Raman spectra of In$_x$Tl$_{1-x}$I substitutional solid solutions

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The structure of Raman spectra of In$_x$Tl$_{1-x}$I substitutional solid solutions (x = 0.2, 0.3, 0.4, 0.5, 0.7) oriented in the (**a,c**) plane has been studied. Basing on the group theory analysis, the symmetry of phonon modes has been classified. The Fano anti-resonances have been revealed in the Raman spectra. The role of free carriers in the mechanism of essential changes in the phonon spectrum structure is discussed as depending on thallium content.

Исследована структура спектров комбинационных рассеяния твердых растворов замещения In$_x$Tl$_{1-x}$I (x = 0,2, 0,3, 0,4, 0,5, 0,7), ориентированных в плоскости (**a,c**). На основе теоретико-группового анализа проведена классификация симметрии фононных мод. Обнаружено антирезонансы Фано в спектрах. Обсуждается роль свободных носителей в механизме существенных изменений структуры фононных спектров в зависимости от содержания таллиевой компоненты.

The phonon subsystem in crystals of variable composition is extremely sensitive to the composition changes, stoichiometry deviations, and structure transformations. Therefore, the vibration spectra investigation of such systems offers a good tool to study the fine phenomena and to elucidate the mechanisms thereof. The phonon spectra of In$_x$Tl$_{1-x}$I substitutional solid solutions remain scarcely studied to date. Only few publications are known aimed at studies of Raman spectra for pure components of the system under consideration [1−3]. The solid solutions on the basis of indium and thallium iodides are of interest, being strongly anisotropic layered structures where the anisotropy extent is much higher than in some other layered crystal types. Moreover, these are relatively novel materials of promise in optoelectronics. The In$_x$Tl$_{1-x}$I crystals were grown by Bridgeman technique. The impurities of initial materials amounted less than 10^{-4} %, as determined by spectral analysis. The measurements were carried out in the reflection geometry. The working surface of bulk samples corresponded to the (**a,c**) crystallographic plane. The **c** axis was perpendicular to the one in the cleavage plane while the **b** axis was normal to the (**a,c**) plane. The setup for Raman spectra measurements was designed basing on a DFS-52 dual monochromator. A LGN-113 He–Ne laser (λ = 6328 Å, P = 15 mW) was used as the exciting source. For In$_x$Tl$_{1-x}$I, the He–Ne laser generation line falls into the transparency region at all the x values. The spectra were measured at room temperature.

The orthorhombic base-centered lattices of In$_x$Tl$_{1-x}$I crystals are described by the asymmorphous space symmetry group D_{2h}^{17} = $Cmcm$, as well as those of pure components InI and TlI. The group theory analysis results in the following classification of the In$_x$Tl$_{1-x}$I lattice vibration modes in the Γ point of the Brillouin zone:

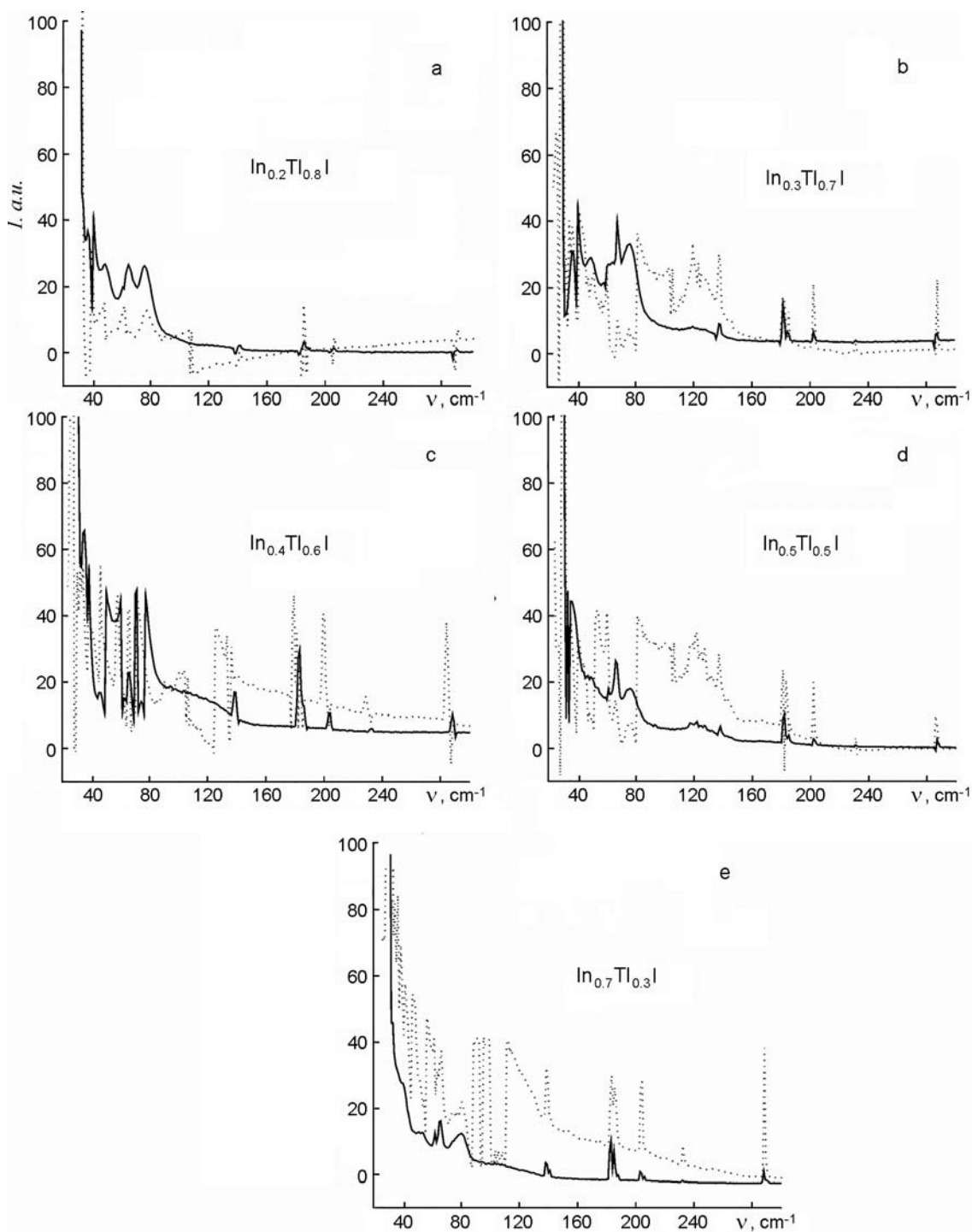$$\Gamma = 2A_g + 2B_{1g} + 2B_{3g} + 2B_{1u} + 2B_{2u} + 2B_{3u}. \quad (1)$$

Fig. 1. Raman spectra of $|In_xTl_{1-x}I|$ at $x = 0.2$ (a), 0.3 (b), 0.4 (c), 0.5 (d), 0.7 (e). Solid lines correspond to $E\|c$ polarization; dotted ones, to $E\|a$.

The B_{1u}, B_{2u} and B_{3u} modes corresponding to the T_X, T_Y and T_Z translations are acoustic. According to (1), nine optical modes answer to normal vibrations, namely, the fully symmetrical ($2A_g$), external translation (B_{1u}, B_{2u} and B_{3u}), and close to libration ($2B_{1g}$ and $2B_{3g}$) ones.

