MECHANISM OF COLOSSAL MAGNETORESISTANCE AND THE ROLE OF ELECTRON CORRELATIONS BY VIRTUAL PHONON EXCHANGE

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Abstract—The connection between the colossal magnetoresistance and the orbitally degenerate d-electron correlation caused by the virtual phonon exchange is explored. This virtual phonon exchange is the result of the combination of the electron-phonon and electron-strain interactions with the phonon dispersion. Two types of polarons are involved in the consideration of electrical conductivity but the virtual phonon exchange and the corresponding electronic states ordering is crucial. © 1998 Elsevier Science Ltd. All rights reserved

The problem of the colossal magnetoresistance is a high concentration mixture of the fundamental physics ideas connected to the structural and magnetic phase transitions, the conductivity in the orbitally degenerate systems, the polaronic phenomena and charge ordering. On the other hand, the important applications of the crystals with colossal magnetoresistance could be easily predicted and some of them have been already discovered.

We suggest that the microscopic mechanism of the colossal magnetoresistance is closely connected with the orbitally degenerate d-electron correlations caused by virtual phonon exchange. The latter is a combination of the phonon dispersion with the electron–phonon and electron–strain interactions and is responsible for the cooperative Jahn–Teller effect.

The idea of the importance of the Jahn–Teller cooperative effect in the colossal magnetoresistance manganites, at first glance, is not new (see a series of very important results obtained in refs. [1–4]). However, in all previous studies, the crystal phonon dispersion was neglected, which, as is well known, leads to the disappearance of the effective electron–electron interaction, or only the totally symmetrical vibrations were considered (so that no structural phase transitions, other than isomorphic transitions in the manganites, can be described).

In the proposed approach, the basic interactions describing the structural ordering in the manganites are

$$\hat{H}_{el-L} = \sum_{m\kappa} (V_{m\kappa}^{E_z}\sigma_z^m + V_{m\kappa}^{E_x}\sigma_x^m)(b_\kappa + b_{-\kappa}^+)$$
$$+ \sum_{m\kappa} V_{m\kappa}^A \sigma_A^m (b_\kappa + b_{-\kappa}^+)$$
$$+ \sum_{\kappa} \hbar\omega_\kappa \left(b_\kappa^+ b_\kappa + \tfrac{1}{2}\right) + \hat{H}_{el-str} + \hat{H}_{str} \quad (1)$$

where the first two terms describe the interaction of the e_g electrons with the E_g- and A_{1g}-symmetry phonons, and the last three terms belong to the energies of the free crystal phonons, the electron–strain interaction and the elastic energy connected to the homogenous strains, (if they exist).

The hopping of the e_g electrons with a constraint prohibiting the double occupancy of the same site is given as

$$\hat{H}_t = \sum_{\substack{mn \\ s\mu\nu}} t_{mn}^{\mu\nu} c_{m\mu s}^+ c_{n\nu s} + h.c. \quad (2)$$

where $c_{m\mu}s(c_{m\mu}s^+)$ is an annihilation (creation) operator of the electrons in doubly degenerate state on site m, orbital μ and spin s.

Our starting model contained additionally terms of the Hund coupling between e_g and t_{2g} electrons, on-site Coulomb interaction of the e_g electrons, inter orbital exchange and the antiferromagnetic coupling of the localized t_{2g} spins. These interactions are not discussed here because we want to focus our attention on the cooperative Jahn–Teller effect. Here we need to mention that in the usual second order perturbation approach [5, 6], the first three terms lead to the effective orbital–orbital and spin–orbital interactions which should be considered as a contribution to the virtual phonon exchange determining the crystal structure.

For crystals with the cooperative Jahn–Teller effect it is convenient to use the canonical shift transformation of the Hamiltonian [7] eliminating the linear electron–phonon interactions. The peculiarity of this transformation in our approach is the necessity to include into the shift $\bar{R}$-operator both types of symmetry of the

phonons

$$\mathrm{e}^{-R}H\mathrm{e}^R = \tilde{H} \quad R = \sum_{m\kappa} g_m^x \sigma_x^m + g_m^z \sigma_z^m + g_m^A \sigma_A^m \quad (3)$$

$$g_m^{x,z} = i \sum_\kappa \frac{V_{m\kappa}^{x,z}}{\hbar\omega_\kappa}(b_{-\kappa}^+ - b_\kappa) \quad g_m^A = i \sum_\kappa \frac{V_{m\kappa}^A}{\hbar\omega_\kappa}(b_{-\kappa}^+ - b_\kappa) \quad (4)$$

