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Lattice Dynamics of the High T_c Superconductor $ErBa_2Cu_3O_7$

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Abstract

The lattice dynamics of the high T_c superconductor $ErBa_2Cu_3O_7$ have been investigated in detail with a modified three-body force shell model. The model accounts for 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 generalised way without making them numerically equal. The values of the phonon frequencies calculated at the zone centre by this new approach are in good agreement with the available Raman and infrared data.

1. Introduction

In general, the lattice dynamics of a high T_c superconductor are described by a frequency–wavevector dispersion relation about the zone centre. Several lattice-dynamical models have been developed to explain the theoretical phonon dispersion curves of high T_c superconductors. These 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. In this paper we present a modified shell model for the calculation of phonon frequencies at the Γ point of the Brillouin zone. The proposed model accounts for charge transfer between neighbouring ions in addition to the dipoles induced on the ions, i.e. the electronic polarisability.

Superconducting properties in $ErBa_2Cu_3O_7$ prepared by the method of powder calcination were studied by Mohan *et al.* (1990). The compounds showed a sharp superconducting transition width ΔT, less than 1 K. The pressure shift of T_c and the a.c. susceptibility measurements were also studied. Recently, we have also done a normal coordinate analysis of the zero-wavevector vibrations of $ErBa_2Cu_3O_7$. In continuation of our work on lattice dynamics, here we present a complete calculation of the lattice vibrations of $ErBa_2Cu_3O_7$, based on the modified three-body force shell model (TSM). Like the shell model, the TSM is also based mainly on the interionic potential consisting of a long-range Coulomb part, for which the potential is exactly known, and a short-range potential of Born–Mayer form.

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2. Theoretical Considerations

The high T_c superconductor $ErBa_2Cu_3O_7$ crystallises in the orthorhombic system which belongs to the space group $P_{mmm}(D_{2h})$. Lehner *et al.* (1982) pointed out that the short-range interionic potentials could be used for the calculation of force constants. Phonon frequencies can then be calculated using the force constants derived from the interionic potentials. These interionic potentials for short-range interactions can be transferred from one structure to another in similar environments. Following Lehner *et al.* (1982), our interionic pair potentials for oxidic pervoskites and metal oxides were taken from known alkali halides and fluoridic pervoskites. Surface dynamics studies of alkali halides (Kress *et al.* 1987) and perovskites (Reiger *et al.* 1987) also confirm this idea of transferability of these potentials from bulk to surface studies, despite the change in distance between interacting ions by surface relaxation.

3. Lattice-dynamical Calculations

Calculation of the lattice-dynamical vibrational frequencies of $ErBa_2Cu_3O_7$ is performed using the TSM developed by Verma and Singh (1969) and Verma and Agarwal (1973), and which is a descendent of early work by Lundqvist (1955). In the TSM, the electronic charge density of an ion in the crystal is taken to be a function of the instantaneous relative positions of that ion's first nearest neighbours. It is assumed that the neighbours produce an isotropic scalar deformation of the charge density of the reference ion. The net effects of these deformations on the cohesive energy and the equations of motion are a renormalisation of the ionic charges, additional short-range two-body forces that can be absorbed into the central force repulsive interactions, and long-range three-body interactions between the vibrating ions (Mahan and Mostoller 1986). The shell model equations are given in the matrix form by

$$\omega^2 MU = (R + ZCZ)U + (T + ZCY)W\,,$$

$$0 = (T' + YCZ)U + (S + K + YCY)W\,.$$

Elimination of W leads to the dynamical matrix

$$D = (R + ZCZ) - (T + ZCY)\,(S + K + YCY)^{-1}(T' + YCZ)\,.$$

The second term in this equation represents the three-body part of the lattice potential. Here M, Z and Y are diagonal matrices representing the mass, ionic charge and the charge on the shell, while R, S and T are matrices specifying the short-range core–core, shell–shell and core–shell interactions respectively. Further, U is the ionic displacement from the equilibrium position and C represents the Coulomb term. In the earlier approaches, the R, S, T elements were considered to be equal to one another, but we expect that there should be some difference in those values (Mohan *et al.* 1986). In the present investigation, we have started with a more general approach such that $R \neq S \neq T$. The T matrix elements are calculated using the relation connecting the parameters $A_{\rm I}, A_{\rm II}, B_{\rm I}$ and $B_{\rm II}$ (Verma and Singh 1971). Then, S matrix elements are calculated using the relation $2T - R = S$. 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. A qualitative analysis shows that this modification is important since they relate the optical and mechanical polarisabilities.

