

THE ORTHORHOMBIC-TO-TETRAGONAL TRANSITION IN $\text{La}_{2-x}\text{M}_x\text{CuO}_4$

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The structural phase diagram in the temperature vs composition plane is obtained for $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M = \text{Sr}, \text{Ba}$) within the model of the oxygen-displacive interaction by assuming an increase of the hole concentration with increasing temperature. It is shown that the orthorhombic-to-tetragonal transition is continuous. The recently reported low-temperature tetragonal phase is also discussed.

1. INTRODUCTION

IT IS WELL-KNOWN [1, 2] that an orthorhombic-to-tetragonal transition occurs in $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M = \text{Sr}, \text{Ba}$) on increasing temperature and the doping level. The critical temperature T_d of this transition is about 533 K for $x = 0$ [3] and vanishes for $x_{cr} \cong 0.23$ [2, 4]. In contrast to the high-temperature tetragonal (HTT) phase the low-temperature orthorhombic (LTO) phase exhibits a non-vanishing tilting of the Cu-oxygen octahedra around the (1 ± 10) crystalline directions [5, 6], as well as a non-vanishing orthorhombicity parameter. Recently, a low-temperature tetragonal (LTT) phase has been reported for the Ba-doped compound [7] (and not yet confirmed for the Sr-doped compounds [8]), which exhibits a greatly diminished or vanishing orthorhombicity parameter, even though the superlattice reflections still persist.

It is shown in the present paper that the tilting angle enters the coupling strength of the interaction between the charge carriers and the sheet-bending mode of the oxygen ions in the basal plane of the Cu-oxygen octahedra. Consequently, a descending exponential is obtained for the x -dependence of both the tilting angle and the Cu-oxygen distances in the basal plane (Cu-O(1) distances), which shows that the above-mentioned structural changes are continuous. Assuming an increase of the hole concentration by thermal activation one obtains, within a simple model, the critical temperature of both the HTT-LTO (T_d) and the LTO-LTT (T'_d) transition as function of x . The phase diagram is thereby sketched qualitatively in the temperature-composition plane. The implications of the present model on the electronic properties of the compounds are briefly discussed.

2. OXYGEN-DISPLACIVE INTERACTION

Within the simplest tight-binding model of electronic structure [9] the relevant orbitals in a single layer of Cu-oxygen octahedra are labelled by the site i of the Cu cation and the spin σ . They arise by the strong hybridization of the Cu- d and oxygen- p orbitals and accommodate a hole concentration that is assumed to be equal to the doping level x . A half-filling gap (one electron per Cu cation) is also assumed in agreement with the experimental evidence. The two-dimensional motion of the charge carriers is described by the Hamiltonian

$$H_{cl} = -t_0 \sum_{\langle ij \rangle \sigma} c_{i\sigma}^+ c_{j\sigma} + U_0 \sum_{i\sigma} n_{i\sigma} n_{i-\sigma} + V \sum_{\langle ij \rangle \sigma \sigma'} n_{i\sigma} n_{j\sigma'}, \quad (1)$$

which includes a transfer (bandwidth parameter t_0) between the nearest neighbours $\langle ij \rangle$, a Hubbard repulsion U_0 and an intersite repulsion V ; $c_{i\sigma}$ ($c_{i\sigma}^+$) is the destruction (creation) operator of the $i\sigma$ -state and $n_{i\sigma}$ stands for the hole occupancy of this state.

A strong coupling is expected to occur [10] between the charge carriers and the localised vibrations of the Cu-oxygen octahedra. Of particular importance, due to their axial symmetry, are, in this respect, the stretching mode of the apical oxygens and the sheet-bending mode of the basal-plane oxygens. The former brings the main contribution to the $\omega = 500 \text{ cm}^{-1}$ optical phonon mode, whereas the $\omega^* = 240 \text{ cm}^{-1}$ mode is associated mainly to the latter [11, 12]. These vibrations are assumed to be described by a set of harmonic oscillators

$$H_{lat} = \sum_i \left(\frac{1}{M} P_i^2 + \frac{1}{4} M \omega^2 Q_i^2 \right)$$

$$+ \sum_{\alpha} \left(\frac{1}{2M} p_{\alpha}^2 + \frac{1}{2} M \omega^{*2} q_{\alpha}^2 \right), \quad (2)$$

where Q_i is the (relative) coordinate of the apical oxygens (mass $M/2$), q_{α} is the coordinate of the basal-plane oxygens labelled by α , and M is the oxygen mass.

