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Calculation of Raman- and infrared-active modes of $Tl_2CaBa_2Cu_2O_8$

A. D. Kulkarni, J. Prade,* and F. W. de Wette
Department of Physics, University of Texas, Austin, Texas 78712-1081

W. Kress
Max-Planck-Institut für Festkörperforschung, Postfach 80 06 65, D-7000 Stuttgart 80, Federal Republic of Germany

U. Schröder
Universität Regensburg, D-8400 Regensburg, Federal Republic of Germany
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We present the frequencies and polarization vectors of the infrared- and Raman-active modes for $Tl_2CaBa_2Cu_2O_8$ (Tl 2:1:2:2). Our calculations are carried out in the framework of shell models, which are based on short-range overlap and long-range Coulomb potentials, as well as ionic polarizabilities. A guiding principle of this work is that the shell models for the different superconducting compounds should be mutually compatible, i.e., the short-range potentials for given ion pairs in equivalent environments should be transferable from one compound to the other. The optical data presented here for Tl 2:1:2:2 are obtained with a model which is applicable not only for six different thallium superconductors, but also for $Bi_2CaSr_2Cu_2O_8$ and $YBa_2Cu_3O_7$. The model for Tl 2:1:2:2 reproduces the measured infrared and Raman data quite well and yields a reliable first approximation for the displacement patterns of the modes at the Γ point. This is far from trivial since a mere force constant fit to the measured eigenvalues may yield rather arbitrary eigenvectors.

This work is part of an ongoing systematic study of the lattice dynamics of the high-temperature superconductors. So far we have reported results for $La_{2-x}M_xCuO_4$,[1] $YBa_2Cu_3O_7$,[2] and $Bi_2CaSr_2Cu_2O_8$ (Bi 2:1:2:2).[3] Our approach is based on the use of long-range Coulomb potentials and short-range repulsive potentials, as well as ionic polarizabilities, in the framework of the shell model. The use of short-range potentials, as opposed to force constants, has important advantages, especially in the case of the high-T_c superconductors: Ordinarily, force constants are determined by least-squares fits to measured phonon dispersion curves, but since force constants are derivatives at lattice positions of otherwise unspecified interaction potentials, the fitting procedure, in general, allows a large degree of flexibility. This problem is exacerbated for the high-T_c superconductors by the fact that only a limited number of infrared and Raman frequencies are available for fitting, while due to the large number of particles in the unit cell, a large number of force constants need to be determined. Since an eigenvalue problem is incompletely defined by the eigenvalues alone, the eigenvectors that are calculated with such a poorly defined force-constant model can be quite arbitrary. This, in our view, renders force-constant models undesirable for these compounds, and a poor choice for uncovering and discussing the similarities and differences between the various high-T_c compounds, and between these and normal compounds. A further guiding principle of our approach is the requirement that the short-range potential of a given ion pair (such as Cu-O) be transferable, to a good approximation, from one compound to the other. For ion pairs with closed-shell electronic configurations, the short-range interactions can be represented by Born-Mayer potentials, which are, to a large extent, independent of the spatial arrangement and the surrounding of the interacting ion pairs. Our previous investigations have shown this to be true for perovskites[4] for which much more complete dynamical information is available.

In the practical implementation of this scheme, our procedure for obtaining the model parameters for a new compound has been to carry over as many short-range potential parameters as possible from the compounds treated earlier. In our starting model for Tl 2:1:2:2 we transferred the Cu-O, O-O, and Ba-O potentials directly from the model for $YBa_2Cu_3O_7$,[2] and the Ca-O potential from the model for Bi 2:1:2:2.[3] This left the problem of determining the Tl-O potential. In order to obtain stable phonon dynamics (explained below), we had to allow for an anisotropic Tl-O potential, i.e., different sets of Born-Mayer parameters for *interplanar* and *intraplanar* Tl-O interactions. The origin of this anisotropy can be understood from the fact that in the structure of Tl 2:1:2:2,[5,6] the interplanar Tl-O distance (2.1 Å) is significantly smaller than the intraplanar distance (2.7 Å). We note that the intraplanar Cu-O distance (1.9 Å) is also significantly smaller than the interplanar Cu-O distance (2.6 Å). However, in this case an anisotropic potential is not necessary since the interplanar Cu-O force constants (calculated from the Born-Mayer parameters in Table I) are almost an order of magnitude smaller than the strongest force constants in the system. Thus, even a moderate anisotropy in the Cu-O interaction would have little effect on the phonon spectrum.

