Polarization properties of stimulated emission from two-photon-pumped PbSe crystals, due to selective filling of the energy valleys

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The polarization characteristics of stimulated recombination radiation of PbSe crystals were investigated at helium temperatures. It was observed that selective population of the energy valleys by linearly polarized radiation of a CO_2 laser ($\hbar\omega = 0.117$ eV) results in unusual polarization dependences of the recombination radiation, which are attributed to a predominant contribution of individual valleys and to enhancement of the polarization modes. The high degree of polarization of the stimulated recombination emission of PbSe (up to 0.54), observed in experiment, greatly exceeds the theoretical possible value for spontaneous linear recombination (0.065), thus indicating a strong enhancement in the PbSe crystal in the stimulated emission regime. The possibility of controlling the amplitude and polarization of the stimulated recombination emission of PbSe by varying the polarization of the pump radiation is demonstrated.

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1. Observation of a number of polarization effects that manifest themselves in an investigation of stimulated recombination emission (SRE) from PbTe ($T \leq 20$ K) in the case of two-photon pumping by linearly polarized emission from a pulsed CO_2 laser was reported earlier.[1-3] The PbTe crystals have cubic symmetry of group O_h. Nonetheless, the change of direction of the linear polarization of the pump radiation (PR) changed substantially the total yield of the SRE. In addition, the SRE turned out to be partially polarized, and the direction (ψ_m) and degree (ρ) of the linear polarization turned out to depend on the direction of the PR polarization. These properties were attributed: 1) to a strong dependence of the rate of excitation of the carriers in two-photon absorption in various energy valleys[1)] of lead telluride on the direction of the PR polarization, 2) to the absence of intervalley transfer at sufficiently low temperatures, and 3) to the onset of stimulated emission.

No investigations of SRE under two-photon pumping were made in lead selenide. At the same time, many studies of the properties of PbSe laser diodes have been reported. PbSe lasers wavelengths can be tuned over a wide range by changing the crystal temperature and the external pressures. The use of two-photon optical pumping for IV–VI crystals makes it possible to obtain from the crystal emission intensities much higher than those of diode lasers. Interest attaches therefore to the polarization properties of the SRE of PbSe and to the possibilities of controlling its polarization.

2. The dependence of the rate of carrier generation in the l-th valley on the direction of the PR polarization in IV-VI compounds can be written in the form [3, 4]:

$$G_l \propto \left[\left(1-a\sum_{i,j}\theta_i^{(l)}\theta_j^{(l)}e_ie_j\right)j_p\right]^2, \tag{1}$$

where $a = 1 - m_\perp/m_\parallel$, $m_{\perp,\parallel}$ are the reduced transverse and longitudinal effective masses in the valleys; e_{ij} are the components of the polarization vector of the PR along the crystal axes; θ_{ij} are the direction cosines of the major semi-axes of the ellipsoids ($l = 1, 2, 3, 4$) which constitute the equal-energy surfaces in k-space ($i, j = x, y, z$).

In particular, an expression is given in Ref. 1 for the angular dependence of the rate of generation in various valleys in the case when the PR propagates along the [100] axis of the crystal:

$$G \propto \left[1-\frac{2}{3}a+\frac{1}{6}a^2 \pm \frac{2}{3}a\left(1-\frac{a}{3}\right)\sin 2\varphi-\frac{a^2}{18}\cos 4\varphi\right]. \tag{2}$$

The plus sign in (2) is chosen for valleys in the directions [1, −1, 1] and [−1, 1, 1], and the minus sign for the valleys in the directions [1, 1, 1] and [−1, −1, 1]; φ is the angle between the direction of the polarization of the PR and the [010] axis of the crystal.

At $\varphi = \pm 45°$, the rate of excitation into two valleys (e.g., [1, −1, 1] and [−1, 1, 1] for $\varphi = 45°$) exceeds the rate of excitation into the two other valleys by a factor $\varkappa = [1 - 4/3a(1 - a/3)]^{-1}$. At $\varphi = 0$ the rate of excitation into all four valleys should be the same.

