

STABILITY OF THE TETRAGONAL AND ORTHORHOMBIC PHASES IN La_2CuO_4

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We have studied the mechanism of the tetragonal to orthorhombic phase transition which is observed in La_2CuO_4 at about 500 K [1] and is destroyed by applying pressure [2]. We have also checked the stability of the orthorhombic structure (ORTHO) at $T = 0$ versus the low temperature tetragonal (LTT) phase observed in neighbouring compounds $\text{La}_{1.9}\text{Ba}_{.1}\text{CuO}_4$ [3] and La_2CoO_4 [4].

THE METHOD :

The method relies upon a development of the total energy of the system as a sum of pair interactions between ions, including a direct Coulomb term, a short range repulsion of the Born Mayer type and a Van der Waals term [25]

$$E = \sum_{i \neq j} \frac{Q_i Q_j}{R_{ij}} + B_{ij} e^{-R_{ij}/\rho_{ij}} - C_{ij}/R_{ij}^6$$

The parameters B_{ij} , ρ_{ij} and C_{ij} were taken so as to be able to reproduce correctly the structures of La_2O_3 and CuO [6] upon the assumption that the ionic charges take integer values (+2 for Copper, +3 Lanthanum and -2 for Oxygen). The interactions are summed by grouping atoms in neutral entities La_2CuO_6 (with the four in-plane Oxygen atoms counting for 1/2). It is worth stressing that a real chemical bond exists between the Lanthanum atoms and the out of plane Oxygen atoms since their distance $d \sim 2.34 \text{ \AA}$ is of the order of the sum of ionic radii. This is to be contrasted with the other eight oxygen atoms surrounding the La which are more remote. The energy is computed with an accuracy better than 10 meV as a function of interatomic distances and angles inside an entity and as a function of the distance z between neighbouring planes (fig. 1) : this amounts to four parameters in the high temperature tetragonal phase (HTT), eight in the ORTHO and seven in the LTT. A minimization procedure is then applied to determine the structural parameters at $T = 0$.

Cohesion in the HTT : The result of the minimization is

$$E = -173.83 \text{ eV/entity}, d = 2.379 \text{ \AA}, d_1 = 2.399 \text{ \AA}, d_2 = 1.897 \text{ \AA}, z = 6.575 \text{ \AA}.$$

It cannot be compared with experiment since this phase is not met at $T = 0$. Yet the decomposition of E into intraplane and interplane interactions reveals that a single plane

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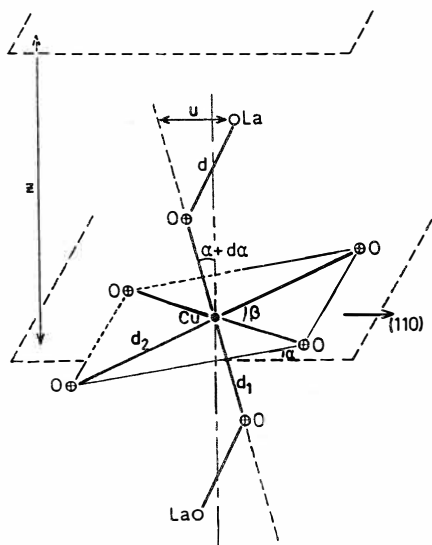


Figure 1 : Representation of the La_2CuO_4 unit in the orthorhombic phase and definition of the eight structural parameters d , d_1 , d_2 , Z , α , dA , β , u

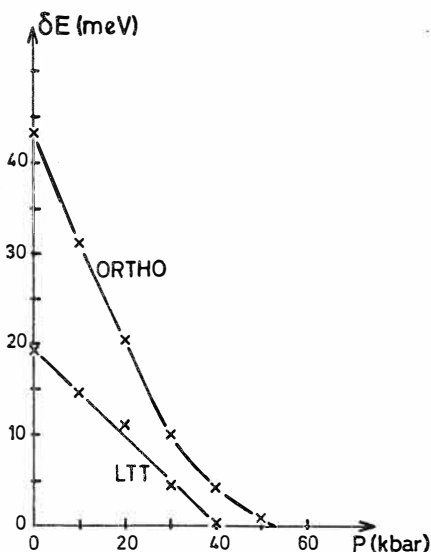


Figure 2 : Energy of stabilization of the orthorhombic (ORTHO) and low temperature tetragonal (LTT) phases, with respect to the high temperature tetragonal one as a function of applied hydrostatic pressure.

of La_2CuO_4 units is unstable, corresponding to strong repulsive interactions ($E_0 = 34.85$ eV) while the cohesion comes predominantly from attractive interactions between neighbouring planes ($E_1 = -208.96$ eV). This may be understood by realizing that the lowest multipolar moment of a La_2CuO_4 unit is a quadrupolar moment, much elongated along the (001) direction; interactions between quadrupoles having a single diagonal component along \vec{c} indeed are repulsive inside an (\vec{a}, \vec{b}) plane, and attractive in most of the neighbouring planes [7].

