

Atomic positional disorder, phonon spectrum, and molecular-dynamics simulation of $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$ and $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$

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(Received 22 August 1991)

The nature of the atomic positional disorder in the high-temperature superconducting ceramic oxides $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$ (Tl 2:1:2:2) and $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ (Tl 2:2:2:3) is studied with the help of an ionic-type interatomic potential and molecular-dynamics computer simulations. The pair distribution function and the phonon spectrum are calculated using this model and compared with results of neutron-scattering experiments on Tl 2:1:2:2. Calculated results on the partial pair distribution function, partial phonon density of states, mean square atomic vibrational amplitudes, and lattice specific heat are also presented.

INTRODUCTION

The phonon mechanism of high-temperature superconductivity in the ceramic oxides continues to be a subject of intense discussion. In this context a detailed understanding of the lattice dynamics and crystal structure is necessary in view of the possible role of certain special features in these ceramics which are not significant in conventional superconductors, e.g., the long-range nature^{1,2} and anharmonicity^{3,4} of the potential energy and positional disorder^{5,6} of certain atoms.

In this paper we shall be interested in the high- T_c oxides $\text{Tl}_2\text{CaBa}_2\text{Cu}_2\text{O}_8$ (Tl 2:1:2:2, $T_c=107$ K) and $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ (Tl 2:2:2:3, $T_c=125$ K), which display significant positional disorder.^{5,6} In particular, the O(3) oxygens in the thallium plane in the unit cell are not located at their ideal (0.5,0.5,z) positions, but instead are disordered with partial occupancies among sites which are shifted from the ideal positions by about 0.05 nm.^{6,7} This feature presents difficulty in treating the lattice dynamics of this material under the usual Born-von Kármán framework as applied to perfect crystals. Note that the average potential of the O(3) atom has a maximum at its ideal average position which is dynamically unstable, and therefore use of this ideal position in the phonon calculation should lead to imaginary phonon frequencies.

It is observed that in Tl 2:1:2:2 and Tl 2:2:2:3 the Debye-Waller factors^{6,7} of several atoms are significantly larger than that in other "ordered" ceramic oxides such as $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Y 1:2:3). This is important since the phonon energies in the two materials are qualitatively similar. An additional contribution to the Debye-Waller factors must come from possible disorder among the atomic sites which are shifted from their ideal sites in the unit cell. The disorder may be static or even dynamic, but on a time scale large compared with that of phonons. Therefore, in considering phonons, the disorder can be assumed to be static on picosecond time scales.

It is thus clear that the lattice dynamics of materials such as Tl 2:1:2:2 should be dealt with in a framework which includes the atomic positional disorder. We proceed from the phenomenological model of Y 1:2:3

(Ref. 4), which is capable of treating such complexities in the structure. We include displacements from the ideal site and positional disorder by using a supercell containing four O(3) atoms among other atoms. The supercell is conveniently chosen to be the tetragonal unit cell, whereas the primitive cell of the space group $I4/mmm$ is smaller. We obtain an interatomic potential model which produces a minimum-potential-energy structure close to that determined by neutron-diffraction experiments.^{6,7} In particular, small displacements from the ideal sites are obtained for many atoms in the unit cell, as may be expected, consistent with the displacement of O(3) atoms. In the analysis of the diffraction experiments, such small displacements from the ideal sites of atoms other than O(3) are believed to be merged in the refined thermal ellipsoids, which are much larger in Tl 2:1:2:2 than in Y 1:2:3 as noted above.

Kulkarni *et al.*⁸ reported earlier a lattice-dynamical calculation of only the optically active modes at the Brillouin-zone center in Tl 2:1:2:2. However, it is not clear whether that calculation takes account of the positional disorder of atoms and the shifts from their ideal sites. The present work has been briefly reported previously.⁹

INTERATOMIC POTENTIAL FOR Tl 2:1:2:2 AND Tl 2:2:2:3

We choose the same potential function for Tl 2:1:2:2 and Tl 2:2:2:3 as previously used⁴ for Y 1:2:3. In order to have a unified study of the various materials, we also use identical values of the potential parameters to the extent possible. The simple unscreened rigid-ion model^{2,4} gives a good account of many of the structural and dynamical properties of Y 1:2:3, indicating that the relevant intera-

TABLE I. Interatomic potential parameters for Tl 2:1:2:2 and Tl 2:2:2:3.

