

Normal co-ordinate analysis of the zero wave-vector vibrations of $\text{DyBa}_2\text{Cu}_3\text{O}_7$

S MOHAN and A SUDHA

Raman School of Physics, Jipmer Campus, Pondicherry University, Pondicherry 605 006, India

MS received 30 March 1991; revised 16 August 1991

Abstract. Using Wilson's F–G matrix method a normal co-ordinate analysis of the spectral frequencies and form of the zero-wave vector vibrations of the high temperature superconductor, orthorhombic $\text{DyBa}_2\text{Cu}_3\text{O}_7$ has been performed. The vibrational frequencies and the potential energy distribution of the 21 infrared-active and 15 Raman-active modes are presented. The potential constants employed here are presented and evaluated vibrational frequencies are compared with the available experimental values.

Keywords. Normal co-ordinate analysis; $\text{DyBa}_2\text{Cu}_3\text{O}_7$.

PACS Nos 74·10; 74·70; 74·90; 78·30

1. Introduction

Ever since Bednorz and Muller (1986) reported the possible existence of a percolative superconductivity in La–Ba–Cu–O system in the 30 K range, Y–Ba–Cu–O, Ho–Ba–Cu–O, Dy–Ba–Cu–O and so on were found to be high temperature superconducting materials. The study of lattice vibrations and the free carrier 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 this new class of superconductors. Although many reports of superconductivity for rare earth atoms have appeared, systematic investigations for the whole rare earth family are scarce. Infrared reflection spectrum of orthorhombic $\text{YBa}_2\text{Cu}_3\text{O}_x$ have been reported by Bonn *et al* (1987). The most important feature is the observation of superconducting gap. Raman study shows the softening of the phonons at 337 cm^{-1} . Such effects are to be expected in normal BCS type superconductors as shown by neutron studies (Shapiro *et al* 1975). Infrared reflection spectra of tetragonal and orthorhombic $\text{MBa}_2\text{Cu}_3\text{O}_x$ (M = rare earths) have been reported by Onari *et al* (1988). Cardona *et al* (1987) have also studied the infrared and Raman spectra of the superconducting cuprate perovskites $\text{MBa}_2\text{Cu}_3\text{O}_7$ (M = Nd, Er, Dy, Tm) and reported the possible origins of phonon softening and the systematics of the variation of phonon frequencies with the ionic radius.

Superconducting properties in $\text{Ba}_2\text{DyCu}_3\text{O}_7$ prepared by the method of calcination was studied by Mohan *et al* (1991). The compounds show a sharp superconducting transition at 95 K and narrow transition width ΔT is less than 1 K. The pressure shift of T_c and a.c. susceptibility measurements for the compound are also studied. Here

we present the result of the normal coordinate analysis frequencies and form of zero-wave vector vibrations for the $\text{DyBa}_2\text{Cu}_3\text{O}_x$ superconductor.

A number of lattice-dynamical calculations have been reported lately for the orthorhombic form (Thomsen 1983; Burns *et al* 1988; Kres *et al* 1988; Chaplot 1988; Bruesch and Buhner 1988) which have yielded descriptions of the normal modes and phonon densities of states. Normal coordinate calculations, which are applicable to zero wave-vector normal mode analysis have the advantage over lattice-dynamical calculations. In normal coordinate calculations, non central forces such as those involved in angle bending can be readily treated. Normal coordinate calculations have been extensively used for various metal oxides (Husson *et al* 1979; Haeuseler 1981; Repelin *et al* 1979; Saine *et al* 1982; Vandenborre *et al* 1982) to study their vibrational analysis. The importance of angle-bending force constants is proportional to the covalency of the compound (Martin 1970) and clearly for copper-oxygen framework of the superconductor cited in title, with an estimated covalency (Pauling 1988) of 0.5, they should be considered.

