

MICROSCOPIC MECHANISM OF STRIPE PAIRING PHASE FORMATION

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Abstract: Stripe phase formation in manganite compounds with the colossal magnetoresistance is discussed on the basis of the cooperative Jahn-Teller effect theory. It is shown that the stripes are the result of a peculiar structural phase transition. The microscopic mechanism of this structural ordering is considered and it is found that the interference of two symmetry types of distortion ordering takes place, that of totally symmetrical and Jahn-Teller distortions. The quadratic electron-phonon interaction after two-mode canonical transformation leads to a three center interaction responsible for the stability of a combination of local distortions around the nearest neighbor Mn^{3+} - Mn^{4+} - Mn^{3+} ions as a structural unit of a stripe. The described combination of the local distortions is in agreement with the experimentally observed electron diffraction pattern.

"Stripe" physics [1] recently came into the focus of attention of physicists in connection with the properties of high-temperature superconductors [2,3] and colossal magnetoresistance manganites [4]. It is believed that the understanding of the stripe formation is fundamentally important for analysis of charge-ordered states, hybridization, and many other different kinds of interactions. Recently a strikingly interesting discovery was made about stripe pairing in manganites [5]. It was shown that in the charge-ordered phase of $La_{1-x}Ca_xMnO_3$ the very stable pairs of Mn^{3+} -stripes separated by the Mn^{4+} -stripes are the dominant motive in the electron diffraction patterns.

Here we are showing that these patterns are the result of a very peculiar cooperative Jahn-Teller effect. The interference of the electron correlations caused by the local (on site) totally symmetrical and the non-totally symmetrical (Jahn-Teller) distortions is typical for the conducting systems with the orbital degeneracy. The unusual stability of the stripe pairs - "stripe pairing" - is caused by the intersite electron correlation through the linear and quadratic electron-phonon interactions.

Let us consider as an example a sample of the $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ crystal with $x=0.5$ that corresponds to the equal numbers of the Mn^{3+} and Mn^{4+} cations. In this situation the Mn^{3+} and Mn^{4+} stripes are alternating in the charge-ordered state of the crystal [5]. We will demonstrate below that this is the result of the cooperative Jahn-Teller structural phase transition.

The Hamiltonian of the system under consideration contains the interactions of the electrons with the totally symmetrical phonons and orthorhombic ($B_{1g}(D_{4h})$) symmetry phonons (to reproduce the experimentally observed two-dimensional pattern it is enough, for simplicity, to consider local tetragonal symmetry of Mn-ions surrounded by the squares of the oxygen atoms)

$$H = H_{ph} + \sum_{m\kappa} V_{m\kappa}^A \sigma_A^m (b_\kappa + b_{-\kappa}^+) + \sum_{m\kappa} V_{m\kappa}^B \sigma_x^m (b_\kappa + b_{-\kappa}^+) + H_{el-str} + H_{str}, \quad (1)$$

where H_{ph} , H_{str} , H_{el-str} are the energies of the free phonons, the elastically strained crystal lattice and the electron-strain interactions. The sums on the sites m formally contain both the Mn^{3+} and the Mn^{4+} ions. As the electronic structures of the Mn^{3+} and Mn^{4+} ions are different, their electron-phonon interaction constants are also different with

$$V^A(\text{Mn}^{4+}) \gg V^A(\text{Mn}^{3+}), V^B(\text{Mn}^{3+}) \gg V^B(\text{Mn}^{4+}). \quad (2)$$

It is convenient to switch to an extended crystal cells containing two Mn-ions. Using the new cell operators, (m is now the cell index, and I, II are the sublattice indices.)

$$\sigma_{\pm}^m = 1/2(\sigma_I^m \pm \sigma_{II}^m) \quad (3)$$

the vibronic part of the Hamiltonian (1) can be written as

$$H_{el-ph} = \sum_{m\kappa} \left[V_{m\kappa}^{A-} \sigma_{A-}^m (b_\kappa + b_{-\kappa}^+) + V_{m\kappa}^{B+} \sigma_{x+}^m (b_\kappa + b_{-\kappa}^+) + V_{m\kappa}^{A+} \sigma_{A+}^m (b_\kappa + b_{-\kappa}^+) + V_{m\kappa}^{B-} \sigma_{x-}^m (b_\kappa + b_{-\kappa}^+) \right] \quad (4)$$

