



Normal CO-Ordinate Analysis Of HTSC La_2CuO_4 .

By

SONAMUTHU. K*, GEENA VIDYA . S

(*J N R Mahavidyalaya, Port Blair, South Andaman, India.744104
Sathyabamal Engineering College, Chennai-600066)

ABSTRACT

Even though a fairly good amount of literature is available on the vibrational spectra of high temperature superconductors, still some specific feature in the experimental vibration spectra could not be assigned reliable to a definite type of vibration. Hence a normal coordinate analysis (NCA) which is applicable to zero wave-vector normal-mode vibrations have been carried out for the high temperature superconductors and the assignment of specific features like phonon softening and hardening were looked in for the clear understanding of the superconducting mechanism in these new class materials.

In the normal coordinate analysis, PED play an important role for characterization of the relative contributions from each internal coordinate to the total potential energy associated with particular normal coordinate of the molecule. The contribution to the potential energy from the individual diagonal elements give rise to a conceptual link between the empirical analysis of infrared spectra of complex molecules dealing with characteristic group frequencies and the theoretical approach from the computation of the normal modes. NCA gives complete assessment of all normal vibration modes of the system.

Key words: High Temperature Superconductor Conductor (HTSC), NCA, Raman and IR-spectroscopy, Brillouin zone, Potential Energy Distribution (PED), etc.,

1. Introduction

High Temperature Superconductor Conductor (HTSC) marks the beginning of a new era of material science. Researchers are looking beyond the simple metals. Their alloys, binary and ternary compounds to the almost limitless range of complex molecular solids, many of which will be based on the rich chemistry of the transition metals. These materials can be expected to have interesting and technologically important electronic and magnetic properties as the familiar materials of modern day technology.

The study of normal coordinate analysis and the free carriers is important for the understanding of the physical nature of high temperature superconductors. Raman and far-infrared studies of these superconductors have contributed significantly to the understanding of new class of superconductors.

The introduction of superconductivity above 30 K in CuO-pervoskites by Bednorz Muller[1] initiated tremendous efforts in solid state physics and material sciences with the aim to isolate the phases which are responsible for the superconductivity and to search for other substances beside the La_2CuO_4 family which exhibit this phenomenon.

These activities succeeded in the discovery of superconductivity in $\text{YB}_2\text{Cu}_3\text{O}_7$ at 92 K by Wu et al.[2] and the observation of a transition temperature above 100 K by Sheng et al.[3].

In this method the frequency of the normal vibration is determined by the kinetic and potential energies of the system. Wilson's GF matrix method [4] is applied for the calculation of optically active vibration frequencies. The kinetic energy is determined by the masses of their individual atoms and their geometrical arrangement in the molecules but the potential energy (PE) arises from interaction between the individual atoms described in terms of the force constants. Assuming reliable potential constants for various bonds, the vibration frequencies have been evaluated. Fine-tuning is done until the available observed frequency and the present evaluated frequency matches perfectly. Internal coordinates like bond length and bond angles are used in the kinetic energy expression. Since the potential and kinetic energies are described in terms of internal coordinates, they have clear physical meaning since these force constants are characteristics of bond- stretching and angle deformation involved[5].

Besides non-central forces such as involved in angle bending can be included in the normal coordinate analysis, which was not possible in the lattice dynamics. Also in NCA, Potential Energy Distribution (PED) indicates the contribution of individual force constants to the vibration energy of normal mode for the clear understanding of the specific vibration the species involved. The normal coordinate calculations were performed to support the assignment of the vibration frequencies and to obtain PED for various mode.

2. Normal Co-Ordinate Analysis Of Superconductor La_2CuO_4 .

The stoichiometric compound La_2CuO_4 crystallize at high temperatures in the K_2NiF_4 structure (D_{4h}^{14} -I4/mmm) with one chemical formula unit per unit cell (Jorgensen et al.[6]). At lower temperatures the crystals undergo a structural phase transition into an orthorhombic phase (D_{2h}^{18} -Cmca) by doubling the unit cell in a $\sqrt{2}a \times \sqrt{2}a$ fashion. The exact transition temperature depends on the oxygen stoichiometry of the sample and occurs between 430 K and 530 K (Johnsoton et al.[7]). Sometimes the structure is also denoted as (D_{2h}^{18} -Bmab). Both assignments may be transferred into each other changing the labels from the orthorhombic axes from abc to acb , respectively [8]. Table I give the results of an analysis of the phonon symmetries at the Γ -point of the reciprocal lattice. In the high temperature phase four Raman-active and seven infrared active modes should be observable. Below the structural phase transition the number of Raman and IR-modes increases because the number of atoms in the unit cell is doubled. 18 Raman and 21 IR active modes are expected. Some of them can be deduced from the zone center modes of the tetragonal phase, the others from zone boundary modes now becoming zone center modes because of the cell doubling.

