

# Raman scattering of light in superconducting $Tl_m Ba_2 Ca_{n-1} Cu_n O_{2(n+1)+m}$ single crystals

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Spectra of the Raman scattering of light by phonons were determined for single crystals of high-temperature superconductors  $Tl_2 Ba_2 CuO_{6-x}$ ,  $Tl_2 Ba_2 CaCu_2 O_{8-x}$ , and  $TlBa_2 CaCu_2 O_{7-x}$  at temperatures from 10 to 300 K. All the recorded modes had the  $A_{1g}$  symmetry. There were no anomalies in the temperature dependences of the frequencies of the phonon modes and the Raman linewidths exhibited no anomalies. A group-theoretic analysis of the phonon mode symmetry at the center of the Brillouin zone was carried out for  $Tl_m Ba_2 Ca_{n-1} Cu_n O_{2(n+1)+m}$  structures with  $m = 1, n = 2$  or  $3$  and  $m = 2, n = 1-3$ . The observed Raman lines were interpreted. The reasons for the absence of the  $B_{1g}$  modes in crystals with two copper–oxygen layers were considered. The asymmetric profiles of some of the Raman lines were attributed to the electron–phonon interaction.

## 1. INTRODUCTION

The discovery of superconductors based on bismuth<sup>1</sup> and thallium,<sup>2</sup> which often have a higher temperature  $T_c$  of the transition to the superconducting state than  $YBa_2 Cu_3 O_{7-x}$  compounds, has stimulated extensive studies of these materials. One of the most important tasks is to establish common features and differences between all the families of high-temperature superconductors, so as to identify the main parameters ensuring the high values of  $T_c$  exhibited by these compounds.

Since the role of phonons in the establishment of high values of  $T_c$  for these superconductors has been ignored so far, it would be particularly desirable to tackle the problems of the similarities and differences between the phonon spectra.

We investigated this aspect using the Raman scattering of light which enabled us to investigate phonons at the point  $\Gamma$  of the Brillouin zone. This investigation was a continuation of earlier work on the Raman scattering of light by phonons in  $YBa_2 Cu_3 O_{7-x}$  (Refs. 3–5) and  $La_2 CuO_4$  (Ref. 6) compounds.

## 2. EXPERIMENTAL METHOD

The Raman scattering spectra were recorded for different faces of single crystals in the backscattering geometry at temperatures from 10 K to the room value. A triple multi-channel spectrometer with a microattachment, which made it possible to focus laser ( $\lambda = 4880 \text{ \AA}$ ) radiation to form a spot of  $\sim 3 \mu\text{m}$  size, was used in these measurements. Heating of the excited region was avoided by limiting the laser radiation power to a few milliwatts. A high spatial resolution made it possible to determine the homogeneity of a sample and to select single-phase samples. Low-temperature measurements were carried out in an optical cryostat where temperatures down to 10 K could be reached. Temperatures were measured to within  $\pm 5 \text{ K}$ .

Single crystals of  $Tl_m Ba_2 Ca_{n-1} Cu_n O_{2(n+1)+m}$  were grown by cooling stoichiometric melts in Alundum capsules. The cooling rates were 5, 150, and 300 K/h in the temperature ranges 1225–975, 975–875, and 675–300 K, re-

spectively. Oxygen was blown through the capsules during growth. Single crystals in the form of rectangular plates with a specularly reflecting basal plane and dimensions up to  $3 \times 3 \times 0.3 \text{ mm}$  were extracted from cavities in a crystallized ingot. The volume of the cavities reached  $1 \text{ cm}^3$ . This method made it possible to prepare practically homogeneous samples of three compositions:  $TlBa_2 CaCu_2 O_{7-x}$  (Tl-1212),  $Tl_2 Ba_2 CuO_{6-x}$  (Tl-2201), and  $Tl_2 Ba_2 CaCu_2 O_{8-x}$  (Tl-2212). The crystal symmetry of these samples was checked by x-ray diffraction. It was found that Tl-1212 crystals had the primitive tetragonal structure  $D_{4h}^1$  ( $P4/mmm$ ) with the lattice parameters  $a = 3.855 \text{ \AA}$  and  $c = 12.711 \text{ \AA}$ , whereas Tl-2201 and Tl-2212 crystals had the body-centered tetragonal structure  $D_{4h}^{17}$  ( $I4/mmm$ ) with  $a = 3.859 \text{ \AA}$ ,  $c = 23.152 \text{ \AA}$  and  $a = 3.856 \text{ \AA}$ ,  $c = 29.340 \text{ \AA}$ , respectively. The transition to the superconducting state in Tl-2201, Tl-1212, and Tl-2212 samples occurred at  $T_c = 30, 70$ , and  $110 \text{ K}$ , respectively.

