Proc. Indian natn. Sci. Acad., **62**, A, No. 6, 1996, pp. 539-545.

LATTICE DYNAMICS AND NORMAL COORDINATE ANALYSIS OF $NdBa_2Cu_3O_7$

S MOHAN AND R KANNAN*

Raman School of Physics, Pondicherry University, Pondicherry 605 014, *India*

(*Received* 18 *October* 1995; *Revised* 11 *March* 1996; *Accepted* 16 *April* 1996)

The lattice dynamics of the high T_c superconductor $NdBa_2Cu_3O_7$ has been investigated in detail based on the modified three body force shell model (TSM). The TSM employed here takes care of the effect of many body interactions in the lattice potential. The aim of the present work is to treat the various interactions between the ions in a more general way without making them numerically equal. The values of the phonon frequencies calculated at the zone centre by the new approach are in agreement with the available Raman and infrared data. A normal coordinate analysis has also been carried out for this superconductor using Wilson's F-G matrix method for the confirmation of our present investigations. The vibrational frequencies and the potential energy distribution (PED) of the optically active phonon modes are also reported.

Key Words: Lattice Dynamics; Normal Coordinate Analysis; $NdBa_2Cu_3O_7$; Superconductor; Wilson's F-G Matrix

Introduction

In general, the lattice dynamics of a high T_c superconductor are described by a frequency-wave vector dispersion relation about the zone centre. The phonon dispersion curves about the zone centre give a better insight into the role of phonons for high transition temperatures, and also throw some light on the electron-phonon pairing mechanism. Optical spectroscopy, especially Raman and infrared experimental techniques offer themselves as wonderful tools for the study of optical phonons in the long wavelength limit. Although a number of reports on this system have appeared, the phonon observations are not unique. Hence, theoretical calculations have been attempted here in order to present a complete picture of the vibrational assignments of the phonon frequencies using TSM. Our lattice dynamical approach is similar to that reported for $ErBa_2Cu_3O_7$.[1] The normal coordinate calculations are performed to support the assignment of the vibrational frequency and to obtain the PED for various modes.

Lattice Dynamics of $NdBa_2Cu_3O_7$ based on the Modified Shell Model

The TSM has been explained elsewhere[1]. Calculation of the lattice dynamical vibrational frequencies of $NdBa_2Cu_3O_7$ is performed using the modified three body force shell model. The TSM of Verma *et al.*[2&3] is a descendent of early

*Department of Physics, Pondicherry Engineering College, Pondicherry 605 014, India

works by Lundqvist[4]. In the earlier approaches, the R, S, T elements were considered to be equal to one another. In the present investigation, we have started with a more general approach such that $R \neq S \neq T$[5]. The dynamical matrix of the model consists of the long range coulomb and three body interactions and the short-range overlap repulsions. The off-diagonal elements of this matrix along the symmetry directions contain a completely new term having a significant contribution for unequal R, S and T.

The lattice dynamical calculation of high T_c superconductor is explained here using interionic potentials consisting of a long-range coulomb part and a short-range potential of Born-Mayer form

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

Phonon frequencies can then be calculated using the force constants derived from the interionic potentials. Following Lehner *et al*.[6] interionic pair potentials for short-range interactions can be transferred from one structure to another in similar environments. The force constants evaluated by this method are in agreement with the values in the literature[7]. Lattice dynamical calculations were performed with these values as model parameters.

Normal Coordinate Analysis of $NdBa_2Cu_3O_7$

The high T_c Superconductor $NdBa_2Cu_3O_7$ belongs to orthorhombic system, space group P_{mmmm} (D_{2h}) like other $MBa_2Cu_3O_7$ (M-Rare earth atom) system. Thirteen atoms of the unit cell yield 36 vibrational modes of optical phonons and three zero frequency translational modes. Vibrational states of optical phonons are characterised by their symmetry, from the group theoretical analysis and the total representation is given by

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

All gerade modes are Raman active (A_g, B_{2g} and B_{3g}) and the B_{1u}, B_{2u} and B_{3u} are infrared active. 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.

