

PHONON FREQUENCY SPECTRUM OF HTSC : EuBaCuFeO₅

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ABSTRACT

The assignments of spectral features to specify lattice vibrations are an important step to understand their role of superconductivity. Raman and infrared studies have contributed significantly for the understanding of high T_c superconductors. Normal coordinate calculations have been employed to study the vibrational analysis of metal oxide EuBaCuFeO₅. The phonon frequency spectrum is also attempted by means of theoretical model of lattice dynamics in addition to normal coordinate calculations. A shell model is developed in the present work which takes care of the effect of many body interactions between the ions and they are treated in a more general way without making them numerically equal. These calculations using infrared and Raman results have allowed us a detailed assignment of the lattice vibrations in the superconducting system EuBaCuFeO₅.

INTRODUCTION

The very exciting discovery of high temperature superconductivity in copper oxides, directed the researchers to find the higher T_cs, with new materials for various applications as well as to understand the underlying mechanism. The mechanism of high temperature superconductivity in layered oxides is still a challenge for theorists. After the discovery of high temperature superconductors by Bendnorz and Muller [1], many attempts have been made to obtain better systems and to understand superconducting mechanism. Besides very high transition temperatures, the YBaCuO family of compounds shows hardly any isotope effect, high electronic anisotropy, strong dependence of the sample preparation conditions, oxygen deficiency and neutron radiation. Sometimes even total replacement of Y by magnetic rare earth has no significant effect on superconductivity [2]. On the other hand, partial replacement of a 3d-transition metal at the Cu site decreases the critical temperature [3]. Atanassova et al. [4] have reported the vibrational spectrum of YBaCuFeO₅ in the framework of interatomic interactions. An attempt has been made in the present work to calculate phonon frequencies of EuBaCuFeO₅ through the GF matrix analysis and shell model calculations.

The high T_c superconductor EuBaCuFeO_5 crystallizes in the tetragonal system which belongs to the space group of $P4/mmm(D_{4h})$. The 9 atoms of the unit cell yield a total of 18 optical vibrational modes. All of our calculations have been made for the phonons at $q=0$. These normal modes are classified as follows:

$A_{2u} + E_u$	From the motion of Eu atom
$A_{2u} + E_u$	From the motion of Ba atom
$A_{1g} + E_g + A_{2u} + E_u$	From the motion of Cu, Fe atoms
$A_{2u} + E_u$	From motion of O(1) atoms
$A_{1g} + B_{1g} + 2 E_g + A_{2u} + B_{2u} + 2E_u$	From motion of four O(2) atoms.

The species belonging to A_{1g} , B_{1g} and E_g are Raman-active modes whereas A_{2u} and E_u are infrared-active modes. Out of five modes in A_{2u} , one corresponds to acoustical mode. Similarly one mode in E_u is acoustical mode out of six modes. Subtracting the translational modes $A_{2u} + E_u$, the $q = 0$ optical modes involved in an irreducible representation become as follows:

$$\Gamma_{\text{tot}} = 2A_{1g}(\text{R}) + B_{1g}(\text{R}) + 3E_g(\text{R}) + 4A_{2u}(\text{IR}) + B_{2u}(\text{silent}) + 5E_u(\text{IR}).$$

EXPERIMENTAL METHOD

A fairly good amount of literature is available on the vibrational spectra of high temperature superconductors. Yet, some specific features in the experimental vibrational spectra could not be assigned reliably 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 normal modes are looked into for the clear understanding of the superconducting mechanism. The normal coordinate analysis provides a more quantitative description of the vibrational modes. In this method, non central forces such as angle bending can be readily used. 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 (5) modified by Shimanouchi et al (6) for solids is applied for the calculation of optically active vibrational frequencies. The kinetic energy is determined by the masses of the individual atoms and their geometrical arrangements in the molecule 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 vibrational frequencies have been evaluated. Fine tuning is done until the available observed frequency and the present evaluated frequency matches perfectly. Internal coordinates namely, bond lengths and bond angles, are used in the kinetic and potential energy expressions. The calculations are carried out using Simple General Valance Force Field (SGVFF) for the following reasons: (a) SGVFF has been

