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Interatomic potential, phonon spectrum and molecular-dynamics simulation up to 1300 K and 10 GPa in $YBa_2Cu_3O_{7-\delta}$ for $\delta = 0$ to 1

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Abstract. An empirical interatomic potential for $YBa_2Cu_3O_{7-\delta}$ is determined for different oxygen contents ($\delta = 0$ to 1), consisting of Coulomb and short-range interactions. The calculated structure and phonon spectrum, and the results of molecular-dynamics computer simulation on the orthorhombic-to-tetragonal phase transition are in fair agreement with reported experiments.

Keywords. $YBa_2Cu_3O_{7-\delta}$; lattice dynamics; molecular-dynamics simulation.

1. Introduction

An interatomic potential model can help in the study of a variety of observed properties in a single framework. Such properties include the structure, phonons, their temperature and pressure dependence, phase transitions and related physical properties. Further, the model is capable of being used in the molecular-dynamics computer simulations which can provide direct detailed insight at the microscopic atomic level. We have recently (Chaplot 1989) determined an empirical potential model for $YBa_2Cu_3O_{7-\delta}$(YBCO) for $\delta = 0$. Since the YBCO system exists with different values of oxygen contents, we extend the model for use with such systems and present its various applications.

2. Interatomic potential, lattice statics and dynamics

We use the unscreened rigid ion model (Chaplot 1988) which is found reasonable for the YBCO class of ceramic compounds. The total potential energy ϕ is expressed as the lattice sum over two body functions of the following form (Chaplot 1989).

$$V_{kk'}(r_{ij}) = Z(k)Z(k')e^2/(4\pi\varepsilon_o r_{ij}) + a\exp[-br_{ij}/(R(k)+R(k'))] - w/r_{ij}^6 - cD\exp[-n(r_{ij}-r_o)^2/(2cr_{ij})].$$

Here r_{ij} is the distance between the two atoms i and j of species k and k' respectively. $Z(k)$ and $R(k)$ are effective charges and radii parameters respectively. Other details and the values of parameters for the case of $\delta = 0$ are given in Chaplot (1989). With the loss of one oxygen for the case of $\delta = 1$, the only parameters which change from $\delta = 0$ are: Z(Ba) from 1·5 to 1·25, $Z(Cu_1)$ from 1·4 to 0·6, R(Ba) from 0·23 nm to 0.21 nm, and $R(Cu_1)$ from 0·12 to 0·11 nm. The potential parameters have been determined from the requirement of producing reasonable crystal structure and maximum phonon frequency. The values of the parameters for intermediate oxygen contents are interpolated from the values for $\delta = 0$ and 1.

The potential is used to calculate the minimum-energy ($\phi + PV$) structure and phonon frequencies at various pressures P using the current version of the program

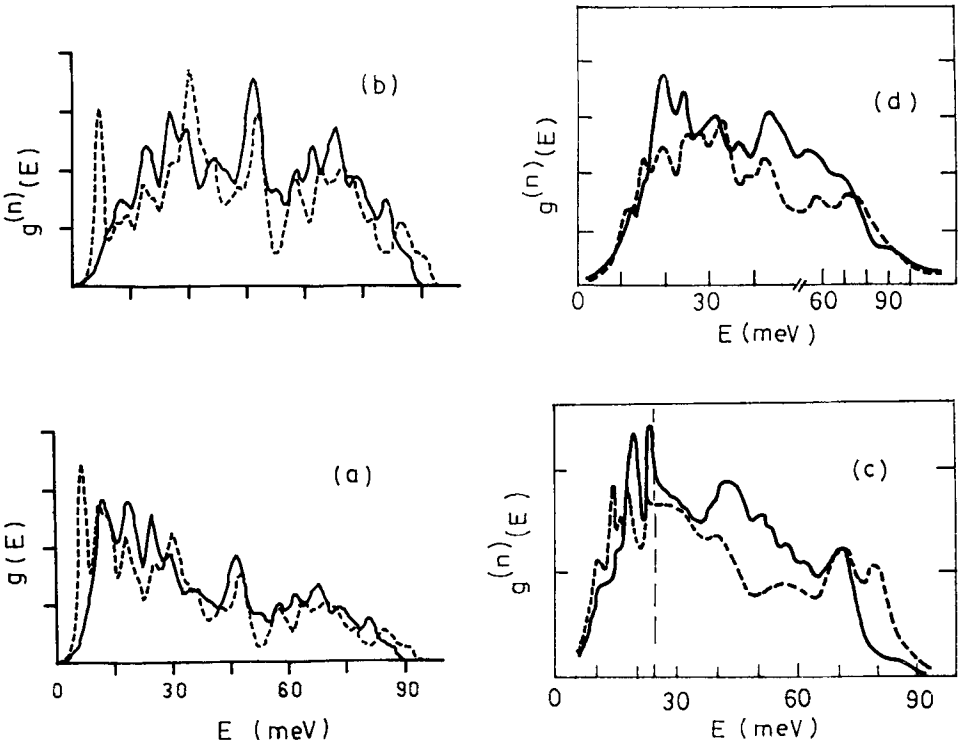

Figure 1. Calculated (**a**) phonon density of states, and (**b**) neutron-weighted density of states. The latter may be compared with experimental spectra (**c**) from Renker *et al* (1988) and (**d**) from Natkaniec *et al* (1988). The full and dashed lines correspond to $\delta = 0$ and 1 respectively.

