

# The influence of hydrostatic compression on the lattice dynamics of thallium-based high-temperature superconductors

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The influence of hydrostatic compression on the Raman spectra of the thallium-based high-temperature superconductors  $\text{TlBa}_2\text{CaCu}_2\text{O}_7$ ,  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$ , and  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$  has been studied. Pressure in the range used does not produce phase transitions in the crystals studied. Analysis of the Raman shifts with pressure indicates the applicability of the Grüneisen model for high-temperature superconductors. It is shown that pressure leads to inhomogeneous deformation of the elementary cell.

## 1. INTRODUCTION

With the discovery of high-temperature superconductors based on thallium,<sup>1</sup> in a number of cases with a higher transition temperature  $T_c$  to the superconducting state than the compounds  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  and  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ , diversified investigations started on these materials. Since the role of phonons and electron-phonon coupling in the realization of a high  $T_c$ , which grows with increasing pressure, is so far not elucidated, it is essential to study the structure of phonon spectra and its transformation under various influences which change the critical temperature.

The method of Raman scattering of light (RS) is one of the most powerful for studying phonon spectra and electron-phonon interaction. Phonons at the  $\Gamma$ -point of the Brillouin zone can be studied in this way. Pressure achieves a stronger perturbation than the other thermodynamic variable, temperature. Besides, the application of pressure produces a cleaner perturbation of the system, since the effect of temperature leads also to a simultaneous change in specimen volume and a redistribution of the phonon population, while pressure changes only the volume. Results of studies of RS under pressure can produce a test of different microscopic theories of lattice dynamics and thereby significantly clarify the role of electron-phonon interaction in the appearance of high-temperature superconductivity.

There are few RS investigations of high-temperature superconductors under pressure. They are limited to the system  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  (Refs. 3 and 4) and to one of the crystals of the thallium system.<sup>5</sup> We have therefore undertaken a systematic study of the effect of hydrostatic compression over a wide pressure range (up to 30 kPa) on thallium-system superconductors that differ in the number of  $\text{CuO}_2$  and  $\text{TlO}$  layers.

## 2. CRYSTAL STRUCTURE AND SYMMETRY OF THE PHONON MODES IN $\text{Tl}_m\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2(n+1)+m}$ CRYSTALS

There are two series of superconducting phases in the system  $\text{Tl}_1\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+3}$  [ $\text{Tl-12}(n-1)n$ ] and  $\text{Tl}_2\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$  [ $\text{Tl-22}(n-1)n$ ], which differ from one another in the spatial symmetry of the lattice and in the number of intercalated  $\text{TlO}$  layers. Crystals of the series  $\text{Tl-22}(n-1)n$  have the body-centered tetragonal structure  $D_{4h}^{17}$  (Ref. 6) with two formula units to the elementary cell. The primitive cell is half the size and consists of one formula unit. Crystals of the series  $\text{Tl-12}(n-1)n$  have the simple

tetragonal structure  $D_{4h}^1$  (Ref. 6) with one formula unit to the cell. Within the limits of each series the structures differ among themselves in the number  $n$  of copper-oxygen layers, separated from one another by calcium ions. In both series the Ba ions are positioned over and under outer layers of  $\text{CuO}_2$  in a nine-coordinated surroundings of oxygen ions, while the Tl ion is surrounded by 6 oxygen ions, forming a distorted octahedron.

The number of phonon modes is determined by the number of ions in the primitive cell, so that for crystals of both series it is equal to triple the number of ions in the formula unit. Since the structures are centrosymmetric, only even ( $g$ -type) modes are active in RS. It follows from a group-theoretical analysis<sup>7-9</sup> that vibrations of only those ions which have point symmetry  $C_{4v}$  or  $C_{2v}$  make a contribution to RS. Each pair of ions with  $C_{4v}$  point symmetry gives then one  $A_{1g}$  and one  $E_g$  vibration, while each two pairs of ions with  $C_{2v}$  positional symmetry give ( $A_{1g} + B_{1g} + E_g$ ) vibrations. Vibrations of ions with  $D_{2h}$  or  $D_{4h}$  positional symmetry do not appear in RS in perfect crystals because of the alternating exclusion rule. Summary analyses in the irreducible representation are shown in Table I for phonons in the structures investigated.