Doping La_2CuO_4 with Sr (or Ba) shifts the tetragonal orthorhombic transition to lower temperatures and yields the superconducting material $(\text{La}_{1-x}\text{Sr}_x)_2\text{CuO}_4$ with the highest transition temperature in this series of 40 K for $x \sim 0.075$.

The interest in the high- T_c superconducting cuprate-crystal is stimulated, on the one hand, by the possibility of phonons taking part in carrier pairing processes and, on the other hand, by peculiar dynamic properties of these complex compounds with a layered structure. It is not surprising; therefore, that many papers report studies of thermal excitations of the crystal lattice of high T_c superconducting cuprates and related compounds. In particular, the La_2CuO_4 crystal lattice oscillations are experimentally studied by means of neutron [9-11] and optical [12-13] spectroscopy. The results of inelastic neutron-scattering experiments giving information about phonon dispersion relation [5] or phonon spectral

density [7-9] are usually interpreted in terms of collective oscillating excitations in each of which all the atoms take part. The information about the oscillations of individual atoms of the compound is thus lost.

Analysis of the literature shows that two approaches are used to get information about oscillating properties of single atoms of a complex compound. The first is based on model calculations of crystal-lattice dynamics, and the second on the analysis of indirect information about thermal atomic motions, obtained by neutron recoil spectroscopy for neutrons of energy $\approx 1 \text{ eV}^{10}$ by resonance neutron absorption and by neutron diffraction. All these methods suffer from an important short coming, namely the characteristics of thermal atomic motion are determined as fitting procedure parameters, together with a lot of other parameters, which, in some cases, can substantially affect the final result. Moreover, neutron diffraction data do not allow distinguishing between static and dynamic atomic displacements from equilibrium in the crystal lattice. The most reliable information about thermal motion of a definite type (i) of atoms in a complex compound can be obtained from the partial oscillating spectrum $g_i(E) = g(E) \langle |e_i|^2 \rangle$, where e is the polarization vector of the i th atom when the latter oscillates with energy E . Thus, the partial spectrum is determined by superposition of all normal modes with weight allowing for the i th atom displacement in lattice oscillations with energy E .

As shown in Parshin *et.al* [12] and Soldatov *et.al* [13], the method of isotopic contrast in inelastic neutron scattering makes it possible to experimentally restore the partial oscillating spectra of single atoms. In the present study this method was used to investigate the oscillations of Cu, La, and O atoms in La_2CuO_4 .

3. Normal Coordinate Analysis of Zero Wave Vector Vibration of La_2CuO_4

Cardona and coworkers [14] studied the infrared and Raman spectra of the super conducting cuprate perovskites MBaCu_2O_2 ($M = \text{Nd, Er, Dy, Tm and Eu}$) and reported the possible origins of phonon softening and the systematic variation of phonon frequencies with the ionic radius. Here an attempt has been made to perform the normal coordinate analysis for the phonon frequencies and the form of the zero wave vector vibrations for the La_2CuO_4 superconductors.

The high T_c superconductor La_2CuO_4 System crystallizes in the body-centered tetragonal (bct) system, which belongs to the space group $14/\text{mmm}$ (D_{4h}^{17}). The simple tetragonal (bct) unit cell of La_2CuO_4 and the numbering of the atoms are shown in Fig.1. The 6 atoms of the unit cell yield a total of 14 optical vibrational modes. All the above calculations are made at $q=0$. Once of A_{2u} and E_u modes corresponds to acoustic vibrations with frequency $\omega = 0$. These normal modes are distributed as follows.

$A_{1g} + A_{2u} + E_g + E_u$	from the motion of 2 La atoms
$A_{2u} + E_u$	from the motion of Cu atoms
$A_{2u} + B_{2u} + 2 E_u$	from the motion of O (1) atoms
$A_{1g} + A_{2u} + E_g + E_u$	from the motion of O (2) atoms

Subtracting the translation modes $A_{2u} + B_{2u} + E_u$ the $q = 0$ optical modes involved in an irreducible representation are as follows.

$$\Gamma_{\text{opt}} = 2A_{1g} + 2E_g + 4A_{2u} + 5E_u + B_{2u}$$

The species belonging to A_{1g} and E_g Raman active modes whereas A_{2u} and B_u are infrared active modes. The A_{2u} and A_{1g} modes involve displacement along crystallographic c-axis, the B_{2u} and E_g modes along the b-axis and E_u modes along the a-axis. The normal coordinate calculation was performed using the programs GMAT and FPERT given by Fuhrer et al [15]. The general agreement between the evaluated and observed normal frequencies of La_2CuO_4 is good. The calculated force constants using the above programs are given in Table 1. It is interesting to note that the evaluated frequencies given in Table.2, agree favorably with the experiment values.

