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# NORMAL COORDINATE ANALYSIS OF THE ZERO-WAVE VECTOR VIBRATIONS OF Er $Ba_2$ $Cu_3O_7$

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Using Wilson's FG matrix method, a normal coordinate analysis of the spectral frequencies and form of the zero-wave vector vibrations of the high temperature superconductor $ErBa_2Cu_3O_7$ have been performed. The vibrational frequencies and potential energy distribution of 21 infrared active and 15 Raman active modes are presented. The potential constants employed here are given and the evaluated vibrational frequencies are compared with the available experimental values.

***Key words:*** Normal coordinate, Analysis, $ErBa_2Cu_3O_7$.

## Introduction

Ever since Bednorz and Muller [1] reported the possible existence of a percolative superconductivity in La–Ba–Cu–O system in the 30K range, Y–Ba–Cu–O, Ho–Ba–Cu–O, Er–Ba–Cu–O and so on were found to be high temperature superconducting materials. The study of lattice vibrations and the free carriers is important for understanding the physical nature of high temperature superconductors.

Raman and far-infrared studies have contributed significantly to the understanding of these high temperature superconductors. Although many reports of superconductivity for rare earth atoms have appeared, systematic investigations for the whole rare earth faily are scarce. Raman [2] and infrared reflection spectrum [2-4] of $YBa_2Cu_3O_7$ have been reported earlier. From the infrared reflection spectra measured at 10K in the 100-300 $cm^{-1}$ range, the superconducting gap was found to be about 210 $cm^{-1}$ for $ErBa_2Cu_3O_7$ [5]. Raman studies showed the softening of the phonons at 337$cm^{-1}$. This band appeared in all theCu samples and corresponded to Cu–O vibrational mode.

Superconducting properties in $ErBa_2$ $Cu_3$ $O_7$ prepared by the method of powder calcination were studied by Mohan *et al.* [6]. The compounds showed a sharp superconducting transition at 95K and a narrow transition width $\Delta T$, less than 1K. The pressure shift of $T_c$ and a.c susceptibility measurements were also made. In continuation of that work, the results of normal coordinate analysis and form of zero-wave vector vibrational frequencies for the $ErBa_2Cu_3O_7$ superconductor are presented here.

*Theoretical considerations.* The high $T_c$ superconductor $ErBa_2Cu_3O_7$ cyrstallizes in the orthorhombic system which belongs to the space group $P_{mmm}$ ($D_{2h}$). The orthorhombic unit cell of $ErBa_2Cu_3O_7$ and the numbering of atoms are shown in Fig. 1. The 13 atoms of the unit cell yield a total of 36 optic vibrational modes and three zero frequencies translational modes involving the following sublattice displacements:

| | |
|---|---|
| $B_{1u} + B_{2u} + B_{3u}$ | From the motion of Er atom |
| $A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$ | From the motion of 2 Ba atoms |
| $A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$ | From the motion of 2 Cu atoms sandwiched by Er and Ba atoms |
| $B_{1u} + B_{2u} + B_{3u}$ | From the motion of Cu atom surrounded by 4 Ba atoms |
| $2A_g + 2B_{2g} + 2B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$ | From the motion of 4 O atoms between the layers of Er and Ba |
| $A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$ | From the motion of 2 O atoms on the Cu-O line along the c-axis |
| $B_{1u} + B_{2u} + B_{3u}$ | From the motion of O atom on the linear Cu-O chain in the b-axis direction |

Subtracting translational modes $B_{1u} + B_{2u} + B_{3u}$, the q=0 optic modes involve the irreducible representations as:

$$\Gamma = 5A_g + 5B_{2g} + 5B_{3g} + 7B_{1u} + 7B_{2u} + 7B_{3u}$$

The species belonging to $A_g$, $B_{2g}$ and $B_{3g}$ are Raman active modes while $B_{1u}$, $B_{2u}$ and $B_{3u}$ are infrared active modes. The $B_{1u}$ and $A_g$ modes involve displacement along the crystallographic c -axis, the $B_{2u}$ and $B_{3g}$ modes along the b-axis, and the $B_{3u}$ and $B_{2g}$ modes along the a-axis.

## Results and Discussion

The normal coordinate analysis is performed using Wilson's FG matrix method along with the modifications introduced by Shimanouchi *et al.* [7]. A simple valence force field is used. The structural parameters employed here to carry

out these calculations are given in Table 1. The initial set of force constants [8,9] are adjusted by a least square technique in accordance with the position of the peak in the Raman and infrared spectra. The computer programs CART, GMAT and FPERT [10] are utilized with suitable modifications to carry out the normal coordinate calculations.

According to group theory, the atoms involved in the Raman active vibrations are Ba, Cu(2), O(2), O(3) and O (4).

