LATTICE DYNAMICS AND NORMAL COORDINATE ANALYSIS OF HTSC $Tl_2Ba_2Cu_1O_6$

S. Mohan[1], K. Sonamuthu[2]* and Sujin P. Jose[1]

[1]Annai Fathima College, Madurai 625 706, India
[2]Raman School of Physics, Pondicherry University, Pondicherry 605 014, India

*Corresponding author: smoh14@rediffmail.com

Abstract: *The lattice dynamics of the high temperature superconductors $Tl_2Ba_2Cu_1O_6$ have been investigated on the basis of the three body-force shell model (TSM). The various interactions between ions are treated in a general way without making them numerically equal. The phonon frequencies at the zone center of Brillouin zone are presented and the vibrational assignments are discussed. Further, the normal coordinate calculation has also been employed to study the vibrational analysis of this compound. The normal coordinate analysis of the superconductor $Tl_2Ba_2Cu_1O_6$ has been calculated by using the Wilson's FG-matrix method, which is useful for the confirmation of our present investigation. The vibrational frequencies and the potential energy distribution (PED) of the optically active phonon modes are also presented.*

Keywords: lattice dynamics, phonon frequencies, $Tl_2Ba_2Cu_1O_6$, Raman and infrared spectroscopy

1. INTRODUCTION

The study of the lattice dynamics of the high-temperature superconductors is of importance not only for the overall physical characterization of these compounds but also for an assessment of the role played by the phonons, i.e., the superconducting phenomenon. A lattice dynamical study requires the knowledge of the crystal structure and the particle interactions. Usually the crystal structure is determined using X-ray diffraction (XRD). For particle interactions one has to use models, which represent the characteristic of the electronic structure and its effect on ionic interaction in a relevant manner. In lattice dynamics, the ionic interactions are expressed in terms of force constants.

Cox et al. [1] have refined the structure of high-temperature superconductors $Tl_2Ba_2Cu_1O_6$ using neutron and powder diffraction data. Raman and infrared active modes of $Tl_2Ba_2Cu_1O_6$ have been calculated by Kulkarni et al. [2] in the frame work of shell models. Belosludov et al. [3] have calculated vibrational spectrum of $Tl_2Ba_2Cu_1O_6$ using interatomic interactions. A high

resolution neutron diffraction study on $Tl_2Ba_2Cu_1O_6$ is contributed by Ogborne et al. [4].

In the present work we start with a more general approach in the frame work of the three body-force shell model (TSM) with *R#S#T* to calculate the lattice dynamics frequencies. The values of the phonon frequencies calculated in this present work at the zone center by the TSM is in good agreement with the available Raman and infrared values. Further, a normal coordinate analysis has also been attempted for the superconductor $Tl_2Ba_2Cu_1O_6$ using the Wilson's FG matrix [5,6] method for the confirmation of our present investigations. The vibration frequencies and the potential energy distribution (PED) of the optically active modes are also reported.

2. THEORETICAL CONSIDERATION

2.1 Latice Dynamics of $Tl_2Ba_2Cu_1O_6$ Based on the Shell Model

The calculation of lattice dynamical vibration frequencies of $Tl_2Ba_2Cu_1O_6$ system is performed by using the TSM calculations. In the TSM calculation, the equations of the motion for the core coordinate *U* and the shell coordinate *W* are expressed as follows:

$$-M\omega^2 U = (R + ZC'Z)\, U + (T + ZC'Y)\, W \tag{1}$$

$$0 = (T' - YC'Z)\, U\, (S + K + YC'Y)\, W \tag{2}$$

With $ZC'Z = Z\,[Z + 2\,f(a)]C + V$ where *M*, *Z* and *Y* are diagonal matrices representing the mass ionic charge on the shell. *R*, *S* and *T* are matrices specifying short-range core-core, shell-shell and core-shell interactions, respectively [7]. *V* is the matrix describing the three-body overlap interactions and $f(a)$ is related to overlap integrals of electron wave function [8]. *U* and *W* are the vectors describing the ionic displacements and deformations, respectively.

