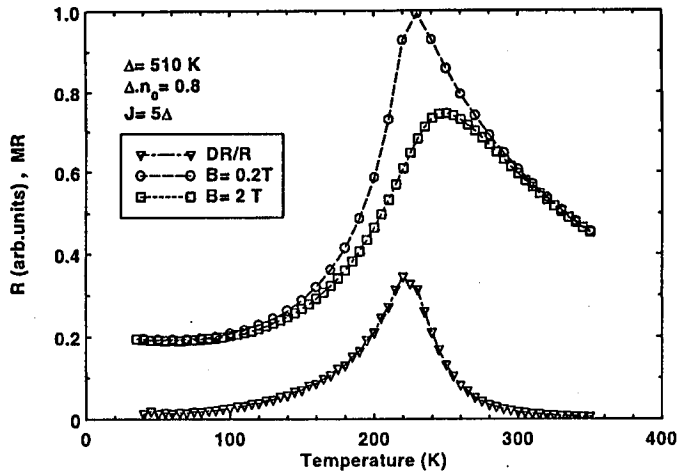

Fig. 2. Resistivity for 0.2 T and 2 T for $La_{0.67}Ca_{0.33}MnO_3$ calculated within the phenomenological model. Δ is the SC gap, J is the $s-d$ exchange coupling constant, n_0 is the density in the s-band. Triangles refer to the relative magnetoresistance.

observed experimentally. When the gap is large and cannot be closed by the magnetic induction, or when the ground state is not ferromagnetic, the SC regime is only modified at the Curie temperature. A metamagnetic transition in the ordered range can then occur if the ground state is close to ferromagnetism, and drives the SC–metal transition.

Acknowledgments

This work was sponsored by the Committee for Scientific Research (Poland) through the grant no. 2 P302 10307 and by French-Polish Scientific and Technological Cooperation Joint Project for 1996 (no. 6516). We thank F. Robaut and S. Misat for magnetoresistance measurements.

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