At low temperatures the tilting mode of the octahedra softens [6] leading to a non-vanishing tilting angle θ , whose square may be considered as a non-dynamical, order parameter of the tilted phase [13]. As a consequence of this tilting a coupling will arise between the vibration modes included in (2) and some other modes of lattice vibrations. However, we neglect this coupling since its main effect is only the renormalization of the frequencies ω and ω^* . On the contrary, the tilting angle gives rise to a non-trivial coupling of the in-plane charge carriers and the ω^* -mode. Indeed, this interaction is proportional to the parallel-to-plane component θq_x of the coordinate q_x of this mode. An interaction of the same nature is also considered for the apical oxygens, which, however, involves the perpendicular-to-plane component Q of the stretching mode. Therefore, the interaction Hamiltonian reads

$$H_{\text{int}} = g \sum_{i\sigma} Q_i n_{i\sigma} + G\theta \sum_{\langle i\alpha \rangle \sigma} q_{\alpha} n_{i\sigma}, \quad (3)$$

where g and G are coupling constants and $\langle i\alpha \rangle$ denotes the Cu-oxygen nearest neighbours.

The canonical transformation generated by

$$S = - \frac{2g}{M\omega^2} \sum_{i\sigma} P_i n_{i\sigma} - \frac{G\theta}{M\omega^{*2}} \sum_{\langle i\alpha \rangle \sigma} p_{\alpha} n_{i\sigma}, \quad (4)$$

eliminates the interaction (3), leaves unchanged H_{latt} given by (2) and takes the electronic Hamiltonian (1) into

$$H_{\text{el}} = - \sum_{\langle ij \rangle \sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_{i\sigma} n_{i\sigma} n_{i-\sigma} + (V - J) \sum_{\langle ij \rangle \sigma \sigma'} n_{i\sigma} n_{j\sigma'}, \quad (5)$$

where

$$t_{ij} = t_0 \exp \left[-i \frac{2g}{M\omega^2} (P_i - P_j) - i \frac{G\theta}{M\omega^{*2}} \left(\sum_{\langle i\alpha \rangle} p_{\alpha} - \sum_{\langle j\alpha \rangle} p_{\alpha} \right) \right],$$

$$U = U_0 - g^2/M\omega^2 - 4J, \quad J = G^2\theta^2/2M\omega^{*2}. \quad (6)$$

The discussion of the effective electron-electron attraction that appears in (5), and which may lead to superconductivity, is beyond the aim of the present paper; partly, it has been done elsewhere [10]. We focus here on the effect of the oxygen-displacive interaction on the crystalline structure of these compounds.

The canonical transformation given by (4) displaces the equilibrium positions of the oxygen vibrations as follows:

$$Q_i \rightarrow Q_i - \frac{2g}{M\omega^2} \sum_{\sigma} n_{i\sigma}, \quad (7)$$

$$q_{\alpha} \rightarrow q_{\alpha} - \frac{G\theta}{M\omega^{*2}} \sum_{\langle i\alpha \rangle \sigma} n_{i\sigma}. \quad (8)$$