In structures with  $D_{4h}^{17}$  lattice symmetry, as also for  $D_{4h}^1$ , oscillations along the  $c$  axis are responsible for  $A_{1g}$ - and  $B_{1g}$  modes, while the vibrations of the  $E_g$  modes are polarized in the  $ab$  plane.<sup>7-11</sup>  $B_{1g}$  modes only appear in structures with  $n > 1$  copper-oxygen layers and correspond to anti-phase vibrations of oxygen ions of a  $\text{CuO}_2$  plane, while  $A_{1g}$  modes correspond to in-phase vibrations.

For our investigations we chose  $\text{Tl-1212}$ ,  $\text{Tl-2201}$  and  $\text{Tl-2212}$  crystals. With such a choice of crystals we could follow the transformation of the phonon spectrum and its change with the increase in pressure for structures differing in the number of  $\text{CuO}_2$  and  $\text{TlO}$  layers. As an example to illustrate the quality of the spectra, the RS spectra of a  $\text{Tl-2212}$  single-crystal are shown in Fig. 1 for two different pressures.

The number of lines in the polarized  $ZZ$  spectra is four in  $\text{Tl-2212}$  and  $\text{Tl-2201}$  and is six in  $\text{Tl-2212}$  (Refs. 7–12). In  $\text{Tl-1212}$  the frequencies of the lines at atmospheric pressure are 116, 146, 404 and  $520\text{ cm}^{-1}$ , in  $\text{Tl-2201}$  they are 122, 167, 495 and  $612\text{ cm}^{-1}$  and in  $\text{Tl-2212}$  109, 132, 158 and  $600\text{ cm}^{-1}$ .

Oxygen ions are the lightest and the vibrations associat-

TABLE I. Decomposition into irreducible representations for phonons at the  $\Gamma$  point of the Brillouin zone.

Crystal	Lattice symmetry	Vibration symmetry
TlBa <sub>2</sub> CaCu <sub>2</sub> O <sub>7</sub>	$D_{4h}^1$	$4A_{1g} + B_{1g} + 5E_{1g} + 7A_{2u} + B_{2u} + 8E_u$
Tl <sub>2</sub> Ba <sub>2</sub> CuO <sub>8</sub>	$D_{4h}^{17}$	$4A_{1g} + 4E_g + 6A_{2u} + B_{2u} + 7E_u$
Tl <sub>2</sub> Ba <sub>2</sub> CaCu <sub>2</sub> O <sub>8</sub>	$D_{4h}^{17}$	$6A_{1g} + B_{1g} + 7E_g + 7A_{2u} + B_{2u} + 8E_u$

ed with them are in the frequency region above  $300 \text{ cm}^{-1}$  (Refs. 7–12). The most intense lines of ZZ polarization are assigned to oxygen stretching oscillations. There is only one such mode in Tl-1212 crystals with a single intercalated TlO layer—oscillations of O<sub>2</sub> ions located in BaO layers. The only intense high-frequency line at  $520 \text{ cm}^{-1}$  relates to it. In Tl-2201 and Tl-2212 crystals with two intercalated TlO layers there are pairs of valence oscillations of oxygen—oscillations of O<sub>2</sub> and O<sub>3</sub> ions. Correspondingly in the ZZ-spectra of these crystals intense modes are observed in pairs; 485 and  $600 \text{ cm}^{-1}$  in Tl-2212 and 495 and  $612 \text{ cm}^{-1}$  in Tl-2201. These modes are classified in the following way: the highest frequency modes  $600 \text{ cm}^{-1}$  in Tl-2212 and  $612 \text{ cm}^{-1}$  in Tl-2201 correspond to vibrations of O<sub>3</sub> ions located in a Tl-O layer, while lines of lower frequency correspond to vibrations of O<sub>2</sub> ions located in Ba-O layers. This attribution is based on an analysis of polarization ratios of RS lines for XX and ZZ polarizations.<sup>8,9</sup>

Apart from the valence oscillations of oxygen ions in structures with two copper-oxygen planes (Tl-2212 and Tl-1212) discussed above, there is another  $A_{1g}$  mode, associated with O<sub>1</sub> oxygen of a copper-oxygen layer, ascribed to in-phase vibrations of two oxygen ions out of each CuO<sub>2</sub> plane. This oscillation is related to a deformation type. The relatively weak lines in the region of  $400 \text{ cm}^{-1}$ , which are only observed in crystals with two copper-oxygen planes, Tl-2212 ( $410 \text{ cm}^{-1}$ ) (Fig. 1) and Tl-1212 ( $404 \text{ cm}^{-1}$ ) (Refs. 8,9), and are absent in Tl-2201 crystals with one CuO<sub>2</sub> plane, are associated with it.