Further, a very important criterion for arriving at a parameter set for a given compound is the requirement of stable phonon dynamics, i.e., real phonon frequencies for

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

Interaction	a (eV)	b (Å^{-1})	Ion	$Z(\|e\|)$	$Y(\|e\|)$	$k(e^2/v_a)$
Tl-O [a]	3000	2.80	Tl	2.70	2.00	1000
Tl-O [b]	3000	3.55	Ba	2.00	2.32	207
Ba-O	3225	2.90	Ca	2.00	−0.50	1357
Ca-O	2513	3.10	Cu	2.00	3.22	1253
Cu-O	1260	3.35	O [c]	−1.93	−2.70	316
O-O	1000	3.00	O [d]	−1.93	−2.70	2100
			O [e]	−1.93	−2.70	316 ($k_\parallel$)
						2100 ($k_\perp$)

[a]For Tl and O in the same plane (intraplanar interaction).
[b]For Tl and O in adjacent planes (interplanar interaction).
[c]For O in the Cu-O planes.
[d]For O in the Tl-O planes.
[e]For O in the Ba-O planes (for the O in these planes we assume anisotropic polarizability with force constants $k_\parallel$ parallel to the Cu-O-Tl directions and $k_\perp$ perpendicular to those directions).

all wave vectors in the Brillouin zone. This criterion usually requires small parameter changes for potentials that had been accepted for a compound treated earlier. In order to have models that are compatible and consistent for all compounds treated so far, we then went back and checked whether the modified potentials remained compatible with the compounds treated earlier. The model presented here for Tl 2:1:2:2 is such a model. Thus, starting from the models for $YBa_2Cu_3O_7$ and Bi 2:1:2:2, we modified them in such a way that the potentials give stable dynamics for these compounds, for Tl 2:1:2:2, as well as for the five additional thallium superconductors $Tl_2Ba_2CuO_6$ (Tl 2:0:2:1), $TlCaBa_2Cu_2O_7$ (Tl 1:1:2:2), $TlCa_2Ba_2Cu_3O_9$ (Tl 1:2:2:3), $Tl_2Ca_2Ba_2Cu_3O_{10}$ (Tl 2:2:2:3), and $TlCa_3Ba_2Cu_4O_{11}$ (Tl 1:3:2:4). The fact that we were able to develop a unified set of potentials for these *eight* structures is confirmation of the viability of our approach to the lattice dynamics of these compounds. It gives us an assurance that the eigenvalues and eigenvectors for these compounds must be very close to the actual ones (apart from effects resulting from screening, which was not considered here). Furthermore, it should be pointed out that the requirement of stable dynamics for this entire series of compounds is extremely demanding and it severely restricts the parameter space. The parameters listed in Table I are obtained by minimizing, within the restricted parameter space, the relative errors between the calculated and measured[7,8] Raman A_{1g} modes for Tl 2:1:2:2. References 9 and 10 also report Raman measurements on Tl 2:1:2:2. However, Ref. 9 reports only three Raman active modes and Ref. 10 reports eight modes—one more than predicted by group theory. Hence, the fit was carried out only to the modes reported in Refs. 7 and 8, which are the most complete and unambiguous Raman measurements available for the thallium superconductors.