At zero temperature we may take the average occupancy per spin $\bar{n}_{i\sigma} = x/2$, according to the above assumption. For convenience, we neglect the deviations from x of the average hole concentration brought about by the oxygen deficiency, disorder effects, defects, magnetic correlations, etc. We also place ourselves in the metallic phase corresponding to $x \gtrsim 0.05$ [14]. Under these circumstances one straightforwardly obtains from (7) the distance between the Cu cation and apical oxygen anion

$$d_2 = \text{const} - \frac{g}{M\omega^2} x, \quad (9)$$

the factor 2 being lost since Q_i is the relative (oxygen-oxygen) vibration coordinate. Experimentally [1], the slope of $d_2(x)$ is about 0.1 \AA , so that, for $\omega = 500 \text{ cm}^{-1}$ ($M\omega^2 = 15 \text{ eV/\AA}^2$), one gets from (9) $g = 1.5 \text{ eV/\AA}$. This yields $g^2/M\omega^2 = 150 \text{ meV}$ which, in the polaronic picture of (5), agrees excellently with the polaronic binding energy suggested by the photoinduced infrared spectroscopy ($2g^2/M\omega^2 \sim 0.3\text{--}0.4 \text{ eV}$) [15]. The reduced bandwidth parameter corresponding to the polarons associated to the apical oxygens is obtained from (6) as

$$\bar{t}_{ij} = t_0 \exp \left[- \frac{2g^2}{M^2\omega^4} \langle (P_i - P_j)^2 \rangle \right] = t_0 \exp (-g^2/M\omega^3).$$

The band-width of $\sim 5 \text{ eV}$ [9] corresponds to $t_0 \cong 0.6 \text{ eV}$ for our band model ($\epsilon_k = -2t_0(\cos k_x + \cos k_y)$), which yields $\bar{t}_{ij} = 54 \text{ meV}$ for $g = 1.5 \text{ eV/\AA}$ obtained above. This reduced bandwidth parameter is satisfactorily close to 36 meV , derived within our electronic structure model from the density of states $\sim 30/\text{Ry} \cdot \text{cell}$ required for describing the normal-state properties [16]. One can say that the polaronic picture associated to the apical oxygens may apply to these compounds. We note that, according to (9), the recently reported [12] anomalous oxygen-isotope effect in ω could also be seen in the Cu-oxygen distance d_2 .

The variation of the tilting angle with the hole concentration can readily be obtained from (8) as

$$\delta\theta = - \frac{2G\theta}{aM\omega^{*2}} \delta\bar{n}_i, \quad (10)$$

whence

$$\theta = \theta_0 \exp(-\bar{n}_i/x_{cr}), \quad (11)$$

where $\bar{n}_i = 2\bar{n}_{i0}$, $x_{cr} = (2G/aM\omega^{*2})^{-1}$ and a is the distance between the Cu cation and the basal-plane oxygens in the undistorted phase. As one can see from (11) the tilting angle never vanishes, which indicates that the orthorhombic-to-tetragonal transition is continuous. The distance between the Cu cation and the basal-plane oxygens in the tilted phase can be given by

$$d_i = a/\cos \theta \cong a(1 - \theta_0^2 x/x_{cr}), \quad (12)$$

where \bar{n}_i has been replaced by x (at low temperatures) and the linear approximation to (11) has been used. Making use of $\theta_0 = 5^\circ$ (the tilting angle for the undoped compound) [3, 5] the expression given by (12) reproduces satisfactorily the experimental dependence [17] $d_i = 1.9 - 0.06 \times \text{\AA}$ for $a = 1.9 \text{\AA}$ and $x_{cr} = 0.24$, which agree with the values obtained from the structural studies [1, 2]. Moreover, it follows that the tilting angle is reduced by the factor e for $x = x_{cr} = 0.24$, which is consistent with the orthorhombic-to-tetragonal threshold reported experimentally [2, 4]. It is also worth noting that on increasing pressure the coupling constant G may increase, leading thus to a lower value of x_{cr} , i.e., to the suppression of the orthorhombic phase, in agreement with the experimental observations [4]. From $x_{cr} = (2G/aM\omega^{*2})^{-1}$ and using the data found above and $\omega^* = 240 \text{ cm}^{-1}$ one obtains $G \cong 13.7 \text{ eV/\AA}$, which indicates a rather strong in-plane coupling. However, its effect on the charge carriers is strongly reduced by the very small tilting angle (as one can see from J given by (6)), so that a rather weak polaron effect might be expected from the coupling to the basal-plane oxygens. It is worth noting in this respect that θ^2 and, consequently (according to (6)), the in-plane polaronic effect are reduced by the same factor e for $x = x_{cr}/2 = 0.12$, i.e., exactly where several anomalies have recently been reported in these compounds [7, 8, 12].