shown to be very effective in normal coordinate analysis of superconductors (7) (b) Valence force constants can be transferred between the related molecules. The normal coordinate calculations were performed by utilizing the program of Fuhrer et al. (8) with suitable modifications for computing the G and F matrices (GMAT and FPERT) and for adjusting a set of independent force constants [9-11]. The programs interface so that the output from one serves as part of the input to the next. GMAT sets up the kinetic energy matrix and FPERT calculates and refines the vibrational frequencies. Also, in NCA, potential energy distribution (PED) indicates the contribution of an individual force constant to the vibrational energy of each normal mode. This technique is adopted here to study the phonon spectrum of EuBaCuFeO_5 . Phonons are useful in the study of the electron-phonon interaction in order to establish their role in the mechanism of superconductivity. Lattice dynamical calculations [12] for the high T_c superconductors have been performed for mainly two purposes. The first was to calculate the electron phonon interaction and its influence on the increased transition temperature for high temperature superconductors. Secondly, a correct assignment on the phonon excitations is necessary for a number of experiments on the phonon spectra. Apart from these studies of electron-phonon interaction, several authors have attempted to calculate the phonon frequencies [13-17] for a comparison with experimental results. An attempt has been made in this paper to study phonon frequencies in the EuBaCuFeO_5 high temperature superconductor in the frame work of modified three body force shell model (TSM). The calculations are based on the use of long-range coulomb potentials, short-range repulsive Born-Mayer potentials and the ionic polarizabilities. With the shell model calculation, the equation of the motion for the core coordinates U and shell coordinate W are expressed by the following equations as [16],

$$-M\omega^2 = (R+ZC'Z) U + (T+ZC'Z)W$$

$$0 = (YC'Z + T) U + (YC'Y + S) W$$

with $ZC'Z = Z [Z + 12 f(a)] C + V$ where M, Z and Y are diagonal matrices representing the mass, ionic charge and the charge on the shell. R, S and T are matrices specify short range core-core, shell-shell and core-shell interactions respectively. V is the matrix describing the three body overlap interactions and $f(a)$ is related to overlap integrals of electron wave function. U and W are the vectors describing the ionic displacements. C represents the coulomb terms.

The earlier investigators have assumed short range core-core, shell-shell and core-shell interactions are equal. But our rigorous and detailed calculations on the matrices revealed differences in these interactions [18]. R and C matrix elements have been worked out using the expression given by Kellermann [19]. T matrix elements are calculated using the short range force constants A_1 , A_{11} , B_1 , B_{11} which have been introduced from our work in a simple manner. The constants connecting T, R and S enabled us to calculate matrix elements. We have also kept the variation of T, R and S to be identical with respect to symmetry directions. It is interesting to note that R, S and T values show a difference from each other. With this modification, attempts have been made to evaluate phonon frequencies. This new approach with $R \neq T \neq S$ is introduced

for the first time and has been applied to alkaline earth oxide crystals and transition metal ions in our earlier work [20-23].

The short-range interactions between neighboring ions *are* represented by Born-Mayer potentials

$$V_{ij}(r) = a_{ij} \exp(-b_{ij} \cdot r),$$

where *i* and *j* label the ions and *r* is their distance. We have determined the parameters *a_{ij}* and *b_{ij}* of other pair potentials as well as the parameters *Y_{ij}* and *k_i* which determine the electronic polarizabilities. It is encouraging to note that the evaluated phonon frequencies of EuBaCuFeO₅ agree quite well with Raman data, wherever they are available. Further, the evaluated phonon frequencies of EuBaCuFeO₅ from lattice dynamical calculation agree quite well with the phonon frequencies evaluated from normal coordinate analysis.

