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Calculation of Raman- and infrared-active modes of $Bi_2CaSr_2Cu_2O_8$

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We studied the lattice dynamics of the high-T_c superconductor $Bi_2CaSr_2Cu_2O_8$ in the framework of a shell model which uses short-range overlap and long-range Coulomb potentials. The phonon frequencies and polarization vectors at the Γ point of the Brillouin zone, which are of interest for the interpretation of the infrared and Raman spectra, are presented.

INTRODUCTION

The study of the lattice dynamics of the high-T_c superconductors is of importance, not only for the overall physical characterization of these compounds, but also for an assessment of the role played by the phonons in the superconducting phenomenon. In this paper we report some results of a lattice-dynamical calculation on the new Bi compounds. We concentrate here on the phonons of small wave vectors since they are of particular interest for the experimental Raman and infrared (ir) studies. Our lattice-dynamical approach, which we already applied to $La_{2-x}M_xCuO_4$ (Ref. 1) and $YBa_2Cu_3O_{7-x}$,[2] is based on the use of short-range repulsive potentials and Coulomb potentials in the framework of the shell model (SM). The parameters for these potentials are obtained from the interaction in similar but better known compounds, containing the same ion pairs. In this procedure we derive short-range Born-Mayer potentials for the various ion pairs, from known SM's available for perovskites and metal oxides, and then transfer these potentials as well as the charges for the Coulomb interactions to the new compound. Comparing the structures of $Bi_2CaSr_2Cu_2O_8$ and $YBa_2Cu_3O_7$ (cf. Fig. 1), we see that they contain the same type of Cu-O planes and similar perovskitelike oxygen arrangements. We can, therefore, transfer the Cu-O and O-O potentials directly from our model for $YBa_2Cu_3O_7$. In addition, we have the Ca-O, Sr-O, and Bi-O interactions; for these we start with potentials similar to those for the Y-O and Ba-O interactions in $YBa_2Cu_3O_7$. It should be noted that for the Ca-O interaction very similar potential parameters are obtained from the measured phonon dispersion curves of CaO.[3] These potentials are then slightly modified in order to get stable phonons for $Bi_2CaSr_2Cu_2O_8$ at the high-symmetry points of the Brillouin zone (BZ). The potential parameters so obtained are given in Table I.

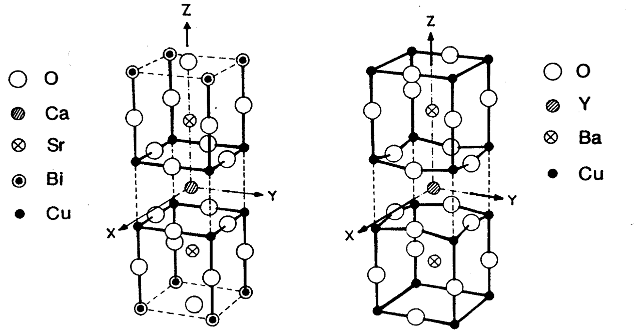

FIG. 1. Comparison of the characteristic elements of the structure of $Bi_2CaSr_2Cu_2O_8$ and $YBa_2Cu_3O_7$.

Screening has not been taken into account in these calculations. The effective Coulomb interactions are of rather short range, so that a dilute gas of free carriers will not affect the vibrational spectrum. Our eigenfrequencies were calculated for small but finite wave vectors; the neglected screening would at most have only a minor effect on the ir modes, while the Raman modes remain completely unaffected. The experimental ir data on $La_{2-x}M_xCuO_4$ and $YBa_2Cu_3O_{7-x}$ show LO-TO splitting, so at least for these compounds there is experimental justification for neglecting screening.

