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An impurity resistivity of doped manganese perovskites

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Abstract

We present a two-time of relaxation approach at an analysis of a magnetoresistance in ferromagnetic manganese perovskites $La_{1-x}(Ca,Sr)_xMnO$. To explain a change in the low-field response from predominantly quadratic $dR/dH|_{H\to 0} = 0$ for $T > T_c$ to linear $dR/dH|_{H\to 0}$ for $T < T_c$ as noted in the measurements in thin films $La_{0.7}Ca_{0.3}MnO_3$ we calculated field and temperature dependences of a impurity contribution to a carrier mobility in a framework of the 2p(O)- and 3d(Mn)-scattering model elaborated for manganese perovskites. We obtained the field-dependent impurity contribution to the overall scattering of carriers that show a transition in the low-field (H) dependence of R from quadratic above T_c to linear below consistent with an experiment. The calculated negative magnetoresistance ratio is sharply peaked at a temperature near T_c or below.

Keywords: Manganese perovskites; Mobility; Linear and quadratic magnetoresistance

Recently, a sharp transition in the low-field (H) dependence of magnetoresistance $R(H)$ from quadratic ($\sim H^2$) above T_c to linear ($\sim H$) below has been observed in the films of doped perovskite manganese oxides [1]. The exact mechanisms responsible for both the phenomenon and the observed larger magnetoresistance effects are not clearly understood at the moment. However, the fact that the peak in the magnetoresistance ratio $\Delta R/R$ in the films $La_{0.67}Ca_{0.33}MnO_3$ occurs not near the ferromagnetic transition temperature [2], where the magnetization is already substantial suggests that the spin-disorder scattering is not the main mechanism. At least two channels of carrier scattering by 2p- and 3d-states of the valence-band edge are likely to exist in the presence of defects. The temperature and field dependencies of a resistivity may be calculated in the framework of the model Hamiltonian method [3]. The Green's function formalism and impurity diagram technique are used for practical purposes of calculating the linear response [4]. Following the model of magnetic semiconductor [3] the Hamiltonian can be written as a superposition of the periodic Anderson model and the s–d exchange model

$$H = H_0 + H_1 + H_2;$$

$$H_1 = \sum_f \left\{ - J\sigma_f S_f + V\sum_\sigma (p^+_{f\sigma} d_{f\sigma} + \text{h.c.}) \right\}.$$

$$H_0 = \sum_{k\sigma} \xi_k p^+_{k\sigma} p_{k\sigma} + \sum_f (E_n - n\mu)\sum_\gamma X^{\gamma\gamma}_f + (E_{n-1} - (n-1)\mu)\sum_\Gamma X^{\Gamma\Gamma}_f, \quad (1)$$

$X^{pq}_f = |fp\rangle\langle fq|$ are Hubbard's operators; E_n and E_{n-1} energies of the basic configurations d^n and d^{n-1} of the magnetic ion; indices γ and Γ refer to the orbital degeneration of these terms; V and J are the hybridization and exchange interaction parameters for p- and d-electrons. In concrete calculations we will consider only $d^3(Mn^{4+}:{}^4A)$ and $d^4(Mn^{3+}:{}^5E)$ configurations. In transport of an "extra" hole, electric current-carriers, via many-electron ^5E-states, $Mn^{4+}(d^3)$ ions are formed. As is known, the effect of magnetic ordering in an ordinary band theory is confined to driving apart spin subband. Within our approach the magnitude of the d-peak

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$\Omega = E_4 - E_3 - \mu$ corresponding to the one electron transition $^4A \leftrightarrow {}^5E$, varies without changing the energy of d-states. The difference in temperature behavior between the density of p-valence-band- and d-states is the key to further understanding; therefore, we will explain in more detail the physical reason for this fact in our approach to the compound $La_{1-x}(Ca,Sr)_xCuO_3$. In paramagnetic phase all $|d^4, S_z = -2 \div 2\rangle$-states of a $Mn^3 + (d^4)$-ion, differing in spin projection, are equally probable. However, as temperature of ferromagnetic phase is lowered, the $|d^4, S_z = 2\rangle$-state is mainly populated, and the one-particle density of states loses its symmetry with respect to spin–flip transition. The reason is that only one of the $d_{f\sigma-}$ operators acting upon one and the same initial state $|d^4, S_z = 2\rangle$, place a carrier into three-particle $|d^3, S_z = 3/2\rangle$-state. As a result there is a zero density of states at $T \to 0$ for hole-carrier with one of spin projections. The structure of the top $E^{\pm}_{k\sigma}$-valence bands is given by