The most important part of the effective intersite electron interaction describing the possible structural ordering in the manganites can be written as

$$H_{\mathrm{int}} = - \sum_{mn} A_{mn}(\sigma_z^m \sigma_z^n + \sigma_x^m \sigma_x^n) + B_{mn}\sigma_A^m \sigma_A^n \quad (5)$$

where the $\sigma_{z,x,A}$ are matrices given on the basis of the ground orbital doublet

$$\sigma_z^m = \begin{pmatrix} 1 & 0 \\ 0 & -1 \end{pmatrix} \quad \sigma_x^m = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} \quad \sigma_A^m = \begin{pmatrix} 1 & 0 \\ 0 & 1 \end{pmatrix} \quad (6)$$

and the parameters A_{mn} and B_{mn} are the virtual phonon exchange constants caused by E_g - and A_{1g}- symmetry phonon modes. Transformation (3) leads to additional terms of the form $\sigma_A^m \sigma_{z,x}^n$ that are not taken into account in the Hamiltonian (Eq. (5)) because this term contributes only to the system dynamics and is not important for the static structural ordering. The modes are determined by the formulae

$$A_{mn} = \sum_\kappa \frac{V_{m\kappa}^{E_z} V_{n\kappa}^{E_z} + V_{m\kappa}^{E_x} V_{n\kappa}^{E_x}}{\hbar\omega_\kappa} + \frac{1}{N} g_{0E}^2 \delta_{mn}$$

$$B_{mn} = \sum_\kappa \frac{V_{m\kappa}^A V_{n\kappa}^A}{\hbar\omega_\kappa} + \frac{1}{N} g_{0A}^2 \delta_{mn}$$

(the $g_{0E,A}$ are the contributing electron strain interaction constants).

The first term in Eq. (5) describes the possible structural orderings of the Jahn–Teller MnO_6 octahedra. After switching to the two sublattice crystals and after applying some cubic symmetry operations, this term can be rewritten in part as

$$\hat{H}_{\mathrm{Anti}} = - \sum_{\substack{mn \\ \alpha\alpha' = I, II^{mn}}} A_{mn}^{\alpha\alpha'} \left[\left(-\tfrac{1}{2}\sigma_z^{m\alpha} + \tfrac{\sqrt{3}}{2}\sigma_x^{m\alpha} \right) \right.$$

$$\times \left(-\tfrac{1}{2}\sigma_z^{n\alpha'} - \sigma_x^{n\alpha'} \right) + \left(-\tfrac{\sqrt{3}}{2}\sigma_x^{m\alpha} - \tfrac{1}{2}\sigma_z^{m\alpha} \right)$$

$$\left. \times \left(\tfrac{\sqrt{3}}{2}\sigma_x^{n\alpha'} - \tfrac{1}{2}\sigma_z^{n\alpha'} \right) \right] \quad (7)$$

in the case of the in-plane antiferrodistortive ordering. Here, the operator in the first set of parentheses corresponds to the x direction elongation of the $m\alpha$-octahedra and the operator in the second set of parentheses corresponds to the elongation in the y direction. The second term in Eq. (5), in the case of the two sublattice

crystal is,

$$\hat{H}_A = - \sum_{\substack{mn \\ \alpha\alpha' = I, II}} B_{mn}^{\alpha\alpha'} \sigma_A^{m\alpha} \sigma_A^{n\alpha'}$$

$$= - \sum_{mn} (B_{mn}^{(1)}\sigma_{A+}^m \sigma_{A+}^n + B_{mn}^{(2)}\sigma_{A-}^m \sigma_A^n) \quad (8)$$

where $\sigma_{A\pm}^m = \sigma_A^{mI} \pm \sigma_A^{mII}$.

The first term describes the isomorphic structural transition accompanied by the appearance of the totally symmetric homogenous strain and is of no interest. The second term in Eq. (8) describes the virtual phonon exchange between two m-atom cells caused by an odd optical phonon mode and can lead to a structural transition accompanied by charge ordering. The interplay of this interaction with the other E_g-type Jahn–Teller and magnetic ordering is definitely important for the colossal magnetoresistance systems.

Applying the transformation (3) to the e_g-electron transfer, the Hamiltonian leads to the vibronic reduction of the transfer integrals

$$t_{mn}^{\mu\nu} \to t_{mn}^{\mu\nu} \gamma_{mn}^{A\mu\nu} \gamma_{mn}^{E\mu\nu}; \quad \gamma_{mn}^{A\mu\nu}, \gamma_{mn}^{E\mu\nu} < 1 \quad (9)$$

$$\gamma_{mn}^{A,E} = \left\langle \exp\left[\sum_\kappa \frac{V_{m\kappa}^{A,E} - V_{n\kappa}^{A,E}}{\hbar\omega_\kappa}(b_{-\kappa}^+ - b_\kappa) \right] \right\rangle \quad (10)$$

This t-reduction is nothing but the polaronic effect. It is interesting to note that if the interaction of electrons with the totally symmetric vibrations prevails, the regular polaron effect takes place. However, if that is not the case, there is a Jahn–Teller polaron or a mixture of Jahn–Teller and regular polarons. Since the magnetic exchange parameter can be reduced similarly, this result can explain the isotopic effect of the magnetic critical temperature.

Finally, we would like to mention that the Hamiltonians discussed above form the basis for understanding the effect of colossal magnetoresistance. We believe that two factors are most important: (1) the change of the structural ordering (as a function of temperature and magnetic field) leads to a change of the electronic structure more favorable for electronic conductivity, (the overlap of the electron functions is bigger); (2) the virtual phonon exchange electron correlations can support the conductivity drastically by increasing the current–current correlations.

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