Excitons deep in the intrinsic absorption region of $TlGaSe_2$ single crystals

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A new absorption line has been discovered deep in the intrinsic absorption region, at $E_B = 2.3804$ eV, at $T = 1.8$ K. This line is shown to be due to the formation of direct free excitons at point Γ at the center of the Brillouin zone. The sharp change in the absorption coefficient at $T = 105$ K, accompanied by a vanishing of exciton absorption peak B, is attributed to structural phase transitions in the $TlGaSe_2$ single crystals.

The existence of excitons deep in the intrinsic absorption region and manifestations of these excitons in the optical spectra of semiconductors have recently attracted increased interest. Studies of the absorption spectra deep in the intrinsic absorption region are known to require very thin crystals, which are not always feasible. The pronounced anisotropy of the chemical bonds of layered $TlGaSe_2$ single crystals significantly simplifies the problem of synthesizing thin single-crystal films of large dimensions with high-quality natural surfaces. On the other hand, this material is particularly suitable for the excitation of excitons deep in the intrinsic absorption region because the absorption coefficient above the fundamental edge is low (~ 300 cm^{-1}) in comparison with that of III–VI (Ref. 1) and II–V (Ref. 2) single crystals. There is, accordingly, interest in optical studies for the purpose of obtaining information on exciton states deep in the intrinsic absorption region in layered semiconducting compounds of the III–III–VI_2 group (e.g., $TlGaSe_2$), which have received little study, over a broad temperature range.

The crystal structure of $TlGaSe_2$ has been studied in detail.[3,4] According to the data of Ref. 3, layered $TlGaSe_2$ single crystals crystallize in a monoclinic structure with space group C_S^4. Its absorption spectrum near the fundamental absorption edge has been studied in several places.[5,7]

In this paper we report the first study of the spectrum of the absorption coefficient of $TlGaSe_2$ single crystals deep in the intrinsic absorption region over the temperature interval 1.8–110 K.

The $TlGaSe_2$ single crystals are grown by the Bridgman-Stockbarger method. The crystals have a layered structure, a p-type conductivity, and a room-temperature resistivity of 10^8–10^9 $\Omega \cdot$ cm. In the experiments we use glass and metal cryostats equipped with a temperature regulation system for experiments over the temperature intervals 1.8–4.2 and 6–110 K, respectively. The spectra are recorded by a photoelectric method with a DFS-12 spectrometer. To record the transmission spectra of the $TlGaSe_2$ single crystal deep in the intrinsic absorption region we use thin samples, with thickness $d \approx 2$–10 μm, cleaved from single crystals from a massive bar. The thicknesses of the samples are determined under a microscope and from an analysis of the transmission interference pattern.

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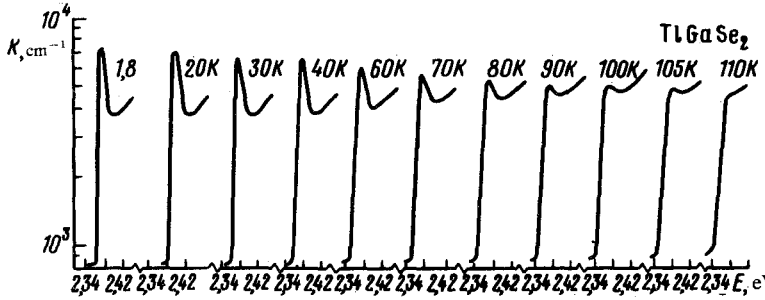

FIG. 1. Absorption spectra of $TlGaSe_2$ single crystals deep in the intrinsic absorption region in the temperature interval $T = 1.8$–110 K. The unpolarized light is incident along the normal to the plane of the layer.

Figure 1 shows absorption spectra deep in the intrinsic absorption region of $TlGaSe_2$. In these measurements, unpolarized light was incident perpendicular to the plane of the layer in the temperature interval $T = 1.8$–110 K. In this interval we observe a peak in the absorption spectrum at $E_B = 2.3804$ eV at $T = 1.8$ K. It can be seen from Fig. 1 that as the temperature is lowered the spectral structure becomes sharper and shifts upward along the energy scale; i.e., $\Delta E/\Delta T$ is of the form characteristic of most III–VI layered semiconductors. Table I shows the energy positions of the absorption lines in the temperature interval 1.8–110 K.

The temperature coefficient of the energy position of the exciton deep in the intrinsic absorption region differs from that of the energy position of the edge direct exciton absorption line. Figure 2 shows the temperature dependence of the energy position of the direct exciton line B in $TlGaSe_2$ single crystals.

TABLE I. Energy positions of absorption lines B in $TlGaSe_2$ single crystals.

T (K)	E_B (eV)
1, 8	2,3804
5,0	2,3803
10	2,3799
20	2,3794
30	2,3790
35	2,3785
40	2,3781
45	2,3767
50	2,3758
60	2,3749
70	2,3731
80	2,3713
90	2,3699
100	2,3690
105	2,3681
110	2,3667

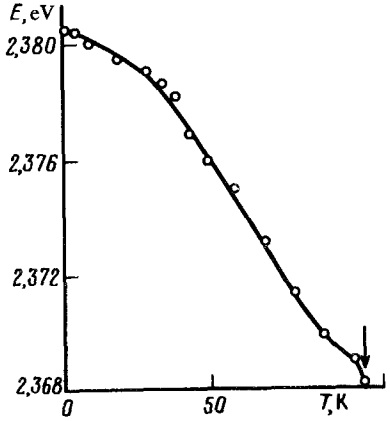

FIG. 2. Temperature dependence of the energy position of direct exciton line B in $TlGaSe_2$ single crystals.

From the temperature-induced shift of the exciton peak deep in the intrinsic absorption region we find

$$\frac{\Delta E_B}{\Delta T} = -1{,}23 \times 10^{-4} \text{ eV/deg}.$$

This line is more sensitive to changes in the temperature and disappears at 105 K (but remains in the form of a plateau), while the line near the fundamental absorption edge is observed as a peak up to 210 K.

The half-width of line B deep in the intrinsic absorption region is smaller ($\sim$0.013 eV at 1.8 K) than that of the line of the main exciton peak at the fundamental absorption edge ($\sim$0.025 eV at 1.8 K).

We thus see that the lifetime of the excitons deep in the intrinsic absorption region is about twice as long; this result can be attributed to the dynamic stability of these excitons.

These results on the temperature dependence, the data on the half-width of the observed structural feature, and preliminary calculations of the band structure of $TlGaSe_2$ single crystals suggest that the observed line B deep in the intrinsic absorption region is due to the formation of electron-hole pairs at point Γ at the center of the Brillouin zone.

Interestingly, the sharp change in the absorption coefficient and the disappearance of the exciton absorption peak B occur in the temperature interval 105–110 K (Fig. 2). Taking into account the data of Refs. 8 and 9 on the occurrence of a phase transition in $TlGaSe_2$ single crystals, we might suggest that this behavior is due to a structural phase transition which gives rise to fluctuations of the crystal lattice and thereby intensifies the exciton-phonon interaction.

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