$B_{1u} + B_{2u} + B_{3u}$ from the motion of Nd atoms

$A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$ from the motion of two Ba atoms

$A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$ from the motion of two Cu atoms sandwiched by Nd and Ba atoms

$B_{1u} + B_{2u} + B_{3u}$ from the motion of Cu atom surrounded by four Ba atoms

$2A_g + 2B_{2g} + 2B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}$ from the motion of four oxygen atoms between the layers of Nd and Ba

$A_g + B_{2g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$ from the motion of two 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

In the normal coordinate analysis the PED plays an important role for characterisation of the relative contribution from each internal coordinate to the total potential energy associated with a particular normal coordinate of the molecule. The contribution to the potential energy from the individual diagonal elements gives rise to a conceptual link between the empirical analysis of vibrational spectra of complex molecules dealing with the characteristic group of frequencies and the theoretical approach from the computation of the normal modes.

The normal coordinate calculations are carried out using Wilson's F-G matrix method and the G-mat and FPERT computer programmes given by Fuhrer *et al*[8]. are utilised for this purpose. The data[9&10] given in Table II is utilised for the calculations. It is interesting to note that the evaluated frequencies (Table III) agree favourably with the experimental values[11]. The potential energy distribution is calculated using the equation.

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

where P.E.D is the contribution of the ih symmetry coordinate to the potential energy of the vibration whose frequency is ν_a. F_{ii} = potential constants, L_{ia} = L matrix elements and $\lambda_a = 4\pi^2 C^2 \nu_a^2$

Results and Discussion

The lattice dynamical calculations based on the modified TSM reproduces very well the observed frequencies of Raman and Infrared active modes which are given in Table I. The evaluated frequencies are assigned to different modes of vibration based on lattice dynamical calculations and other available reports.

The lowest calculated Raman active A_g mode at 149cm^{-1} is due to the vibration of the Ba atoms and this agrees well with the observed value at 153cm^{-1}. The Raman modes around 312 and 430cm^{-1} have been observed consistently in all rare earth superconducting materials (123 systems) and are attributed to pure bond bending vibrations of Cu(2)-O(3)-O(4), with O(3) and O(4) atoms moving out of phase and in-phase respectively. From the lattice dynamical calculations these values are predicted at 315 and 434cm^{-1}. The wave number at 510cm^{-1} is due to the bond stretching vibrations of O(2) atoms and is associated with the observed mode at 512cm^{-1}. The highest calculated mode for A_g symmetry is at 560cm^{-1}.

Although the B_{2g} and B_{3g} modes have different frequencies, they have similar vibration characteristics except the fact that the B_{2g} mode involves the motion of atoms along the *b*-axis where as the B_{3g} one is due to the motion in the *a*-axis. The lowest B_{2g} and B_{3g} modes calculated at 160 and 111cm^{-1} are attributed to the vibrations of Ba atoms. The $B_{2g} - B_{3g}$ pair at 312 and 278cm^{-1} involve the vibration of O(2) atoms. The frequencies above 500cm^{-1} are assigned to the stretching vibrations of Cu – O.

The observed IR frequencies are at 123, 160, 235, 277, 318 and 588cm^{-1}. The calculated IR active mode at 120cm^{-1} (B_{1u}) is due to the vibrations of Ba atoms and this agrees with the observed peak around 123cm^{-1}. The peak at 160cm^{-1} is assigned to the motion of Nd atoms. According to our calculation this mode is at 164cm^{-1}. The frequency observed at 277cm^{-1} is predominant-

Table I

Vibration frequencies obtained by the TSM calculation on $NdBa_2Cu_3O_7$ *with the observed Raman and IR frequencies in parantheses*[11]

Raman active modes (cm^{-1})			Infrared active modes (cm^{-1})					
A_g	B_{2g}	B_{3g}	B_{1u}		B_{2u}		B_{3u}	
			TO	LO	TO	LO	TO	LO
560	561	569	610	618	618	624	610	612
510(512)	550	542	575	580(588)	608	612	579	584
434(430)	525	440	472	478	560	567	554	560
315(312)	312	278	418	424	550	559	452	455
149(153)	160	111	328	330	272	279(277)	315	320(318)
			159	164(160)	228	234(235)	135	138
			115	120(123)	114	119	100	115

