

Raman Active Phonons in the High- T_c Superconductors: A Global Point of View

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The two most widely studied families of high-temperature superconductors are $TlBa_2Ca_{n-1}Cu_nO_{3+2n}$ called 1-Tl(n) and $Tl_2Ba_2Ca_{n-1}Cu_nO_{4+2n}$ called 2-Tl(n). We consider the structures of each family and show how some of the Raman active phonons are independent of n and some should have certain regularities depending on n . Further, we show which Raman active phonons should be essentially the same in both families of compounds. © 1990 Academic Press, Inc.

Introduction

George Honig has always tried to take a global point of view of problems in solid state science. It is not as though he is afraid of details, he and his many graduate students have determined their share. However, the bottom line of George's thinking is to understand the basic aspects of a subject from a broad point of view. It is with this stimulus that we discuss phonons in the high-temperature superconductors. The high- T_c superconductors have complicated structures by solid state scientists' standards. Yet, by appreciating the components of the various structural families, insight into the structures and lattice vibrations can be gained.

To understand phonons in any complicated structure, it is important to start with the fundamental concept that *a crystal structure is a lattice convoluted with a basis*. Also, for most of the high- T_c materials the

basis is just one formula unit (I). By using just these facts, considerable insight can be obtained.

Structures of 1-Tl(n)

Figures 1a and 1b show the crystal structures of two members of the single Tl layer, high- T_c material. The relations between the shorthand, descriptive abbreviations, and the nominal chemical formulae are given in Table I. This primitive tetragonal structure has space group $P4/mmm - D_{4h}^1$ and one formula unit in the unit cell ($Z = 1$).

For 1-Tl($n = 1$) the important structural components in one unit cell can be thought of as the CuO_2 atoms which make up the Cu–O plane (labeled Cu_p and O_p), the Ba– O_z plane of atoms directly above and below, then the Tl–O plane of atoms (the atoms in the plane are labeled Tl and O_{octa}). Thus, this simplest structure in the 1-Tl(n) family can be thought of as composed of Cu–O

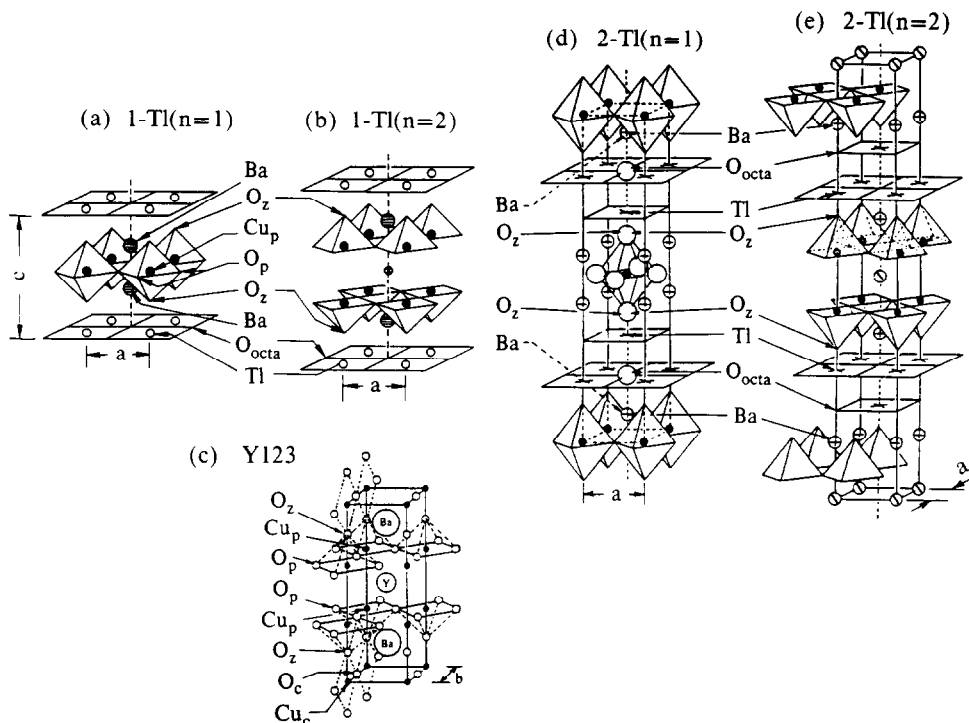


FIG. 1. The structures of some of the crystals discussed in the text. Some of the atoms not in the Cu-O planes are labeled. The figure shows how the environment for these atoms is similar both within and between the 1-Tl(n) and 2-Tl(n) families of structures. Note that Raman active modes indicated with atom labels Tl and O_{octa} in the 2-Tl(n) crystals have no counterparts in the 1-Tl(n) family.