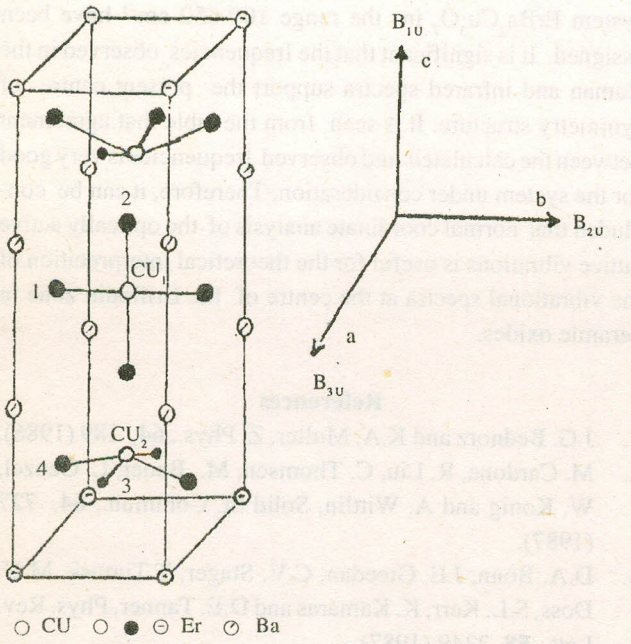


Fig. 1. Orthorhombic unit cell of $ErBa_2Cu_3O_7$.

TABLE 1. FORCE CONSTANTS FOR $ErBa_2Cu_3O_7$.

| Force constants | Bond type | Distance (A°) | Values |
|---|---|---|---|
| $f_a$ | Cu(1)-O(1) | 1.945 | 1.4 |
| $f_b$ | Cu(1)-O(2) | 1.827 | 1.6 |
| $f_c$ | Cu(2)-O(3) | 1.930 | 1.4 |
| $f_d$ | Cu(2)-O(4) | 1.964 | 1.4 |
| $f_e$ | Cu(2)-O(2) | 2.332 | 1.1 |
| $f_g$ | Ba-O(1) | 2.911 | 0.8 |
| $f_h$ | Ba-O(2) | 2.753 | 1.0 |
| $f_k$ | Ba-O(3) | 2.945 | 0.8 |
| $f_l$ | Ba-O(4) | 2.945 | 0.8 |
| $f_m$ | R-O(3) | 2.421 | 0.77 |
| $f_n$ | R-O(4) | 2.380 | 0.79 |
| $f_p$ | Cu(2)-Cu(2) | 3.374 | 0.5 |
| $f_\alpha$ | O(1)-Cu(1)-O(2) | — | 1.3 |
| $f_\beta$ | O(3)-Cu(2)-O(4) | — | 1.3 |
| $f_\gamma$ | O-Cu(1)-O | — | 0.5 |

Force constants unit : Stretching $10^2$ $Nm^{-1}$. Bending $10^{-18}$ Nm $rad^{-2}$

The highest calculated mode for $A_g$ symmetry is at 561 $cm^{-1}$. From the PED, it is clear that this mode is solely due to the symmetric Cu(2)-O(2) stretch. The $A_g$ mode at 482 $cm^{-1}$ is also due to the bond stretching vibrations of O(2) and is associated with the observed mode at 504 $cm^{-1}$. And it is clear from Table- 2 that this frequency increases with increasing ionic radius of the rare earth. Raman modes observed at 442 and 320 $cm^{-1}$ have been observed consistently in all rare earth

TABLE 2. CALCULATED PHONON FREQUENCIES FOR $ErBa_2Cu_3O_7$.

| Symmetry species | Frequency ($cm^{-1}$) | PED (%) |
|---|---|---|
| $A_g$ | 561 | $f_b$ (55) $f_e$ (40) |
| | 482 (504) | $f_e$ (48) $f_d$ (28) |
| | 428 (442) | $f_\beta$ (45) $f_c$ (24) $f_d$ (24) |
| | 320 (320) | $f_\beta$ (58) $f_c$ (20) $f_d$ (15) |
| | 149 (150) | $f_l$ (58) $f_h$ (23) |
| $B_{2g}$ | 560 | $f_d$ (49) $f_c$ (21) $f_g$ (19) |
| | 546 | $f_c$ (62) |
| | 471 | $f_d$ (59) $f_c$ (18) $f_h$ (16) |
| | 310 | $f_\beta$ (56) $f_d$ (16) |
| | 158 | $f_h$ (45) $f_\beta$ (21) |
| $B_{3g}$ | 552 | $f_d$ (54) $f_c$ (23) |
| | 532 | $f_c$ (59) $f_d$ (19) |
| | 430 | $f_d$ (46) $f_e$ (24) |
| | 280 (280) | $f_\beta$ (51) $f_d$ (20) |
| | 104 | $f_h$ (48) $f_e$ (30) |
| $B_{1u}$ | 635 | $f_a$ (48) $f_b$ (31) |
| | 550 | $f_a$ (69) $f_b$ (16) |
| | 484 | $f_b$ (47) $f_m$ (22) $f_n$ (20) |
| | 418 | $f_m$ (34) $f_n$ (24) $f_p$ (17) |
| | 262 (278) | $f_\beta$ (52) $f_b$ (15) |
| | 191 (166) | $f_m$ (55) $f_h$ (21) $f_p$ (17) |
| | 109 | $f_\alpha$ (28) $f_\beta$ (18) $f_g$ (15) |
| $B_{2u}$ | 640 | $f_b$ (65) $f_a$ (17) |
| | 631 | $f_b$ (44) $f_a$ (23) $f_g$ (12) |
| | 585 (583) | $f_c$ (45) $f_d$ (31) |
| | 562 | $f_c$ (41) $f_d$ (28) $f_k$ (17) |
| | 180 | $f_g$ (54) $f_m$ (27) $f_n$ (13) |
| | 165 | $f_\alpha$ (59) $f_n$ (23) |
| | 110 | $f_\gamma$ (63) $f_\alpha$ (25) $f_\beta$ (14) |
| $B_{3u}$ | 624 | $f_a$ (33) $f_b$ (27) $f_h$ (24) |
| | 520 | $f_c$ (65) $f_d$ (15) |
| | 512 | $f_d$ (63) $f_b$ (16) |
| | 441 (456) | $f_l$ (45) $f_k$ (22) $f_d$ (19) |
| | 181 | $f_g$ (46) $f_n$ (20) $f_p$ (15) |
| | 168 (165) | $f_\alpha$ (44) $f_m$ (36) $f_e$ (13) |
| | 109 | $f_\gamma$ (39) $f_\alpha$ (24) $f_m$ (20) |