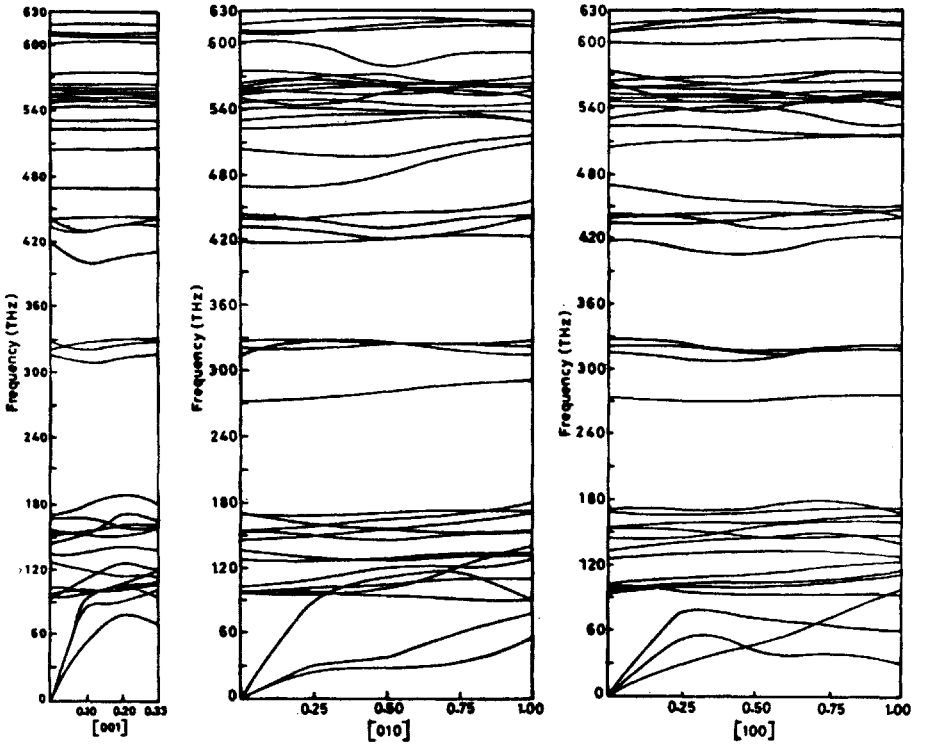

Fig. 1 Dispersion curves of $NdBa_2Cu_3O_7$ in the [100], [010] and [001] directions

ly due to the deformation modes of Cu(2)−O(3)−O(4). The corresponding calculated TO and LO frequencies are 272 and 279cm^{-1} respectively. The observed peak at 588cm^{-1} is assigned to the bond stretching vibrations of Cu(1) and O(1) atoms. The calculated TO and LO modes at 575 and 580cm^{-1} agrees well with the reported value.

The observed frequencies reported in the literature[11] are well accounted with the calculated frequencies in the present work. The phonon dispersion curves of $NdBa_2Cu_3O_7$ in the three symmetry directions obtained in this work are depicted in Fig. 1.

The zone centre phonon frequencies of $NdBa_2Cu_3O_7$ calculated using normal coordinate analysis is given in Table III, along with the observed values and calculated PED. The initial set of force constants used for the calculation are tabulated in Table II.

Table II *Force constants for* $NdBa_2Cu_3O_7$

Potential constants	Bond type	Distance Å	Initial Value*
f_a	Cu(1) – O(1)	1.95	1.44
f_b	Cu(1) – O(2)	1.80	1.62
f_c	Cu(2) – O(3)	1.98	1.47
f_d	Cu(2) – O(4)	1.96	1.38
f_e	Cu(2) – O(2)	2.34	1.09
f_g	Ba – O(1)	2.95	0.70
f_h	Ba – O(2)	2.80	1.16
f_k	Ba – O(3)	2.94	0.84
f_l	Ba – O(4)	2.84	0.98
f_m	Nd – O(3)	2.43	0.81
f_n	Nd – O(4)	2.52	0.78
f_p	Cu(2) – Cu(2)	3.40	0.49
f_α	O(1) – Cu(1) – O(2)	–	0.99
f_β	O(3) – Cu(2) – O(4)	–	1.01
f_τ	O – Cu(1) – O	–	0.39

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

Table III *Calculated (NCA) Phonon frequencies of* $NdBa_2Cu_3O_7$

Symmetry species	Frequency cm^{-1}	Potential energy distribution[a], %
A_g	152(153)	$f_l(65) f_h(21)$
	309(312)	$f_\beta(55) f_d(22) f_c(18)$
	428(430)	$f_\beta(61) f_c(15) f_d(17)$
	515(512)	$f_e(61) f_d(23)$
	552	$f_d(55) f_c(38)$
B_{2g}	168	$f_h(55) f_\beta(24)$
	310	$f_\beta(63) f_d(20)$
	528	$f_d(62) f_c(18) f_h(21)$
	545	$f_c(71) f_d(11) f_e(12)$
	569	$f_d(40) f_c(24) f_g(13)$