Expansion of the Γ_α representation gives

$$\Gamma_\alpha = 2A_g + 2B_{1g} + 2B_3g. \qquad (2)$$

The Raman-active A_g modes correspond to non-zero diagonal elements of the polarizability tensor while the α_{xy} and α_{yz} components correspond to B_{1g} and B_{3g} modes.
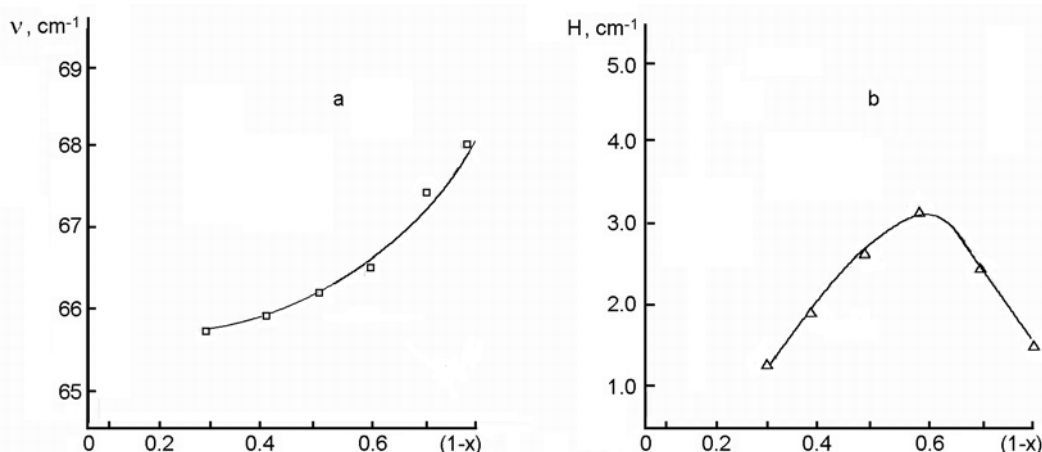
Fig. 2. Maximum position ν (a) and halfwidth H (b) of the band near 68 cm^{-1} as functions of thallium content in $In_xTl_{1-x}I$.

Fig. 1 presents the Raman spectra of $In_xTl_{1-x}I$ samples in the 20–300 cm^{-1} region for two scattering variants, $X(ZY)\overline{X}$ and $X(ZZ)\overline{X}$. For the samples with various thallium content, the main parameters of bands have been determined: the maximum position ν_i, halfwidth H_i and intensity I_i. In Fig. 2, presented are the $\nu_i(x)$ and $H_i(x)$ dependences for the band with a maximum near 68 cm^{-1}. As the thallium content increases, the band becomes shifted towards higher frequencies. This is explained by a higher polarizability of thallium as compared to indium, that results in increased force constant. A similar trend takes place for the bands near to 38, 45 and 62 cm^{-1}. In contrast, the 53 and 78 cm^{-1} bands are shifted towards lower frequencies as x decreases. The band halfwidth variations are complicated enough, thus evidencing a local disordering of the cell and its statistical character at the substitution of InI and TlI components in the mixed system.

The low-frequency modes of InI and TlI are especially sensitive to structure transformations of the layered cell. A characteristic intensity change of 22.5 and 29.6 cm^{-1} bands of the orthorhombic TlI under compression of the sample has been shown to reflect the transition to a $CsCl$ type cubic phase [4]. A hysteresis was observed due to the structure transformation at $P = 4.5$ kbar and the reciprocal transition at $P = 1.1$ kbar. From the 22.5 cm^{-1} band shift, the Grueneisen constant has been estimated to be $\gamma = 3.0$. A similar phase transition was observed in InI at temperature variation: the transition from the rhombic to cubic phase has been revealed at $T = 478$ K indicated by the behavior of

39.0 cm^{-1} Raman band [1]. Judging from the behavior of parameters for the most characteristic Raman bands as functions of x, the $In_xTl_{1-x}I$ system can be characterized as the two-mode model [5]. As to the Raman spectra of the samples with $(1 - x) > 0.5$ taken in the $X(ZY)\overline{X}$ geometry, the narrow band at $\nu \approx 40$ cm^{-1} ($H \approx 2$ cm^{-1}) is worth of attention. Its intensity is several times higher as compared to other bands. To elucidate its origin, the measurements under excitation near to the resonance one are necessary.

As to the scattering configuration $X(ZZ)\overline{X}$, the anti-resonance at $\nu \approx 80$ cm^{-1} is to be noted for $In_{0.5}Tl_{0.5}I$ and $In_{0.3}Tl_{0.7}I$ samples (Fig. 3). The 80 cm^{-1} band is described by the Breit-Wigner-Fano asymmetric contour

$$I(\nu) = I_0[1 - \left(\frac{\nu - \nu_0}{qH}\right)]^2[1 + \left(\frac{\nu - \nu_0}{H}\right)]^{-2}, \quad (3)$$

where ν_0 is the renormalized resonance frequency [7]; H, the band halfwidth; q, the Fano parameter (at $q^{-1} \to 0$, the symmetric Lorentzian contour is recovered).

