# Distinctive features of the electron *d* states and structural transition in $La_2CuO_4$ high-temperature superconductors

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A microscopic model for structural phase transitions in high-temperature superconductors of the $La_2CuO_4$ type is proposed. This model links these transitions with a mixing of copper *d* levels which are split in the crystal field (a pseudo–Jahn-Teller effect). Certain consequences of this model for superconductivity are discussed.

It is now generally accepted that the basic properties of the high-temperature superconductors of the $La_2CuO_4$ and $YBa_2Cu_3O_7$ types are determined by the electrons of copper-oxygen layers (or chains). In view of the nature of the splitting of the *d* levels by the crystal field, it is customary to consider only the electrons from a single nondegenerate *d* band of the $(x^2 - y^2)$ type. When this approach is taken, however, it becomes difficult to explain several aspects of the behavior of these systems, in particular, the nature of the structural phase transition from the tetragonal modification to the orthorhombic modification (the *T–O* transition) in $La_2CuO_4$ (Ref. 1). Arguments based on particular features of the Fermi surface in a nondegenerate two-dimensional *d* band[1,2] can hardly explain this transition: The distortions which are actually observed at this transition do not lead to a splitting of states or to the appearance of a gap at the Fermi surface (as follows in most general form from the conservation of the helical axis in the low-temperature phase of $La_2CuO_4$; Ref. 3).

Other attempts have also been made to explain the structural transition in $La_2CuO_4$, e.g., in a model of resonant valence bonds.[4] In the model discussed in Ref. 4, however, a corresponding phase apparently does not occur.[5]

  

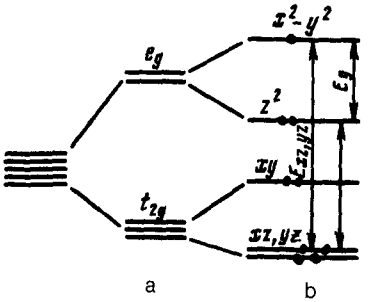


FIG. 1. Scheme of one-electron levels. a—Splitting of $d$ levels in a crystal field of cubic symmetry (undistorted octahedron); b—the same, but in the tetragonal case (elongated octahedron), which corresponds to the situation in $La_2CuO_4$. The filling of levels in the ground state of the $Cu^{2+}$ ion (the $d^9$ state) is illustrated. The arrows show which states are mixed by the corresponding vibrations.

We would like to show that several aspects of the behavior of these systems, in particular, the $T$–$O$ transition in $La_2CuO_4$, can be explained in a natural way by considering the structure of the $d$ levels in more detail. In our analysis we start from a picture of localized $d$ states; there are now many arguments in favor of such a description.[6]

The distortions accompanying the $T$–$O$ transition in $La_2CuO_4$ consist primarily of antiphase rotations of $CuO_6$ octahedra around the [110] axis. These rotations correspond to doubly degenerate $E_g$ ($D_{4h}$) vibrations $E_{xz,yz}$ (in the tetragonal phase, the local vibrations $T_{2g}$ are split into double $E_{xz,yz}$ vibrations and a single $A_{xy}$ vibration). In addition, there is a macroscopic deformation, which generates the usual orthorhombic symmetry. It is a simple matter to show that these distortions could result from a mixing of $d_{x^2-y^2}$ and $d_{xz,yz}$ terms, i.e., from a mixing of excited states with the $|x^2-y^2\rangle$ ground-state configuration (Fig. 1). From this standpoint, the structural transition in $La_2CuO_4$ may be thought of as a consequence of a cooperative pseudo–Jahn-Teller effect. Specifically, it follows from symmetry considerations that the matrix elements satisfy

$$\langle x^2-y^2|E_{xz,\,yz}|xz,yz\rangle \neq 0, \tag{1}$$

This point can also be verified directly, by noting that by virtue of the Wigner–Eckart theorem we have, for example,