	Tl	Ca	Ba	Cu	O
Z	1.6	1.2	1.6	1.4	-1.3
R (nm)	0.155	0.180	0.230	0.120	0.174

ionic interactions are substantially ionic in nature. While a detailed discussion is given in Ref. 2, it may be stated here that the model involves adjustable effective ionic charges and short-range potential parameters which are able to mimic the relevant physics, namely, the crystal structural stability and dynamics. A two-body potential function of the following form is used:

$$V_{kk'}(r_{ij}) = \frac{e^2 Z(k)Z(k')}{4\pi\epsilon_0 r_{ij}} + a \exp\left[\frac{-br_{ij}}{R(k)+R(k')}\right] - \frac{w}{r_{ij}^6} - cD \exp\left[\frac{-n(r_{ij}-r_0)^2}{2cr_{ij}}\right]. \quad (1)$$

We summarize from Ref. 4: $e^2/(4\pi\epsilon_0)=144$ eV/nm, $a=1822$ eV, $b=12.364$, r_{ij} is the distance between the two atoms i and j of species k and k' , $w=50\times 10^{-6}$ eV nm⁶, $c=0.5$, $D=1$ eV, $n=80$ nm⁻¹, and $r_0=0.18$ nm. The third term in Eq. (1) is assumed to act only between the oxygen atoms. The fourth term is assumed to act between the copper-oxygen pairs existing in the CuO₂ planes or in the CuO₃ chain networks as in Y 1:2:3. The short-range interaction parameters $R(k)$ and relative values of the charges $Z(k)$ are determined from the requirement of obtaining a stable and reasonable crystal structure. The parameters are suitably scaled to ensure the maximum of the phonon frequencies to be approxi-

TABLE II. Calculated and experimental structure and the mean-square vibrational amplitudes of Tl 2:1:2:2. The experimental data are at 300 K.

	Calculated	Experimental ^a	Experimental ^b	Experimental ^c
a (nm)	0.379	0.3856	0.3856	0.3852
c (nm)	3.059	2.9260	2.9420	2.9210
Fractional coordinates				
Tl x	0.51	0.5	0.5	0.5
y	0.60	0.5	0.5	0.5
z	0.215	0.2125	0.2129	0.2147
Ca x	0.0	0.0	0.0	0.0
y	0.0	0.0	0.0	0.0
z	0.0	0.0	0.0	0.0
Ba x	0.01	0.00	0.00	0.00
y	0.00	0.00	0.00	0.00
z	0.122	0.1210	0.1210	0.1236
Cu x	0.51	0.5	0.5	0.5
y	0.50	0.5	0.5	0.5
z	0.056	0.0551	0.0536	0.0524
O(1) x	0.51	0.5	0.5	0.5
y	0.00	0.0	0.0	0.0
z	0.055	0.0528	0.0526	0.0527
O(2) x	0.51	0.5	0.5	0.5
y	0.49	0.5	0.5	0.5
z	0.152	0.1447	0.1455	0.1488
O(3) x	0.62	0.626	0.603	0.658
y	0.47	0.5	0.5	0.5
z	0.278	0.2806	0.2803	0.2844
Isotropic temperature factors ^d at 300 K, $8\pi^2\langle u^2 \rangle / 3$ (Å ²)				
Tl	2.1	1.8	0.8	4.9
Ca	0.6	1.2	0.0	3.3
Ba	0.6	1.0	0.6	2.7
Cu	0.5	0.4	0.1	3.9
O(1)	0.6	0.6	0.4	2.6
O(2)	1.0	1.2	0.8	1.0
O(3)	2.5	3.8	0.5	1.8

^aReference 6(a).

^bReference 6(b).

^cReference 7.

^dThe thermal parameters given by Hewat *et al.* (Ref. 6) in column 2 may be more accurate as they have included a much larger number of reflections than those given in columns 3 and 4 by others.

mately of the right magnitude. No other dynamical information is utilized to obtain the parameter values. The rigid-ion model imposes charge neutrality on the unit cell.