Vibrations of Ba and Cu ions correspond to fully symmetric oscillations of metallic ions in Tl-1212, vibrations of Ba and Tl ions in Tl-2201 and vibrations of Ba, Tl and Cu in Tl-2212. The modes at  $132 \text{ cm}^{-1}$  in Tl-2212 and  $167 \text{ cm}^{-1}$  in

Tl-2201 correspond to vibrations of Tl. The lowest frequency line ( $122, 109$  and  $116 \text{ cm}^{-1}$  for Tl-2201, Tl-2212 and Tl-1212 respectively) refers to oscillations of Ba in all high-temperature superconductors based on thallium. The remaining low-frequency modes— $146 \text{ cm}^{-1}$  in Tl-1212 and  $158 \text{ cm}^{-1}$  in Tl-2212 must be ascribed to oscillations of copper ions. Such an attribution is confirmed by calculations of the lattice dynamics, carried out in the shell approximation mode,<sup>14,15</sup> and by the results of experiments of various groups.<sup>7–12</sup>

It follows from a group-theoretical analysis that in all the Tl-1212, Tl-2212, and Tl-2201 crystals there is also a large number of vibrations which are allowed in depolarized RS spectra. These are mainly  $E_g$  modes which should appear in ZX (ZY) polarizations and  $B_{1g}$  modes, allowed in X'Y' polarization. However, it has up to now not been possible to record them reliably at atmospheric pressure in the polarized RS line spectra, which could be associated with non-diagonal modes. A mode of  $B_{1g}$  symmetry, in which Ca displacement dominates, has been recorded in Tl-2223 (Ref. 10). The weak activity of RS  $E_g$  modes in crystals of the  $Tl_m Ba_2 Ca_{n-1} Cu_n O_{2(n+1)+m}$  system<sup>8,9</sup> correlates with equally small activity of  $E_g$  modes in  $YBa_2 Cu_3 O_{7-x}$  crystals studied earlier.<sup>13</sup> The absence of a  $B_{1g}$  mode in RS spectra corresponding to the antiphase oscillations of oxygen ions in a CuO<sub>2</sub> plane is characteristic of  $Tl-m2(n-1)n$  structures and is connected with the weak corrugation and low asymmetrical perturbation of a CuO<sub>2</sub> layer.<sup>8,9</sup>

### 3. EXPERIMENTAL SECTION

$Tl_m Ba_2 Ca_{n-1} Cu_n O_{2(n+1)+m}$  single-crystals were grown by cooling melts of stoichiometric composition in an oxygen stream. The single crystals were in the shape of rectangular plates with mirror basal plane with dimensions  $3 \times 3 \times 0.3 \text{ mm}$ . The method used enabled practically uniform specimens of the three compositions Tl-1212, Tl-2201 and Tl-2212 to be obtained. The symmetry and lattice parameters of the single crystals were monitored by x-ray diffraction. Tl-1212 crystals had a primitive  $D_{4h}^1$  ( $P4/mmm$ ) tetragonal structure,  $a = 3.855 \text{ \AA}$ ,  $c = 12.711 \text{ \AA}$ , while Tl-2201 and Tl-2212 crystals had a  $D_{4h}^{17}$  ( $I4/mmm$ ) body-centered tetragonal structure  $a = 3.859 \text{ \AA}$ ,  $c = 23.152 \text{ \AA}$ , and  $a = 3.9856 \text{ \AA}$ ,  $c = 29.340 \text{ \AA}$  respectively. The Tl-2201, Tl-1212, Tl-2212 specimens had transitions to the superconducting state at  $T_c = 30, 70$  and  $110 \text{ K}$  respectively.