It is seen from the presented expressions that the ratio $\varkappa$ of the rates of generation in the indicated pair of valleys is determined essentially by the valley anisotropy parameter a. For PbTe we have $a \approx 0.9$ (Ref. 1) and $\varkappa = 6.25$. The large value of $\varkappa$ causes at $\Delta n \gtrsim n_0$ a substantial difference between the carrier recombination rates in the indicated pairs of valleys. As a result, and also on account of the strong anisotropy of the valleys, the emission from the crystal should be considerably polarized (in the absence of intervalley relaxation). In Ref. 2 is given an expression that determines, under these conditions, the connection between the flux of the spontaneous interband recombination radiation (RR) from the crystal (I_{RR}), the direction φ of the PR polarization, and the angle of rotation of the analyzer in front of the photoreceiver that measures the RR. For the case when the investigated crystal is cut in the (100) plane and the RR is measured in a direction perpendicular to this plane we

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have

$$I_{RR} \propto \left\{ \left[1 - \frac{a}{3}(1+\sin 2\psi) \right] \left[1 - \frac{a}{3}(1+\sin 2\varphi) \right]^{2n} + \left[1 - \frac{a}{3}(1-\sin 2\psi) \right] \left[1 - \frac{a}{3}(1-\sin 2\varphi) \right]^{2n} \right\}; \tag{3}$$

Here $n = 1, 2$ for linear and quadratic recombination, respectively; the angles φ and ψ are measured from the [010] direction in the crystal.

It follows from (3) that for PbTe at $\varphi = \pi/4$, even in the case of linear recombination, the degree of polarization ρ of the luminescence should be ~0.3. Under SRE conditions, however, the experimental value of ρ reached in some cases ~0.85 (Ref. 2).

The effective-mass anisotropy in PbSe is small,[5] $a \approx 0.47$ and $\varkappa \approx 2.1$. The degree of linear polarization of the spontaneous luminescence in PbSe cannot exceed ~0.065 and ~0.11 for linear and quadratic recombination, respectively. On the other hand, under SRE conditions the value of ρ is determined also by the gain in the crystal. It should depend both on the angle φ and on the pump radiation intensity j_p.

The foregoing conclusions are valid in the absence of intervalley exchange of carriers. This asumption, however, is not trivial. Since the minimum energy, in PbSe, of a phonon with momentum sufficient for an intervalley transition with scattering by a phonon is 4.35 meV (Ref. 6), such an exchange is considerably suppressed for thermalized carriers at low temperatures ($T \leq 30$ K). However, intervalley transitions, due to scattering by impurity centers, to electron-hole scattering, and to "re-emission" processes[7] are not very effective in PbSe because of the large dielectric constant and the very low ionization energy of the shallow impurity levels. For "hot" carriers, which are thrown high into the band by light photons, there are no stringent restrictions whatever on intervalley transitions. What is important here is the relation between the intravalley (τ_I) and intervalley ($\tau_{II'}$) relaxation times, and also the carrier lifetime (τ). Under SRE conditions the question of selective population of valleys and the associated effect of polarizability of the radiation, its dependence on the direction of the polarization of the PR can be determined only in experiment.

3. Experimental investigations of SRE under two-photon pumping were performed on polished plane-parallel samples of n-PbSe ($n \approx 1.8 \times 10^{17}$ cm^{-3}) of thickness ~0.8 mm, cut in the (100) plane. To prevent external deformations, the samples were freely mounted in the chamber of a helium cryostat in a stream of helium vapor. The experiments were performed at a temperature $T = (7 \pm 1)$ K. The emission of the pulsed (pulse duration $t_p = 10^{-7}$ sec) CO_2 laser was focused on the crystal by a lens of focal length $F = 18$ cm. The direction of the linear polarization of the PR was varied with a halfwave plate of CdS. The SRE of the PbSe crystals was registered "in transmission" by a Ge:Au photoreceiver[2)] in front of which the analyzer was placed. The laser emission ($\lambda = 10.6$ μm) passing through the crystal was separated from the investigated SRE of the PbSe ($\lambda \approx 8.5$ μm) by an LiF-crystal filter mounted in front of the photoreceiver.

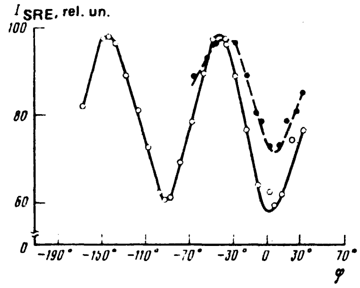

FIG. 1. Dependence of the SRE flux of PbSe on the angle φ between the direction of the polarization of the PR and the [010] axis of the crystal n-PbSe at $j_{p1} = 0.6 \times 10^{25}$ cm$^{-2}\cdot$sec^{-1} (○); $j_{p2} = 0.9 \times 10^{25}$ cm$^{-2}\cdot$sec^{-1} (●); $n = 1.8 \times 10^{17}$ cm^{-3}, $T = (7 \pm 1)$ K.