To check whether the chosen set of vibrational frequencies makes the maximum contribution to the potential energy associated with the normal coordinate frequencies of the super conducting material, the potential energy distributions was calculated using the equation.

$$\text{PED} = (\mathbf{F}_{ij} \mathbf{L}_{ik}^2) / \lambda_k$$

Where PED is the combination of the i-th symmetry coordinate to the potential energy of the vibration whose frequency is ν_k . \mathbf{F}_{ij} are potential constants, \mathbf{L}_{ik} are L matrix elements and $\lambda_k = 4\pi^2 C^2 \nu_k^2$.

4. Result and Discussion

4.1. Normal coordinate analysis of La_2CuO_4

The G-matrix elements have been calculated from the equilibrium geometry. The initial force constants were taken from the related molecules. The final sets of potential constants provide the stability of the crystal in relation to all vibrational modes. The vibrational frequencies and potential energy distribution values are presented in this work. The potential energy distribution indicates the contribution of an individual force constant to the vibrational energy of normal modes. It clearly indicates that there is mixing of the internal displacement coordinates.

The evaluated frequencies using the normal coordinate analysis method listed in table.2 agrees favourably with the calculated normal coordinate analysis frequencies and observed experimental frequencies.

The calculated Raman phonon frequency at 218 cm^{-1} in A_{1g} symmetry is due to the vibration of La atom. The highest calculated phonon frequency at 553 cm^{-1} is due to the vibration of O(1) atoms and it is due to the stretched vibration of Cu-O(2) atoms

The lowest calculated phonon frequency at 105 cm^{-1} in E_g symmetry mode is due to the vibration of La atom and is due to the stretched vibration of O(1) –O(2)atoms

The calculated Raman phonon frequency at 333 cm^{-1} in E_g symmetry is due to the vibration of Cu atom and it is due to the stretched vibration between La and Cu atoms. The lowest calculated infrared phonon frequency at 163 cm^{-1} in A_{2u} symmetry is due to the vibration of La atoms and it agrees very well with the experimental values at 169 cm^{-1} and it is due to the stretched vibration of La–Cu atom. The calculated infrared phonon frequency at 305 cm^{-1} is due to the vibration of Cu atom and it is due to the bending vibration of O(1)-Cu-O(2) atom: The highest phonon frequency at 549 cm^{-1} in A_{2u} symmetry is due to the vibration of O(2) atoms and it agrees very well with the experimental values at 569 cm^{-1} and it is due to the bending vibration of O(2)-Cu-O(3) atom.

The lowest calculated phonon frequency at 120 cm^{-1} is in E_u symmetry is due to the vibration of La atom and it agrees well with the experimental frequency at 135 cm^{-1} and it is due to the stretched vibration of La-O(1) atoms.

The next calculated infrared phonon frequency at 179cm^{-1} in E_u symmetry is due to the vibration of Cu atom and it agrees well with the experimental frequency at 196cm^{-1} and it is due to the vibration of Cu–O(1) atom. The next calculated phonon frequency at 263cm^{-1} is due to the vibration of O(1) atom and it agrees very well with the experimental values at 283cm^{-1} . Here the La atom vibrates at 180° degree out of phase to Cu–O(1) atoms. The highest calculated phonon frequency at 547cm^{-1} in this symmetry is due to the vibration of O(2) atoms and it is due to the stretched vibration of O(2)–O(3) atoms. The calculated phonon frequency at 206cm^{-1} in B_{2u} symmetry is due to the vibration of O(1) atom.

5. Conclusion

In this work the normal coordinate analysis technique have been adopted to give the evidence for electron, phonon interaction in the La_2CuO_4 . It is observed from the tables that the agreement between the calculated and observed frequencies were in good agreement with the systems that are considered here. This fact supports that the present vibrational assignments made for the infra red and Raman spectra are adequate. Therefore it is concluded that the normal coordinate analysis is the optically active vibrations of the vibrational spectra in cuprate oxides.

Lastly, these calculations yielded not only the zone center phonon modes but also the stable dispersions. Hence, it also supports the strong electron phonon interaction in high temperature super conductor (HTSC). The vibrational frequencies calculated by the method of normal coordinate analysis are compared theoretically and experimentally, and they appears to be in good agreement that are further confirmed by the potential energy distribution calculation.