A chamber with diamond anvils (Fig. 2) was used to provide the high pressure. Specific features of the construction were the large (up to  $90^\circ$ ) angle of the optical entrance aperture and minimal (6 mm) distance from the chamber axis to the anvils. This made it possible to use a micro-objective with large aperture from the micro-attachment of the spectrometer in the back scattering geometry, which is im-

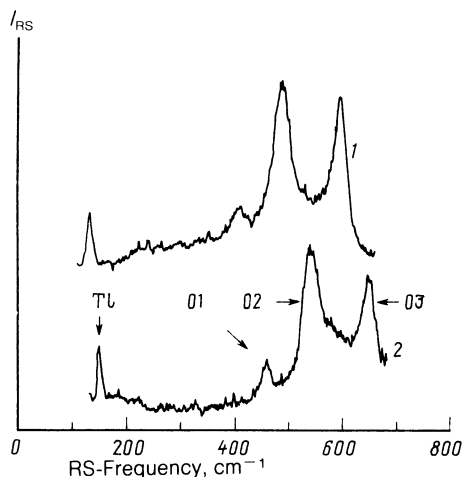


FIG. 1. RS spectra of a Tl<sub>2</sub>Ba<sub>2</sub>CaCu<sub>2</sub>O<sub>8</sub> crystal at different pressures: 1)  $10^{-4}$  GPa and 2) 15.8 GPa.

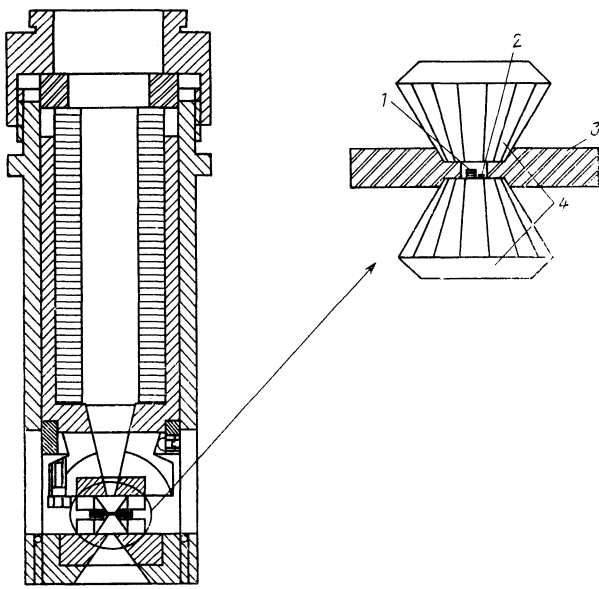


FIG. 2. Diamond high-pressure chamber: 1) specimen and 2) ruby placed in the pressure-transmitting medium (helium), 3) gasket (hardened steel), 4) diamond anvils (diameter of working area 0.4 mm, 4 mm at base).

portant for recording weak RS signals from single-crystal microspecimens. As a result the signal on positioning the specimen in the chamber is not less than half compared with the signal observed outside the chamber. Radiation of one of the lines of an  $\text{Ar}^+$  laser (wavelength 488 nm) was focused on the specimen in a patch with dimensions about  $3 \mu\text{m}$ . In order to avoid heating, the exciting region of the laser beam power (at the entrance to the chamber with diamond anvils) did not exceed fractions of a milliwatt.

The RS spectra were recorded with a "Microdil-28" Raman spectrometer made by Dilor. The system for recording the spectrum was multichannel. The receiver consisted of a microchannel plate (image intensifier), optically coupled with a self-scanning line of photodiodes and cooled to  $-28^\circ\text{C}$ .

The pressure was applied by compressing helium, which is a practically ideal hydrostatic medium in the pressure range studied.<sup>16</sup> The pressure in the chamber was measured by the shift in the  $R_1$  fluorescence line of ruby.<sup>16</sup> This

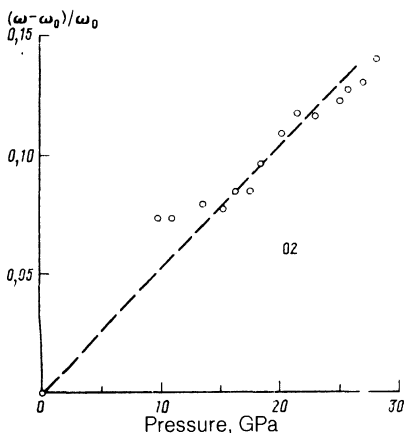


FIG. 3. Pressure dependence of the relative frequency shift  $(\omega - \omega_0)/\omega_0$  for the  $A_{1g}$  mode studied in a  $\text{TlBa}_2\text{CaCu}_2\text{O}_7$  crystal.