In the earlier approaches, the *R*, *S* and *T* elements were considered to be equal to one another. In the present investigation, we have started with an approach such that *R#S#T* [9]. The various interactions between the ions are treated in a more general way without making them numerically equal. The dynamical matrix of the model consists of the long-range Coulomb and three-body interactions and the short-range overlap repulsion. The secular equation to be solved and other details are the same as those given in our earlier paper [9].

The lattice dynamical calculation of high-temperature superconductors is explained using an inter-ionic potential consisting of the long-range Coulomb part and the short-range Potential of Born-Mayer form [10].

$$V_{ij} = a_{ij} \exp(-b_{ij} r) \tag{3}$$

where i, j label the ions and r is their separation. The parameters a_{ij} and b_{ij} are the pair potentials and the parameters Y and K determine the electronic polarizabilities. The parameters Z, Y and K used in the present calculations are given in Table 1. Phonon frequencies are calculated using the force constants derived from the inter-ionic potential. Following Lehner et al. [11] inter-ionic pair potentials for short-range interactions can be transferred from one structure to another in similar environments [9]. The force constants evaluated by this method are in good agreement with the evaluated values [12].

Table 1: Parameters of the model: a, b are Born-Mayer constants; Z, Y, K are ionic charge, shell charge and on-site core-shell force constant of the ion; V_a is the volume of the unit cell

Interaction	a (eV)	b (Å^{-1})
Tl-O (same plane)	3000	2.80
Tl-O (adj plane)	3000	3.55
Ba-O	3220	2.90
Cu-O	1260	3.35
O-O	1000	3.00

Ion	Z ($\|e\|$)	Y ($\|e\|$)	K (e^2/V_a)
Tl	2.70	2.00	1000
Ba	2.00	2.32	207
Cu	2.00	3.22	1248
O (Cu-O) plane	–1.90	–2.70	310
O (Tl-O) plane	–1.93	–2.70	210
O (Ba-O) plane	–1.93	–2.70	310 ($K_{\|\|}$)
			2100 ($K_{\square}$)

2.2 Normal Coordinate Analysis of the Zero Wave Vector Vibrations of $Tl_2Ba_2Cu_1O_6$

The study of lattice vibrations and the free carriers are 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. Thomsen et al. [13] studied the infrared and Raman spectra of the superconducting cuprate perovskites MBaCu$_2$O$_2$ (M = *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 $Tl_2Ba_2Cu_1O_6$ superconductors.

The high T_c superconductor $Tl_2Ba_2Cu_1O_6$ system crystallizes in the body-centered tetragonal (bct) system which belongs to the space group $14/_{mmm}(D^{17}_{4h})$. The bct unit cell of $Tl_2Ba_2Cu_1O_6$ and the numbering of the atoms are shown in Figure 1. The 11 atoms of the unit cell yield a total of 22 optical vibrational modes. All the above calculations are made at $q = 0$. One of A_{2u} and E_u modes corresponds to acoustic vibrations at frequency $\omega = 0$. These normal modes are distributed as follows:

$A_{1g} + E_g + A_{2u} + E_u$	from the motion of 2 Tl atoms
$A_{1g} + E_g + A_{2u} + E_u$	from the motion of 2 Ba atoms
$A_2 + E_u$	from the motion of Cu(1) atoms
$E_g + A_{2u} + B_{2u} + 2E_u$	from the motion O(1) atoms along c-axis
$A_{1g} + E_g + A_{2u} + E_u$	from the motion O(2) atoms along b-axis
$A_{1g} + E_g + A_{2u} + E_u$	from the motion O(3) atoms along a-axis

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

$$\Gamma_{opt} = 4A_{1g} + 4E_g + 6A_{2u} + B_{2u} + 7E_u \quad (4)$$

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. [14]. The general agreement between the evaluated and observed normal frequencies of $Tl_2Ba_2Cu_1O_6$ is good. The calculated force constants using the above programs are given in Table 2. It is interesting to note that the evaluated frequencies given in Table 3 agree favorably with the experimental values.