2. Theoretical considerations

The high T_c superconductor $\text{DyBa}_2\text{Cu}_3\text{O}_7$ crystallizes in the orthorhombic system which belong to the space group $P_{mmm}(D_{2h})$. The orthorhombic unit cell of $\text{DyBa}_2\text{Cu}_3\text{O}_7$ and numbering of atoms are shown in figure 1. The 13 atoms of the unit cell yield a total of 36 nonzero vibrational frequency modes. The symmetry species to which displacements of different sublattices belong are:

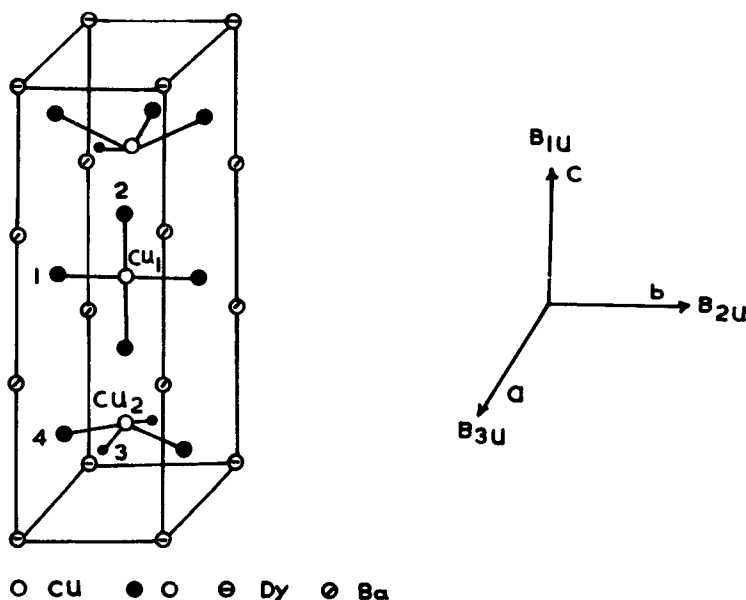


Figure 1. Orthorhombic unit cell of $\text{DyBa}_2\text{Cu}_3\text{O}_7$.

$B_{1u} + B_{2u} + B_{3u}$	From motion of Dy atom
$A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$	From motion of 2 Ba atoms
$A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$	From motion of 2 Cu atoms sandwiched by Dy and Ba atoms
$B_{1u} + B_{2u} + B_{3u}$	From motion of Cu atom surrounded by 4 Ba atoms
$2A_g + 2B_{2g} + 2B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$	From motion of O atoms between the layers of Dy and Ba
$A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$	From motion of 2 O atoms on the Cu–O line along the C-axis
$B_{1u} + B_{2u} + B_{3u}$	From 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 normal modes correspond to the irreducible representations as follows:

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

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.

A preliminary normal coordinate calculations of orthorhombic $YBa_2Cu_3O_7$ have been performed using the data given in table 1. The potential constants f_m ($Y-O(3) =$

Table 1. Force constants for $DyBa_2Cu_3O_7$.

Potential constants	Bond type	Distance (Å)	Initial value*
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_i	Ba—O(4)	2.945	0.8
f_m	Dy—O(3)	2.400	1.0
f_n	Dy—O(4)	2.300	1.0
f_p	Cu(2)—Cu(2)	3.374	0.5
f_α	O(1)—Cu(1)—O(2)	—	1.3
f_β	O(3)—Cu(2)—O(4)	—	1.3
f_γ	O—Cu(1)—O	—	0.5
	Out of plane bending		

*Force constant units are: Stretching 10^2Nm^{-1} and bending $10^{-18} \text{Nm rad}^{-2}$.

Table 2. Calculated frequencies (cm^{-1}) for Y-Ba-Cu-O.