To verify that no considerable shift of the energy valleys took place as a result of internal stresses in the crystal (a relative shift of one or two valleys downward in energy by more than ~4.3 meV makes the population of these valleys much higher than in the "upper" valleys), the SRE was measured with the PR circularly polarized. The rate of generation of carriers in all the valleys was the same and in the absence of a shift of the valleys the emission from the crystals should not be linearly polarized. Experiment has shown that the degree of linear polarization ρ of the SRE was quite small ($\rho \leq 0.035$). Since the degree of circular polarization of the PR was ~0.96, it can be assumed that the deviation of ρ from zero is due precisely to this circumstance.

Figure 1 shows plots of the total SRE yield (without the analyzer) against the direction of polarization of the PR at two values of the PR intensity. It is seen that these dependences are periodic functions with a period ~90°. At lower PR intensity, the modulation of the SRE flux turns out to be deeper: $I_{RR}^{max}/I_{RR}^{min} \approx 1.6$. Such a periodic dependence, observed earlier also for PbTe (Ref. 1), is explained by the fact that when the energy valleys are selectively filled the gains in the valleys are different. In the experimental geometry employed at $\varphi = \pm\pi/4$ the rate of excitation of carriers into two valleys was 2.1 times larger than into the two others. Accordingly the gain in them was much higher. At $\varphi = 0°$ the rate of generation was the same in all valleys. In each of them the number of carriers excited is 1.35 times smaller than in the two valleys in the preceding ($\varphi = \pm 45°$) case. As a result, the gain in each valley is smaller and the total emission yield is less.

Figure 2 shows plots of $I_{RR}(j_p)$ for $\varphi = 0°$ and 45°, as well as for circularly polarized PR. At $\varphi = 0°$ and circularly polarized PR, the plots practically coincide. This is quite understandable, since in these two cases the rate of generation into all valleys is the same. The plot of $I_{RR}(j_p)$ at $\varphi = 45°$ rises higher, and at small j_p it turns out to be less steep.

The dashed lines in Fig. 2 show two values of the intensity $j_{p1,2}$ at which the angular dependences $I_{RR}(\varphi)$ were measured. The lower intensity (j_{p1}) corresponds to the steeper section of the plot, and accordingly the

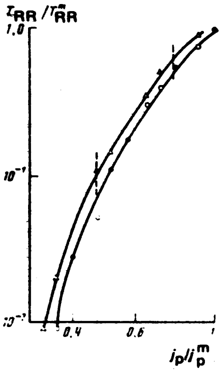

FIG. 2. Dependence of the SRE flux of PbSe on the pump radiation intensity j_p: ○) circularly polarized PR, $j_p^{max} = 1.15\times 10^{25}$ $cm^{-2}\cdot sec^{-1}$; ●) linearly polarized PR, $\varphi = 9°$; △) linearly polarized PR, $\varphi = -40°$.

depth of modulation of $I_{RR}(\varphi)$ turns out to be larger. The $I_{RR}(\varphi)$ dependence at $j_p = j_{p2}$ turns out to be shifted somewhat relative to $I_{RR}(\varphi)/j_{p1}$. Its minimum was observed at $\varphi \approx 10°$. A Laue diffraction pattern plotted for this sample to determine its orientation more accurately, has shown that the plane of the plate is inclined away from the (100) plane by 4.0°. Therefore the rates of generation into different valleys are not exactly the same at any angle φ. This circumstance, as well as the fact that the radiation yield upon recombination in different valleys does not have the same dependence on G (and by the same token on φ and j_p) can be assumed to explain the indicated behavior of the functions $I_{RR}(\varphi)$ at different j_p.