RESULT AND DISCUSSION

Table 1: Bond distance and force constants for EuBaCuFeO₅

	Bond type	Distance (Å)	Initial value- Potential constants	Final value- Potential constants
<i>f_a</i>	Ca-O(1)	2.12	1.41	1.482
<i>f_b</i>	Cu-O(2)	1.96	1.40	1.471
<i>f_c</i>	Cu-O(3)	1.98	1.40	1.476
<i>f_d</i>	Ba-O(1)	2.74	0.80	0.943
<i>f_e</i>	Ba-O(2)	2.80	1.00	1.187
<i>f_g</i>	Ba-O(3)	2.91	0.80	0.861
<i>f_h</i>	Eu-O(1)	2.42	0.61	0.621
<i>f_k</i>	Eu-O(2)	2.42	0.56	0.564
<i>f_i</i>	Cu-Fe	3.55	0.85	0.876
<i>f_m</i>	Fe-O(1)	1.99	2.71	2.890
<i>f_n</i>	Fe-O(2)	1.98	2.62	2.814
<i>f_p</i>	Cu-Cu	3.41	0.50	0.542
<i>f_o</i>	O(1)-Cu(1)- O(2)	-	1.34	1.356
<i>f_p</i>	O(2)-Cu(1)- O(3)	-	1.34	1.361

Table 2: Calculated phonon frequencies of EuBaCuFeO₅

Symmetry Species	Frequency (cm ⁻¹) Using normal Coordinate Analysis
A _{1g} (Raman)	104
	208
B _{1g} (Raman)	171(178)
E _g (Raman)	108(114)
	145(141)
	190(192)
A _{2u} (IR)	218(221)
	351(360)
	450(454)
	658(650)
B _{2u}	333(340)
E _u (IR)	284(276)
	338(340)
	354(360)
	538(541)
	572(568)

The fourteen initial force constants used in the Normal coordinates program is given in Table 1. It is interesting to note that evaluated frequencies given in Table 2 agree favourably with the experimental values [24]. The model parameters obtained using the three body force shell model for EuBaCuFeO₅ is listed in Table 3. The lattice vibrational

frequencies at the r point are obtained and are given in Table 4. The observed and calculated phonon frequencies and the potential energy distribution for EuBaCuFeO₅ is given in Table 5.

Table 3: Parameters of the model: a,b are Born-Mayer constants; Z,Y,k: 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 ($\text{\AA}^{-1}$)
Eu-O	3010	3.00
Ba-O	3225	2.90
Cu-O	1260	3.29
Fe-O	1203	3.11
O-O	1000	3.00

Ion	Z(e)	Y(e)	k(e^2/v_a)
Eu	2.61	2.90	895
Ba	1.90	2.32	179
Cu	1.80	3.22	1351
Fe	1.71	3.18	1285
O(1),O(2)	-1.81	-2.70	252
O(2), O(3)	-1.81	-2.70	252($k_{ }$) 1675($k_{\perp}$)

Interaction	A($e^2/2v_a$)	B($e^2/2v_a$)
Cu-O(2)	576	-90.8
Eu-O(2)	563	-80.5
Ba-O(2)	114	-13.2
Fe-O(2)	95	-10.5
O(3)-O(2)	62	-7.5

Table 4: Calculated phonon frequencies of EuBaCuFeO₅

Symmetry species	Frequency (cm ⁻¹) Using lattice dynamical Calculations
A _{1g} (Raman)	110
	203
B _{1g} (Raman)	171
E _g (Raman)	103
	140
	187
A _{2u} (IR)	214
	343
	454
	653
B _{2u}	333
E _u (IR)	292
	323
	361
	531
	571