$$E^{\pm}_{k\sigma} = 1/2(\xi_{k\sigma} + \Omega \pm \sqrt{(\xi_{k\sigma} - \Omega)^2 + 4K_\sigma V^2}),$$

$$\xi_{k\sigma} = \xi_k - \sigma J\langle S_z\rangle/2,$$

$$K_\sigma = \langle d^+_{k\sigma}d_{k\sigma} + d_{k\sigma}d^+_{k\sigma}\rangle = \tfrac{1}{4}(2 + \sigma\langle S_z\rangle), \quad \sigma = \pm 1,$$

$\langle S_z\rangle$ is the average spin of the Mn^{3+}-ion. The effective spin-down pd-hybridization $K_\downarrow V^2|_{T\to 0} \to 0$ too. Of a variety of processes involving electron scattering by impurities, we will take into account only the conventional potential scattering of carriers with potential Δ_1 in p-valence-band states (Sr,Ca-impurities) and fluctuations of d-level energies Δ_2 (O-vacancies):

$$H_2 = \sum_{kfq} p_{1f} e^{-if(k-q)} p^+_{k\sigma} b_{q\sigma} \Delta_1(\boldsymbol{k} - \boldsymbol{q}) + \sum_{f\sigma} p_{2f}\Delta_2(\boldsymbol{f}) d^+_{f\sigma} d_{f\sigma} \tag{2}$$

Here p_{1f} and p_{2f} are projection operators equal to zero in the absence of impurities and to unity in the immediate vicinity of an impurity atom or a defect. The second summand in H_2 assumes random fluctuations of the crystal field strength without alteration of its symmetry. The usual transport relaxation time approach for the effective two-band model results in: $\sigma = e\sum_\sigma n_\sigma u^2_\sigma \mu_{\text{eff}}$, where the effective mobility is given by

$$\mu_{\text{eff}} = \frac{e}{m}\left(\frac{u^2_\sigma}{\tau_{\text{tr}}} + \frac{K_\sigma v^2_\sigma}{\tau_{\text{d}}}\right)^{-1} = \left(\frac{u^2_\sigma}{\mu_S} + \frac{K_\sigma v^2_\sigma}{\mu_{\text{d}}}\right)^{-1}. \tag{3}$$

the inverse transport relaxation time is given by $\tau^{-1}_{\text{tr}} = c_1 g_0 \int d\Omega |\Delta_1(\theta)|^2 (1 - \cos(\theta))/4\pi$ and $1/\tau^\sigma_{\text{d}} = K_\sigma v^2_{k\sigma}/u^2_{k\sigma}\,(1/\tau^\sigma_2)$ is the effective rate of carrier relaxation in the d-channel. In accordance with Matthiessen's rule, the effective relaxation rate in Eq. (3) is additive with respect to relaxation rates τ^{-1}_{tr} and $(\tau^\sigma_{\text{d}})^{-1}$ with weights u^2_σ and $K_\sigma v^2_\sigma$.

$$u^2_{k\sigma} = \frac{\partial E^+_{k\sigma}}{\partial \xi_{k\sigma}} = \frac{E^+_{k\sigma} - \Omega}{E^+_{k\sigma} - E^-_{k\sigma}},$$

$$v^2_{k\sigma} = 1 - u^2_{k\sigma}, \quad (u_{k\sigma}v_{k\sigma})^2 = \frac{K_\sigma V^2}{(E^+_{k\sigma} - E^-_{k\sigma})^2}. \tag{4}$$