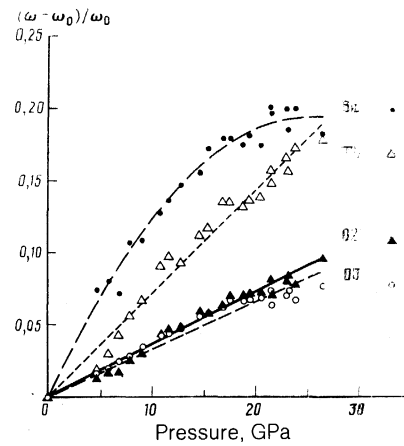


FIG. 4. Pressure dependence of the relative frequency shift  $(\omega - \omega_0)/\omega_0$  for the  $A_{1g}$  modes studied in a  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$  crystal.

method is ideal for experiments on RS, since the pressure can be measured rapidly without changing the measuring apparatus and the experimental geometry. The accuracy in measuring the  $R$  line was  $1.5 \text{ cm}^{-1}$ .

On account of the characteristics of the diamond chamber, specimens with dimensions not more than  $30 \times 30 \times 15 \mu\text{m}$  could be used. It was important that the crystals should not be contaminated in the process of preparing specimens of the required size and housing them in the chamber (especially various organic materials). The quality of the faces of these small specimens must satisfy the conditions of a RS experiment—a mirror reflectance of the surface and a fixed orientation of the crystallographic axes. Specimens of dimensions approximately  $20 \times 20 \times 10 \mu\text{m}$  were obtained by punching out. The quality of the surface and the orientation of the specimen were monitored by the RS spectra after placing the specimens in the diamond chamber.

#### 4. EXPERIMENTAL RESULTS

Only lines corresponding to fully symmetrical  $A_{1g}$  vibrations were recorded in measuring RS of high-temperature superconductors based on thallium. All measurements were carried out for ZZ polarization. It was possible to measure the pressure dependence of the frequency for all  $A_{1g}$  modes in Tl-2201, for four of the six modes in Tl-2212 and

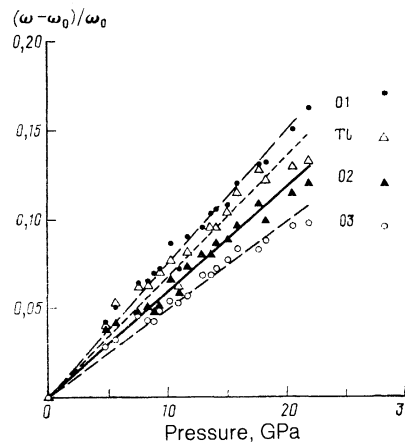


FIG. 5. Pressure dependence of the relative frequency shift  $(\omega - \omega_0)/\omega_0$  for the  $A_{1g}$  mode studied in a  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$  crystal.

TABLE II. Mode parameters of the crystals studied. Experimental uncertainties are shown in brackets.

	$(\partial\omega/\partial P)\omega^{-1}, 10^{-2} \text{ GPa}^{-1}$			Grüneisen parameters			
	Tl-1212	Tl-2201	Tl-2212	Tl-1212	Tl-2201	Tl-2212	
O3	0,51(0,001)	0,330(0,008)	0,494(0,008)	0,7	0,45	0,68	
O2		0,364(0,006)	0,59(0,01)		0,5	0,81	
O1			0,754(0,009)			1,03	
Tl		0,71(0,01)	0,68(0,02)			0,97	0,93
Ba		0,92(0,03) *				1,26	

\*For the pressure dependence of the logarithmic derivative the best approximation is the quadratic  $(\partial\omega/\partial P)\omega^{-1} = aP + bP^2$ , where  $a = 1.53 \cdot 10^{-2}$ ,  $b = 3.0 \cdot 10^{-4}$ .

one of the four vibrations of Tl-1212. The pressure dependence of the oscillations of Cu and Ba in Tl-2212 and Tl-1212 were not studied, due to their small RS effectiveness.<sup>7,8</sup> The pressure dependence of the frequency in Tl-1212 was only studied for modes of the bridging O2 oxygen, since the in-phase oscillations of O1 ions in ZZ polarization have low intensity, due to their small mixing coefficient with O2 oscillations in Tl-1212.<sup>17</sup>