Table 5: Phonon frequencies of EuBaCuFeO₅

Symmetry species	Frequency (cm ⁻¹)		Potential Energy Distribution.(%)
	Using lattice dynamics	Using normal Coordinate Analysis	
A _{1g} (Raman)	110	104	f _a (60), f _c (23)
	203	208	f _a (41), f _d (24), f _n (18)
B _{1g} (Raman)	171 (178)	171	f _b (48), f _c (24), f _d (18)
E _g (Raman)	103 (114)	108	f _c (62), f _g (26)
	140 (141)	145	f _b (54), f _k (21)
	187 (192)	190	f _a (34), f _g (29), f _n (20)
A _{2u} (IR)	214 (238)	218	f _d (46), f _n (26)
	343 (360)	351	f _m (49), f _n (31)
	454 (454)	450	f _c (52), f _g (19)
	653 (650)	658	f _b (59), f _k (20), f _g (18)
B _{2u}	(340)	333	f _a (38), f _d (24), f _n (28)
E _u (IR)	292 (276)	284	f _g (46), f _p (32)
	323 (340)	338	f _k (45), f _a (29), f _b (21)
	361 (360)	354	f _b (43), f _g (30), f _k (22)
	531 (541)	538	f _c (44), f _g (27), f _a (19)
	571 (568)	572	f _a (72), f _n (21)

In high temperature superconductors, a large number of Raman scattering studies have been reported [25], aimed at clarifying the characteristics of the phonon structure of the materials considered. These studies have been attempted to draw more information from the various results on the physical properties of the materials which are more or less directly related to the mechanism of superconductivity. The highest calculated mode is the A_{1g} symmetry at 208 cm^{-1} , which is due to Cu/Fe vibrations. From the Table-1 the bond lengths for Cu-O(2) [$1.96\text{ \AA}$] and Fe-O(2) [$1.98\text{ \AA}$] remains practically same in the case of EuBaCuFeO_5 . Although the bond length are the same, one expects Cu/Fe in A_{1g} mode to become strong as the result of significant Cu-O(l) (Fe-O(l)) bond lengths, the present evaluated frequency supports the assignments.

The calculated frequency 145 cm^{-1} , observed in the E_g Raman spectra involves the motion of Cu/Fe atoms in the Cu/Fe-O(2) planes.

The observed frequencies at 360 and 450 cm^{-1} agree quite well with the calculated values of 351 and 450 cm^{-1} , which are due to out phase and in phase vibrations of O(2) oxygen atoms along c-axis respectively.

The calculated frequencies of 354 and 572 cm^{-1} are the in phase and out phase in-plane Cu/Fe-O(2) vibrations in the E_u symmetry. These values agree quite well with the observed values available in the literature. The frequency in the A_{2u} species at 658 cm^{-1} is due to the modes involving mainly Ba-O(l) plane only. The calculated frequencies at 284 cm^{-1} in the E_u species is due to O(l)vibration in Ba-O(l) plane.

The potential energy distribution is shown for EuBaCuFeO_5 material in the last column of Table 5. It also indicates whether the concerned mode is a pure or a mixed mode involving contributions from the other modes. All the above calculated frequencies in the present work agrees quite well with the observed Raman and infrared frequencies. Hence, the SGVFF field adopted in the present work yields a reasonable phonon frequencies for the EuBaCuFeO_5 superconductor.

In the present approach, the lattice dynamics of high temperature superconductor EuBaCuFeO_5 has been investigated on the basis of modified Three-body-force shell model (TSM). This model reproduces the observed values fairly well for the modes of EuBaCuFeO_5 .

The observed frequency in the B_{1g} symmetry at 178 cm^{-1} is due to the vibration of O(2) atom which vibrates 180° out of phase with O(1) atom. This agrees quite well with the normal coordinate analysis and lattice dynamical calculation frequency at 171 cm^{-1} . The three calculated Raman frequencies in the E_g symmetry mode at 103 , 140 and 187 cm^{-1} , which are due to the vibrations of Ba, Eu, Fe / Cu and Eu atoms agree well with the normal coordinate analysis frequencies at 108 , 145 and 190 cm^{-1} respectively. It also agrees reasonably with the observed frequencies.