## 3. SYMMETRY OF PHONON MODES IN $Tl_m Ba_2 Ca_{n-1} Cu_n O_{2(n+1)+m}$

Two series of superconducting phases have been investigated most so far in the  $Tl_m Ba_2 Ca_{n-1} Cu_n O_{2(n+1)+m}$  system:  $TlBa_2 Ca_{n-1} Cu_n O_{2n+3}$  [Tl-12( $n-1$ ) $n$ ] and  $Tl_2 Ba_2 Ca_{n-1} Cu_n O_{2n+4}$  [Tl-22( $n-1$ ) $n$ ], differing in respect of the spatial symmetry of the lattice. Crystals of  $Tl_2 Ba_2 Ca_{n-1} Cu_n O_{2n+4}$  have the body-centered tetragonal structure  $D_{4h}^{17}$  (Refs. 7–9) with two formula units per unit cell (Fig. 1). The primitive cell of these crystals is half that and contains only one formula unit. Crystals of  $TlBa_2 Ca_{n-1} Cu_n O_{2n+3}$  have the primitive tetragonal structure  $D_{4h}^1$  (Refs. 9–11) with one formula unit per cell (Fig. 1). Within each row of the structure we can distinguish  $n$  copper–oxygen layers separated by calcium layers. It is clear from Fig. 1 that the main difference between Tl-22( $n-1$ ) $n$  and Tl-12( $n-1$ ) $n$  structures is the number of intercalated Tl–O layers: there are two such layers in the  $D_{4h}^{17}$  structure and one in  $D_{4h}^1$ . In both structures the Ba ions are located above and below the outer  $CuO_2$  layers in a nine-coordination environment of oxygen ions. The Tl ion in either struc-

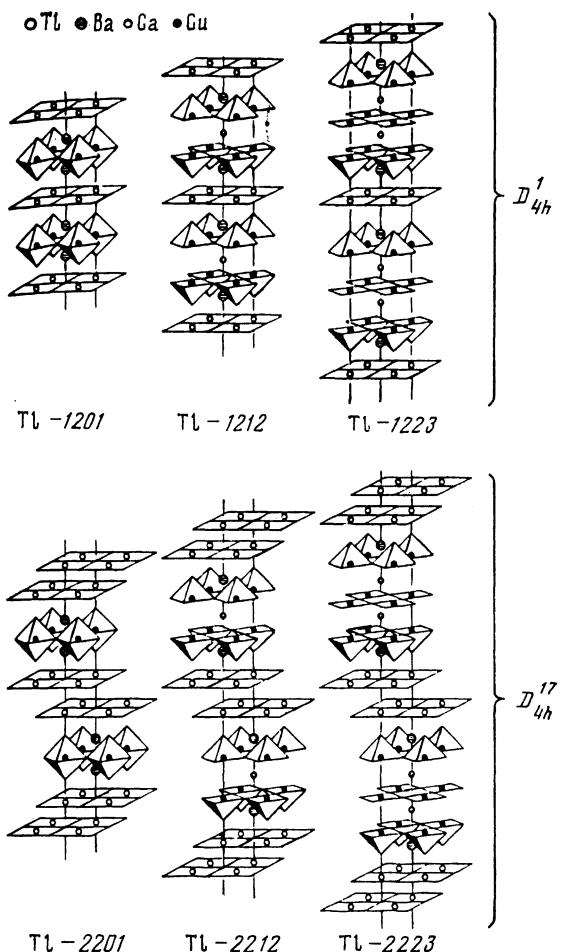


FIG. 1. Unit cells of  $Tl_mBa_2Ca_{n-1}Cu_nO_{2(n+1)+m}$  compounds.

ture is surrounded by six oxygen ions forming a distorted octahedron.

The number of the phonon modes in a lattice is governed by the number of atoms in a primitive cell, so that in the case of Tl-base semiconductors with the  $D_{4h}^1$  or  $D_{4h}^{17}$  structures it is equal to triple the number of atoms in the formula unit. Since the structures are centrosymmetric, only the even (g-type) modes are Raman-active. A group-theoretic analysis shows that only the ions with the positional symmetry  $C_{4v}$  or  $C_{2v}$  contribute to the Raman-active vibrations. Each pair of ions with the positional symmetry  $C_{4v}$  gives rise to one  $A_{1g}$  vibration and one  $E_g$  vibration (doubly degenerate), whereas two pairs of ions with the  $C_{2v}$  positional symmetry give rise to two vibrations ( $A_{1g} + B_{1g}$ ) and one doubly degenerate  $E_g$  vibration. The vibrations of ions with the positional symmetry  $D_{2h}$  or  $D_{4h}$  are not manifested in the Raman spectra because of the alternative forbiddensness rule. The combined expansions into irreducible representations of the  $Tl-m2(n-1)n$  structures are listed in Table I. The vectors of the normal vibrations of the ions corresponding to the  $A_{1g}$ ,  $B_{1g}$ , and  $E_g$  modes in  $Tl_mBa_2Ca_{n-1}Cu_nO_{2(n+1)+m}$ , are analogous to those exhibited by  $YBa_2Cu_3O_{7-x}$ .

