

Observation of photoluminescence bands with $E_{\max} > E_g$ in CdTe⟨Se⟩ and CdTe⟨Zn⟩ crystals

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Resonant levels manifested by emission bands with $E_{\max} > E_g$ have been observed in CdTe⟨Se⟩ and CdTe⟨Zn⟩ crystals. The anisotropy of the centers responsible for the new bands is evidence that these centers have a complex structure.

An effective method for controlling the physical properties of semiconductors is to dope them with isovalent impurities.¹ Isovalent impurities may introduce local levels in the band gap of the semiconductor (impurities of the first kind) or participate in the formation of allowed bands, forming solid solutions (impurities of the second kind). Theoretical work predicts that isovalent impurities of the second kind can, at low concentrations, also form quasilocal levels in an allowed band of the semiconductor, i.e., levels which are at resonance with the continuous band spectrum.² The effect of isovalent impurities on the formation of local levels in the band gap and on the formation of bound exciton states has been studied in some detail (in Ge, Si, InP, GaP, CdS, and ZnTe crystals). In terms of experimental observations of resonant levels in wide-gap semiconductors, in contrast, the only studies which have been reported are those by Solov'eva *et al.*³ and Bachenov *et al.*,⁴ who reported the observation of an additional peak with $E_{\max} = 2.1$ eV in the photoconductivity spectrum of GaAs_{1-x}Sb_x ($x \leq 0.02$). Their peak was interpreted as a manifestation of an antimony level 0.6 eV below the top of the valence band. It was pointed out later,¹ however, that this interpretation requires further proof.

In the present letter we are reporting data on the observation of radiative centers with $E_{\max} > E_g$ in CdTe crystals doped with an isovalent impurity of Se or Zn. The

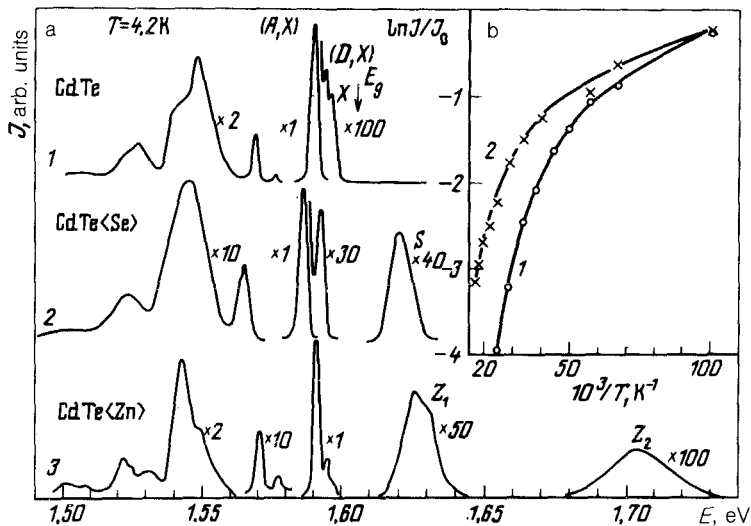


FIG. 1. a: Photoluminescence spectra of single crystals at $T = 4.2$ K. 1—CdTe; 2—CdTe(Se) ($N_{Se} = 10^{20}$ cm $^{-3}$); 3—CdTe(Zn) ($N_{Zn} = 10^{19}$ cm $^{-3}$). The arrow marks the position of the edge of the band gap in pure CdTe. b: The functional dependence $\ln(I/I_0) = f(10^3/T)$. 1—For the S and Z_1 photoluminescence bands; 2—for the Z_2 band.

doping was carried out during the crystal growth (by the Bridgman method) by adding elemental selenium or zinc to the cell holding the previously synthesized material. The dopant concentration in the melt was $N_{Se} \approx 10^{17} - 10^{20}$ cm $^{-3}$ or $N_{Zn} \approx 10^{19}$ cm $^{-3}$.