The normalized relative frequency shift  $(\omega - \omega_0)/\omega_0$  ( $\omega_0$  is the frequency at atmospheric pressure) for all the  $A_{1g}$  modes studied is shown in Figs. 3–5 as a function of pressure. As can be seen from these, the frequencies of all modes increases with increase in pressure. The pressure dependence of the frequency of Ba oscillations is nonlinear in the region of pressures above 15 kPa. The frequencies of Tl oscillations change with increases of pressure in approximately the same way for crystals with two intercalated TlO layers. A similar dependence is observed for stretching oscillations of oxygen ions in crystals with two  $\text{CuO}_2$  planes. The relative frequency shifts of the O2 mode in Tl-2212 and Tl-2201 somewhat exceed the values for O3. The mode of in-phase oscillations of oxygen (deformation oscillations) is the most sensitive to pressure in Tl-2212 crystals. Results of measuring the pressure dependences and the Grüneisen parameters for all the modes studied are summarized in Table II. In calculating the Grüneisen parameters the value of the bulk compressibility of a Tl-2223 crystal was used.<sup>18</sup> Since a growth in the compressibility is observed with an increase in the number of  $\text{CuO}_2$  planes in different classes of high-temperature superconductors,<sup>18</sup> the values shown in the table are a lower limit.

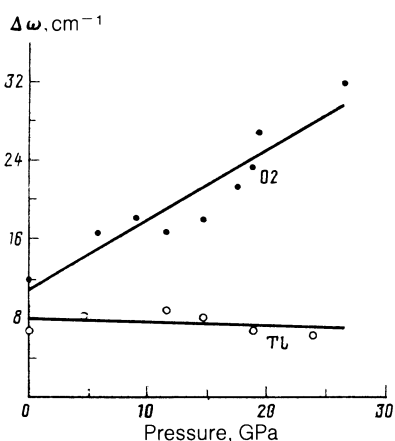


FIG. 6. Pressure dependence of the half-width of lines of the O2 and Tl modes in a  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$  crystal.

A broadening of the lines of all the phonon modes studied is observed with increase in pressure, reaching (for oxygen modes at 20 GPa)  $\approx 100$ : (Fig. 6). In addition, a change occurred in the line intensities in Tl-2201 corresponding to oscillations of Tl and Ba. At atmospheric pressure the intensity of the Tl mode is approximately three times larger than the intensity of the Ba line. However, at a pressure of 10 GPa their intensities are of the same order, i.e., with a growth in pressure a reduction occurs in the intensity of the Tl line and an increase in the intensity of the Ba line relative to the oxygen peaks.

On increasing the pressure above 20 GPa the quality of the spectra deteriorates, being reestablished on decreasing the pressure.

## 5. DISCUSSION OF THE RESULTS

The monotonic (without discontinuities) change in frequencies of fully symmetric modes shows that no phase transitions occur in the pressure range studied (up to 30 GPa). This fact is evidence that the structures of high-temperature superconductors based on thallium are stable at high pressures up to 30 GPa, when the relative volume changes are  $\approx 20\%$ .

As can be seen from the curves of Fig. 4 and from Table II, the relative frequency shifts for Tl oscillations in Tl-2201 crystals are about twice as large as for oxygen stretching oscillations. It follows from such a difference in pressure dependences that the frequency of the Tl mode is not determined by short-range interlayer interactions ( $\approx 2 \text{ \AA}$ ) along the  $c$  axis, but by long-range interlayer interactions ( $\approx 3 \text{ \AA}$ ) in the basal plane.