$$\langle x^2-y^2|E_{xz}|xz\rangle \sim \int (x^2-y^2)xzxzdxdydz \neq 0.$$

For the diagonal matrix element, on the other hand, we have $\langle x^2-y^2|E_{xz,yz}|x^2-y^2\rangle = 0$, and this circumstance corresponds to the difficulty which we mentioned earlier in the description of the $T$–$O$ transition in the single-band model. The effective electron-phonon interaction which describes the mixing of ($x^2$–$y^2$) and $xz,yz$ states is

$$H_{int} = g\Sigma[a^+_{x^2-y^2}a_{xz,\,yz}(b^+_{xz,\,yz}+b_{xz,\,yz})+\text{H.a.}], \tag{2}$$

and the temperature of the structural transition is

$$T_{str}\sim\Delta\operatorname{arctanh}^{-1}\left(\frac{\Delta}{g^2/\omega}\right), \qquad \Delta = \epsilon_{x^2-y^2}-\epsilon_{xz,\,yz}\ , \tag{3}$$

where $\omega$ is the characteristic frequency of the $E_{xz,yz}$ vibrations, and $\varepsilon_\alpha$ is the energy of the corresponding electronic terms. Under the condition $\Delta \ll g^2/\omega$ we have

$$T_{\text{стр}} \sim \frac{g^2}{\omega}\left[1-\frac{1}{3}\frac{\Delta^2}{(g^2/\omega)^2}\right], \tag{4}$$

while at $\Delta \rangle g^2/\omega$ we have $T_{\text{str}} = 0$.

Deformations of $E_{xz,yz}$ also mix $d_{xz,yz}$ states with $d_{z^2}$ states. A filling of the $|z^2\rangle$ levels either in the ground state[7] or as the temperature is raised may thus promote the transition, since there would be a decrease in the second term in (4). It is possible that this circumstance is linked with the nonmonotonic behavior of the orthorhombic distortion, with a maximum at finite temperatures, as observed in Ref. 4.

The orthorhombic deformation, which transforms under the representation $B_{2g}$, is related quadratically to the main order parameter $\langle E_{[110]}\rangle = \langle E_{xz} + E_{yz}\rangle$ and stems from a term $\hat{O}_{B2g}E^2_{[110]}$. Correspondingly, it should vary as $(T_{\text{str}} - T)$ near the transition. Combined with the initial tetragonal distortion of the octahedron, these deformations give rise to a local monoclinic symmetry, in agreement with experiment.[1]

From the standpoint of this mechanism, a structural transition resulting from the mixing of partially filled and filled (or vacant) orbitals should be observed in $La_2NiO_4$, for example (the $Ni^{2+}$ ion has the configuration $t_{2g}^6 d_{x^2-y^2}^1 d_{z^2}^1$), but not in $La_2MnO_4$ (all of the $d$ levels are singly occupied in the $Mn^{2+}$ ion). A transition from a tetragonal phase to an orthorhombic phase, precisely similar to that observed in $La_2CuO_4$, has in fact been observed[9] in $La_2NiO_4$. It would be interesting to see whether a similar transition occurs in $La_2MnO_4$.

The suppression of the $T$–$O$ transition upon doping of $La_2CuO_4$ can, in this model, explain the similar suppression of antiferromagnetism[6]: The introduction of mobile holes suppresses both the spin and orbital ordering of the localized electrons, since the kinetic energy of the holes in the ordered phases is reduced.

Incorporating the complex structure of the $d$ states and the additional mechanisms for an electron-phonon interaction which appear here [see (2)] might also promote a superconducting pairing. In addition to the interaction of $(x^2-y^2)$electrons with a "breathing" mode, which is customarily invoked, in this case we would even add interaction (2) with $E_{xz,yz}$ vibrations and also an interaction with $E_g$ modes (in cubic symmetry), which lead to a repulsion and mixing of the $(x^2-y^2)$ and $z^2$ levels (Fig. 1). Whether these interactions would be enough to explain such high values of $T_c$ of course remains an open question. In any case, the incorporation of these interactions should promote a superconductivity. It may be that the arguments presented above may be important for other superconducting oxides of transition metals also, e.g., yttrium or bismuth oxides.

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