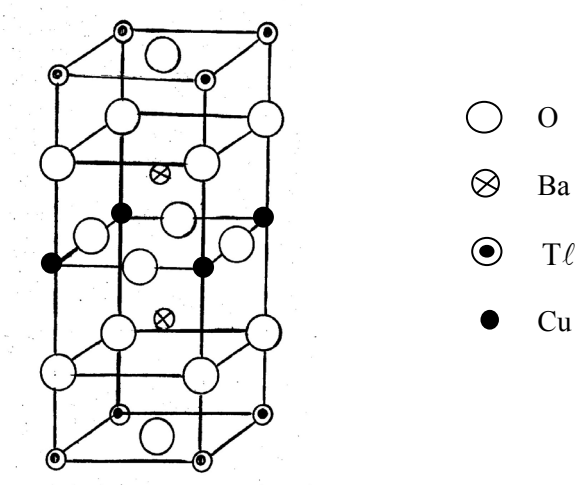

Figure 1: $Tl_2Ba_2CuO_6$ (unit cell)

Table 2: Force constants for $Tl_2Ba_2Cu_1O_6$ in units of 10^2 Nm^{-1} (stretching) and 10^{-18} Nm rad^{-2} (bending)

Potential constant	Bond type	Distance (Å)	Force constant initial value	Stretching/ bending
f_b	Ba-O(1)	2.798	0.75	Stretching
f_c	Ba-O(2)	2.819	1.10	Stretching
f_d	Ba-O(3)	2.851	0.81	Stretching
f_e	Tl-O(1)	2.003	0.30	Stretching
f_g	Tl-O(2)	2.097	0.30	Stretching
f_h	Tl-O(3)	3.108	0.61	Stretching
f_k	Tl-O(3)	2.402	0.48	Stretching
f_l	Cu-O(1)	1.932	145	Stretching
f_m	Cu-O(2)	2.648	1.65	Stretching
f_n	Tl-O(3)-Tl	–	0.31	Bending
f_p	O(1)-Cu-O(1)	–	0.25	Bending
f_α	Tl-O(2)-Ba	–	0.46	Bending
f_β	O(2)-Tl-O(3)	–	0.80	Bending

Table 3: Calculated phonon frequencies of $Tl_2Ba_2Cu_1O_6$

Symmetry species	Frequency (cm^{-1}) using lattice dynamics	Using normal coordinate analysis	Potential energy distribution (%)
A_{1g}(Raman)	124(125)	121	$f_\beta(60)f_d(20)f_k(10)$
	153(165)	161	$f_l(70)f_d(11)f_p(10)$
	470(485)	482	$f_e(55)f_\alpha(31)$
	601(603)	602	$f_a(58)f_e(30)f_m(11)$
E_g	100	106	$f_c(61)f_e(11)\, f_\beta(15)$
	131	134	$f_m(70)f_i(21)$
	388	400	$f_a(45)f_g(31)f_n(20)$
	491	499	$f_n(64)f_h(21)f_m(15)$
A_{2u} (IR)	108(108)	115	$f_n(70)f_\alpha$ (12)
	141(143)	139	$f_m(65)f_\alpha$ (19)$f_d(15)$
	335(341)	351	$f_p(59)f_n(30)$
	443(451)	441	$f_p(62)f_\beta$ (19)$f_n(15)$
	656(648)	641	$f_a(60)f_e(21)f_m(16)$
B_{2u}	259	270	$f_p(51)f_n(24)f_e(16)$
E_u	84	89	$f_b(70)f_e(14)$
	162(163)	168	$f_a(65)f_e(22)$
	320(326)	321	$f_a(49)f_d(17)f_e(21)$
	411(419)	406	$f_a(60)f_b(22)f_k(11)$
	445(451)	448	f_β (66)$f_p(21)$
	559(563)	561	$f_n(62)f_\alpha$ (20)

Note: Values in the parentheses are experimental frequencies

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 superconducting material, the PED was calculated using the equation

$$\text{PED} = (F_{ij} L^2_{ik}) / \lambda_k \tag{5}$$

where PED is the combination of the i-th symmetry coordinate to the potential energy of the vibration whose frequency is v_k, F_{ij} are potential constants, L_{ik} are L matrix elements and $\lambda_k = 4\pi^2 C^2 v^2_k$.

