Free exciton and exciton-impurity complexes of monoclinic zinc diphosphide

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The reflection spectra near E_g at 4.2, 80, and 293 K and the transmission and photoluminescence spectra at 4.2 K have been investigated for monoclinic ZnP_2 crystals. The free-exciton states with $n = 1, 2, 3$, and 4 and exciton-impurity complexes have been observed for the first time. Their basic parameters are evaluated.

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The monoclinic modification of ZnP_2 is presumed to be a straight-band semiconductor with the possible appearance of a free exciton with $n=1$.[1] We have used the method of Ref. 2 to investigate the reflection spectra near E_g at 80 and 293 K for $\mathbf{E}\parallel\mathbf{c}$ and $\mathbf{E}\perp\mathbf{c}$ polarizations, the reflection and transmission spectra at 4.2 K on a PGS-2 spectrograph, and the photoluminescence spectra at 4.2 K on an SDL-1 apparatus.

Structures corresponding to the free-exciton state with $n=1, 2$, and 3 have been observed in the reflection spectra at $\mathbf{E}\parallel\mathbf{c}$ and 80 K (curve 1 in Fig. 1). The first two dispersion structures have the classical shape, from which we can easily calculate, by using the method of Ref. 3, the energy E of the absorption maximum, the absorption coefficient μ at the maximum and the oscillator strength f of the unit cell of a crystal: $E_1 = 1.5536$ eV, $\mu_1 = 6.1 \times 10^5$ cm^{-1}, and $f_1 = 0.084$ for the most intense structure, and $E_2 = 1.5831$ eV, $\mu_2 = 0.7 \times 10^5$ cm^{-1}, and $f_2 = 0.0034$ for the second structure.

The most intense free excitons of semiconductors have been identified in CdSe-type crystals.[4] For example, for the A_1 exciton ground state of CdSe at 80 K the reflection at the maximum is about 23% for a continuous background of about 17–

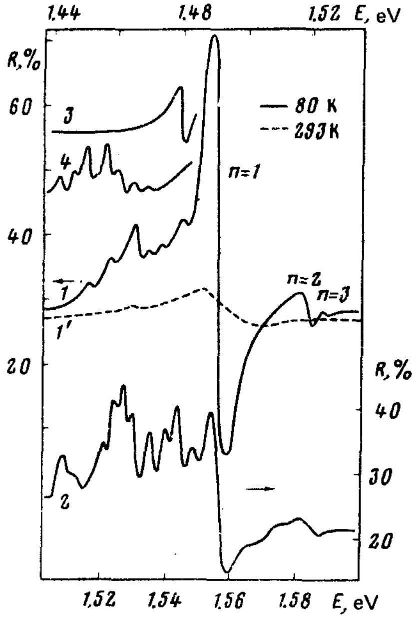

FIG. 1. Reflection spectra for four ZnP_2 samples for $\mathbf{E} \parallel c$ and 80 K (energy scale at bottom). For samples 3 and 4 only the region to 1.55 eV is shown, and their spectra are displaced upward by 30 and 20%, respectively, relative to curve 1. The spectrum at 293 K is shown for sample 1 (energy scale at top).

18%, $\mu_1 = 1.1 \times 10^5$ cm^{-1}, and $f_1 = 0.0075$. For other crystals of the type GaAs, Ge, and GaSe the value of f_1 is 10–100 times smaller. The almost metallic reflection observed by us at the maximum of the fundamental band (up to 70%) and its enormous oscillator strength (0.084) for semiconductors indicate that there is an anomalously intense, free exciton in the monoclinic ZnP_2. Assuming that the absorption bands with maxima at E_1 and E_2 are caused by free excitons with $n = 1$ and $n = 2$, we can easily calculate from the hydrogen formula for the energy of exciton states the binding energy of the exciton with $n = 1$ (E_{bind}), predict the location of the state with $n = 3$ (E_3) in the spectrum and determine the value of E_g at 80 K: $E_{\text{bind}} = 0.0394$ eV, $E_3 = 1.5885$ eV, and $E_g = 1.593$ eV. In the reflection spectrum we actually observe a weak peak at 1.588 eV, which coincides well with E_3 in energy and profile. This accurately indicates that the exciton terms of ZnP_2 have a hydrogen-like nature. According to Elliot's theory, the intensity of the exciton bands falls off as n^{-3}. According to our data, however, a much stronger n dependence is observed for ZnP_2: $f_1 = 25 f_2$ and $f_2 > 10 f_3$, instead of $f_1 = 8 f_2$ and $f_2 = 3.5 f_3$, as predicted by Elliot. This is apparently attributable to the strong anisotropy of the monoclinic ZnP_2.

