Resonance Raman scattering in ZnTe at high excitation levels

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The interaction of *LO* phonons with plasma oscillations of nonequilibrium carriers generated as a result of resonance, two-photon excitation ($\hbar\omega_{\text{laser}} \leqslant E_g$) in ZnTe single crystals was observed. The resonance nature of the RS spectrum is strengthened with increasing excitation level.

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A resonance interaction that forms mixed plasmon-phonon modes can be observed in polar semiconductors at a high concentration of the carriers when the plasma frequency $\omega_p = (4\pi n^2/\epsilon_\infty m)^{1/2}$ is comparable to the frequency of the longitudinal optical phonon ω_{LO}. At plasma frequencies that are low as compared with the ω_{LO}, the interaction primarily takes the form of line broadening of the *LO* phonon. As the concentration of the carriers increases and $\omega_p \to \omega_{LO}$, we observe a shift of the mixed plasmon-phonon mode in the direction of high frequencies. This effect was studied in detail in strongly doped semiconductors.[1,2]

It is of interest to investigate the plasmon-phonon interaction in the nonequilibrium case at high level of laser pumping when the lifetime of the nonequilibrium carriers is 10^{-9} sec.

The dependence of the line shape of the *LO* phonon in the RS spectrum of GaAs on the pumping intensity was studied in Ref. 3. However, the plasma frequency corresponding to the density of the nonequilibrium carriers in this semiconductor proved to be much smaller than the frequency of the *LO* phonon. Therefore, the observed variations of the Raman scattering spectrum were negligible.

In this paper we investigate the reconstruction of the RS spectra of ZnTe single crystals. In this case the plasma frequency corresponding to the density of the nonequilibrium carriers generated by the optical pumping may exceed the frequency of the *LO* phonon.[4] Moreover, the YAG:Nd laser used as the second-harmonic excitation source (HE) at a temperature of the sample $T = 6$ K provided a resonance enhancement of the scattering because of the proximity of the exciting quantum $\hbar\omega_{\text{laser}}$ to the forbidden band $E_g (E_g - \hbar\omega_{\text{laser}} \approx 2\hbar\omega_{LO})$. As a result, we realized both a high generation efficiency of the nonequilibrium carriers due to two-photon absorption and a high efficiency of RS.

Investigations were conducted with use of bulk crystals. The measurements were performed using a CDL-1 spectrometer in the "backward scattering" geometry in conjunction with a stroboscopic photorecording system. The maximum pumping intensity, which was determined by the destruction threshold of the sample, was $I_0 = 30$–35 MW/cm^2. The obtained spectra are shown in Fig. 1.

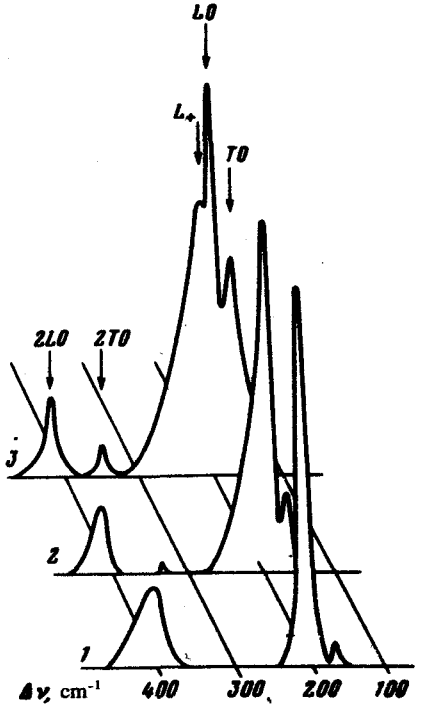

FIG. 1. RS spectra of ZnTe single crystals for different excitation levels: 1, $I_H = 0.3\ I_0$; 2, $I_H = 0.6\ I_0$; 3, $I_H = I_0$.

At pumping levels of $\sim 0.3\ I_0$ (curve 1), we observe an intense line of the *LO* phonon $\nu = 205\ \text{cm}^{-1}$, a weak line of the *TO* phonon $\nu = 176\ \text{cm}^{-1}$, and a broad band $\nu = 400\ \text{cm}^{-1}$ corresponding to the 2 *LO* pumping. An enhancement of the pumping level leads to a reconstruction of the RS spectrum due to formation of a new L_+ band, whose half-width increases with increasing pumping, and the maximum is shifted in the direction of high frequencies, reaching a value $\nu = 230\ \text{cm}^{-1}$ at maximum pumping (Fig. 2).[1)]

An increase of the pumping level increases the intensity of the *TO* and 2 *TO* lines more rapidly as compared to that in the region of the *LO* (L_+) and 2 *LO* oscillations. In addition, a noticeable narrowing of the 2 *LO* band is observed.