The structures with the  $D_{4h}^{17}$  symmetry, like those with the  $D_{4h}^1$  symmetry, have  $A_{1g}$  and  $B_{1g}$  vibrations along the Z

axis, whereas the  $E_g$  vibrations are in the  $XY$  plane. The  $B_{1g}$  vibrations appear only in the structures with a number  $n > 1$  of copper–oxygen layers and they correspond to antiphase vibrations of the oxygen atoms in these planes, whereas in-phase vibrations of oxygen atoms in these planes correspond to the  $A_{1g}$  vibrations. In spite of the fact that the vibrations of ions in the  $A_{1g}$  modes occur only along the Z axis, these vibrations should be active not only in the ZZ polarizations, but also in the XX and YY polarizations, and the XX and YY spectra are identical in view of the tetragonal symmetry of the crystals, so that the tensor of the totally symmetric Raman component is

$$\begin{pmatrix} a & 0 & 0 \\ 0 & a & 0 \\ 0 & 0 & b \end{pmatrix}.$$

The ratios of the intensities of the  $A_{1g}$  vibrations of the ions in the ZZ and XX spectra depend on the electron configuration and are different for different ions.

The investigated set of Tl-1212, Tl-2212, and Tl-2201 crystals allowed us to follow the changes in the phonon spectrum both due to a change in the number of copper–oxygen layers and due to a change in the number of the intercalated Tl–O layers.

#### 4. RAMAN SPECTRA OF Tl-1212, Tl-2201, and Tl-2212 CRYSTALS AT ROOM TEMPERATURE

The room-temperature Raman spectra of all the investigated single crystals are plotted in Figs. 2–4. The number of well-resolved lines in the polarized Raman spectra was four for Tl-1212 and Tl-2201 and six for Tl-2212. The frequencies of the lines were 116, 146, 404, and 520  $\text{cm}^{-1}$  for Tl-1212 (Fig. 2), 122, 167, 495, and 612  $\text{cm}^{-1}$  for Tl-2201 (Fig. 3), and 109, 132, 158, 410, 485, and 600  $\text{cm}^{-1}$  for Tl-2212 (Fig. 4). Scanning of the surface of a sample with a laser beam revealed a slight (within 3–4  $\text{cm}^{-1}$ ) change in the line frequencies. The integral intensity of the lines along the ZZ direction was considerably higher than for the XX polarization and this was true of all these single crystals. There were also differences between the background in the spectra with the XX and ZZ polarizations. All the lines listed above were due to the totally symmetric  $A_{1g}$  vibrations.

A group-theoretic analysis indicated that all the Tl-1212, Tl-2212, and Tl-2201 crystals investigated should exhibit a large number of vibrations allowed in the depolarized Raman spectra. This was particularly true of the  $E_g$  mode, which should appear in the ZX(ZY) polarizations, and the  $B_{1g}$  mode allowed in the X'Y' polarization. However, we were unable to record experimentally the depolarized Ra-

TABLE I. Expansion of vibrations into irreducible representations at the point  $\Gamma$  of the Brillouin zone.

Crystal	Complete expansion
Tl-1212	$4A_{1g} + B_{1g} + 5E_g + 7A_{2u} + B_{2u} + 8E_u$
Tl-1223	$5A_{1g} + B_{1g} + 6E_g + 9A_{2u} + 11E_u + 2B_{2u}$
Tl-2201	$4A_{1g} + 4E_g + 6A_{2u} + B_{2u} + 7E_u$
Tl-2212	$6A_{1g} + B_{1g} + 7E_g + 7A_{2u} + B_{2u} + 8E_u$
Tl-2223	$7A_{1g} + B_{1g} + 8E_g + 9A_{2u} + 2B_{2u} + 11E_u$

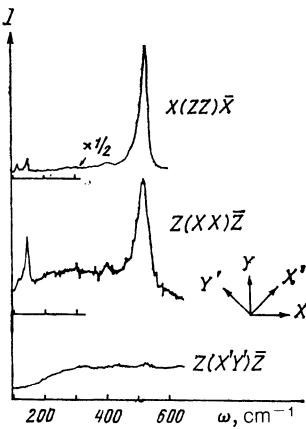


FIG. 2. Raman spectra of  $\text{TlBa}_2\text{CaCu}_2\text{O}_{7-x}$  ( $D_{4h}^1$  symmetry) at room temperature; here,  $I$  is the line intensity.

man lines which could be attributed to the  $E_g$  or  $B_{1g}$  modes. In the case of the  $X'Y'$  spectra we recorded lines with positions coinciding with the positions of the frequencies of the  $A_{1g}$  modes. However, these were due to the “polarization leakage” when objectives with a large numerical aperture ( $\approx 0.95$ ) were used. The weak activity of the  $E_g$  modes in the Raman spectra of  $\text{Tl}_m\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2(n+1)+m}$  crystals<sup>12</sup> agreed with a similar low activity of the  $E_g$  modes in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  crystals investigated earlier.<sup>3,4</sup>