While ensuring the above criteria, it is found to be possible to use identical parameters for the common atoms among Y 1:2:3, Tl 2:1:2:2, and Tl 2:2:2:3 except for one parameter. Table I gives the values for the thallium systems where only the charge on the Ba atom of 1.6 is chosen slightly different from the value of 1.5 as used for Y 1:2:3.⁴ We believe it would be possible to readjust the charges in Y 1:2:3 to include the slight modification of the Ba charge.

STRUCTURE

The potential as given in Table I produces a minimum for the structure given in Tables II and III for Tl 2:1:2:2 and Tl 2:2:2:3, respectively, which shows good agreement with the observed structure. The shift produced for the O(3) atom from the $(\frac{1}{2}, \frac{1}{2}, z)$ site is about 0.05 nm, which is in excellent agreement with experiments. The calculated shift for the Tl atom is only 0.038 nm. This is slightly larger than what could be easily absorbed in the large Debye-Waller factor in the Rietveld analysis of the experimental data. However, this value is close to the shift of 0.037 nm in magnitude as suggested⁵ on the basis of the experimental pair distribution function. Reference 5, however, suggested these shifts of Tl and O(3) to be along the $\langle 110 \rangle$ direction as opposed to that of O(3) in the $\langle 100 \rangle$ direction as determined from Rietveld analysis⁶ and the present calculation. For all other atoms the

TABLE III. Calculated and experimental structure and vibrational amplitudes of Tl 2:2:2:3. The experimental data are at 13 K.

	Calculated	Experimental ^a
<i>a</i> (nm)	0.378	0.3847
<i>c</i> (nm)	3.737	3.5630
Fractional coordinates		
Tl	(0.51,0.60,0.221)	(0.5,0.5,0.2197)
Ca	(0.00,0.00,0.045)	(0.0,0.0,0.0454)
Ba	(0.01,0.00,0.145)	(0.0,0.0,0.1445)
Cu(2)	(0.50,0.50,0.00)	(0.5,0.5,0.0)
Cu(1)	(0.51,0.50,0.091)	(0.5,0.5,0.0884)
O(4)	(0.50,0.00,0.00)	(0.5,0.0,0.0)
O(1)	(0.51,0.00,0.091)	(0.5,0.0,0.0881)
O(2)	(0.52,0.49,0.169)	(0.5,0.5,0.1650)
O(3)	(0.62,0.47,0.273)	(0.592,0.5,0.2756)
Isotropic temperature factors at 13 K, $8\pi^2\langle u^2 \rangle / 3$ (\AA^2)		
Tl	0.2	0.8
Ca	0.2	0.1
Ba	0.1	0.7
Cu(2)	0.1	0.2
Cu(1)	0.1	0.1
O(4)	0.3	0.4
O(1)	0.3	0.9
O(2)	0.3	1.0
O(3)	0.5	0.2

^aReference 6(b).

shifts from their ideal sites are less than 0.01 nm, which could be absorbed in their Debye-Waller factors.

As discussed earlier, the available experimental Debye-Waller factors need to be treated with caution, particularly in the samples involving significant substitutional disorder. For example, the values given by Cox *et al.*⁶ are quantitatively similar in the three cases which they have studied, namely, Tl 2:1:2:2 at 293 K and Tl 2:2:2:3 at 13 and 150 K, respectively, which means the values may not be indicative of the vibrational amplitudes, but are determined by the disorder. Further, we may note that the experimental temperature factors given in Table II for Tl 2:1:2:2 differ widely, the differences being several times the experimental errors quoted in the original papers. A clearer picture would emerge when neutron-diffraction data become available from good quality single crystals.

PHONON SPECTRUM AND SPECIFIC HEAT

The lattice-dynamical calculations are performed using the current version of the computer program DISPR.¹¹ The calculated phonon density of states and its partial components corresponding to the different atoms and polarizations are given in Figs. 1–3. The latter are used to calculate the vibrational amplitudes of the different atoms as presented in Tables II and III, which are in satisfactory agreement with experiments in view of the earlier discussion.