3. ORTHORHOMBIC-TO-TETRAGONAL TRANSITION

As the tilting angle never vanishes the orthorhombic-to-tetragonal transition is continuous. Conventionally, one can define the borderline between the two phases by

$$\bar{n}_i = x_{cr} \quad (13)$$

which corresponds to the reduction of the tilting angle in the HTT phase by a factor e . There are some indications, especially from Hall effect measurement [18, 19], that the hole concentration \bar{n}_i increases with

temperature. The reduction of the electron number, may arise from the pseudogap caused by the anti-ferromagnetic fluctuations [20] or by disorder effects, especially at higher values of x [21]. Adopting such a point of view could be consistent with the continuous character of the structural transition in these compounds. One may suggest, in a very schematic model, that the electronic structure may be approximated by two energy levels, ε_1 and ε_2 ($\varepsilon_2 > \varepsilon_1$) the former corresponding to the conduction electrons, while the latter being associated to the localized electrons which are practically lost for the transport properties. This rather rough approximation is only intended to show that the critical temperature of the orthorhombic-to-tetragonal transition may be qualitatively obtained by assuming an increase of the hole concentration with increasing temperature, and emphasizes once more the importance of the detailed knowledge of the electronic structure for describing the properties of these compounds. The thermal distribution among the two levels reads

$$1 = \frac{1}{y+1} + \frac{1}{Ay+1}, \quad (14)$$

where $y = \exp(\beta\varepsilon_1)$, $A = \exp(\beta\delta)$, $\delta = \varepsilon_2 - \varepsilon_1$ and β being the reciprocal temperature. Since there are $1-x$ electrons on the ε_1 level it follows that the average hole concentration is given by

$$\bar{n}_i = 1 - (1-x) \frac{1}{y+1}, \quad (15)$$

which is such as $x < \bar{n}_i < 1$. From (14) and (15) one readily obtains

$$\bar{n}_i = x + (1-x)/(\sqrt{A}+1), \quad (16)$$

whence, making use of (13), one derives the critical temperature

$$T_d = \frac{\delta}{2} \{ \ln [(1-x_{cr})/(x_{cr}-x)] \}^{-1}, \quad (17)$$

for the LTO-HTT phase transition. For $x_{cr} = 0.24$ the reduced temperature T_d/δ given by (17) is plotted in Fig. 1 (curve a) as a function of x . One obtains $\delta \cong 74 \text{ meV}$ by requiring $T_d(x = 0.15) = 200 \text{ K}$, as observed experimentally [2]. With this value of δ one obtains $T_d(x = 0) \cong 370 \text{ K}$ from (17), which is sensibly lesser than the experimental value 533 K [3]. However, for $x \lesssim 0.05$ the effects of electron localization are dominant, which would lead to a higher value of \bar{n}_i and, consequently, to a higher value of the critical temperature. This supports our assumption of increasing hole concentration with increasing temperature as a result of the electron localization by disorder effects.

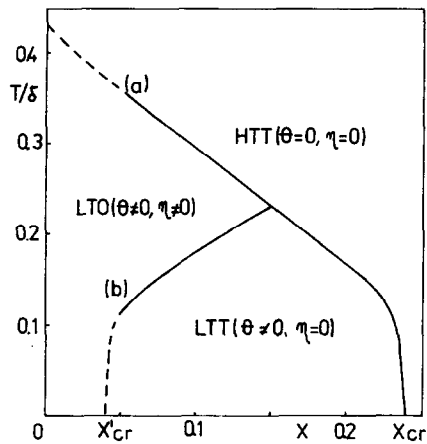


Fig. 1. Sketch of the structural "phase diagram" in the plane of the reduced temperature (T/δ) vs doping level x for $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M = \text{Sr}, \text{Ba}$). The curves (a) and (b) correspond to the "critical" temperature given by (17) and, respectively, (20) for $x_{cr} = 0.24$ and $x'_{cr} = 0.04$.