The absence of the  $B_{1g}$  mode, representing antiphase vibrations of the oxygen ions in copper–oxygen planes, from the Raman spectra was specific to  $\text{Tl}-m(2(n-1)n$  structures, because in the case of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  similar vibrations were manifested in the Raman spectra of both the tetragonal nonsuperconducting phase and the orthorhombic superconducting phase.<sup>3–5</sup> The reason for the low efficiency of the Raman scattering in the case of the  $B_{1g}$  vibrations can be understood if we consider the conditions for the appearance of this mode in superconducting structures containing  $\text{CuO}_2$  planes. The symmetry of a single plane, ignoring its corrugations, in all high-temperature superconductors is at

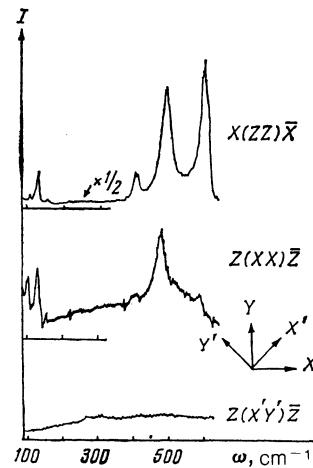


FIG. 4. Raman spectra of  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8-x}$  ( $D_{4h}^{17}$  symmetry) at room temperature.

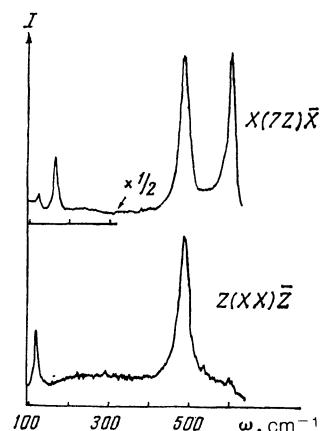


FIG. 3. Raman spectra of  $\text{Tl}_2\text{Ba}_2\text{CuO}_{6-x}$  ( $D_{4h}^{17}$  symmetry) at room temperature.

most  $D_{4h}$ , so that expansion of the representation which governs the transformation of the  $p$  function of the oxygen atom, belonging to a  $\text{CuO}_2$  plane, does not have the even ( $g$ -type) representations. Consequently, the Raman scattering is allowed in the  $C_{4v}$  group, which is in fact used to describe the symmetry of any single  $\text{CuO}_2$  plane with an allowance for corrugations entirely due to perturbations. Such perturbations may be: 1) a crystal field asymmetric along the  $Z$  axis; 2) corrugation of the  $\text{CuO}_2$  plane; 3) the interaction of the  $\text{CuO}_2$  planes with one another and with the intercalation surface [ $\text{Cu}(1)-\text{O}(1)$  chains in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , and  $\text{Tl}-\text{O}$  and  $\text{Bi}-\text{O}$  layers in superconductors based on  $\text{Tl}$  and  $\text{Bi}$ , respectively]. All these perturbations decrease on transition from  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  to  $\text{Tl}-m(2(n-1)n$ : the field of the  $\text{Y}^{3+}$  ion is stronger than that of  $\text{Ca}^{2+}$ , the  $\text{CuO}_2$  planes become flatter, the distance between the planes increases,<sup>7</sup> and the coupling of the planes to the intercalated layer falls (this is demonstrated by an increase in the ratio of the intensities of the bridge oxygen modes and of in-phase vibrations of oxygen in the  $\text{CuO}_2$  plane in a  $ZZ$  polarization<sup>4,12,13</sup>). Since the scattering cross section is proportional to the perturbation amplitude, which activates a vibration, the efficiency of the  $B_{1g}$  mode decreases.

##### 5. INTERPRETATION OF $A_{1g}$ MODES

The number of the  $A_{1g}$  modes observed in the Raman spectra of all the investigated crystals is equal to the number of the  $A_{1g}$  modes found from the group-theoretic analysis: four for  $\text{Tl}-2201$  and  $\text{Tl}-1212$  and six for  $\text{Tl}-2212$ . A correct interpretation of the  $A_{1g}$  vibrations is possible only if we bear in mind the difference between the masses of the vibrating ions and allow for the differences between the coupling constants representing the interactions between different ions. Additional information can also be obtained from a comparison of the relative intensities of the lines obtained in the  $XX$  and  $ZZ$  polarizations. From this point of view it is useful to consider also an analogy between the vibrations in  $\text{Tl}_m\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2(n+1)+m}$  superconductors and the vibrations in similar  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and  $\text{La}_2\text{CuO}_4$  structures.