The photoluminescence spectra were studied by a method of synchronous detection over the temperature range $T = 4.2 - 70$ K in samples cleaved along $[110]$ plane in liquid helium. Figure 1a shows spectra of the near-edge photoluminescence of CdTe single crystals, both undoped (1) and doped with Se (2) and Zn (3). In the photoluminescence spectrum of the undoped crystal we can clearly see the well-known emission lines of free excitons (X) and bound excitons (D,X), (A,X), along with their phonon repetitions. We also see a complex band at 1.54–1.56 eV, which is due to (conduction band)-acceptor and donor-acceptor transitions.⁵ The doping of the CdTe crystals with selenium or zinc does not give rise to any new lines in the photoluminescence spectrum at energies below E_g . On the other hand, we do observe a substantial redistribution of the intensity among the exciton and impurity photoluminescence bands. In particular, as the selenium concentration is raised from 10^{17} to 10^{19} cm $^{-3}$, we observe a sharp relative attenuation of the line of an exciton bound to a donor and of the band from donor-acceptor transitions. These changes seem to be evidence of a gettering action of selenium by an uncontrolled donor impurity. A further increase in the selenium concentration results in an intensification of all of the photoluminescence bands. This effect can be attributed to a gettering of impurities and defects which are effective centers of radiationless recombination.¹⁾

The most important result of the doping of CdTe with isovalent impurities is the

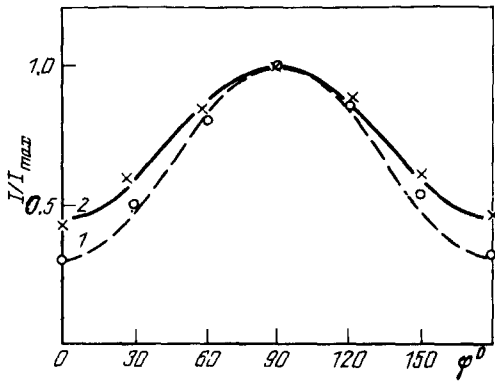


FIG. 2. Intensities of the Z_1 (O) and Z_2 (X) photoluminescence bands versus the angle (φ) between the vector \mathbf{E} of the luminescence and the plane of incidence.

appearance of some new photoluminescence bands with $E_{\max} > E_g$: $E_{\max} = 1.621$ eV (the S band) in the case of doping with selenium and $E_{\max} = 1.626$ eV (the Z_1 band) and $E_{\max} = 1.704$ eV (the Z_2 band) during doping with zinc (Fig. 1a). The intensities of the new bands are roughly two orders of magnitude lower than that of the lines of bound excitons. A study of the temperature dependence of the intensity of these new bands revealed that they shrink exponentially as the temperature is raised from $T = 4.2$ K to $T = 40$ – 60 K, with activation energies $E_i^S \approx 7$ meV, $E_i^{Z_1} \approx 7$ meV, and $E_i^{Z_2} \approx 11$ meV (Fig. 1b). These energies are significantly smaller than the energy separations between the peaks of these bands and the edge of the band gap.

Polarization studies of the photoluminescence made it possible to establish that the centers responsible for the new bands are anisotropic. Figure 2 shows the intensities of bands Z_1 and Z_2 versus the angle φ , between the vector \mathbf{E} and the plane of incidence. A similar behavior was observed for the S band. As the angle φ increases, the intensities of the S , Z_1 and Z_2 bands increase, reaching a maximum at $\varphi = 90^\circ$. The intensities of the other photoluminescence bands remain essentially constant. The degree of polarization P , defined as $P = (I_\perp - I_\parallel) / (I_\perp + I_\parallel)$, is 53% for the S and Z_1 bands and 38% for the Z_2 band.

In summary, some resonant levels which fall in allowed energy bands have been detected in the photoluminescence spectra of $\text{CdTe}\langle\text{Se}\rangle$ and $\text{CdTe}\langle\text{Zn}\rangle$ crystals. The anisotropy of the centers responsible for these new bands is evidence that these centers have a complex structure. This structure is apparently a consequence of an association of isovalent impurities with uncontrolled impurities or clusters of isovalent impurities.

¹A change in the concentration of local centers as a result of isovalent doping is also characteristic of III-V semiconductors.^{6,7}

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