It is worth emphasizing that the orthorhombicity parameter $\eta = (d_1 - a)/a \cong \frac{1}{2}\theta^2$, where d_1 is given by (12), vanishes much faster than the tilting angle with increasing x and temperature. Indeed, at zero temperature we have

$$\eta = \frac{1}{2}\theta^2 = \frac{1}{2}\theta_0^2 \exp(-2x/x_{cr}), \quad (18)$$

where (11) has been used with $\bar{n}_i = x$. Taking, conventionally, the reduction of θ_0^2 in (18) by the same factor e as for the tilting angle θ_0 , one gets the threshold

$$x'_{cr} = \frac{x_{cr}}{2} (1 - \ln 2) \cong 0.04, \quad (19)$$

which may be taken as the point separating the LTO phase ($\theta \neq 0, \eta \neq 0$) from the LTT phase ($\theta \neq 0, \eta = 0$). A rather arbitrary "critical" temperature T'_d , for the LTO-LTT phase transition can therefore be obtained from (17) by replacing $x_{cr} \rightarrow x'_{cr}$ and $x \rightarrow 2x'_{cr} - x$,

$$T'_d = \frac{\delta}{2} \left\{ \ln \left[\frac{1 - x'_{cr}}{x - x'_{cr}} \right] \right\}^{-1}, \quad (20)$$

which is plotted in Fig. 1 (curve b as function of x). Although qualitatively consistent with the experimental data one should, however, stress upon the arbitrary character of both T_d and T'_d given by (17) and, respectively, (20), and the phase diagrams represented in Fig. 1. The main point is that the tilting angle decreases exponentially on increasing both the temperature and the doping level and, as such, its square and, consequently, the orthorhombicity parameter η falls out much faster than θ . Apart from the HTT and LTO phases one may have therefore an additional structural

modification, referred to as the LTT phase, with the tilting angle θ sensibly greater than the orthorhombicity parameter η . In addition, we note that the experimental data [1, 2] follow quite closely the temperature dependence of $\eta = \frac{1}{2}\theta^2$ as obtained using (11) and (16).

4. DISCUSSION

We may conclude that the tilting of the Cu-oxygen in $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ induces a coupling between the holes and the sheet-bending mode of the basal-plane oxygens that displaces the equilibrium positions of the latter such as to produce a descending exponential x -dependence of the tilting angle. A similar decreasing is obtained for the tilting angle with increasing temperature when allowing for the increase in the hole concentration as caused by the electron localization. Magnetic correlations or disorder effects may account for such a reduction in the number of electrons, which would be consistent with both the continuous character of the structural transformations and the sign reversing of the charge carriers in the Hall effect. The tilting angle decreases on a much slower scale than the orthorhombicity parameter, which, naturally, allows three structural "phases" to be accommodated in the (x, T) -plane: HTT ($\theta = 0, \eta = 0$), LTO ($\theta \neq 0, \eta \neq 0$) and LTT ($\theta \neq 0, \eta = 0$). The dividing "critical" lines of these phases are, however, of a much conventional character, which would explain the uncertainties and the conflictual data in the experimental reports.

In the formal derivation of the critical temperatures T_d and T'_d as given by (17) and, respectively (20) the fluctuation effects have been neglected. Although it is difficult to estimate these effects at this level of knowledge one can expect a sensible reduction in the critical temperatures, especially at higher values of x , due to thermal fluctuations. This reduction may be as great as to completely spoil the LTT phase (or, at least, to push it toward very low temperatures), as it may be the case for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$. However, one should notice that as weak as this phase may show itself in the structural properties it may sensibly affect the electronic properties (as, for example, the superconductivity). Indeed, as one can see from (6), these properties depend on the tilting angle square θ^2 (like the orthorhombicity parameter η) and it exactly this parameter which greatly diminishes in the LTT phase. This may explain the recently reported anomalies in the superconducting properties of both Sr- and Ba-doped compounds [8, 12]. The implications of this structural transformation on the superconducting properties will be discussed in a forthcoming paper.

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