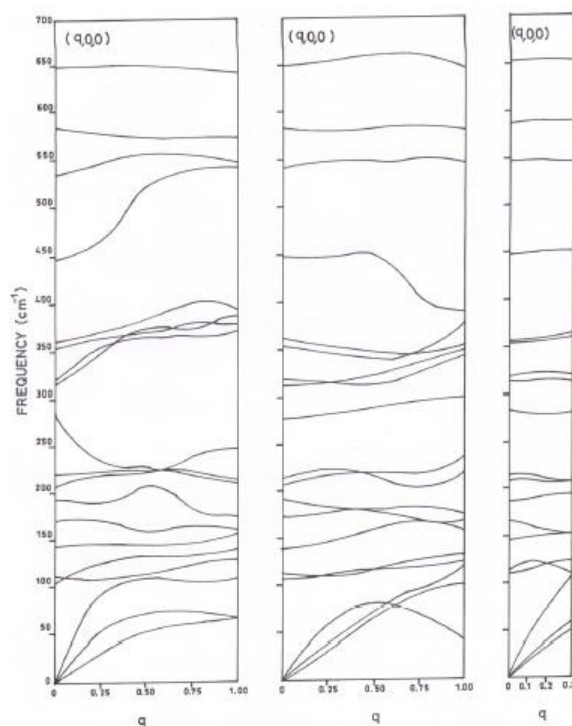


Figure 1: Dispersion curve of EuBaCuFeO_5

The same tendency is obtained for the A_{2u} , B_{2u} and E_u species. These species give rise to frequencies in the infrared spectra. Interestingly the frequencies at 361 and 571 cm^{-1} are due to the vibrations of O(2) and Cu atoms and these atoms vibrate in Cu-O(2)-Fe plane and agrees well with the observed and normal coordinate analysis frequencies. The vibration of O(2) in Cu-O(2)-Fe plane is identified at 323 cm^{-1} and 531 cm^{-1} by the lattice dynamical calculation. This agrees well with the normal coordinate analysis as well as with observed frequencies. A lattice dynamical calculation yields descriptions of normal modes. Hence, zone center phonon frequencies obtained in the present work are compared with the available IR and Raman data. Figure 1 gives the calculated phonon dispersion relation for EuBaCuFeO_5 for the wave vectors along the three main symmetry directions $(0,0,q)$, $(0,q,0)$ and $[q,0,0]$. The important criterion for arriving at a parameter set for a given compound is the requirement of real phonon frequencies for all wave vectors in the Brillouin zone. Hence parameters are varied systematically to obtain stability throughout the Brillouin zone which gave a reasonable fit to the zone center frequencies. Normal coordinate calculations have been used extensively for metal oxides and have greatly aided in their vibrational analysis [26]. Hence, GF matrix technique has been used here to arrive at the zero wave vector normal mode vibrations. Each of the reliable observed frequencies reported in the literature are well accounted by the calculated frequencies from two different methods in the present work.

CONCLUSION

It is not uncommon in physics that two different methods yield the same result. In the present work, two different methods viz, lattice dynamical study and normal coordinate analysis yielded the same phonon frequency for EuBaCuFeO_5 high temperature superconductor. It is also seen from the tables, that the agreement between the calculated and observed frequencies wherever available are very good for the system under consideration. This fact supports that the present vibrational assignments made for the infrared and Raman Spectra are adequate. Therefore, it is concluded that normal coordinate analysis of the optically active lattice vibrations is very useful for the theoretical interpretation of the vibrational spectra at the center of the Brillouin zone in cuprate oxides. Further it is also a good method to characterize the high temperature superconductors.

It is also shown that it is possible to obtain is a fairly reasonable representation of the lattice vibration in EuBaCuFeO_5 . Using the three-body force shell model, with the assumption of unequal short-range interactions, the present approach leads to yields a complete phonon frequency of high T_c superconductor under consideration in the present work. Summarisingly, the theoretical phonon frequencies obtained by the lattice dynamics and the normal co-ordinate analysis agree very well with the available Raman and infrared frequencies.

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