Lattice dynamics calculation of infrared active modes of cuprate superconductors

T. Hasegawa [a,*], N. Ogita [a], T. Kondo [b], H. Kawashima [c], J. Akimitsu [c], M. Udagawa [a]

[a] *Faculty of Integrated Arts & Sciences, Hiroshima University, Higashi-Hiroshima, 739-8521, Japan*
[b] *Venture Business Laboratory of Hiroshima University, Higashi-Hiroshima, 739-8527, Japan*
[c] *Department of Physics, Aoyama-Gakuin University, Sagamihara, Kanagawa 229-8558, Japan*

Abstract

We have calculated the highest-energy infrared active $E_{\rm u}$ mode for three cuprate compounds with and without apical ions, in order to investigate the experimental energy-difference between T- and T'-structures. The calculated energies show the similar Cu-O bond length dependence to the experimental results. The calculated spin densities of the T-structure have more electrons in the $d_{x^2-y^2}$ orbital than that of the T'-structure. This means that the CuO_2 plane in the T-structure is compressed, in comparison with the T'-structure even with the same Cu-O bond length. This compression increases the energy of the $E_{\rm u}$ mode in the T-structure. This is the clear evidence that the block layer is important for the electric state on the CuO_2 plane.

Key words: *ab-initio* calculation, phonon, cuprate, apical oxygen

Recently we have reported that the highest-energy infrared active $E_{\rm u}$ mode has larger energy by 45cm^{-1} for the T-structure cuprates than that for the T'-structure ones even with the same Cu-O bond length[1]. This mode is the stretching vibration of the Cu-O bond along the CuO_2 plane. This energy difference suggests that the electric state in the CuO_2 plane is different between them, since this mode has the same atomic displacement for both structures. To investigate a relationship between this energy difference and the electric state, we performed first-principles calculations of lattice vibrations at q=0 for three compounds, i.e. La_2CuO_4 with T-structure (abbreviated by T-LCO), $Sr_2CuO_2Cl_2$ with T-structure (T-SCOC), and La_2CuO_4 with hypothetical T'-structure (T'-LCO).

The present results were obtained by the ABINIT code [2], which is based on *ab-initio* pseudopotentials and a plane-wave basis set in the framework of the density-functional formalism. All calculations were performed with the local spin density approximation (LSDA) parameterized by Perdew and Wang [3]. The space group Bmab was used for all calculated compounds to produce an antiferromagnetic order in the CuO_2 plane. The phonon energy was calculated by the density functional perturbation theory [4]. At the first step, the optimized structures were calculated in the space group Bmab and then we proceeded phonon calculations using these structures.

The optimized lattice structures of T-SCOC and T'-LCO are consistent with the symmetries of ideal T- and T'- structure even if the symmetry of Bmab was assumed in the calculations. The calculated structures show good agreement with the experimental results for T-LCO and T-SCOC, and the difference in the lattice constants and atomic positions between the calculated and experimental results is less than 3%. The calculated energies of the E_u mode are shown in Fig. 1, where the reported experimental results are also plotted. In the figure, we draw four lines with the same slope of 1.78×10^3cm^{-1}/Å. The calculated results is plotted by dotted lines and the experimental ones solid lines for

* T. Hasegawa. Fax: 8182-424-0757
Email address: hase@hiroshima-u.ac.jp (T. Hasegawa).

both T- and T'-structures. All data are on the corresponding lines. The same energy difference of 45cm^{-1} between T-structure and T'-structure are found for both calculated and experimental results. We note the absolute energy difference of 30cm^{-1} between the calculations and the experiments is caused by the energy determination accuracy in the calculation. This accuracy is the same for the T- and T'- structures. Thus, this result shows the calculation can reproduce correctly the experimental Cu-O bond dependence.

In order to discuss the origin of the energy difference, we have also calculated spin densities of T-LCO and T'-LCO and the results are shown in Fig. 2. The spin density corresponds to the density of the hole wavefunction, since only one electron plays a dominant role for the Cu^{2+} case. As clearly seen, the hole wavefunction in T-LCO includes small amount of $d_{3z^2-r^2}$ orbital, while that in T'-LCO is almost $d_{x^2-y^2}$ orbital. This means that a small amount of electronic charge is transferred from $d_{3z^2-r^2}$ to $d_{x^2-y^2}$ orbitals due to the existence of the apical ions in the T-structure. This electronic charge transfer increases the Cu-O bond length in the CuO_2 plane in terms of Jahn-Teller distortion. However, the Cu-O bond length can not be freely relaxed, since the length is determined only by optimization of energy against the size of the block layer. In fact, the Cu-O bond length in the T-LCO is shorter than that in the T'-LCO. These facts indicate that the CuO_2 plane in the T-structure is compressed in comparison with that in the T'-structure even with the same Cu-O bond length. This compression increases the E_u mode energy in the T-structure. The present results clearly show the importance of the block layers on the electric state at the CuO_2 plane through their size and charge distribution.

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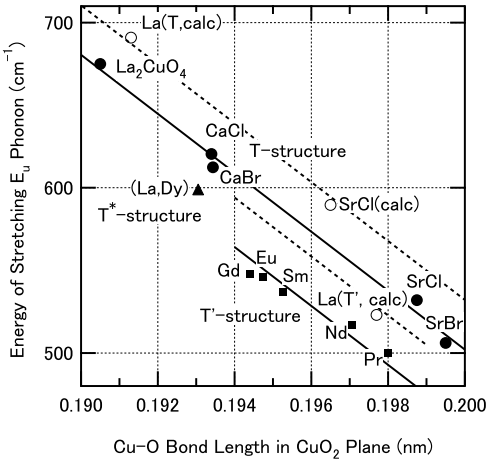

Fig. 1. Bond length dependence of the energy of the stretching Cu-O vibration along the CuO_2 plane. The closed circle, triangle, and square symbols are experimental data for T-structure, T*-structure, and T'-structure, respectively, taken from Refs. [1], [5], and [6]. The open circle symbols are calculated results. For R_2CuO_4 compounds, only rare earth ion R is presented, while for $R_2CuO_2X_2$ compounds they are abbreviated by RX.

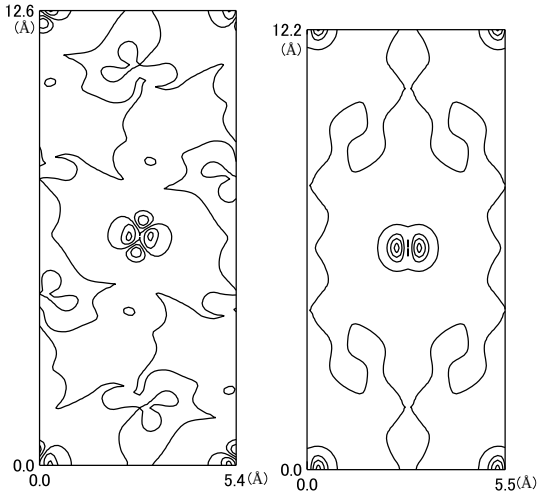

Fig. 2. The spin densities of T-LCO (left) and T'-LCO (right) on ac-plane. The Cu ions locate on center and corners. The contours are drawn by the interval of 0.01 μ_B/Bohr^3.