For comparison with the phonon spectrum which may be observed¹² by neutron inelastic scattering, we have given in Fig. 4 the neutron-weighted phonon density of states, which is the weighted sum of the partial density of states for the different atoms. The neutron weights $4\pi b^2/m$ (b =scattering length and m =mass) for the atoms Tl, Ca, Ba, Cu, and O are 4.8, 7.8, 2.5, 11.8, and

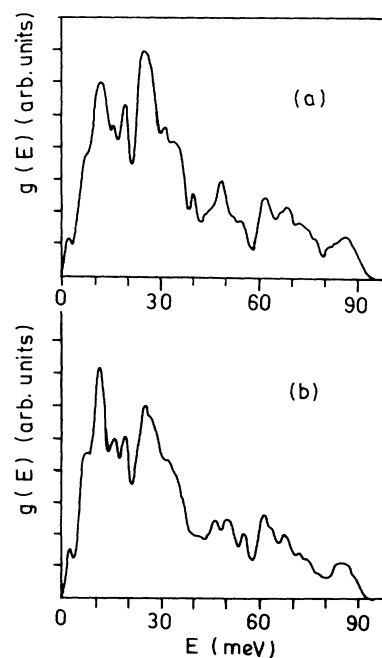


FIG. 1. Calculated phonon density of states in (a) Tl 2:2:2:3 and (b) Tl 2:1:2:2.

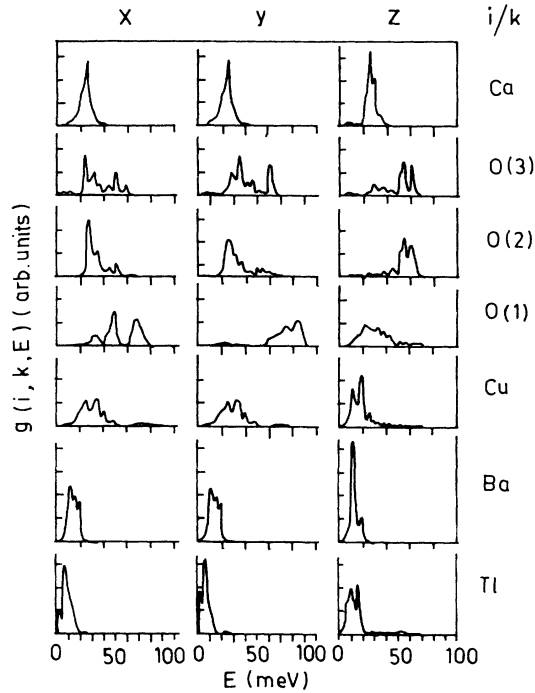


FIG. 2. Calculated partial components $g(i, k, E)$ of the phonon density of states in Tl 2:1:2:2 corresponding to the different atoms k and polarization along the different directions i .

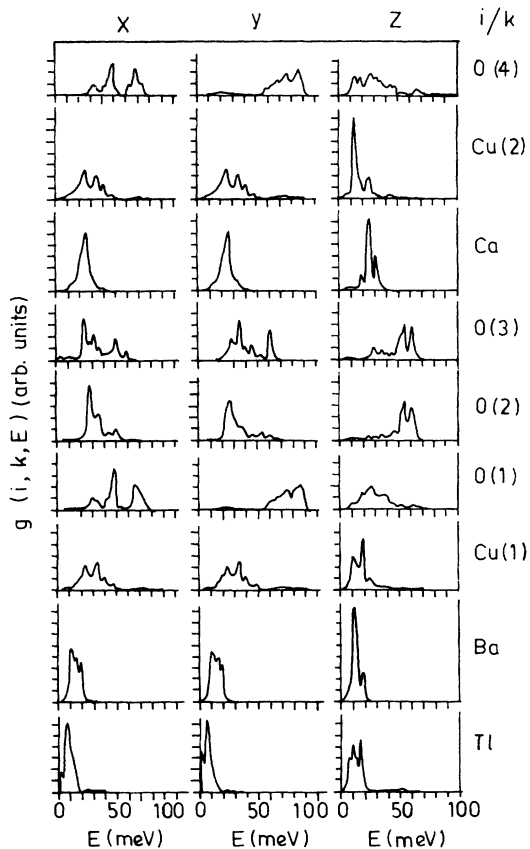


FIG. 3. Same as in Fig. 2 for Tl 2:2:2:3.