3. RESULT AND DISCUSSION

3.1 Lattice Dynamical Calculation Using Shell Model

The lattice dynamical calculations based on the modified TSM reproduced the observed frequencies of Raman and infrared active modes, which are given in Table 3. The calculated frequencies are in good agreement with the available experimental values. The lowest calculated Raman active A_{1g} mode frequency at 124 cm^{-1} is due to the vibration of Ba atoms and this agrees very well with the experimental frequency at 125 cm^{-1}. Similarly, the calculated Raman frequency, A_{1g} symmetry at 153 cm^{-1} and 470 cm^{-1} are due to the vibration of Tl and O(2) atoms respectively and the observed frequencies at 165 and 485 cm^{-1} agrees very well with the calculated frequency. The highest calculated Raman frequency 601 cm^{-1} in A_{1g} symmetry is due to the vibration of O(3) atoms, which also agrees very well with the observed frequency at 603 cm^{-1}.

Further, we have investigated the following zone center frequencies in the Raman active mode in the symmetry at 100, 131 and 388 cm^{-1}, and these are due to the vibration of Ba, Tl and O(1) atoms respectively. The maximum vibrational frequency in E_g symmetry is 491 cm^{-1}, which is due to the vibration of O(2) atoms.

The calculated infrared frequency is A_{2u} symmetry at 108 cm^{-1} is due to the vibration of Cu(1), Ba and Tl atom whereas the atom Tl vibrates at 180º out of phase to Ba and Cu(1) atom and the observed frequency 108 cm^{-1} agrees very well with the experimental values. The infrared phonon frequency at 141 cm^{-1} is due to the vibration of Ba and Cu(1) atoms and its experimental value is 143 cm^{-1}. The evaluated phonon frequency at 335 cm^{-1} is due to the vibration of Cu(1) and O(1) atoms and its experimental value is 341cm^{-1}. The evaluated infrared frequency at 443 cm^{-1} is due to the vibration of O(2), O(1) and Cu atoms in which O(1) atom vibrates at 180º out of phase to O(2) and Cu atoms. The highest evaluated phonon frequency in A_{2u} symmetry is 656 cm^{-1} which is due to the vibration of O(3) atom and its observed frequency at 648 cm^{-1} in A_{2u} symmetry modes agrees very well with each other. The evaluated phonon frequency in B_{2u} symmetry mode at 259 cm^{-1} is due to the vibration of O(1) atoms.

The calculated infrared phonon frequency at 84 cm^{-1} in E_u symmetry is due to the vibration of Tl and Cu(1) atoms and its experimental frequency at 80 cm^{-1} agrees very well with the evaluated values. The infrared phonon frequency at 162 cm^{-1} is due to the vibration of Cu(1) and Ba atoms and its observed frequency at 163 cm^{-1} agrees very well with the calculated frequency.

The infrared phonon frequency at 320 cm^{-1} is due to the vibration of O(1) atom, which performs bending bond vibrations and its observed frequency at 326 cm^{-1}, agrees very well with the calculated frequency. The highest infrared frequency at 559 cm^{-1} is due to stretching vibration of O(1) atoms and its experimental values at 563 cm^{-1} agrees very well with its observed frequency.

3.2 Normal Coordinate Analysis

The G-matrix elements have been calculated from the equilibrium geometry. The initial force constants were taken from the related molecules. The final set of potential constants provides 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.

Vibrational modes on the region of 400–500 cm^{-1} are attributed to the Ba-O stretching. The present potential energy distribution confirms our conclusion. The lower frequency modes involve the small displacement of Cu-O and Ba-O and the angular displacement of O-Ba-O. The evaluated frequencies using the normal coordinate analysis method listed in Table 3 agrees favorably with the calculated lattice dynamical frequencies and observed experimental frequencies.

4. CONCLUSION

The theoretical phonon frequencies obtained by the lattice dynamics and the normal coordinate analysis method agree very well with the available Raman and infrared frequencies. The calculation reveals not only the phonon frequency in the center of the Brillouin zone but also supports the strong electron-phonon interaction in the high-temperature superconductor $Tl_2Ba_2Cu_1O_6$.

5. REFERENCES

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