Taking into account only the ground orbital doublet for the Mn^{3+} ion ($\phi_{1,2}^{3+}$) and the two lowest separated by a big gap electronic states of the Mn^{4+} ion ($\phi_{3,4}^{4+}$) on the basis of the tunnel functions $\psi_{1,2,3,4} = 1/2(\phi_{1,2}^{3+} \pm \phi_{3,4}^{4+})$ the electronic operators σ_{\pm} are given as

$$\sigma_{A-} = \begin{pmatrix} 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \end{pmatrix}, \sigma_{x+} = \begin{pmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 1 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 \end{pmatrix}, \sigma_{x-} = \begin{pmatrix} 0 & 0 & 0 & 1 \\ 0 & 0 & 1 & 0 \\ 0 & 1 & 0 & 0 \\ 1 & 0 & 0 & 0 \end{pmatrix} \quad (5)$$

The vibronic coupling for totally symmetrical vibrations in the systems with the transfer of the electrons between the different crystal sites is much stronger than the coupling to the low symmetry Jahn-Teller distortions ($V^A(Mn^{4+}) \gg V^B(Mn^{3+})$). At this situation the quadratic vibronic interaction is important

$$H_{vib}^{(2)} = \sum_m \{ W_m^{B-AB} \sigma_x^m Q_m^B Q_m^A + W_m^{A-BB} \sigma_A^m Q_m^{B2} \} \quad (6)$$

On the basis of the tunnel functions of the expanded crystal two ion cells the operator (6) can be rewritten as

$$H_{vib}^{(2)} = \sum_{m\kappa\xi\pm} \{ W_{m\kappa\xi}^{B-AB\pm} \sigma_{x\pm}^m (b_{\kappa} + b_{-\kappa}^+) (b_{\xi} + b_{-\xi}^+) + W_{m\kappa\xi}^{A-BB\pm} \sigma_{A\pm}^m (b_{\kappa} + b_{-\kappa}^+) (b_{\xi} + b_{-\xi}^+) \} \quad (7)$$

In the following equations, the interaction of the electrons with the totally symmetrical, Q_{\pm} , distortions of the expanded crystal cell will be ignored as its contribution is negligible due to the crystal structure containing the common oxygen atom as the nearest neighbor of the Mn-ions. Taking into account that all operators in (5) are commuting it is possible to subject the Hamiltonians (1), (4) and (7) to the shift canonical transformation [6]

$$\tilde{H} = e^{iR} H e^{-iR}, R = \sum_m (g_m^{(1)+} \sigma_{x+}^m + g_m^{(1)-} \sigma_{x-}^m + g_m^{(2)-} \sigma_{A-}^m); \quad (8)$$

$$g_m^{(1,2)\pm} = i \sum_{\kappa} \frac{V_{m\kappa}^{B\pm, A-}}{h\omega_{\kappa}} (b_{-\kappa}^+ - b_{\kappa}), \quad (9)$$

after which the electron correlation caused by the virtual phonon exchange is described as

$$\begin{aligned}
\tilde{H} = & - \sum_{mn} A_{mn}^{(1)} \sigma_{x-}^m \sigma_{x-}^n - \sum_{mn} B_{mn} \sigma_{A-}^m \sigma_{A-}^n - \sum_{mn} A_{mn}^{(2)} \sigma_{x+}^m \sigma_{x+}^n - \\
& - \sum_{mn} (C_{mn}^{(1)} \sigma_{x-}^m \sigma_{A-}^n + C_{mn}^{(2)} \sigma_{x+}^m \sigma_{A-}^n + C_{mn}^{(3)} \sigma_{x+}^m \sigma_{x-}^n) - \sum_{mnk} (D_{mnk}^{(1)} \sigma_{x-}^m \sigma_{A-}^n \sigma_{x+}^k + \\
& + D_{mnk}^{(2)} \sigma_{x+}^m \sigma_{A-}^n \sigma_{x-}^k) - \sum_{mnk} (E_{mnk}^{(1)} \sigma_{x-}^m \sigma_{A-}^n \sigma_{x-}^k + \dots) - \Delta E_A - \Delta E_B. \quad (10)
\end{aligned}$$

In the Hamiltonian (10) the last two terms correspond to the stabilization energies ("polaronic" energies) caused by the totally symmetrical and the Jahn-Teller phonon modes, the remaining quadratic in phonons on site vibronic interaction is neglected as not important for the questions under discussion. While there are many terms in the Hamiltonian (10), only few of them can contribute to the stability of the static distortion configuration. For symmetry reasons all terms with the constants $C_{mn}^{(1,2)}$ and $E_{mnk}^{(1,\dots)}$ are equal to zero in the static limit.