A_g	121 (132)	B_{1u}	122 (130)
	157 (159)		209 (208)
	351 (347)		184 (199)
	378 (373)		313 (319)
	509 (515)		417 (423)
			527 (518)
			565 (555)
B_{2g}	73 (70)	B_{2u}	145 (156)
	156 (160)		104 (106)
	351 (348)		211 (237)
	481 (541)		357 (355)
	565 (510)		451 (485)
			548 (534)
			573 (576)
B_{3g}	91 (94)	B_{3u}	75 (62)
	140 (158)		120 (115)
	440 (462)		221 (240)
	502 (510)		304 (337)
	551 (573)		369 (454)
			548 (555)
			142 (138)

2.421 Å) and $f_n(\text{Y-O}(4)) = 2.38 \text{ \AA}$) are taken as $0.77 \times 10^2 \text{ Nm}^{-1}$ and $0.79 \times 10^2 \text{ Nm}^{-1}$ respectively. The programmes G-MAT and FPERT given by Fuhrer *et al* (1976) have been utilized for performing this calculation. It is interesting to note that the calculated frequencies listed in table 2 for Y-Ba-Cu-O system agree favourably with the experimental values which are given in parantheses.

Hence the same programme is used with the data given in table 1 to perform normal coordinate calculations of $\text{DyBa}_2\text{Cu}_3\text{O}_7$. The general agreement between the evaluated and the observed normal frequencies of the $\text{DyBa}_2\text{Cu}_3\text{O}_7$ is good.

3. Result and discussion

The G-matrix elements have been calculated from the equilibrium geometry as given in table 1. A simple valence force field was adopted to evaluate the vibrational frequencies of $\text{DyBa}_2\text{Cu}_3\text{O}_x$. The 16 initial force constants were taken from the related molecules. The Cu-O stretching, O-Cu-O bending force constants, Ba-O stretching force constants, Dy-O stretching force constants, Cu-O out of plane bending force constants are all taken from Bates and Eldridge (1987), Bates (1989). The initial force constants used in the present work are also given in table 1. The calculated frequencies and the potential energy distribution are given in table 2.

All the modes above 500 wave numbers are mainly described as Cu-O stretches. The wave number at 561 is mainly due to the symmetric Cu-O stretch while the rest of the vibrations are attributed to asymmetric stretch. These frequencies arise approximately around 625 cm^{-1} . These modes couple with Ba-O or Dy-O stretches to yield a higher frequency mode at 550 cm^{-1} . The former is due to the motion of Cu and adjacent Ba or Dy atoms in phase, while the latter is due to the motion in opposite direction.

Table 3. Calculated frequencies for DyBa₂Cu₃O₇.

Symmetry species	$\nu \text{ cm}^{-1}$	Potential energy distribution (%)*	Symmetry species	$\nu \text{ cm}^{-1}$	Potential energy distribution (%)*
A _g	567	$f_b(48)f_e(44)$	B _{2u}	445	$f_n(39)f_k(26)f_m(19)$
	442(440)	$f_i(51)f_k(25)$		270	$f_e(58)f_b(17)$
	430	$f_k(41)f_n(48)$		212	$f_i(39)f_k(20)f_n(15)$
	320(330)	$f_p(62)f_a(20)f_e(15)$		114	$f_a(28)f_b(18)f_g(14)$
	149	$f_g(61)f_i(22)$		640	$f_b(46)f_c(31)f_m(17)$
B _{2g}	628	$f_c(49)f_m(21)f_b(19)$	625	$f_a(84)f_g(18)$	
	580(580)	$f_c(74)$	585	$f_d(79)$	
	474	$f_h(79)$	558	$f_h(39)f_i(32)f_a(19)$	
	310(330)	$f_b(59)f_i(24)$	184	$f_a(54)f_k(21)$	
	158(150)	$f_g(49)f_n(32)$	172	$f_m(55)f_b(28)$	
B _{3g}	641(640)	$f_c(52)f_a(28)$	102	$f_k(56)f_a(28)$	
	585(580)	$f_c(64)f_n(19)$	642	$f_b(46)f_m(21)f_c(15)$	
	569	$f_h(84)$	590	$f_c(70)f_m(18)$	
	280	$f_p(58)f_i(22)$	518	$f_h(75)$	
	111	$f_g(39)f_m(24)f_i(14)$	441	$f_g(64)f_f(17)$	
B _{1u}	641	$f_b(48)f_b(20)f_m(24)$	192	$f_f(71)$	
	551	$f_b(72)f_b(19)$	182	$f_n(52)f_b(40)$	
	448	$f_k(46)f_a(31)$	111	$f_i(68)f_a(21)$	

* Contributions greater than 15% are included. Values in parantheses are the observed Raman frequencies.