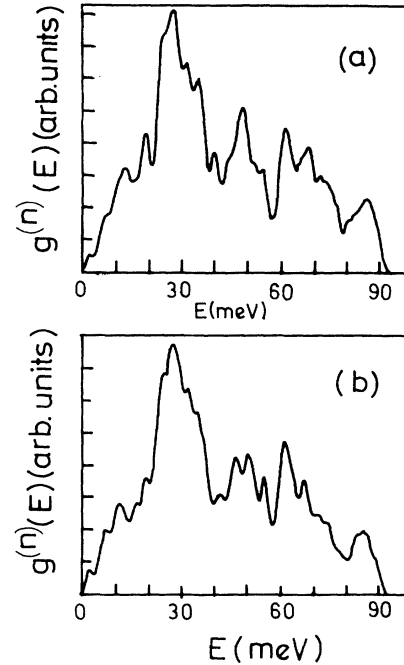


FIG. 4. Calculated neutron-weighted phonon density of states in (a) Tl 2:2:2:3 and (b) Tl 2:1:2:2.

26.5 (in units of 10^{-2} barn/amu), respectively, the largest being for the oxygen atoms. Figure 5 shows good agreement between the neutron experiment^{12(a)} and calculation for Tl 2:1:2:2. An experimental phonon spectrum of Tl 2:2:2:3 is not available to our knowledge.

It is worthwhile to make a comparison with the phonon spectrum in Y 1:2:3. In Fig. 6 we reproduce the calculated⁴ and experimental¹³ spectra, which are in good agreement with each other. Comparing Figs. 4(b), 5, and

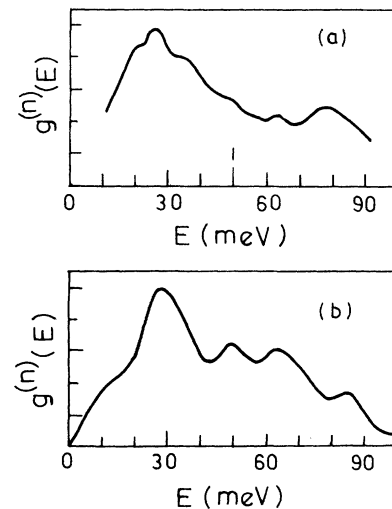


FIG. 5. Comparison of the (a) experimental [Ref. 12(a)] and (b) calculated phonon spectra as weighted for neutron scattering for Tl 2:1:2:2. Both spectra include multiphonon scattering. The experimental energy resolution varies from 6 to 28 meV for energies of 10–90 meV, respectively. The calculated spectrum is obtained from Fig. 4(b) by Gaussian smoothing of 6 meV and including the multiphonon scattering [after Ref. 12(a)].

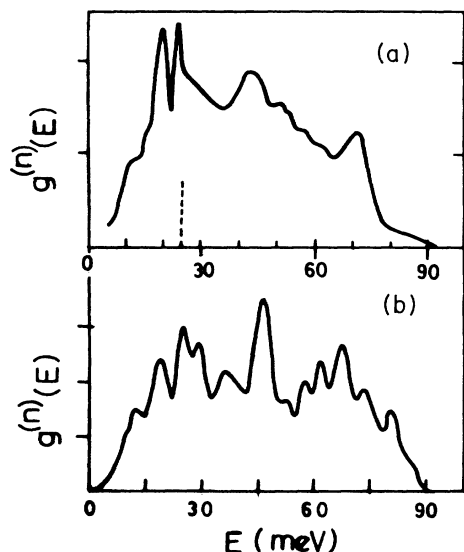


FIG. 6. Comparison of the (a) experimental (Ref. 13) and (b) calculated phonon spectra as weighted for neutron scattering for Y 1:2:3 (Ref. 4). The experimental energy resolution was estimated to be 3 and 10 meV for energies below and above 25 meV, respectively.