6. References

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Table . 1

Force Constants for LaCuO₄ (in units of 10² Nm⁻¹(Stretching) and 10⁻¹⁸Nm rad⁻² (bending)).

Force	Bond Type	Distance (O)	Initial Value
f _o	Cu-o(1)	1.945	1.41
f _o	Cu-O(2)	1.827	1.40
f _o	La-O(1)	1.625	1.49
f _d	La-O(2)	1.723	0.80
f _e	La-O(3)	1.732	1.00
f _g	La-La	1.852	0.80
f _n	Cu-La	4.30	0.40
f _k	O(1)-O(2)	1.99	0.08
f _l	O(2)-O(3)	1.98	0.57
f _m	O(2)-O(3)	3.41	0.5
f _α	O(1)-Cu(1)-O(2)	-	1.32
f _β	O(1)-Cu(1)-O(3)	-	1.30

Table .2

Calculated Phonon Frequencies of La₂CuO₄

(Values in the parentheses are experiment frequencies)

Symmetry Species	Using Normal Co-ordinate Analysis(Cm ⁻¹)	Potential Energy Distribution (%)
A _{1g} (Raman)	218	f _c (57), f _e (20), f _g (18)
	553	f _b (70), f _a (11), f _β (10)
E _g	105	f _k (74), f _e (30)
	333	f _n (70), f _m (21), f _β (14)
A _{2u}	163(169)	f _n (81), f _a (12)
	305(498)	f _α (74), f _a (19), f _β (15)
	549 (569)	f _β (59), f _a (30),f _m (16)
	120(135)	f _c (70), f _k (20), f _β (14)
E _u	179(196)	f _a (65),f _e (22)
	263(283)	f _a (49), f _d (17), f _e (21)
	547(617)	f _α (60), f _m (22), f _k (11)
	206	f _g (40), f _d (24), f _b (12)
B _{2u}		

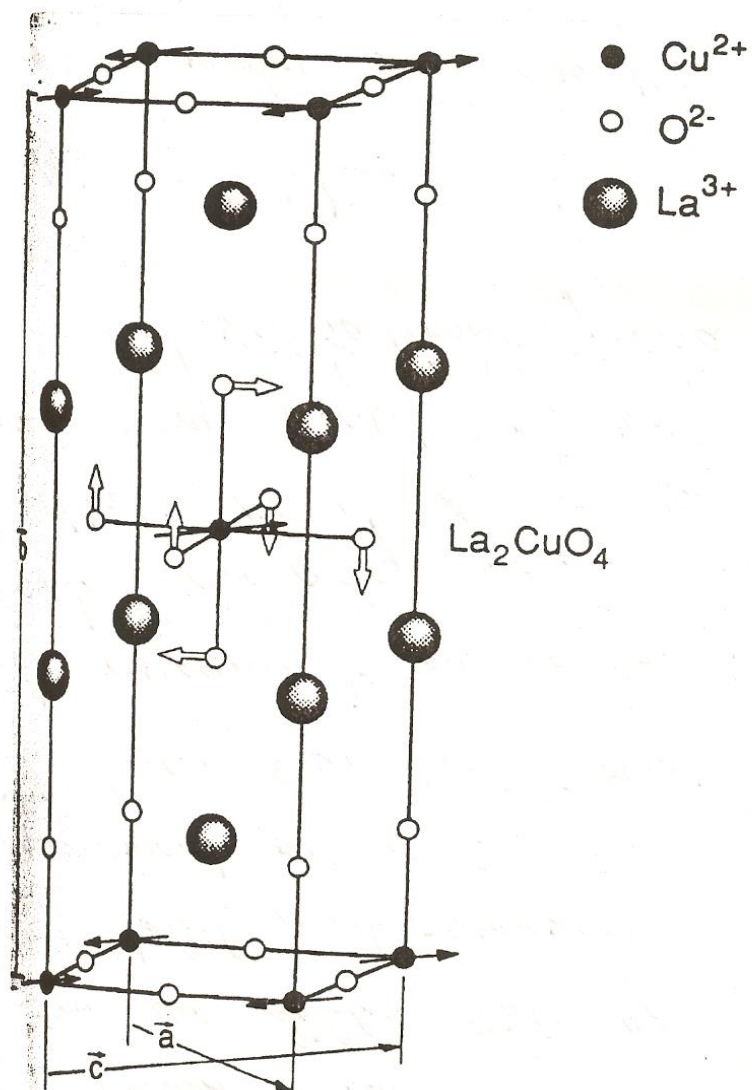


Fig: 1 The Structure of La_2CuO_4