planes separated by a Ba-O plane, then a Tl-O plane, followed by another Ba-O plane, before one returns to a Cu-O plane. We refer to these three planes as "isolation planes" because they isolate the Cu-O planes from each other. Since the electrical conductivity is associated with the Cu-O planes, the isolation planes have only a secondary role as far as superconductivity is concerned.

For 1-Tl($n = 2$) the structure follows easily from that of 1-Tl($n = 1$). Starting with the latter, another Cu-O plane is inserted so that there are two immediately adjacent Cu-O planes ($\sim 3.2 \text{ \AA}$ apart) with a sparsely occupied Ca-atom plane between them (Fig. 1b). The isolation planes remain the same.

For 1-Tl($n = 3$), not shown, the same

procedure is continued. Namely, starting with 1-Tl($n = 2$), another immediately adjacent Cu-O plane is inserted between the other two with another sparsely occupied Ca plane. The isolation planes remain the same. Of course, this is consistent with the general formula for 1-Tl(n), namely $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{4+2n}$. To go from n to $n + 1$, only $\text{CuO}_2 + \text{Ca}$ are added, which results in an additional Cu-O plane plus a sparsely occupied Ca plane.

Phonons in 1-Tl(n)

We consider only the Raman active phonons with motion along the c axis, that is, only the A_{1g} and B_{1g} modes. In the high- T_c materials, generally only these modes have

TABLE I
A LIST OF THE HIGH-TEMPERATURE
SUPERCONDUCTORS DISCUSSED IN THIS PAPER
USING THE IDEAL CHEMICAL FORMULA

Formula	T_c (K)	n	Notations	
(a)				
TlBa ₂ CuO ₅	0–50	1	1-Tl($n = 1$)	Tl1201
TlBa ₂ CaCu ₂ O ₇	80	2	1-Tl($n = 2$)	Tl1212
TlBa ₂ Ca ₂ Cu ₃ O ₉	110	3	1-Tl($n = 3$)	Tl1223
TlBa ₂ Ca ₃ Cu ₄ O ₁₁	122	4	1-Tl($n = 4$)	Tl1234
YBa ₂ Cu ₃ O ₇	92	2	Y123	YBCO
(b)				
Tl ₂ Ba ₂ CuO ₆	0–80	1	2-Tl($n = 1$)	Tl2201
Tl ₂ Ba ₂ CaCu ₂ O ₈	108	2	2-Tl($n = 2$)	Tl2212
Tl ₂ Ba ₂ Ca ₂ Cu ₃ O ₁₀	125	3	2-Tl($n = 3$)	Tl2223
(La _{2-x} Sr _x)CuO ₄	38	1	La($n = 1$)	214

Note. For each material we list the range of critical temperatures reported (T_c), and the number of immediately adjacent Cu–O planes (n). Then, typical notations are given, but we use only the first one listed. (a) These materials have a primitive tetragonal structure, space group $P4/mmm(D_{4h})$. (b) These materials have a body-centered tetragonal (bct) structure, space group $I4/mmm(D_{4h}^*)$.

been observed. Modes with motion perpendicular to the c axis transform as the E_g irreducible representation, and are much weaker.