The force constants for the short-range interionic potentials between Cu and O, Ba and O, Er and O and between the neighbouring oxygen atoms are calculated using the Born–Mayer potential

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

where i, j label the ions and r their separation. The force constants evaluated by this method are in agreement with values in the literature (Kress *et al.* 1988). The parameters a_{ij} and b_{ij} of the pair potentials and the parameters Y_i and K_i which determine the electronic polarisabilities were computed and agree well with those of Kress *et al.* (1988).

The ionic charges are +3, +2 and +2, for Er, Ba and Cu, while for oxygen the value is determined using the charge neutrality condition. Lattice-dynamical calculations were performed with these values as model parameters.

Table 1. Vibration frequencies obtained by the TSM calculation on $ErBa_2Cu_3O_7$ with the observed Raman and IR frquencies in parentheses (Cardona *et al.* 1988)

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
562	622	641(640)	622	631	638	642	640	652(630)
449(442)	591(580)	591	552	563(550)	618	628(630)	582	591
418	471	584	468	484	574	589(580)	515	524
333(320)	312(330)	283	410	420	555	564	414	428
158(150)	160	111	241	262(210)	181	188	169	175
			184	198	161	168	159	162(165)
			101	111	105	111	102	108

4. Results and Discussion

The model parameters obtained by the TSM are in close agreement with the reported values (Kress *et al.* 1988). The calculations reproduce very well the observed frequencies of Raman- and infrared-active modes (Cardona *et al.* 1988). The lattice vibration frequencies at the Γ point are obtained at $q = 0$. The calculated frequencies of the zone-centre phonon modes of $ErBa_2Cu_3O_7$ and the observed Raman and infrared frequencies are presented in Table 1.

$YBa_2Cu_3O_7$ and $ErBa_2Cu_3O_7$ possess similar phonon structures. Hence the vibrational assignments available for $YBa_2Cu_3O_7$ can be applied to $ErBa_2Cu_3O_7$. The evaluated frequencies were assigned to different modes of vibration on the basis of the orthorhombic system and lattice-dynamical calculations. This system yields a total of 36 optic modes distributed as $\Gamma = 5A_g+5B_{2g}+7B_{1u}+5B_{3g}+7B_{2u}+7B_{3u}$. The species belonging to A_g, B_{2g} and B_{3g} are Raman-active modes, while