The observed L_+ band cannot be explained in terms of the broadening and line shift of the *LO* phonon due to heating of the sample by the laser. This is indicated by the fact that the half-width and the energy position of the *TO* phonon line remain almost invariable at all pumping levels. The heating of the sample, moreover, should decrease ω_{LO}. Therefore, the appearance of the L_+ band in the RS spectrum is attributable to the excitation in the crystal of the nonequilibrium electron-hole plasma (EHP) whose oscillations interact with the *LO* phonons, which produces the bound plasmon-phonon modes. It should be noted that the onset of broadening of the *LO* (L_+) line coincides with the appearance in the luminescence spectrum of a line corresponding to the recombination radiation of the EHP.

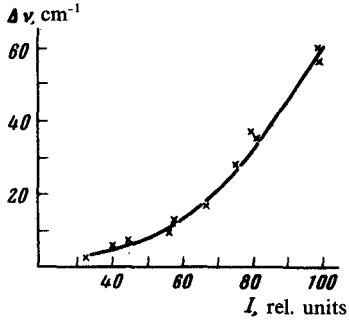

FIG. 2. Dependence of the half width of the L_+ band on the pumping intensity.

However, as seen in Fig. 1 (curve 3), in addition to the shifted plasmon-phonon L_+ mode the unperturbed line of the LO phonon can be observed in the RS spectrum even at maximum excitation levels. This is apparently attributed to the fact that at helium temperatures the non-equilibrium carriers are condensed into an electron-hole liquid. Because of this, the phases in the pumped volume break down into a dense EHL whose plasma oscillations interact with the LO phonons and a region of small carrier density in which the nonequilibrium electron-phonon pairs are bound in the excitons.

The scattering efficiency by the bound plasmon-phonon modes is proportional to the expression[5]:

$$\sigma \sim \{ [\omega^2(\omega_{LO}^2 - \omega^2) - \omega_p^2(\omega_{TO}^2 - \omega^2)]^2 + \omega^2\Gamma^2(\omega_{LO}^2 - \omega^2)^2 \}^{-1}, \qquad (1)$$

where ω_{LO} and ω_{TO} are frequencies of the LO and TO phonons, respectively, and ω_p is the plasma frequency, with allowance for the dispersion, which is determined by the expression

$$\omega_p(q) = \omega_p\left(1 + \frac{3}{10}\frac{q^2V_F^2}{\omega_p^2}\right), \qquad (2)$$

where q is the wave vector of the plasmon, which for the backward-scattering geometry is equal to approximately a doubled wave vector of the laser and V_F is the Fermi velocity of the carriers. The first term in expression (1) vanishes when $\omega = \omega_+$. The plasma frequency, which in this case is equal to 160 cm^{-1}, can be determined from the value of ω_+ (230 cm^{-1}). With allowance for the dispersion, it corresponds to the concentration of the electron-hole pairs $n = 3\times10^{17}$ cm^{-3}. This value is in agreement with the concentration estimated by us from the shape of the emission line of the EHP.

A fast increase of the intensity of the TO and 2 TO lines and also a narrowing of the spectrum of two-phonon 2 LO transitions indicates a strengthening of the resonance interaction, which can be attributed to two mechanisms. 1) A decrease of the width of the forbidden band due to the exchange and correlation interactions, whose estimate for $n = 3\times10^{17}$ cm^{-3}, analogously to Ref. 6, gives $\Delta E_g = 21$ meV. As a result, $E_g' - \hbar\omega_{\text{laser}} \sim \hbar\omega_{LO}$. 2) To explain the narrow and the intensive 2 LO and 2 TO lines in the spectrum of resonance RS of $Ga_xIn_{1-x}P$ and $GaAs_xP_{1-x}$ single

crystals, Balkanski *et al.*[7] proposed a bound exciton-phonon complex[8] as the intermediate state. It is conceivable that in our case of high-level excitation, its contribution to the resonance RS process is increased.

[1)]The half-width of the L_+ band was estimated disregarding the contribution from the LO-phonon line.

[1]E. L. Ivchenko, D. N. Mirlin, and I. I. Peshina, Fiz. Tverd. Tela **17**, 2282 (1975) [Sov. Phys. Solid State **17**, 1510 (1975)].

[2]A. Pinczuk, G. Abstreiter, R. Trommer, and M. Cardona, Solid State Comm. **21**, 959 (1977).

[3]R. S. Turtelli and A. R. B. de Castro, Phys. Stat. Sol. **93**, 811 (1979).

[4]V. A. Korneĭchuk, M. K. Sheĭnkman, and A. M. Yaremko, Fiz. Tverd. Tela **22**, 987 (1980) [in press].

[5]Rasseyanie sveta v tverdykh telakh (Scattering of Light in Solids), edited by M. Cardona, Moscow, Mir, 1979.

[6]V. G. Lysenko, V. I. Revenko, T. G. Tratas, and V. B. Timofeev, Pis'ma Zh, Eksp. Teor, Fiz. **20**, 180 (1974) [JETP Lett. **20**, 77 (1974)].

[7]M. Balkanski, L. M. Falicov, C. Hirlimann, and K. P. Jain, Solid State Comm. **25**, 261 (1978).

[8]I. B. Levinson and É. I. Rashba, Usp. Fiz. Nauk **111**, 683 (1973) [Sov. Phys. Usp. **16**, 892 (1973)].