In considering the phonons, or other properties of these materials, parts of the basis are independent of n (the isolation planes), and parts of the basis vary in a simple manner with n . For 1-Tl(n), the Raman active modes are listed in Table IIa. The table is broken down so that the results from different structural components can be shown separately. Independent of n , $2A_{1g}$ modes are expected arising from the two Ba and two O_z atoms in the two Ba–O planes per unit cell. The one Tl and one O_{octa} atoms per cell, in the Tl–O plane, cannot contribute to the Raman active modes. For 1-Tl($n = 1$) the atoms in the Cu–O plane are at centers of symmetry, and therefore cannot contribute to Raman active phonons. Thus, for 1-Tl($n = 1$) there are only $2A_{1g}$ Raman

TABLE II
THE RAMAN ALLOWED MODES, FOR VIBRATIONS
ALONG THE c AXIS, FOR 1-Tl(n)
AND 2-Tl(n) CRYSTALS

	(a)	1-Tl(1)	1-Tl(2)	1-Tl(3)
Isolation planes		$2A_{1g}$	$2A_{1g}$	$2A_{1g}$
Cu–O planes		—	$2A_{1g} + B_{1g}$	$2A_{1g} + B_{1g}$
Ca planes		—	—	A_{1g}
(b)		2-Tl(1)	2-Tl(2)	2-Tl(3)
Isolation planes		$4A_{1g}$	$4A_{1g}$	$4A_{1g}$
Cu–O planes		—	$2A_{1g} + B_{1g}$	$2A_{1g} + B_{1g}$
Ca planes		—	—	A_{1g}

Note. The modes are separated according to their origin, namely those arising from the atoms in the isolation planes between the n Cu–O planes, those arising from the atoms in the n Cu–O planes, and those arising from the Ca planes that are between the immediately adjacent n Cu–O planes.

allowed phonons (for motion parallel to the c axis), and they arise from atoms in the isolation planes.

For 1-Tl($n = 2$) the atoms in the Cu–O planes are now off the centers of symmetry and contribute $2A_{1g} + B_{1g}$ Raman active modes. Besides these modes, there still are the $2A_{1g}$ modes from the Ba and O_z atoms in the isolation planes. These results are listed in Table IIa.

In going to 1-Tl($n = 3$) the additional atoms in the Cu–O plane are again at centers of symmetry, hence do not contribute to Raman active modes; however, the two Ca atoms now contribute an A_{1g} mode. Of course, the two Cu–O planes off the centers of symmetry still contribute $2A_{1g} + B_{1g}$ modes and $2A_{1g}$ modes still come from the isolation planes. All of these modes for 1-Tl($n = 3$) are listed in Table IIa.

Y123 (Table I) is an interesting special case of 1-Tl($n = 2$). In order to go from 1-Tl($n = 2$) to Y123, the Ca is replaced by Y, and the Tl by Cu and called Cu_c since it is on the chain, and O_{octa} is moved from a position equidistant from four Tl atoms to a position equidistant from just two Cu_c atoms, and so it forms a chain along the b axis. This latter position for O_c causes Y123 to be orthorhombic instead of tetragonal. What is surprising from a phonon point of view is that all of the atoms that are replaced and the new O atom positions are all at centers of inversion. Hence, *the Raman active phonons in 1-Tl($n = 2$) and Y123 are the same, $4A_{1g} + B_{1g}$* as listed in Table IIa, and should have similar eigenvectors since the environments of all of the atoms that move are essentially the same.

Structures of 2-Tl(n)

The situation for 2-Tl(n) is similar to that for 1-Tl(n) except in 2-Tl(n) the basis contains two more atoms (I). These are Tl and O_{octa} atoms which cause 2-Tl(n) to have two Tl-O planes per primitive unit cell, as can be seen in Figs. 1d and 1e. In 2-Tl(n), independent of n , the ordered sequence of isolation planes consists of a Ba-O, a Tl-O, another Tl-O, and another Ba-O plane. Independent of n , these eight atoms in the isolation planes are the same, and have the same environment. Remember 2-Tl(n) has a body-centered tetragonal structure, space group $I4/mmm - D_{4h}^{17}$, thus there are two lattice points (and two complete bases) in the conventional unit cells (I) shown in Figs. 1d and 1e. However, in the primitive unit cell there is only one basis, one formula unit ($Z = 1$) for this material, and hence the situation is just the same as for 1-Tl(n).

Phonons in 2-Tl(n)

For 2-Tl($n = 1$) the 2Tl and $2O_{octa}$ atoms are not at centers of symmetry and contrib-

ute two more A_{1g} modes than we have in 1-Tl($n = 1$). Consider the simplest case in this family of structures, namely 2-Tl($n = 1$). For 2-Tl($n = 1$), the atoms in the isolation planes (2Tl-O and 2Ba-O planes per primitive unit cell) contribute $4A_{1g}$ modes as listed in Table IIb. For 2-Tl($n = 1$) the atoms on the Cu-O planes are at centers of inversion and hence do not move in Raman active modes. Also, for this crystal there are no Ca atoms so there are only $4A_{1g}$ Raman active modes expected (Table IIb).