As the temperature increases from 80 to 293 K, all the exciton structures are broadened drastically, while the dispersion structure of the state with $n = 1$ retains the average displacement temperature coefficient of about -3.2×10^{-4} eV • K^{-1} (curve 1′ in Fig. 1).

We have investigated more than 20 samples. In addition to the free-exciton structures in their reflection spectra at 80 K and $\mathbf{E} \parallel c$, we have observed for the first time narrow peaks in the long-wave region in the immediate vicinity of the exciton maxima with $n = 1$ and $n = 2$. It is shown in Fig. 1 that the number (from 1 to 20) and position of these additional peaks vary from sample to sample. It is interesting that the intensity of the fundamental exciton maximum decreases abruptly by almost a factor of 2 when an additional peak appears at a distance of 0.007–0.002 eV from the free exciton (curve 2 in Fig. 1). This strong "quenching" effect of the free exciton has not been observed previously in semiconductors. According to Ref. 5, the additional reflection peaks clearly indicate that they have an exciton-impurity nature with many binding energies.

Transitions of free excitons with $n > 1$ and exciton-impurity complexes have not been observed at high temperatures such as 80 K in any known semiconductors with resolved excitons. In our case this "tradition" is destroyed because of the enormous oscillator strength of the free exciton with $n = 1$. It turned out that some complexes have been observed even at room temperature, and the exciton with $n = 2$ has been detected at temperatures much higher than 80 K.

Since the reflection bands of some complexes have a well-defined dispersion, all the parameters can be calculated for them by the method of Ref. 3, just as for the free excitons. For example, for the structure at 1.531 eV the absorption at the maximum is equal to 0.96×10^5 cm^{-1}, and the oscillator strength per unit cell of the crystal is $f \approx 0.01$. If we assume that no impurities were added to the crystals, and their concentration does not exceed 10^{-5} of the concentration of the natural components, then the f value of the complex must exceed the f value of the free exciton by a factor of about 10^4. These estimates of the gigantic oscillator strength of the exciton-impurity complexes of ZnP_2 confirm experimently the theoretical prediction.[5]

A decrease of the temperature from 80 to 4.2 K resulted in a narrowing of all

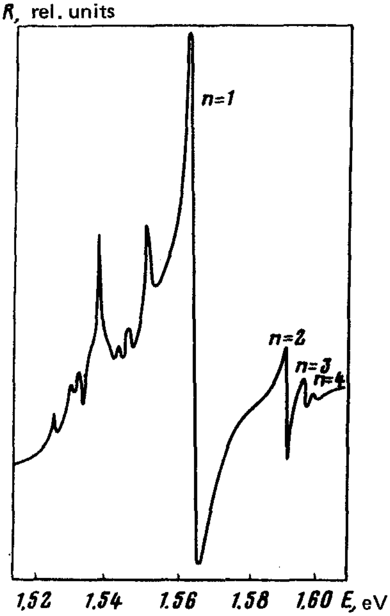

FIG. 2. Reflection spectrum of sample 1 at 4.2 K.

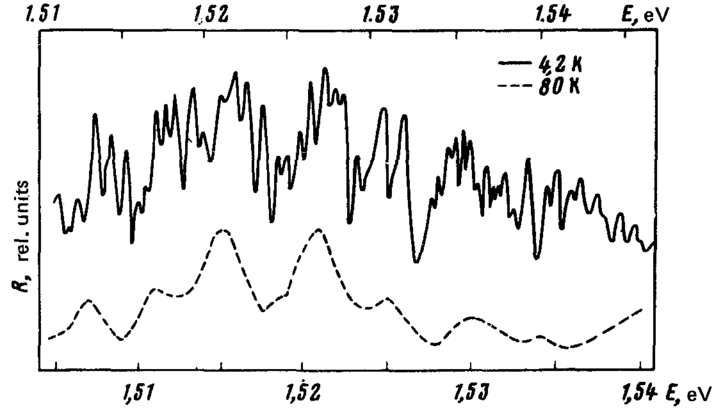

FIG. 3. Reflection spectra of the exciton-impurity complexes of sample 4 at 4.2 K (energy scale at bottom).

the reflection peaks, in a much sharper definition of the free-exciton states with $n=3$ and 4 (Fig. 2), and in the detection of many new bands (belonging in part to the exciton-impurity complexes), whose number approaches 50 in some samples (Fig. 3).

In the transmission spectra for $\mathbf{E}\parallel\mathbf{c}$ we observed additional exciton-impurity absorption lines in the region 1.45–1.57 eV, and in the photoluminescence spectra we observed the resonance-emission band of a free exciton with $n=1$ and more than 20 bands in the region 1.17–1.55 eV.

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