## 1. $A_{1g}$ vibrations of oxygen ions

The oxygen ions are the lightest in these compounds and the associated lattice vibrations are expected at frequencies in excess of  $300\text{ cm}^{-1}$ . By analogy with  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , the Raman lines strongest in the  $ZZ$  polarization should be attributed to the  $Z$  valence (stretching) vibrations of oxygen. In Tl-1212 crystals with one intercalated Tl-O layer, there is only one such mode representing the  $Z$  valence (stretching) vibrations of the O(2) ions in the BaO layers; we shall attribute to these vibrations the isolated strong hf line at  $520\text{ cm}^{-1}$ , which is observed both in the  $ZZ$  and  $XX$  spectra (Fig. 2). Crystals of the Tl-2201 and Tl-2212 types with two intercalated Tl-O layers exhibit two valence vibrations of oxygen: vibrations of the O(2) and O(3) ions. Consequently, the  $ZZ$  spectra of these crystals exhibit two strong hf modes:  $485$  and  $600\text{ cm}^{-1}$  for Tl-2212 and  $495$  and  $612\text{ cm}^{-1}$  for Tl-2201. They can be interpreted as follows: the highest-frequency modes  $602\text{ cm}^{-1}$  of Tl-2212 and  $612\text{ cm}^{-1}$  of Tl-2201 are due to the vibrations of the O(3) ions located in the Tl-O layer, whereas the lines of lower frequency are due to vibrations of the O(2) ions located in Ba-O layers.

This interpretation is based on an analysis of the ratios of the intensities of the Raman lines in the  $XX$  and  $ZZ$  polarizations. It is clear from Figs. 3 and 4 that in the case of the  $600\text{ cm}^{-1}$  line of Tl-2212 and the  $612\text{ cm}^{-1}$  line of Tl-2201 this ratio is very small. It is an order of magnitude smaller than for the  $485\text{ cm}^{-1}$  line of Tl-2212 and  $495\text{ cm}^{-1}$  line of Tl-2201. The Raman spectra of Tl-1212 crystals in which the O(3) ion vibrations are forbidden (Fig. 2) show that the intensity ratio  $I_{XX}/I_{ZZ}$  for the  $A_{1g}$  vibrations of the O(2) ions ( $520\text{ cm}^{-1}$ ) is approximately the same for these crystals as for the  $485$ – $495\text{ cm}^{-1}$  lines in the spectra of Tl-2212 and Tl-2201 crystals.

In addition to these  $Z$  valence vibrations of the oxygen ions in structures with two copper-oxygen (Tl-2212 and Tl-1212) planes, there is one further  $A_{1g}$  mode associated with the oxygen O(1) in the copper-oxygen plane, which corresponds to  $Z$  cophasal vibrations of two oxygen ions in the same  $\text{CuO}_2$  plane. The eigenvector of this normal mode is

$$Z(\text{O}(1_1)) + Z(\text{O}(1_2)) - Z(\text{O}(1_1^*)) - Z(\text{O}(1_2^*)),$$

where the asterisk denotes that the ion belongs to the lower (relative to the center of inversion) part of half-space. This vibration is of the bending type. We shall assume that it is represented by the relatively weak lines in the region of  $400\text{ cm}^{-1}$ , observed only for crystals with two copper-oxygen planes: Tl-2212 ( $410\text{ cm}^{-1}$ ) shown in Fig. 4 and Tl-1212 ( $404\text{ cm}^{-1}$ ) shown in Fig. 2; these lines are not exhibited by Tl-2201 crystals with one  $\text{CuO}_2$  plane (Fig. 3). The ratio of the intensities of these lines in the  $XX$  and  $ZZ$  spectra of both crystals is in order-of-magnitude agreement with the ratio of the intensities of the lines representing vibrations of the O(2) ions ( $520$  and  $485\text{ cm}^{-1}$  for Tl-1212 and Tl-2212, respectively).

The large difference between the intensities of the lines attributed to the  $A_{1g}$  vibrations of the O(1) ions is a striking feature of the spectra of Tl-1212 and Tl-2212. Clearly, this difference indicates that in the case of  $\text{Tl}_m\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2(n+1)+m}$  structures, exactly as in the case of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , the  $ZZ$  polarization activity of in-

phase vibrations of the oxygen ions in copper-oxygen planes is due to their coupling to the valence vibrations of the bridge oxygen O(2) lying in the BaO planes,<sup>4,5</sup> and this activity increases as the difference between the frequencies of such vibrations is reduced. For Tl-2212 crystals, for which the difference between the frequencies of the  $A_{1g}$  vibrations of the O(1) ions ( $410\text{ cm}^{-1}$ ) and the valence vibrations of the bridge oxygen ( $485\text{ cm}^{-1}$ ) is only approximately 20% higher than for  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $435$  and  $502\text{ cm}^{-1}$ ),<sup>4</sup> the ratio of the intensities of the  $410$  and  $485\text{ cm}^{-1}$  lines is close to the ratio of the analogous lines in the case of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . Transition to Tl-1212 increases the difference between the  $A_{1g}$  vibrations of the O(1) and O(2) ions by a factor of 1.5 and the ratio of the intensities decreases by a factor greater than 3.