Values given in parentheses are experimental values [5].

superconducting materials and are attributed to pure bond bending vibrations of O(3) – Cu(2) and O(4)–Cu(2) bonds along the c-axis with O(3) and O(4) neighbours moving in-phase and out-of phase respectively. From the normal coordinate calculation, these values are predicted to be 428 and 320 $cm^{-1}$ which agree with the observed values. A feature that appears to be directly related to superconductivity and also seen in the Raman spectra is the anomalous softening of some modes when the temperature is lowered. When the material is cooled below $T_c$, the phonons associated with stretching-bending vibrations of the Cu-O frames lower their frequency. The observed mode at 320 $cm^{-1}$ is shown to possess such anomaly and this frequency decreases with increasing ionic radius of the rare earth [2]. According to the present calculations, the wave number at 149 $cm^{-1}$ is the lowest calculated mode for $A_g$ symmetry which corresponds to the experimental value at 150 $cm^{-1}$ and is attributed to the Ba-O vibrations. The relative contribution of the force constants involving Ba-O stretch to the vibrational energy of this mode is 58%.

The phonon frequencies evaluated from this calculation for $B_{2g}$ and $B_{3g}$ symmetries are 560,546,471,310,158 and 552,532,430,280,104 $cm^{-1}$ respectively. The contribution of force constants to these modes are shown in Table 2. Although the $B_{2g}$ and $B_{3g}$ modes have different frequencies, they have similar vibration characteristics except the fact that the former mode involves the motion of atoms along the b-axis whereas the latter one is due to the atomic motion in the a-axis. The modes calculated at 560 and 546 $cm^{-1}$ of $B_{2g}$ symmetry and at 552 and 532 $cm^{-1}$ of $B_{3g}$ symmetry are described as asymmetric Cu-O stretches. The weak intensity Raman band observed at 280 $cm^{-1}$ has been assigned to the O-Cu-O deformation modes. From the PED, it is found that this mode is practically due to pure bond-bending vibrations. The observed value agrees well with the calculated value at 280 $cm^{-1}$. The mode at 320 $cm^{-1}$ is also assigned in the same way.

The assignment of the infrared active modes are complicated due to the complexity of the crystal structure. Some weak modes are also observed in the infrared spectrum of these systems. For those modes which involve in-phase and out-of phase types of Cu-O, Ba-O or Er-O stretches, a strong infrared feature is expected for the in-phase motion of the metal atoms. The peak at 165 $cm^{-1}$ is attributed to the vibrations of Er and corresponds to the calculated mode at 158 $cm^{-1}$. The $B_{1u}$ mode calculated at 262 $cm^{-1}$ agrees well with the observed peak at 278 $cm^{-1}$ and is assigned to Cu(2)-O (3)-O(4) in-plane vibration. The infrared peak at 456 $cm^{-1}$ coincides with the calculated value at 449 $cm^{-1}$. The rest of the calculated modes and their corresponding PED are presented in Table 2.

## Conclusion

With the aid of normal coordinate analysis the evaluated vibrational frequencies of the rare earth superconducting system $ErBa_2Cu_3O_7$ in the range 100-650 $cm^{-1}$ have been assigned. It is significant that the frequencies observed in the Raman and infrared spectra support the present centre of symmetry structure. It is seen from the table that agreement between the calculated and observed frequencies is very good for the system under consideration. Therefore, it can be concluded that normal coordinate analysis of the optically active lattice vibrations is useful for the theoretical interpretation of the vibrational spectra at the centre of the Brillouin zone in ceramic oxides.

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