We investigated next the polarization of the SRE. For each value of the angle φ_i we plotted the function $I_{RR}(\psi)$ within the limits of one or two periods. We then determined the quantities

$$\rho(\varphi_i) = (I_{RR}^{max} - I_{RR}^{min})/(I_{RR}^{max} + I_{RR}^{max})$$

and $\psi_m(\psi_i)$, which is the angle that determines the direction of polarization of the SRE. Figure 3 shows plots of $\rho(\varphi)$ and $\psi_m(\varphi)$. It is seen that in a small vicinity near the angle $\varphi = 0$ the direction of the SRE polarization changes jumpwise, and the degree of polarization has a strongly pronounced minimum ($\rho \approx 0.12$). When φ deviates from 0° by $\pm(30-40)°$, the value of ρ increases to ~0.4. The directions of polarization of the SRE at the angles $\varphi \sim 50°$ and +40° differ by approximately 90°, corresponding to emission from different

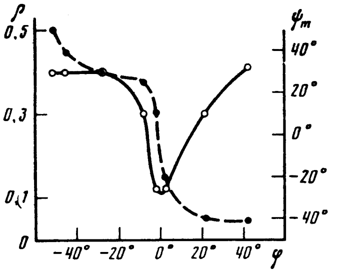

FIG. 3. Dependence of the degree ρ and direction ψ_m of the polarization of the SRE of PbSe on the angle φ between the direction of the polarization of the PR and the [010] axis of the crystal: ○) $\rho(\varphi)$, ●) $\psi_m(\varphi)$; $j_p = 1.15\times 10^{25}$ $cm^{-2}\cdot sec^{-1}$.

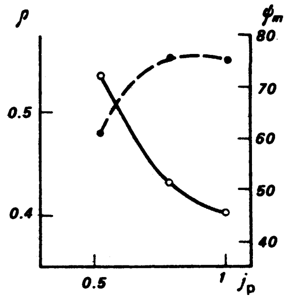

FIG. 4. Dependence of the degree ρ and the direction ψ_m of the polarization of the SRE on the PR intensity j_p: ○) $\rho(j_p)$, ●) $\psi_m(j_p)$; $\varphi = -54°$, j_p is in units of 1.15×10^{25} $cm^{-2}\cdot sec^{-1}$.

pairs of energy valleys. The considerable slope of the $\rho(\varphi)$ plot in the vicinity of $\varphi = 0°$ and the large values of φ at $|\varphi| \gtrsim 10-15°$ indicate a substantial enhancement of the polarization modes in the crystal. Some asymmetry of the plots of $\rho(\varphi)$ and $\psi_m(\varphi)$ is possibly due to the small deviation of the plane of the sample from the (100) plane of the crystal (~4°), and also to internal stresses in the crystal.

The function $\rho(j_p)$ was measured at $\varphi = -54°$, see Fig. 4. It was found that at a given value of the angle φ in the investigated range of PR intensity the degree of polarization of the SRE decreases with increasing j_p. The largest experimentally obtained ρ is ~0.54. With increasing j_p, a change takes place also in the direction of the SRE polarization. This behavior of these dependences can be easily understood. In the presence of a resonator, the radiation becomes amplified from those valleys into which fewer carriers are thrown at a given direction of the PR polarization. On the other hand the radiation yield upon recombination in the two other valleys (into which more carriers were thrown) saturates with increasing j_p. Thus, the relative contributions of the radiation from all the valleys to the measured SRE flux become equalized. The degree of polarization of the SRE decreases correspondingly.

4. From the presented results of the investigation of the SRE of PbSe we can conclude that a considerable enhancement of the polarization modes due to recombination in individual energy valleys was observed under the conditions of the described experiment as they became selectivity filled by linearly polarized PR in two-phonon absorption. The spectral measurements have also shown that one relatively narrow emission line is generated with a quantum energy ~0.1465 eV, corresponding approximately to the "optical" width of the forbidden band at the given temperature. The energy of two photons of the CO_2 emission is 0.234 eV. Thus, the optically excited carriers manage to become thermalized prior to recombination. A comparison of the spectral and polarization measurements yields the relations between the intravalley and intervalley relaxation times, and also of the lifetime at the given level j_p, namely $\tau_I < \tau < \tau_{II'}$.

The data obtained in the present study show that there are ample opportunities for controlling the amplitude and polarization properties of SRE of two-photon-pumped PbSe by varying the polarization of the PR.

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[1)]IV-VI crystals have a multivalley energy spectrum. The valleys are elongated along the [111] directions in the crystal. The effective masses of the electrons and holes are close in magnitude, and the extrema of both bands are at point L of the Brillouin zone.

[2)]The sensitivity of commercial Ge:Au photoreceivers depends strongly on the direction of polarization of the incident radiation. A receiver was therefore produced for these measurements by the author, with a sensitivity independent of the polarization.

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