The eq.(3) expresses the strong interaction of the discrete Raman-active phonon mode with continuous background. The parameter q is defined by the scattering amplitudes on phonons, A_p, and on carriers, A_h:

$$q \approx \frac{A_b}{HA_h}. \quad (4)$$

The method for q determination from the experimental asymmetric $I(\nu)$ contour is described in [6]. As thallium content in the $In_xTl_{1-x}I$ cell increases, the q value has been found to decrease. We have explained this

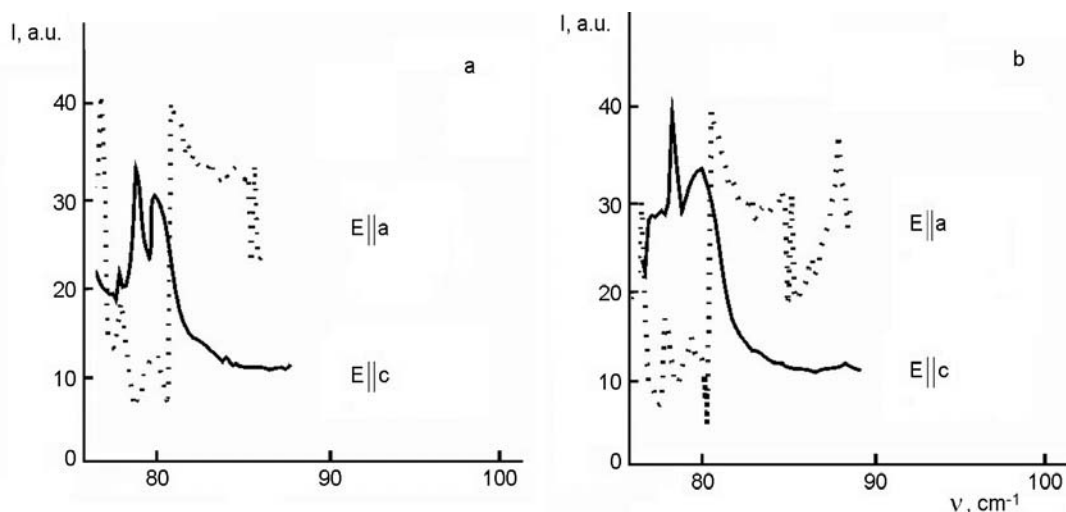Fig. 3. Anti-resonance at $\nu \approx 80$ cm^{-1} in Raman spectra of $In_{0.5}Tl_{0.5}I$ (a) and $In_{0.3}Tl_{0.7}I$ (b) at polarization $E\|\mathbf{a}$ (dotted line) and $E\|\mathbf{c}$ (solid line).

by the fact that at $(1 - x) \geq 0.5$, the concentration of free carriers (holes) increases [7], thus causing the background intensification and the A_h increase. It is still unclear why the free carrier excitation and the Fano effect manifestation is typical only of the $E\|a$. Perhaps the symmetry of wave functions of corresponding subbands is of importance here, taking into account a strong anisotropy of layered $In_xTl_{1-x}I$ lattices. It can be assumed that the intralayer vibrations of B_{1g} type interact intensely with the current carriers localized in those layers.

References

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Спектри комбінаційного розсіяння світла розчинів заміщення $In_xTl_{1-x}I$

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Досліджено структуру спектрів комбінаційного розсіювання твердих розчинів заміщення $In_xTl_{1-x}I$ ($x = 0,2$, $0,3$, $0,4$, $0,5$, $0,7$), орієнтованих у площині (**a,c**). На основі теоретико-групового аналізу проведено класифікацію симетрії фононних мод. У спектрах виявлено антирезонанси Фано. Обговорюється роль вільних носіїв у механізмі суттєвих змін структури фононних спектрів у залежності від вмісту талієвої компоненти.