DISPR (Chaplot 1978) (V is volume). The calculated bulk modules B_0 at $P = 0$ of 109 and 92 GPa for $\delta = 0$ and 1 respectively compare well with various published experimental values in the range of 65–157 GPa. The calculated $\partial B/\partial P$ are 4·1 ($\delta = 0$) and 5·0 ($\delta = 1$). The calculated phonon spectra in figure 1 for $P = 0$ show good qualitative agreement with experiments (figure 1). The calculated partial density of states corresponding to different atoms showed that compared to the $\delta = 0$ system, in the $\delta = 1$ system the spectra shift to lower energies for Ba, Cu_1 and O_1 atoms and to higher energies for O_2 and O_3 atoms, while the O_4 atom is missing.

3. Molecular-dynamics simulation

The high temperature behaviour beyond the harmonic vibrations is calculated by the molecular-dynamics computer simulation, using a program developed by us (Chaplot 1986). Recently for the case of $\delta = 0$ we reported (Chaplot 1989) simulation of the orthorhombic-to-tetragonal (O–T) phase transition, which essentially involves equal distribution of the O_4 oxygens along the **a** and **b** directions, from their ordered arrangement along the **b** direction in the Cu–O_4 chains in the orthorhombic phase. The simulated transition temperatures for the cases of $\delta = 0, 0{\cdot}25$ and 0·5 are 1100 K, 1000 K

and 900 K respectively, compared to the reported experimental value of 970 K for $\delta = 0{\cdot}5$. (For experimental references and details of simulation, see Chaplot 1989). Experimentally, the system loses oxygen when heated under ambient atmospheric pressure. We believe that oxygen loss occurs through the surface of the real system which is not included in the present simulation. The simulation suggests that the oxygen loss may not be a necessary requirement for the O–T transition. Close to the O–T transition the oxygen atoms in the CuO_3 network undergo frequent jump motions (figure 2) at about 10 jumps per nanosec per oxygen atom, which also create vacancies at the O_1 sites which link the Cu_1 and Cu_2 atoms. At higher temperatures jumps among other oxygen sites are also observed while the heavy atoms remain at their equilibrium sites.

The zero-pressure simulation also reproduces the experimental average volume thermal expansion of $6 \times 10^{-5}\,K^{-1}$ between 0 and 1000 K. Simulation at a high pressure essentially reproduced the bulk modules as calculated by lattice statics above.

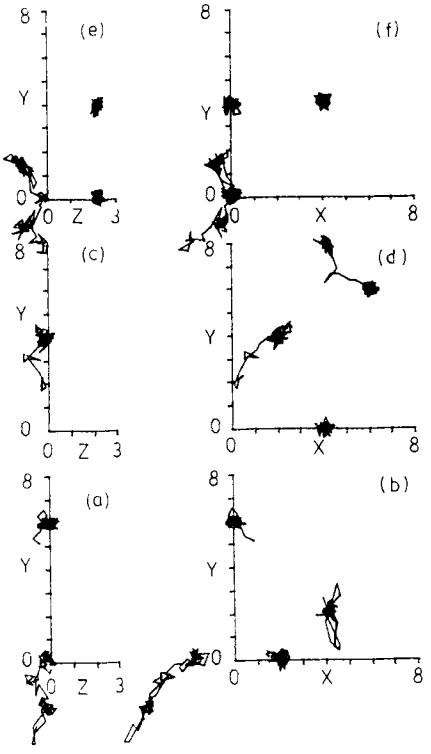

Figure 2. Projections of atomic coordinates from MD simulation at 1000 K for $\delta = 0{\cdot}25$ for a duration of 10 ps. Angstrom units are used. Separate projections are given for the oxygen atoms, which were in different layers along the Z axis at the start of the simulation (time $t = 0$). The projections correspond to $t = 35$ to 45 ps. The XY projections include all atoms in each layer of the $2\mathbf{a} \times 2\mathbf{b} \times \mathbf{c}$ macrocell, while the YZ projections include only those having $0 \leqslant x < a$ at $t = 0$. (**a**) and (**b**) for the atoms starting at the O_1 sites at $z = -0{\cdot}16c$. (**c**) and (**d**) for the atoms starting at the O_4 sites at $z = 0$. (**e**) and (**f**) for the atoms starting at the O_1 sites at $z = 0{\cdot}16c$.

4. Discussion

The various applications of the ionic model for YBCO given in this paper show that such a model can explain most of the observed features of the structure and dynamics in the ceramic superconducting materials. We note that the motion of the O_4 oxygen atom perpendicular to the Cu_1–O_4 chain is found to be highly anharmonic (Chaplot 1988, 1989). Possible connections between highly anharmonic dynamics and superconductivity have been suggested (Plakida *et al* 1987; Hardy and Flocken 1988).

We wish to mention here that our earlier predicted phonon dispersion relation (Chaplot 1988) for $\delta = 0$ turned out to be in good agreement with later neutron scattering determination (Reichardt *et al* 1988) of a few low energy branches of the dispersion relation, with only 10% average discrepancy, when detailed comparison is made taking account of the observed polarization of phonons.

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