Our results for the Raman and infrared (ir) modes calculated using the structure of Ref. 6 are summarized in Fig. 1, in which we give the mode displacement patterns in the center of the rectangular (nonprimitive) cell of the Tl 2:1:2:2 structure. Only the most prominent polarization vectors are indicated. A comparison of the optic modes calculated at Γ with the experimental Raman[7,8] and ir (Ref. 11) data is shown in Table II. The A_{1g} Raman modes with calculated frequencies of 119, 138, and 149 cm^{-1} mainly involve Ba, Tl, and Cu vibrations, respectively (Fig. 1), and are in good agreement with the experiments.[7,8] The 303 and 373 cm^{-1} modes are due to the out-of-phase (B_{1g}) and in-phase (A_{1g}) angle bending vibrations of O in the Cu-O planes, respectively. The B_{1g} mode has been assigned to the Raman band observed at 221 cm^{-1} by Krantz *et al.*,[10] which differs from our prediction by 37%. However, the B_{1g} modes in Tl 1:1:2:2, Tl 1:2:2:3, and Tl 2:2:2:3, predicted by our unified model[12] are within 6, 8, and 11%, respectively, of their measured values.[7,8] In view of this and a similar agreement we find with the other A_{1g} modes,[12] we feel that the B_{1g} mode in Tl 2:1:2:2 needs further experimental investigation. The remaining two Raman modes with calculated frequencies of 439 and 623 cm^{-1} are due to the vibrations of the bridging oxygen and of the oxygen in the Tl-O planes, respectively.

During the course of writing up this work we became aware of the recent ir studies by Renk *et al.*[11] An inspection of Table II shows that the A_{2u} TO modes predicted by our model agree quite well with the experimental ir data. Moreover, Renk *et al.* observe a particularly large oscillator strength at 311 cm^{-1}, which is confirmed by the large TO-LO splitting (355 and 437 cm^{-1}) predicted by our model.

It is shown that for the high-T_c superconductors $YBa_2Cu_3O_7$, $Bi_2CaSr_2Cu_2O_8$, and $Tl_2CaBa_2Cu_2O_8$, quite realistic estimates of the frequencies and displacement patterns of the zone-center phonons can be made on the basis of two-body interaction potentials, taken into account in the framework of a shell model. These potentials remain, to a good approximation, invariant to structural changes and can therefore be transferred from one compound to the other without any, or at most minor modifications. Finally, it should be pointed out that electronic deformations other than dipolar symmetry could very well be in-