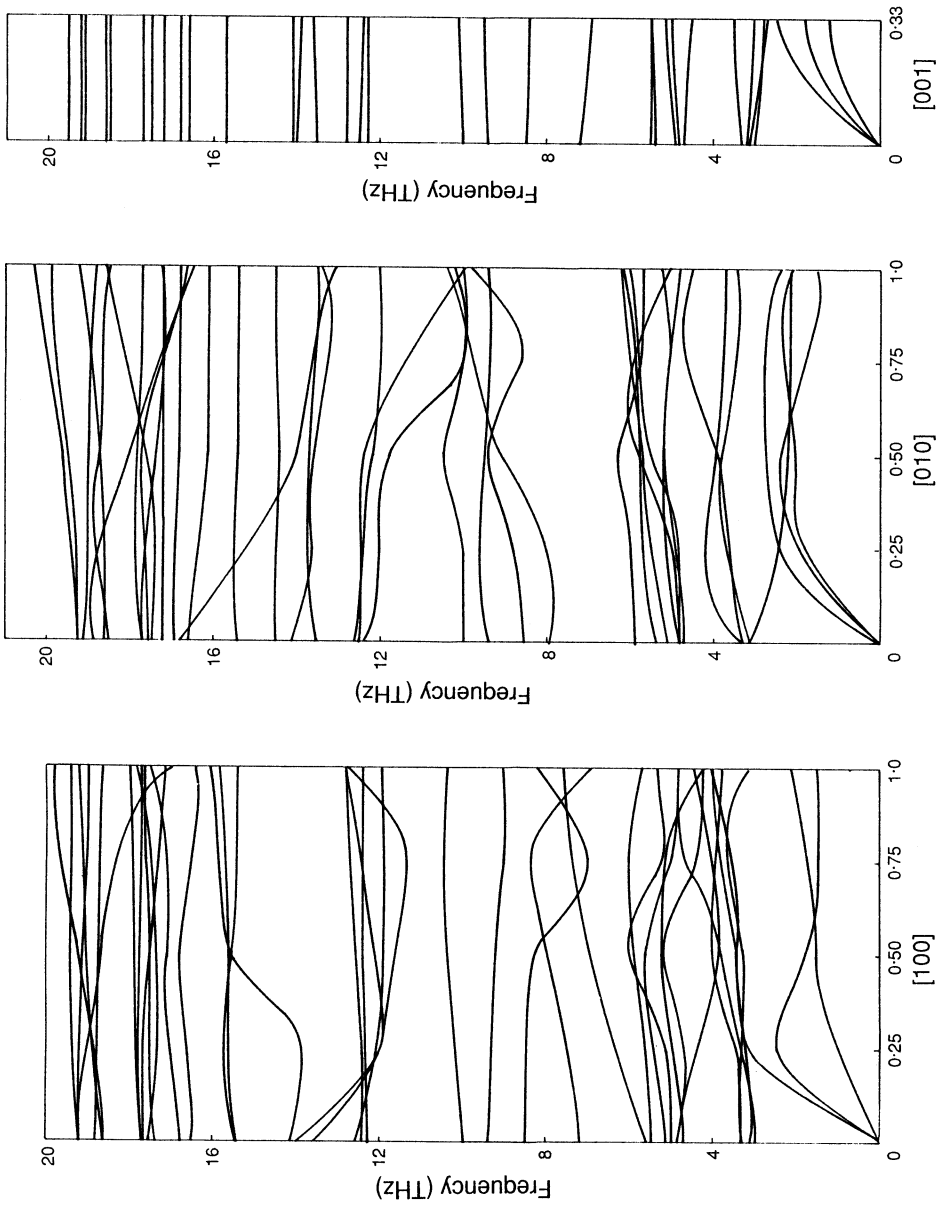

Fig. 1. Dispersion curves of $ErBa_2Cu_3O_7$ in the [100], [010] and [001] directions.

B_{1u}, B_{2u} and B_{3u} are infrared-active modes. Although a number of papers have appeared in the literature concerning experimental and theoretical studies on phonons, they contradict each other. Bengang and Katiyar (1992) resolved the discrepancies in their work on a lattice-dynamical formalism using a rigid ion model for the superconductor $YBa_2Cu_3O_7$. Their conclusions are taken as a guide in assigning the modes of vibration of $ErBa_2Cu_3O_7$ in the present work.

The Raman-active A_g mode of 158 cm^{-1} (Cu–Ba–O motion) is the lowest calculated wavenumber which agrees well with the observed value. Vibrational modes in the region 400 to 500 cm^{-1} are assigned to Ba–O or Er–O stretches. The observed frequency of 320 cm^{-1} due to oxygen motion agrees reasonably well with the calculated frequency of 333 cm^{-1}. The evaluated frequency of 591 cm^{-1} due to the motion of the barium atoms against O(III) is close to the observed frequency of 580 cm^{-1}.

The frequency 312 cm^{-1} is assigned to the bond bending vibrations of O(II)–Cu(II)–O(III), in good agreement with the experimental frequency of 330 cm^{-1}. The lowest phonon frequency of 111 cm^{-1} belongs to B_{3g} symmetry. The observed modes for B_{1u} species are the 210 [Cu(I)–Ba–Er–O(III) vibration] and 550 [Cu–Er–O atom vibration] wavenumbers. The calculated values corresponding to TO and LO modes are at 241 and 262 cm^{-1} wavenumbers and at 552 and 563 cm^{-1}. The calculated frequencies of 184 and 198 cm^{-1} obtained in the present investigation may be due to the motion of barium and erbium atoms against the Cu(I)–O(III)–Cu(II) chain.

The calculated TO and LO frequencies for the infrared-active B_{2u} species are 105, 161, 181, 555, 574, 618 and 638 cm^{-1} and 111, 168, 188, 564, 589, 628 and 642 cm^{-1} respectively. The experimentally observed frequencies of 630 and 580 cm^{-1} agree very well with the calculated frequencies. The frequencies of 161 and 181 cm^{-1} are due to vibrational motion of copper, barium and erbium atoms. As in $YBa_2Cu_3O_7$, the 555 cm^{-1} frequency is due to the motion of oxygen atoms.

For the B_{3u} normal modes, the experimental frequency of 165 cm^{-1} [vibration of copper, barium and erbium atoms against O(III)] and of 630 cm^{-1} agree very well with the evaluated frequency in the present work. The calculated frequency of 515 cm^{-1} in TO and 524 cm^{-1} in LO belong to O(IV) and O(V) vibrations as pointed out by Bengang and Katiyar (1992). The observed frequency of 630 cm^{-1} [640 for TO and 652 for LO] is due to the motion of O(I) against O(III).

Each of the 12 reliable observed freqencies reported in the literature is well accounted for by the calculated frequencies in the present work. The phonon dispersion curves of $ErBa_2Cu_3O_7$ in the three symmetry directions obtained in this work are depicted in Fig. 1.

5. Conclusion

The shell model parameters for $ErBa_2Cu_3O_7$ have been obtained and they provide reasonable agreement with the measured infrared and Raman frequencies. Our lattice-dynamical calculation provided not only the phonon frequency at $q = 0$, but also the phonon dispersion curves in the three main symmetry directions. The theoretical phonon frequency values obtained in this work comply with the available experimental values.

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