## 2. $A_{1g}$ vibrations of metal ions

In the case of Tl-1212 these are the  $Z$  vibrations of the Ba and Cu ions, whereas in the case of Tl-2201 these are the  $Z$  vibrations of Ba and Tl and in Tl-2212 they are the  $Z$  vibrations of the ions Ba, Tl, and Cu. It is clear from Figs. 2–4 that the number of the lf  $A_{1g}$  modes in the spectra of the investigated crystals agrees with the number expected theoretically. Therefore, the main problem is to attribute the modes to the vibrations of specific ions.

A comparison of the Raman spectra of all three Tl-1212, Tl-2212, and Tl-2201 crystals makes it possible to suggest the following distribution of the observed lines to the vibrations of Ba, Cu, and Tl. A comparison of the  $ZZ$  spectra in Figs. 2–4 shows that out of all the lf lines in these spectra, strong lines at  $132\text{ cm}^{-1}$  for Tl-2212 and  $167\text{ cm}^{-1}$  for Tl-2201 are observed. The polarizability of the bonds, the vibrations of which are responsible for these lines, is almost an order of magnitude higher than for the other bonds of the metal ions. Such a situation occurs in Tl-2223 crystals, the Raman spectra of which exhibit an lf line at  $130\text{ cm}^{-1}$  (Refs. 14 and 15), whereas in the case of Tl-1212 there is no analogous line. Similar values of the polarizabilities of the  $132\text{ cm}^{-1}$  vibrations in Tl-2212,  $130\text{ cm}^{-1}$  in Tl-2223, and  $167\text{ cm}^{-1}$  in Tl-2201 allow us to attribute them to the Tl vibrations.

In the case of Tl-2201, in addition to the Tl vibrations, the polarized Raman spectra show only the resolved Ba vibrations. They include the remaining line at the lowest frequency of  $122\text{ cm}^{-1}$ . Since the environment of the Ba ions and the Ba-O bond length change only slightly in the transition from Tl-2201 to Tl-2212 and then to Tl-1212, we have to assume that the frequency of the  $Z$  vibrations of the Ba atoms changes only slightly. We therefore attribute the  $109\text{ cm}^{-1}$  line to the  $Z$  vibrations of the Ba ions in Tl-2212 crystals with two  $\text{CuO}_2$  layers. The Raman spectra of Tl-2223 shown in Refs. 14 and 15 demonstrate that the frequency of the  $Z$  vibrations of the Ba ions in crystals with three  $\text{CuO}_2$  layers decreases to  $92\text{ cm}^{-1}$ . Similarly, out of two lf vibrations  $116\text{ cm}^{-1}$  and  $146\text{ cm}^{-1}$  in Tl-1212, the  $Z$  vibrations of Ba include the  $116\text{ cm}^{-1}$  mode. The remaining lf modes at  $146\text{ cm}^{-1}$  for Tl-1212 and  $158\text{ cm}^{-1}$  for Tl-2212 should be attributed to the  $Z$  vibrations of the copper ions, which are allowed in the Raman scattering spectra. In the case of Tl-2201 crystals with one copper-oxygen plane the Raman scattering by the  $Z$  vibrations is forbidden.

In Tl-2223 crystals with three  $\text{CuO}_2$  planes and in Tl-2212 with two  $\text{CuO}_2$  planes only one  $A_{1g}$  mode of the  $Z$  vibrations of the copper ions is Raman-active. It follows from the Raman spectra of Tl-2223 reported in Refs. 14 and 15 that its frequency remains approximately the same as for Tl-2212. Moreover, the Raman spectra of Tl-2223 (Refs. 14 and 15) and Tl-2212 (Ref. 16) crystals include a line additional to the Raman spectrum of Tl-2212 and it is located in the region of  $275 \text{ cm}^{-1}$ . In our opinion it should be attributed to the  $A_{1g}$  vibrations of the calcium ions which are allowed in the Raman scattering because of the reduction in the positional symmetry of calcium from  $D_{4h}$  to  $C_{4v}$  in the transition from Tl-2212 to Tl-2223.

Our analysis of the polarized Raman spectra of superconducting thallium-base crystals thus allows us to classify all the  $A_{1g}$  vibrations. Our attributions are supported by calculations reported in Ref. 17. The results are presented systematically in Table I. Summarizing, we can point out that the polarized Raman scattering spectra and even the frequencies of the  $A_{1g}$  modes in the spectrum of Tl-2212 agree practically completely with the corresponding parameters of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  crystals investigated earlier and characterized by a similar lattice structure. The appearance of an additional Tl-O valence bond in the structures with two intercalated Tl-O layers gives rise to strong Raman lines in the  $ZZ$  polarization and this is true of the oxygen and thallium ions.