The second term describes the antiferro-type correlation of the local totally symmetrical distortions, when $Q^{A-} \neq 0$ the antiferrodistortive structural transition takes place and it is accompanied by the charge ordering-localization. Additionally the local orthorhombic distortions can be ordered due to electron correlation described by the first and the third terms in (10). They can contribute to the ferro- or antiferro-type ordering of the orthorhombic distortions. However, accepting that the electron correlations caused by the orthorhombic symmetry phonons lead to the antiferrodistortive ordering (as it really takes place in the high Mn3+ concentration compounds), two antiferrodistortive structures could be considered (see Fig.1,2). The structure shown on the Fig.1 is energetically unfavorable because half of the Mn4+ ions lose their totally symmetrical polaron stabilization energy.

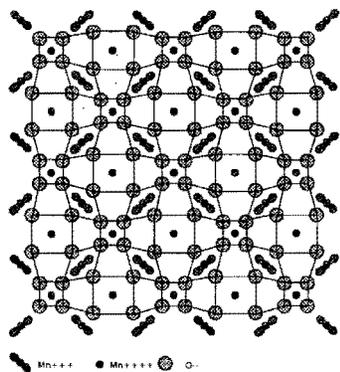


Figure 1. The structurally ordered phase of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ showing only the manganese and oxygen atoms. This phase is energetically unfavorable. See text

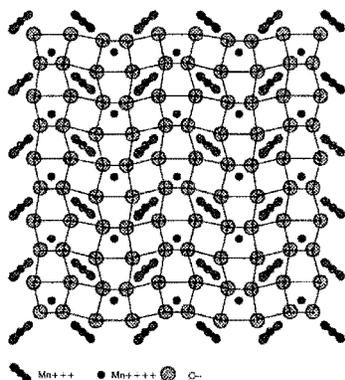


Figure 2. The energetically favorable phase of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ showing the three center interactions. This phase gives rise to stripes

The orthorhombic distortion anti-ferro ordering of the second type (Fig.2) can take place. This is a result of the presence in (10) of the $D_{mnk}^{(1,2)}$ terms that are of primary interest. Actually, the A-terms describe mostly the "direct" $\text{Mn}^{3+} - \text{Mn}^{3+}$ ions interaction of the non-nearest neighbors as the $V^B(\text{Mn}^{4+})$ is a small constant and the values of the A-constants are relatively small (of order of $((V^B)^2 / \hbar\omega_B)\Phi(m-n)$, $n = m \pm 2$, where Φ is some function upon the distance between the next nearest neighbors). At

the same time the three center D-terms describe the interaction of the two Mn^{3+} ions and of one Mn^{4+} ion between them.

The antiferrodistortive interaction of the Mn^{3+} ions is enhanced by the totally symmetrical contraction of the oxygen atoms around the Mn^{4+} ion. And the antiferrodistortive ordering of the orthorhombic distortions in its turn enhances the totally symmetrical distortion ordering of the antiferrotype and correspondingly the localization of the electrons. This type of the three center ordering is governed by the constant D that is of order of $W^{B-AB A-BB}(V^B / \hbar\omega_B)(V^A / \hbar\omega_A)\Phi_1(m, n, k)$ and can be bigger than the A-constants. In the sum over m, n, k in the Hamiltonian (10) there are non-zero D-terms with the equal subscripts for the pairs of the σ -operators that corresponds to the pairs of ions from the same expanded cell. Taking into account that $\sigma_{x-}^m \sigma_{A-}^m = \sigma_{x+}^m$ and $\sigma_{x+}^m \sigma_{A-}^m = \sigma_{x-}^m$, it can be seen that these terms are similar in structure to the A-terms in (10). However, the interaction constant of this orthorhombic distortion interaction of the three center origin is different-it contains a big factor $V_A / \hbar\omega_A$ as mentioned above.

In molecular field approximation the three center interaction generated by the quadratic electron-phonon interaction [6] can be represented as

$$D_{mn} \bar{\sigma}_{A-} (\sigma_{x-}^m \sigma_{x+}^n) \quad (11)$$

It is easy to show that returning to the one center electron operators the D-interaction in (10) can be rewritten as $D\sigma_{xI}^m \sigma_{AII}^m \sigma_{xI}^n$, where I, II are the sublattice indices of the expanded cell m.