The identical growth in the frequencies of oxygen stretching oscillations in crystals with two  $\text{CuO}_2$  layers, exceeding the value for the analogous oscillations in Tl-2201, shows that the main change in the bond lengths takes place near the copper-oxygen layers. This is confirmed by the fact that the heavy ion modes and the oxygen oscillations, belonging to the  $\text{CuO}_2$  planes have the greatest pressure derivatives. Analysis of the pressure dependences of the frequencies of fully symmetrical oscillations shows that the deformation of the elementary cell along the  $c$  axis in the crystals studied occurs because of a reduction in the distance between  $\text{CuO}_2$  layers and compression of Cu–O bonds. With a growth in pressure primarily the bond lengths Tl–O and Cu–O decrease and it is then not impossible that there is an increase in the corrugation of the  $\text{CuO}_2$  and TlO layers. We note that the bending of the Cu–O–Cu bonds with an increase in pressure was observed earlier<sup>19</sup> in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . An increase in asymmetrical disturbances

of a  $\text{CuO}_2$  plane should show up in a growth in the RS efficiency of a mode of oxygen antiphase oscillations of this plane. In fact, in Tl-2223 crystals<sup>20</sup> on substituting calcium for yttrium, i.e., on corrugating and increasing the asymmetrical excitations of the  $\text{CuO}_2$  planes,<sup>21</sup> a mode of antiphase oxygen oscillations was observed. This mode has  $B_{1g}$  symmetry and must therefore be controlled by the basal plane of the crystals. Further experiments on RS at high pressures should elucidate this effect.

The large pressure derivatives for the frequency of the O2 mode relative to O3, in spite of the fact that the Tl-O3 bond length is greater than for Tl-O2, can be explained by the influence of the mixing of the oscillations of oxygen ions. In fact, a model of the mixing of the oscillations of O2 and O1 oxygen ions, belonging to the tetrahedral surroundings of a Cu ion, has been proposed. In this case not only the Tl-O2 bond length is responsible for the energy of the O2 mode oscillations, but also the dynamic O2-O1 interaction, which can change with increase in pressure. However, this model can not explain adequately the sequence of the frequencies of the O2 and O3 modes. In our view it is essential to propose that the O2 and O3 oscillations are combined together in order to describe the magnitudes of the frequencies and the pressure dependences of the modes mentioned above. We note that a similar suggestion was recently used for assigning the oscillations in the high-temperature superconductor  $\text{Pb}_2\text{Sr}_2\text{Y}_{0.75}\text{Ca}_{0.25}\text{Cu}_3\text{O}_8$  (Ref. 25), the structure of which is isomorphous with Tl-2212 studied by us and is confirmed by the results of a calculation of the lattice dynamics.<sup>15</sup>

In our view the nonlinear pressure dependence of the Ba mode is a direct consequence of the inhomogeneous compressibility of the Tl-2201 elementary cell. In fact, according to the lattice dynamics calculations, as well as Ba displacements, displacements of the Cu and Tl ions also enter into the eigenvector. Therefore, different structural blocks of the cell deform sequentially with increase in pressure, first the perovskite, then the intercalated  $\text{Tl}_2\text{O}_2$ , thereby leading to a nonlinear nature of the frequency change of the mixed oscillations. We note that a similar nonlinear pressure dependence of frequency is known for  $A^{\text{III}}B^{\text{V}}$  semiconductors.<sup>22</sup>

Analysis of the set of Grüneisen parameters obtained for the crystals studied shows that with growth in pressure a fairly uniform broadening of the spectrum on an energy scale takes place. This shows that the lattice dynamics is determined by one type of bond and satisfies the Grüneisen law (the values of the mode Grüneisen parameters are close to one another and close to unity in order of magnitude).

It is not possible at present to carry out a quantitative analysis of the line broadening. We note that line broadening under pressure is usually associated with lattice anharmonicity.<sup>23</sup> However, in the crystals studied an inhomogeneous line broadening mechanism is dominant, so that the observed increase in line width with pressure, different for various modes (Fig. 6), is only evidence of the inhomogeneous compressibility of the elementary cell.

The RS studies carried out under pressure make it possible to analyze in detail the effect of temperature on the phonon spectrum in high-temperature superconductors based on thallium. A similar analysis was carried out earlier<sup>24</sup> for the superconductor  $\text{YBa}_2\text{Cu}_2\text{O}_{7-x}$ . It is well known<sup>23</sup> that the influence of temperature on phonon frequencies consists of two components:

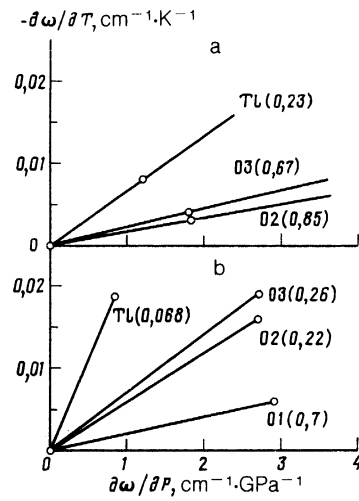


FIG. 7. Correlation between the temperature and pressure derivatives for the frequency of  $A_{1g}$  modes in crystals of a)  $\text{Tl}_2\text{Ba}_2\text{CuO}_6$  and b)  $\text{Tl}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$ . The values of the parameter  $\varphi$  are shown for each mode in brackets.

$$(\partial\omega/\partial T)_p = (\partial\omega/\partial T)_v - (\alpha/\beta) (\partial\omega/\partial P)_T, \quad (5.1)$$

where  $\alpha = (1/V)(\partial V/\partial T)_p$  and  $\beta = -(1/V)_v - (\alpha/\beta)(\partial V/\partial P)_T$ . The first term represents the change in oscillation amplitudes (explicit contribution), while the second, called the implicit contribution, reflects the change in equilibrium distances between the ions. The influence of temperature on the phonon spectra of high-temperature superconductors based on thallium can be interpreted correctly<sup>8</sup> from the ratio of the explicit and implicit contributions. The correlations of pressure and temperature sensitivity<sup>8</sup> of the frequencies of the fully symmetrical modes in the superconductors studied is shown in Fig. 7. Each point on the plots corresponds to a fully symmetrical mode for which values were obtained of the temperature (ordinate axis) and pressure (abscissa axis) derivative. The straight lines which pass through the origin are designated by the magnitude of the dimensionless parameter  $\varphi = (dT/dP)_\omega (\alpha/\beta)$ . In the calculation the values  $\alpha = 1.1 \cdot 10^{-5} \text{ K}^{-1}$  (Ref. 25) and  $\beta = 7.3 \cdot 10^{-3} \text{ GPa}^{-1}$  (Ref. 18) for Tl-2201 crystals were used, so that the values of  $\varphi$  obtained are the lower limit. It can be seen that in the case of the crystals studied (except for the case of the thallium mode in Tl-2201) the trend corresponds more closely to the case of  $\varphi \approx 0.5-1.0$  rather than  $\varphi = 0$  or  $\varphi = \infty$ . It follows from the results that the explicit and implicit contributions are comparable in magnitude with a small preponderance of the latter.

The increase in the RS-mode intensity of Ba in Tl-2201 with increasing pressure can be understood as a change in structure of the electron spectrum (resonance RS reconstructed by pressure). However, since the exact mechanism of scattering and of the coefficients of coupling with the energy structure of the electron spectrum is not known in the crystals studied, it is impossible to be specific about the observed fact.

## 6. CONCLUSION

We shall summarize those conclusions which can be drawn from our work. The investigation of the influence of hydrostatic pressure on the RS spectra shows that pressure

up to 30 GPa does not produce phase transitions in the crystals of the high-temperature superconductors studied. The logarithmic derivatives with respect to pressure of the RS shifts have been determined and estimates made of the Grüneisen parameters for a number of fully symmetrical modes. Analysis of the whole set of mode parameters obtained shows the applicability of the Grüneisen model for high-temperature superconductors. A comparative analysis of the pressure dependences of the frequencies of different modes showed that pressure leads to an inhomogeneous deformation of the elementary cell, in which primarily the perovskite blocks of the cell deform. It is shown that together with Ba displacements, the movements of other ions enter into the normal vector of the lowest frequency mode of the RS spectrum, while the modes of the tetrahedron of oxygen ions surrounding copper and thallium ions are mixed together. It is suggested that as the pressure increases, a corrugation of the CuO<sub>2</sub> and TlO planes takes place and an experimental method for checking the proposed hypothesis is indicated. The results obtained on the pressure dependence of RS shifts made it possible to ascertain that both implicit and explicit components of the shift make a contribution to the temperature dependence of the phonon mode frequencies, but the contribution of the former is more significant. This shows the applicability of the quasiharmonic approximation for describing the lattice dynamics of the crystals studied. A further RS study under pressure (especially of phonon-phonon interactions and resonance effects) both in superconductors based on thallium and in superconductors of other families will enable filling out and generalization of the results obtained in the present work to be made.

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