In proceeding from 2-Tl($n = 1$) to the other members of this family with $n \geq 2$, the situation is identical to that found in the 1-Tl(n) family. This result occurs because *in both families of crystals the isolation planes are independent of n* . As n increases by one, the additional atoms are an additional Cu-O plane (Cu + 2O atoms per primitive unit cell) and an additional Ca atom. Thus, for both the 1-Tl(n) and 2-Tl(n) families, this part of the basis is the same, contributing the same modes. These results can be seen in Table II.

Mode regularities

It is clear from the discussion that we expect a great deal of regularity to be found among the Raman active frequencies and eigenvectors in either of the 1-Tl(n) or 2-Tl(n) families. Also, certain of the 1-Tl(n) modes should be similar to those in 2-Tl(n). Let us explore this point.

1-Tl($n = 1$). For 1-Tl($n = 1$) there are $2A_{1g}$ modes (Table IIa) involving Ba and O_z vibrations along the c axis. Since the masses are so different, we expect a low frequency mode involving mostly Ba motion and a high frequency mode involving mostly O_z motion. However, note that for all of the 1-Tl(n) crystals these same modes, involving the same atoms, occur (Table IIa). Furthermore, the nearest neighbors and general environment for the Ba and O_z atoms is the same throughout the 1-Tl(n) family (Figs. 1a

and 1b). Hence we expect that these same $2A_{1g}$ modes, which occur for all 1-Tl(n) crystals, should have about the same frequencies and eigenvectors. Similarly, for $n \geq 2$, the $2A_{1g} + B_{1g}$ modes come from motion of atoms in the Cu–O plane and this type of motion is the same throughout the 1-Tl(n) family.

2-Tl(n). For 2-Tl(n) the same type of results occur. The basis consists of more atoms from the isolating planes, which yields $4A_{1g}$ modes (Table 2b). However, just as in the 1-Tl(n) materials, the nearest neighbors and general environment for all the atoms in the isolation planes is the same throughout the 2-Tl(n) family. Hence, we also expect that these same $4A_{1g}$ modes, which occur for all 2-Tl(n) crystals, should have about the same frequencies and eigenvectors. For $n \geq 2$, similar statements apply for the modes from the Cu–O planes and Ca planes.

Comparison of 1-Tl(n) and 2-Tl(n). Comparison is intriguing (i.e., between the two families of materials with different space groups). Consider the simplest case, the $2A_{1g}$ phonons in 1-Tl($n = 1$) which are due to motion of the Ba and O_z atoms in the isolation planes, as discussed. Note that in all of the 2-Tl(n) materials these same two atoms occur and have the same nearest neighbors and general environment. Hence, phonons with similar frequencies and eigenvectors should be expected throughout *both* families of crystals. A similar statement applies to phonons due to atoms in the Cu–O planes and Ca planes. On the other hand, 2-Tl(n) materials have $2A_{1g}$ modes due to motion of the very heavy Tl atoms and the

very strongly bonded O_{octa} atoms. Probably, phonons predominantly involving motion of these atoms will be the lowest and highest frequency modes of the entire spectrum for 2-Tl(n). These types of modes should not be expected to be observed in 1-Tl(n), but only in 2-Tl(n) crystals.

Comparison with Experiment

From the structural and symmetry analysis of the 1-Tl(n) and 2-Tl(n) families of materials, we have predicted certain regularities for phonon modes for atomic motion along the c axis. This sort of approach could be taken for other phonon modes and possibly other properties. For the A_{1g} and B_{1g} phonons, a great deal of Raman data has been accumulated and the details of the comparison between these ideas and experiment has been considered (2, 3). We refer the reader to these papers for detailed comparison of the phonon frequencies. In these papers (2,3) the regularities that have been discussed do occur in these materials. Thus, the structural and symmetry approaches discussed here indeed have merit even for the complicated structures encountered in the high- T_c materials.

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