It is seen that the interaction of the type (10) leads to an unusual cooperative Jahn-Teller interference ordering of the different symmetry distortions that is completely in agreement with the electron diffraction pattern observed experimentally in [5] (see Fig.2). Therefore, it is shown that the pairing of the Mn^{3+} ion stripes through the Mn^{4+} stripe is the consequence of the Jahn-Teller structural phase transition. One can quantitatively estimate the D-term in Eq. 10 by rewriting it as

$$D = W \frac{V^B}{\hbar\omega_B} \frac{V^A}{\hbar\omega_A} = W Q_{JT} Q_A = W Q_{JT}^2 \frac{Q_A}{Q_{JT}} \quad (12)$$

Then $D = (0.01 \rightarrow 0.1) E_{JT} \frac{Q_A}{Q_{JT}}$, where E_{JT} is the Jahn-Teller

stabilization energy, which is one or two orders of magnitude larger than W. For $Q_A/Q_{JT}=10$, (a typical ratio of distortions caused by the transfer of charge and the Jahn Teller effect,) we can get $D = (0.01 \rightarrow 0.1)eV$.

The stability of the clusters of five or three transition metal ions related to the stripe formation was under discussion by the authors of [7, 8]. Here we find that the three center electron correlation (10, 11) can be considered as an appropriate mechanism describing the Mn-cluster stability and the stripe phase.

So far, the analysis of the stripe formation in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ system was mostly confined to the $x=0.5$ concentration of Ca^{+2} ions, (or Mn^{4+} cations). It can, however, be generalized to cover any relevant concentration. For simplicity, let us assume that $x/(1-x)=n$, where n is an integer, ($x=0.5; 0.67; 0.75; 0.8\dots$). Then the crystal can be divided into $(n+1)$ sublattices with two Mn ions, (Mn^{3+} or Mn^{4+}) in a cell. Accepting the following hierarchy of interaction magnitudes in (10),

$$\Delta E_p \geq B > E_{JT} \geq A^{(1,2)} \approx D \text{ with } (\Delta E_p \equiv \Delta E_A \text{ and } E_{JT} \equiv \Delta E_B) \quad (13)$$

we conclude that the gain in energy is greatest (smallest) if one of the ions in the cell is a Mn^{3+} and the other is a Mn^{4+} .

In this case, the energy gain (loss) for each crystal cell is

$$-\Delta E = -\Delta E_p - \Delta E_{JT} \quad (14)$$

$$(\Delta E_p \approx \Delta E_p(\text{Mn}^{4+}), \Delta E_{JT} \approx \Delta E_{JT}(\text{Mn}^{3+}))$$

As the B-parameter is positive, ($B>0$ corresponds to the ferro-type ordering of the (Mn^{3+} - Mn^{4+})-pairs), an additional crystal energy $-B(0)\sigma_{A-}^2$ is gained when each cell is characterized by the similar orientation of Mn pairs,

$$B(0) = \frac{1}{N} \sum_{kn} B_{kn} \text{ (sum over cells containing } (\text{Mn}^{3+} \text{ -Mn}^{4+})\text{-pairs).}$$

Therefore, the distribution of atoms at which each Mn^{4+} - ion is surrounded by Mn^{3+} -ions leads to the gain of two main interaction energies, (ΔE_p and B). Moreover, additional energy is gained in this configuration due to the intercell Jahn-Teller distortion interaction of magnitude $A(0)$, ($A(0)$ is maximal at the shortest possible distance between Mn^{3+} -ions, and due to the 3-center interaction $D \approx A$, (which is maximal when the Mn^{4+} -ion is surrounded by Mn^{3+} -ions).

Thus, the stripe structure accounts for the energy gain related to all the terms of the Hamiltonian (10). The increase of the relative amounts of Mn^{4+} -

ions $\left(\frac{x}{1-x}\right)$ is decreasing each interaction's contribution to the total gain.

The "defective" ($\text{Mn}^{4+} - \text{Mn}^{4+}$) pairs are distributed homogeneously around the "correct" ($\text{Mn}^{3+} - \text{Mn}^{4+}$) pairs as in this case there are more boundaries with Mn^{3+} -ions and the energy loss can be partially recovered. Finally, in case $\left(\frac{x}{1-x}\right)$ is not an integer, the stripes will exhibit defects.

In conclusion, we would like to emphasize that the stripe phase stability is the result of a gain in the energy of the crystal electronic subsystem rather than in the elastic energy of the crystal lattice.

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