6, we may note that, in both experiment and calculation, the phonon density of states is much enhanced at low energies in Tl 2:1:2:2 compared with that in Y 1:2:3 and is reduced at high energies. A similar conclusion was also reached earlier^{12(b)} on the basis of the neutron experiments in the two materials. We believe these changes are largely due to the increased positional disorder in the thallium systems as compared to Y 1:2:3, leading to multiple-minima potentials which are rather soft and

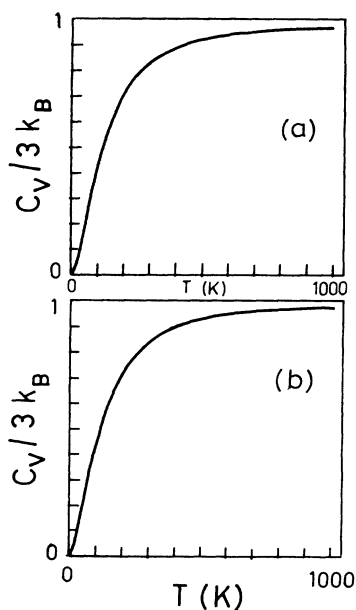


FIG. 7. Calculated lattice contribution to the specific heat in (a) Tl 2:2:2:3 and (b) Tl 2:1:2:2. The specific heat approaches the Dulong-Pettit limit of $3k_B$ per atom (k_B is Boltzmann constant), which is equivalent to 425.3 and 382.3 mJ/(g K) for Tl 2:2:2:3 and Tl 2:1:2:2, respectively.

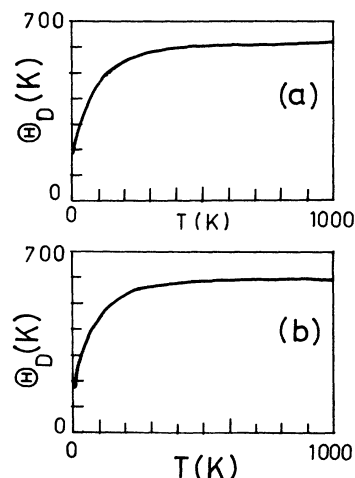


FIG. 8. Calculated Debye temperature in (a) Tl 2:2:2:3 and (b) Tl 2:1:2:2.

anharmonic. Consequently, the energy of some of the oxygen vibrational modes is lowered, resulting in the observed changes in the density of states.

We also note that the lattice-dynamical calculations as presented here are based on the harmonic approximation and therefore strictly correspond to the zero-temperature case. Further, since anharmonic vibrational behavior is expected on the basis of the interatomic potential and minimum-energy structure, renormalization of phonon energies would occur as the temperature is raised. The extent of anharmonicity is comparatively less in Y 1:2:3 than in the thallium systems.

The calculated phonon density of states is used to obtain the lattice contribution to the specific heat as a func-

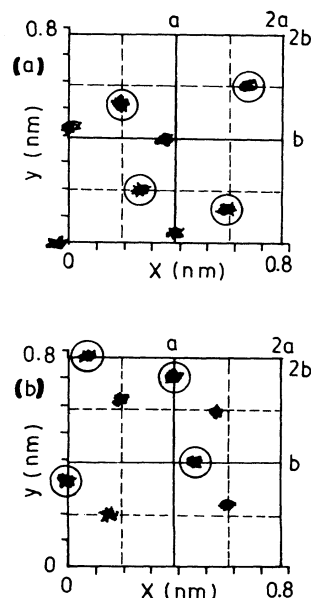


FIG. 9. XY projections of the coordinates of the Tl and O(3) (marked by circles) atoms in the Tl-O(3) planes at (a) $z=0.28$ and (b) $z=0.22$, in Tl 2:1:2:2 for a duration of 10 psec in a molecular-dynamics simulation.

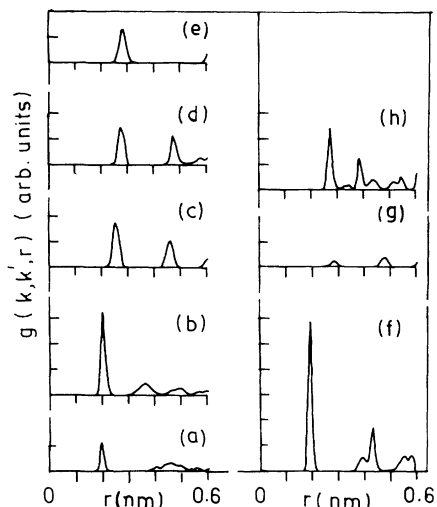


FIG. 10. Calculated partial components $g(k, k', r)$ of the pair distribution function for certain atomic pairs (k, k') in Tl 2:1:2:2. The atoms k, k' are (a) Tl, O(2), (b) Tl, O(3), (c) Ca, O(1), (d) Ba, O(1), (e) Ba, O(2), (f) Cu, O(1), (g) Cu, O(2), (h) O(1), O(1), respectively.