Vibrational modes in the region 400 to 500 cm⁻¹ is generally attributed to Ba–O or Dy–O stretches. The present potential energy distribution confirms this conclusion (Bates *et al* 1989). The lower frequency modes involve small displacements of Ba–O or Dy–O or angular deformations of O–Cu–O angles. The evaluated frequencies are close to the available observed infrared and Raman frequencies, giving further support to the present assignment.

Further testing of the evaluated frequencies which are in the expected range confirm the correctness of an assignment for this compound. To check whether the chosen set of vibrational frequencies contributes maximum to the potential energy associated with normal-coordinate of the superconducting material, the potential energy distribution was calculated using the equation

$$\text{P.E.D.} = (F_{ii}L_{ik}^2)/\lambda_k$$

where P.E.D. is the combination of the *i*th symmetry coordinate to the potential energy of the vibration whose frequency is ν_k . F_{ii} = Potential constants, L_{ik} = *L* matrix elements and $\lambda_k = 4\pi^2 C^2 \nu_k^2$.

4. Conclusion

The evaluated vibrational frequencies in the range 100 to 650 cm⁻¹ have been assigned with same reliability in the present work. It is significant to note that the frequency observed in Raman and infrared supports the present centre of symmetry structure. Peaks reported at 150, 330, 440, 580 and 640 cm⁻¹ agree well with the proposed assignment.

References

- Bates F E and Eldridge J E 1987 *Solid State Commun.* **64** 1435
- Bates F E 1989 *Phys. Rev.* **B39** 322
- Bednorz J C and Müller K A 1986 *Z. Phys.* **B64** 189
- Bonn D A, Greedan J E, Stager C V, Timusk T, Doss M G, Kerr S L, Kamras K and Tanner D B 1987 *Phys. Rev. Lett.* **58** 2249
- Bruesch P and Bührer W 1988 *Z. Phys.* **B70** 1
- Burns G, Dalcol F H, Holtzberg F and Kaiser D L 1988 *Solid State Commun.* **66** 217
- Cardona M, Liu R, Thomsen C, Bauer M, Genzel L, König W and Wittlin A 1987 *Solid State Commun.* **64** 727
- Chaplot S L 1988 *Phys. Rev.* **B37** 7435
- Führer H, Kartha V B, Kidd K G, Krueger P J and Matsch H H 1976 *Computer programs for infrared spectrophotometry, Normal Coordinate Analysis* (Ottawa: National Research Council of Canada) vol. 5
- Haeuseler H 1981 *Spectrochim. Acta* **A37** 487
- Husson E, Repelin Y, Brusset H and Ceyez A 1979 *Spectrochim. Acta* **A35** 1177
- Kress W, Schroder U, Prade J, Kulkarni A D and de Wette F W 1988 *Phys. Rev.* **B38** 2906
- Martin R M 1970 *Phys. Rev.* **B1** 4005
- Mohan S, Radjakoumar T and Gal M 1991 *Mater. Res. Bull.* **26** 3
- Onari S, Hiroaki T, Onshima K, Monma H and Arai T 1988 *Solid State Commun.* **3** 303
- Pauling L 1988 *Phys. Rev. Lett.* **59** 225
- Repelin Y, Husson E, Dao N Q and Brusset H 1979 *Spectrochim. Acta* **A35** 1165
- Shapiro S M, Shirane G and Axe J D 1975 *Phys. Rev.* **B12** 4899
- Saine M C, Husson E and Brusset 1982 *Spectrochim. Acta* **A38** 19
- Thomsen C, Cardona M, Kress W, Liu R, Genzel L, Bauer M, Schonherr E, and Schroder U 1983 *Solid State Commun.* **65** 1139
- Vandenborre E, Husson E and Fourquet J L 1982 *Spectrochim. Acta* **A38** 997