The Tl-O(3) bond is  $sp$ -hybridized with the  $p_z$  orbital of oxygen.<sup>18</sup> Consequently, the polarizability of the system in the basal plane for these vibrations is very low and the ratio of the intensities of the Raman lines in the  $ZZ$  and  $XX$  polarizations is considerably higher than for the O(2) bridge oxygen. For all crystals with more than one copper-oxygen plane it is possible to record reliably also the Raman lines due to the  $A_{1g}$  bending vibrations of the oxygen ions in the  $\text{CuO}_2$  planes. The frequencies of these vibrations depend weakly on the number of copper-oxygen layers and on the number of intercalated Tl-O layers, and they lie in the range  $404$ – $410 \text{ cm}^{-1}$  (in the case of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  crystals this frequency is  $435 \text{ cm}^{-1}$ ). It is clear from Table II that in the case of Tl-22( $n-1$ ) $n$  crystals with  $n=1$ – $3$  the frequencies of the remaining allowed and Raman-active  $A_{1g}$  vibrations of the oxygen ion remain unchanged.

The greatest changes are observed in the frequency of the  $A_{1g}$  vibrations of the Ba ions. The frequencies of these vibrations decrease from  $122 \text{ cm}^{-1}$  for Tl-2201 characterized by  $T_c \approx 30 \text{ K}$  to  $92 \text{ cm}^{-1}$  for Tl-2223 characterized by

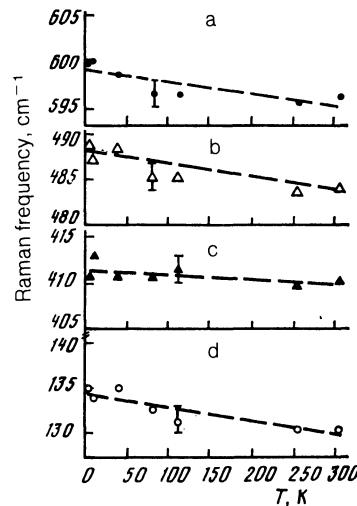


FIG. 5. Temperature dependence of the frequencies of the Raman lines at  $\sim 600 \text{ cm}^{-1}$  (a),  $\sim 485 \text{ cm}^{-1}$  (b),  $\sim 410 \text{ cm}^{-1}$  (c), and  $\sim 132 \text{ cm}^{-1}$  (d) obtained for  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_{8-x}$  in the temperature range 5–300 K.

$T_c \approx 110 \text{ K}$ . The lower frequency of the  $Z$  vibrations of Ba compared with Cu is correlated for all the crystals with the large mass of the Ba ions. The frequency of the vibrations of the heaviest thallium ions in all Tl-22( $n-1$ ) $n$  crystals is higher than for the Ba ions [ $M(\text{Tl}) \approx 2M(\text{Ba})$ ]. This high frequency of the vibrations of the thallium ions is associated with the short Tl-O(3) bond length. On the other hand, a comparison of the frequencies of the  $Z$  vibrations of the Ba and Tl ions in Tl-22( $n-1$ ) $n$  structures characterized by  $n=1$ – $3$  with the corresponding bond lengths in these crystals gives rise to two problems. Firstly, it is clear from Table II that the frequency of the  $Z$  vibrations of the Tl ions increases strongly (by  $\sim 20\%$ ) on transition from Tl-2212 to Tl-2201, although the Tl-O(3) bond length is practically unaffected.<sup>7–9</sup> Simple comparison of the bond lengths cannot account either for the strong softening of the frequency of the  $Z$  vibration of the Ba ions in the Tl-2201, Tl-2212, and Tl-2223 series, because the thickness of the  $\text{CuO}_2$ –TlO layer containing the Ba ions does not increase, but conversely decreases as the number of copper-oxygen layers in the structure increases. Clearly, these experimental observations cannot be explained without allowing for the changes in the nature of hybridization of the orbitals of the metal ions with oxygen ions.

TABLE II. Interpretation of totally symmetric vibrations.

Crystal	vibration mode	Tl	Ba	Ca	Cu	O(1)	O(2)	O(3)
Tl-2212	$A_{1g}$	—	116	—	146	404	520	otc.
Tl-2201	$A_{1g}$	167	122	abs	—	—	495	612
Tl-2212	$A_{1g}$	132	109	—	158	410	485	600

Note. Here, abs shows that a given atom is absent from the structure and a dash means that the vibration of a given type in an atom is missing from the expansion.

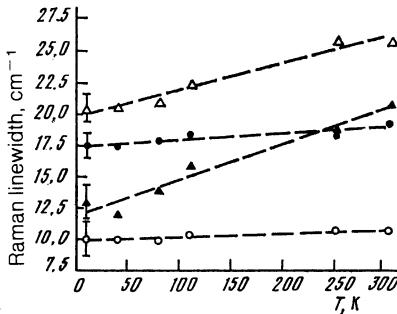


FIG. 6. Temperature dependence of the widths of the Raman lines  $\Delta\omega$  obtained for  $Tl_2Ba_2CaCu_2O_{8-x}$  at temperatures 5–300 K using the lines at  $\sim 600\text{ cm}^{-1}$  (●),  $\sim 485\text{ cm}^{-1}$  (△),  $\sim 410\text{ cm}^{-1}$  (▲), and  $\sim 132\text{ cm}^{-1}$  (○).