STRUCTURE

Various structures have been proposed for the new Bi compounds.[4-7] These structures all contain more or less the same building blocks, meaning that local environments are very similar, but in slightly different stackings. We have here calculated only *one* structure ($Bi_2CaSr_2Cu_2O_8$), namely, the primitive cell of the structure of Tarascon *et al.*[4] Using this simple structure means that we get the smallest number of Raman and ir modes at Γ. Of course, for a less symmetric structure additional Raman- and ir-active modes may appear (as they are folded to Γ from the boundary of the BZ of the primitive structure). However, we expect that this will lead to only minor changes in the spectrum, because in these extended structures the vibrating subunits are rather separated so

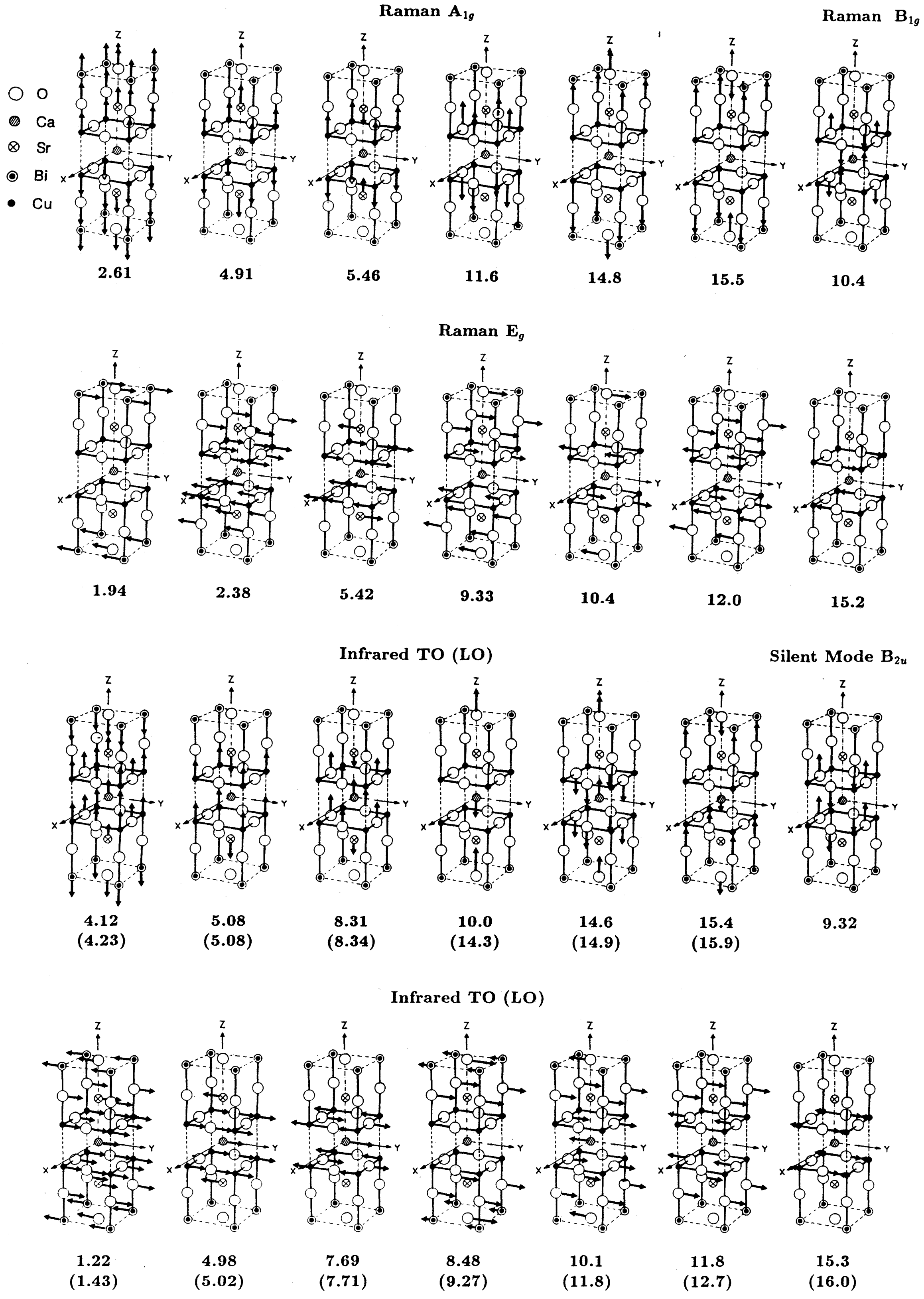

FIG. 2. Phonon frequencies (in THz) and schematic representation of the most important polarization vectors of the optical modes for infinitesimal wave vectors. The values of the LO frequencies are given in parentheses; note that the notation LO and TO refers to the direction of the propagation vector.