tion of temperature, which is plotted in Fig. 7 for Tl 2:1:2:2 and Tl 2:2:2:3. The lattice specific heat at each temperature may be related to an effective Debye temperature. Figure 8 shows the considerable variation of the Debye temperature as a function of temperature, which essentially indicates the inadequacy of the Debye model.

MOLECULAR - DYNAMICS SIMULATION AND PAIR DISTRIBUTION FUNCTION

The static and dynamic correlations between various atoms at a finite temperature are conveniently studied by computer simulation based on the molecular-dynamics technique.¹⁰ In Tl 2:1:2:2 the short-range correlations which arise from the positional disorder and shifts from the ideal sites are of main interest. We have simulated this behavior at 300 K in a simulation run for 20 000 time steps of 0.005 psec on a macrocell made of $2a$, $2b$, and c with periodic boundary conditions (a , b , and c are the tetragonal unit-cell vectors). This macrocell is considered sufficient for studying short-range correlations.

Figure 9 shows the projection of the Tl and O(3) atoms in various Tl-O(3) planes in Tl 2:1:2:2. At the time scale of 100 psec of the simulation run, no atomic jumps are observed between equivalent sites at 300 K. This corresponds to an energy barrier of ≥ 0.2 eV, which is consistent with that calculated from the present potential.

The pair distribution function for various atomic pairs is calculated from the simulation. This result for certain atomic pairs is given in Fig. 10. The calculated neutron-scattering-weighted total pair distribution function is shown in Fig. 11 and compared with the experimental data.⁵ The agreement between the two is quite satisfactory in view of the simplicity of the potential used. However, a detail comparison in Fig. 11 indicates some

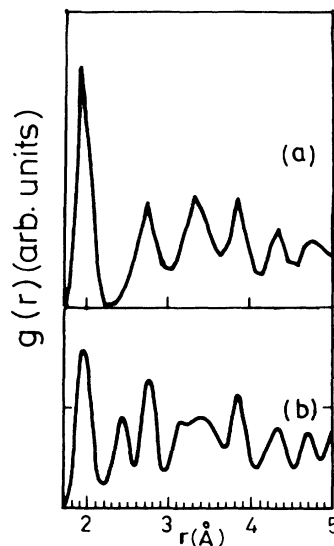


FIG. 11. Neutron-scattering-weighted total pair distribution function in Tl 2:1:2:2. (a) Calculated and (b) experimental (Ref. 5).

discrepancy in the second peak which needs further theoretical and experimental investigation. In fact, the projections in Fig. 9 give an atomic distribution showing the Tl and O(3) shifted along the $\langle 100 \rangle$ axes, which is closer to the crystallographic Rietveld analysis^{6,7} of the neutron-diffraction experiments than the suggestion⁵ of $\langle 110 \rangle$ shifts put forward to explain the pair distribution function observed by neutron diffraction. The magnitude of the shifts observed in the simulation is similar to the result from both Rietveld and pair distribution analyses.

CONCLUSION

From the studies reported in this paper on the thallium systems and in an earlier paper⁴ on the yttrium systems, it appears that fairly simple interatomic potentials can be constructed for rather complex systems such as the ceramic superconductors for a reasonable description of their structure, dynamics, and related thermodynamical properties. The complexity of the structures has, for the time being, restricted us to the use of a simple form of the potential and thus ignore certain features, namely, screening, polarizability, and many-body interactions, which may be important in describing some of the properties. For the yttrium and thallium systems, we have used an essentially common potential function, except for a modification due to the charge balance. It would be desirable to obtain a general interatomic potential which may be used with other ceramic superconductors as well to the extent possible.

ACKNOWLEDGMENT

The author appreciates the encouragement given by Dr. K. R. Rao and Dr. B. A. Dasannacharya.

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