Stability of ORTHO : We have minimized the energy with respect to the eight structural parameters represented on figure 1. The results show that the ORTHO phase has a lower energy than the HTT, as experimentally observed but the distance d_2 in the Copper Oxygen plane is found larger by $\sim .04 \text{ \AA}$ than the observed one. We assign this difference to the neglect of covalency effects, obviously present in the (\vec{a}, \vec{b}) plane, and, in order to account for them, we add a new attractive term in the total energy, $-Ae^{-qd_2}$, varying exponentially with d_2 in order to mimick the distance dependence of hopping integrals. The values of A and q leading to a best fit with the experimental structural parameters are unambiguously found equal to 25 eV for A , 1.5 \AA^{-1} for q , which corresponds to a covalent energy of about 1.44 eV per Copper atom. It is satisfactory that this quantity be

of the same order of magnitude as the one obtained by band structure calculations [8], although slightly smaller : correlation effects might be responsible for this fact.

The validity of our description is then checked by studying pressure effects, which amounts to minimizing the enthalpy $E+PV$ with V the volume associated to a La_2CuO_4 entity. At small values of the pressure the compressibility coefficients are found equal to: $4.31 \cdot 10^{-4}\text{kbar}^{-1}$, $3.71 \cdot 10^{-4}\text{kbar}^{-1}$, $3.12 \cdot 10^{-4}\text{kbar}^{-1}$ along respectively \vec{a} , \vec{b} , \vec{c} to be compared with the experimental determination [9]: $1.8 \cdot 10^{-4}\text{kbar}^{-1}$, $4.2 \cdot 10^{-4}\text{kbar}^{-1}$, $0.86 \cdot 10^{-4}\text{kbar}^{-1}$.

It is seen that correct orders of magnitude are found, but the figures should not be considered too seriously since our accuracy on distances is less than 10^{-3} Å. By comparing the energy of the ORTHO with respect to HTT we find that ORTHO gets progressively destabilized until a critical pressure P_c of about 50 kbars. This is in good agreement with the value derived by extrapolation of X Ray data [2].

Stability of the LTT : Without changing the parameters for Born Mayer, Van der Waals and covalency terms, we have studied the relative stability of the LTT phase compared to the HTT and ORTHO. The results, shown on figure 2, indicate that LTT has a lower energy than HTT but higher than ORTHO. It is also destabilized by pressure effects and its critical pressure is $P_c \sim 40$ kbars. Figure 2 is consistent with the fact that LTT was never observed in La_2CuO_4 in the whole pressure range. This phase presents a special interest due to the occurrence of two different Cu–O distances in the basal plane (d and $d \cos \alpha$) required to fulfill a tetragonal symmetry. This may induce changes in the density of states and eventually affect the superconductivity.

Mechanism of the HTT to ORTHO phase transition : The flexibility of our method of calculation allows a careful examination of the microscopic origin of the ORTHO phase. First we have looked for the primary order parameter of the transition : we have found that a rigid tilt α of the units (keeping the Cu–O–La atoms aligned) is never able to stabilize ORTHO, nor is a rigid tilt accompanied by a shear distortion of the basal plane ($\beta \neq \pi/2$ in fig. 1). A rotation of the La–O bond, keeping approximately its length constant (described in fig.1 by a displacement u of the La atom) is required. The primary order parameter thus has three components (α , $d\alpha$, u), while the shift of β from the value $\pi/2$ and the readjustment of all bond lengths are secondary ones. It is possible to obtain numerically a Landau development of the energy as a function of α , $d\alpha$ and u . The lowest order terms in α^2 , $d\alpha^2$ and u^2 have positive coefficients indicating that no phase transition can be driven by a single distortion. On the other hand, coupling terms, eg. $\alpha u \dots$ are large and indeed are responsible for the stabilization of the orthorhombic phase.

The origin of such a behaviour can be looked for in individual interactions. As concerns the rigid tilt, we find that two forces oppose its occurrence : first it decreases appreciably the distance between two La atoms belonging to neighbouring entities in the same plane, which leads to a strong repulsion ; second, it strongly enhances the Born Mayer repulsion

between the "central" entity and its neighbours along the (001) direction.

On the other hand, a displacement u of the La atoms obviously suppresses these unwanted effects and the stabilization of the ORTHO phase may be understood as a competition between an increase of short range repulsion (the HTT seems to optimize these terms) overcompensated by an increase of Coulomb attraction. This latter has various origins : first, thanks to the displacements u , the La atoms come closer to the four in-plane Oxygen atoms inside their own unit ; second, considering intraplane interactions, the tilt is as a whole favourable because it decreases the quadrupolar diagonal component and avoids the strong repulsion of parallel quadrupolar ; third, as for interplanar interactions, the slight contraction of distances which comes with the tilt, allows an increase of interplane Coulomb attractions. A more detailed account of this work will be published elsewhere [7].

As a conclusion, it may be said that, although relying on a partly empirical set of parameters, checked for other structures, this method is well suited to a study of the mechanisms of phase transitions. We intend to develop the study of the LTT phase and of the alloys $\text{La}_{2-x}\text{M}_x\text{CuO}_4$ ($M = \text{Sr}, \text{Ba}, \text{Ca}$) in a next future.

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