(*Table III contd*)

(*Contd. of Table III*)

B_{3g}	110	$f_h(40)f_e(24)$
	283	$f_g(60)f_d(21)$
	447	$f_d(62)f_c(18)$
	535	$f_c(68)f_d(15)$
	562	$f_d(55)f_e(25)$
B_{1u}	118(123)	$f_\alpha(30)f_\beta(21)f_g(20)$
	165(160)	$f_m(48)f_h(21)f_\alpha(18)$
	329	$f_\beta(55)f_b(28)$
	421	$f_m(50)f_n(22)f_p(20)$
	474	$f_b(48)f_m(30)f_n(16)$
	575(588)	$f_a(69)f_b(24)$
	616	$f_a(51)f_b(28)$
B_{2u}	113	$f_\tau(35)f_\alpha(34)f_\beta(20)$
	230(235)	$f_\alpha(63)f_n(28)$
	271(277)	$f_g(62)f_m(19)f_n(12)$
	551	$f_c(50)f_d(21)f_k(24)$
	565	$f_c(50)f_d(34)$
	611	$f_b(49)f_a(21)f_g(28)$
	622	$f_b(55)f_a(24)$
B_{3u}	109	$f_\tau(72)f_\alpha(12)f_m(10)$
	130	$f_\alpha(55)f_m(24)f_e(16)$
	320(318)	$f_g(42)f_n(22)f_p(16)$
	451	$f_1(64)f_k(20)f_d(14)$
	552	$f_d(42)f_b(30)$
	585	$f_c(71)f_d(18)$
	605	$f_a(44)f_b(24)f_h(18)$

[a] Only contributions greater than 10% are included

The calculated Raman active A_g modes are at 152, 309, 428, 515 and 552cm^{-1} respectively. The lowest mode at 152cm^{-1} agrees well with the observed 153cm^{-1} Raman mode. From PED it is clear that the mode is due to the vibration of Ba and oxygen atoms. The calculated A_g mode at 309cm^{-1} is due to the out of plane vibrations of O(3)−Cu(2)−O(4) atoms, and this is associated with the observed mode around 312cm^{-1}. The most prominent peak observed at 512cm^{-1} is due to motion of axial O(2) atoms. The relative contribution of the force constants involving O(2) stretch to the vibration energy of this mode is 61%. Similar way, the rest of the assignments can be explained based on the calculated PED given in the Table III.

The observed Raman and infrared frequencies reported so for are well accounted for, by the calculated frequencies in the present work.

Conclusion

The vibrational frequencies calculated by the methods of lattice dynamics and the normal coordinate analysis agree well with the measured Raman and IR frequencies. The calculations yield not only the phonon frequencies at the centre of the Brillouin zone but also the phonon dispersion curves in the three high symmetry directions. It can, therefore, serve as a tool for the investigation

of the role of phonons for the high T_c in the superconducting system. It is also shown that it is possible using a rather simple model to obtain a fairly good overall representation of the superconducting system.

References

1 S Mohan and R Kannan *Aust J Phys* **47** (1994) 103
2 M P Verma and R K Singh *Phys Stat Solidi* **33** (1969) 769
3 M P Verma and S K Agarwal *Phys Rev* **B8** (1973) 4880
4 S O Lundqvist *Ark Fys* **9** (1955) 435
5 S Mohan, S Durai and G Vaidyanathan *Indian J Phys* **60A** (1986) 137
6 N Lehner, H Rauh, K Strobel, R Geick, G Heger, J Bouillot, B Renker, M Rousseau and W J Stirling *J Phys* **C15** (1982) 6545
7 S Onari, A Ono, T Arai and T Mori *Physica* **B** (165-166) (1990) 1235
8 H Fuhrer, V B Kartha, K G Kidd, P J Krueger and H H Matsch *Computer Programs for Infrared Spectrophotometry Normal Coordinate Analysis* National Research Council of Canada Ottawa Vol. 5 (1976)
9 F E Bates *Phys Rev* **B39** (1989) 322
10 G Collin, P A Albouy, P Monod and M Ribault *Phys France* **51** (1990) 1163
11 M Cardona, R Liu, C Thomsen, M Bauer, L Genzel, W Konig, A Wittlin, U Amador, M Barahona, F Fernandez, C Otero and R Saez, *Solid State Commun* **65** (1988) 71