They have a meaning of the probability with which a carrier participates in scattering by the corresponding potential for p-valence band or d-states. Moreover, these coefficients depending on temperature and applied field, the resulting conductivity is also temperature and field dependent. The calculated mechanism of magnetoresistance is observed in the form of a uniform shift (without essential changes in shape) of the mobility versus temperature curve to the higher temperatures upon applying a magnetic field. As a consequence, the magnetoresistance ratio is sharply peaked at a temperature near T_c. We proposed $V = 0.1$ eV, $J = 0.8$ eV, $E_g = 1.6$ eV, $\Omega = E_4 - E_3 = -0.45$ eV, measured from the middle of semiconductor gap, $\mu_S \approx 10\,\text{cm}^2/\text{Vs}$ and $\mu_d \approx 0.5\,\text{cm}^2/\text{Vs}$. To explain a change in the low-field response from predominantly quadratic $dR/dH|_{H\to 0} = 0$ for $T > T_c$ to linear $dR/dH|_{H\to 0} < 0$ for $T < T_c$ as noted in the measurements in thin films $La_{0.7}Ca_{0.3}MnO_3$ [1] we calculate magnetoresistance (Fig. 1a,b). However, while the linear low-field dependence occurs at $T < T_c$, to get the quadratic low-field dependence ($T > T_c$) it is necessary to include the intersite d-electron hopping ($d^+_i d_j$-contribution): $\sigma_{\text{tot}}(H) = \sigma(H) + \sigma_{\text{dd}}$. The quadratic dependence (Fig. 1b) is observed if a scattering mechanism of the additive *d*-current channel depends on temperature

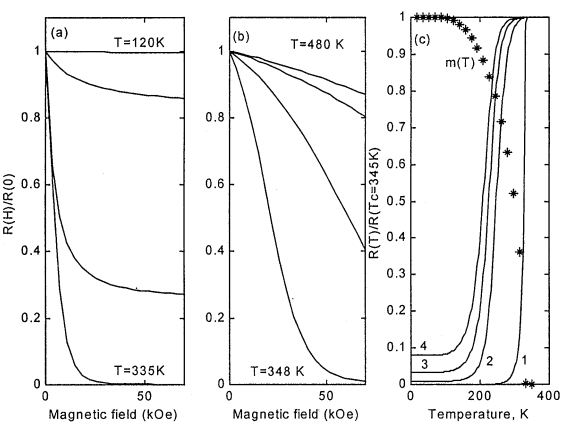

Fig. 1. Calculated magnetoresistance as a function of temperature and applied field: (a) $T < T_c$ and (b) $T > T_c$; (c) normalized resistivity as function of temperature and mobility in the additive shunt current channel: 1, $\mu_{\text{dd}} = 0$; 2, $\mu_{\text{dd}} = 0.05\mu_d$; 3, $-\mu_{\text{dd}} = 0.2\mu_d$; 4 $-\mu_{\text{dd}} = 0.5\mu_d$. $m(T)$, – normalized magnetization.

very slowly and $\mu_{dd} = 0.05\mu_d$. Moreover, the linear dependence remains valid as before (Fig. 1a) because d–d contribution is negligible at low T. Varying μ_{dd} we find the jump of the resistivity with increasing temperature may occur at $T_p \leqslant T_c$ (Fig. 1c) in accordance with the fact that peak in $\Delta R/R$ in the $La_{0.67}Ca_{0.33}MnO_3$ films occurs not near the magnetic transition temperature but in the temperature region where the magnetization is already substantial [2]. The $T_p \to T_{cross}$ with increasing μ_{dd} where T_{cross} is temperature of valence-p-band top and d-level Ω crossing. As a result, $u^2_{k\sigma}|_{T=T_p} = v^2_{k\sigma}$. Of particular interest is the theoretical impurity-concentration dependence of mobility. With decreasing the defect concentration c_1(La,Sr) in the La-cation sublattice, $\mu_{eff}(\sim 1/c_1)$ becomes higher at low temperatures ($u^2 \to 1$, $T \to 0$), when carrier scattering mainly occurs via the impurity potential scattering channel. We assume the concentration of oxygen vacancies c_2 is constant under the action of the Sr,Ca-doping. Therefore, only at high temperatures ($v^2 \to 1$, $T \gg T_c$)$\mu_{eff} \sim 1/c_2$ is constant too.

The experimental resistivity has a semiconductor-like temperature dependence $T > T_p$. However, the semiconductor-like temperature dependence of the resistivity cannot be correctly obtained from the theory in the degenerate semiconductor approximation $\mu > \hbar/\tau$.

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