TABLE I. Parameters of the model. *a*,*b*: Born-Mayer constants; *Z*, *Y*, and *k*: ionic charge, shell charge, and on-site core-shell force constant of the ion (v_a is the volume of the unit cell).

Interaction	*a* (eV)	*b* (Å^{-1})	Ion	$Z(\lvert e\rvert)$	$Y(\lvert e\rvert)$	$k(e^2/v_a)$
Bi-O	3000	3.00	Bi	2.60	2.42	1117
Sr-O	3010	2.90	Sr	2.35	2.32	212
Ca-O	2513	3.06	Ca	2.00	−2.50	1387
Cu-O	1259	3.50	Cu	2.00	3.22	1281
O-O	1000	3.00	O[a]	−1.99	−2.70	323
			O[b]	−1.99	−2.70	2146
			O[c]	−1.99	−2.70	323 ($k_\parallel$) 2146 ($k_\perp$)

[a] For O in the Cu-O planes.

[b] For O in the Bi-O planes.

[c] For O in the Sr-O planes. (For the O in these planes we assume anisotropic polarizability with force constants $k_\parallel$ parallel to the Cu-O-Bi directions and $k_\perp$ perpendicular to those directions.)

that the zone boundary modes will be practically degenerate with the modes at Γ.

RESULTS

Our results for the Raman and ir-active modes at Γ are summarized in Fig. 2, in which we give the mode displacement pattern in the center of the rectangular (not primitive) cell of the structure of Ref. 4. A first comparison of these results should be made with those of $YBa_2Cu_3O_7$ (Refs. 2 and 8) and of the oxygen-deficient compound $YBa_2Cu_3O_6$.[9] The main structural difference between the three compounds is the structure and composition of the pure Cu plane of $YBa_2Cu_3O_6$, which in $YBa_2Cu_3O_7$ has two additional oxygens forming the Cu-O chains, while in $Bi_2CaSr_2Cu_2O_8$ the corresponding plane contains Bi and O (see Fig. 1). It is, in fact, precisely the structure of this plane which is still very much under discussion. Since the building elements of the structures (except for the abovementioned planes) are so similar, the potentials of all three compounds also have very close similarities. As a result, it is not surprising that the modes involving these planes show strong similarities both in regard to frequencies and polarizations. We also find additional A_{1g} modes in the Bi compound at 2.61 and 15.5 THz. The experimental determination of these particular modes would, therefore, be of interest for a better determination of the short-range Bi-O potentials. A comparison of our results with the Raman data[10,11] shows rather close agreement for the four modes which, according to our calculations, do not involve displacements in the Bi-O planes.

We point out, however, that a comparison of our results with experiments should be done with caution, because the experiments may have been performed on structures which differ in detail from the primitive structure for which these calculations have been performed (see, for example, the Raman data in Ref. 12). Strictly speaking, only experimental and theoretical results for the exact same microscopic structure can be compared in detail. Nevertheless, since different actual structures all contain the same building elements, we expect much of what we present here to be valid for a wide class of Bi compound structures.

SUMMARY

We have been able to develop a lattice dynamical model for $Bi_2CaSr_2Cu_2O_8$. With so little experimental information available, it is obvious that the choice of potential parameters is not unique. However, the ordering of the mode frequencies and the mode displacement pattern at Γ are almost exclusively determined by the local symmetry of the structure and the hierarchy of the interactions, and are relatively insensitive to small parameter changes. On the other hand, the requirement of stable phonons severely restricts the range in parameter space in which the parameters can be varied. Since the balance of forces in these perovskitelike structures is so delicate, minor variations of the parameters will easily cause phonon instabilities. This had the result that calculations which we carried out with different sets of parameters which also give stable dynamics, lead to the same hierarchy of ir and Raman modes, with the same displacement patterns, and frequencies which differed by at most 10%. This statement does not say anything about a comparison with experiment, unless the experiment is performed on the same structure as the calculations.

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