The results of a study of the influence of temperature on the Raman spectra are presented in Figs. 5 and 6 to illustrate the case of Tl-2212. It is clear from Fig. 5 that all the  $A_{1g}$  modes observed in the range 300–15 K demonstrate the usual temperature dependence: the frequency increases as a result of cooling. There are no singularities on transition through the point  $T_c$ . This behavior of the  $A_{1g}$  modes is analogous to that reported for  $YBa_2Cu_3O_{7-x}$  in Ref. 19. In the case of superconducting  $YBa_2Cu_3O_{7-x}$  crystals the reduction in the frequency in the transition across  $T_c$  is exhibited by just one Raman-active mode corresponding to antiphase vibrations of oxygen in the  $CuO_2$  plane.<sup>19,20</sup> It is not possible to follow the behavior of this mode ( $B_{1g}$ ) in  $Tl_mBa_2Ca_{n-1}Cu_nO_{2(n+1)+m}$  crystals because of the very low activity of this mode in the Raman spectra.

Cooling alters also (reduces) the intensities of If phonon modes (Fig. 7). In the case of the scattering process accompanied by the emission of a phonon, theory generally predicts a reduction in the intensity as a result of cooling, which should be proportional to  $[1 + n(\omega)]$ , where  $n(\omega)$  is the occupancy number of the phonon states of energy  $\hbar\omega$ :

$$n(\omega) = (\exp(\hbar\omega/kT) - 1)^{-1}. \quad (1)$$

This dependence is represented by the dashed line in Fig. 7 and it applies to the  $132\text{ cm}^{-1}$  mode of Tl-2212. It is clear from Fig. 7 that, within the limits of the experimental error, the points fit well the dependence (1).

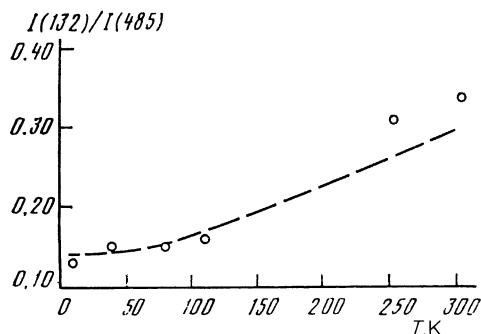


FIG. 7. Temperature dependence of the relative intensity  $I(132\text{ cm}^{-1})/I(485\text{ cm}^{-1})$  in the spectrum of  $Tl_2Ba_2CaCu_2O_{8-x}$ . The dashed curve represents the theoretical dependence described by Eq. (1).

Cooling reduces by a factor  $\sim 1.5$  the Raman linewidths corresponding to the valence  $Tl-O(3)$  vibrations (line in the region of  $612\text{ cm}^{-1}$ ) at both Tl-2201 and Tl-2212. An even greater (almost threefold) reduction in the width is exhibited also by a line in the region of  $410\text{ cm}^{-1}$  in the Tl-2212 spectrum (in-phase vibrations of the oxygen ions in a copper–oxygen plane), as demonstrated in Fig. 6. These vibrations are Raman-inactive in the case of Tl-2201. The  $612\text{ cm}^{-1}$  line is asymmetric at room temperature and the asymmetry is retained right down to helium temperatures. Moreover, the  $520\text{ cm}^{-1}$  line in the Tl-1212 spectrum is asymmetric.

The line profile asymmetry is a manifestation of the electron–phonon interaction which mixes a phonon with an electron continuum. A similar effect (Fano interference<sup>21</sup>) in superconducting  $YBa_2Cu_3O_{7-x}$  crystals is observed only for the  $XX(X'Y')$  polarizations (lines  $335$  and  $115\text{ cm}^{-1}$  reported in Refs. 19, 20, and 22) when the electric vector lies in the conducting basal plane. The Raman lines of  $Tl-m(n-1)n$  crystals display an asymmetry in the  $ZZ$  polarizations.

## 6. CONCLUSIONS

Polarization measurements, symmetry considerations, and also allowances for the masses and bond lengths of the atoms participating in vibrations were used to identify all the totally symmetric modes emitted by our Tl-2201, Tl-1212, and Tl-2212 crystals. An analysis was made of the similarity and difference between the phonon mode symmetries in  $Tl_mBa_2Ca_{n-1}Cu_nO_{2(n+1)+m}$ ,  $YBa_2Cu_3O_{7-x}$ , and  $La_2CuO_4$  compounds. The low Raman efficiency of the  $B_{1g}$  modes in Tl-1212 and Tl-2212 was due to a reduction in the asymmetric perturbations of the  $CuO_2$  plane. A study of the temperature dependences of the frequencies and half-widths of the phonon modes showed that all the totally symmetric modes exhibited a slight increase in the frequency as a result of cooling and the half-widths decreased. It was found that a number of lines in the Raman spectra of Tl-base superconductors have asymmetric profiles. The line asymmetry could be attributed to the Fano interference in the course of the interaction of a phonon with an electron continuum.

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