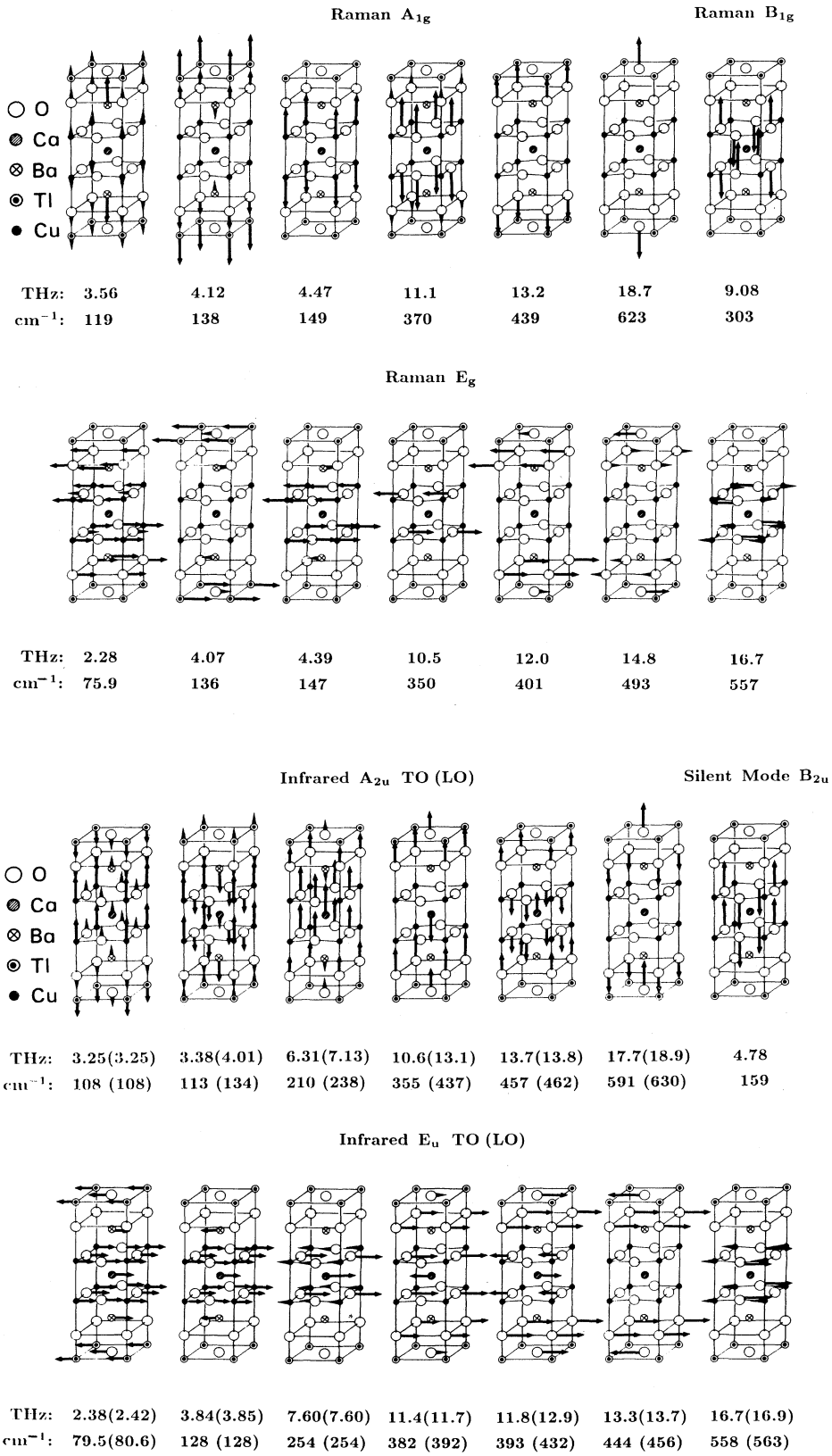

FIG. 1. Polarization diagrams of Raman and ir modes. Long, medium, and short arrows indicate large, intermediate, and small amplitudes, respectively (amplitudes not to scale).

TABLE II. A comparison of the calculated and measured optic modes. Measurements are taken from Refs. 7, 8, and 11.

Raman-active modes (cm^{-1})			Infrared-active modes (cm^{-1})				
This work		Refs. 7 and 8	This work				Ref. 11
			E_u		A_{2u}		
E_g	A_{1g}	A_{1g}	TO	LO	TO	LO	A_{2u}
75.9	119	108	79.5	80.6	108	108	75
136	138	130	128	128	113	134	142
147	149	158	254	254	210	238	222
350	370	407	382	392	355	437	311
401	439	494	393	432	457	462	460
							520
493	623	599	444	456	591	630	565
557	303 [a]		558	563	159 [b]	159 [b]	

[a] B_{1g} mode.
[b] B_{2u} mode (silent).

volved in the lattice vibrations for large wave vectors, and that the charge carriers may cause screening effects for phonons with very small wave vectors. Since the potentials for such deformations are not known at present, the coupling parameters of these deformations can only be obtained from measurements of the dispersion curves throughout the Brillouin zone. In any case, such deformations, if at all present, would lead to a wavelength- and polarization-dependent renormalization of the phonon frequencies at larger wave vectors than shown here. In contrast, screening would affect the TO-LO splitting of the infrared modes.

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*Permanent address: Universität Regensburg, D-8400 Regensburg, Federal Republic of Germany.

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