Excited states of acceptors in gallium phosphide

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The fine structure of photoexcitation spectra of acceptor centers in gallium phosphide has been observed for the first time. The exact values of the ionization energies of Cd, Zn, Mg, and Be have been determined. The results point to the need for determining more accurately the ionization energy of the indirect exciton in GaP.

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The combination of the physical and chemical properties of gallium phosphide has turned out to be so favorable, that many of the interesting optical effects, observed in it for the first time and connected primarily with the impurity states, could be explained not only qualitatively but also quantitatively (see., e.g., the reviews[1]). The energy states of the donors were determined from the photoexcitation spectra.[2] A detailed analysis of the fine structure of the spectra of the interimpurity radiative recombination has made it possible to determine, with accuracy 0.2 meV, the values of $E_g - E_D - E_A$ for more than 20 donor-acceptor pairs. Only the lack of direct data on the acceptor states has made it impossible to obtain the complete quantitative picture of the energy spectrum of the impurity centers in GaP.

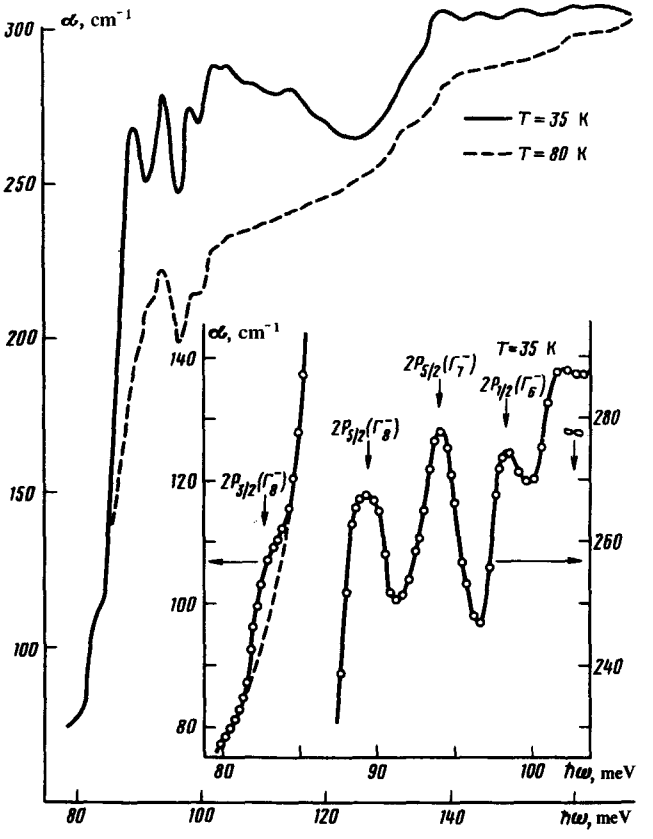
The presence of strong two-phonon lattice-absorption bands,[3] which make the investigations more complicated, has made it necessary to use relatively strongly doped samples. However, since the Bohr radii of the impurity centers are much smaller in GaP than in germanium, the fine structure should be preserved here up to relatively high impurity concentrations. We have investigated single crystals of GaP doped with Cd, Zn, Mg, and Be to a level 10^{18} cm^{-3} by crucibleless zone melting.

The fine structure of the photoexcitation spectra manifests itself best in samples doped with cadmium (see the figure). The three strongest lines correspond to allowed transitions to $2P$ states split by the spin-orbit interaction. The step near 82 meV corresponds to a forbidden transition. The relative positions of all the observed lines agree well with the results of a recent theoretical calculation.[4] With increasing temperature, the structure in the spectrum of the impurity absorption has vanished. We note that all the lines due to the strongest $1S-2P$ transitions were observed in the experiment.

The table lists the ionization energies of all the investigated acceptors, obtained from the analysis of the experimental data, together with the presently accepted values of E_A. A comparison of the presented data shows that the values obtained by us exceed systematically, by 8 ± 2 meV, the ionization energies determined from the analysis of the interimpurity recombination spectra. In the latter case, the calculate $(E_D + E_A)$ it is necessary to know the exact value of the forbidden band

Ionization energies of acceptors in GaP.

Acceptor	E_A, meV	
	Present work	Analysis of interimpurity recombination spectra[8]
Cd	102.7 ± 0.7	94.3
Zn	71 ± 2	61.7
Mg	60 ± 2	52.0
Be	56 ± 2	48.7



Impurity absorption spectrum of GaP: Cd. All the curves are shown after subtraction of the absorption by the lattice vibration. The insert shows on a larger scale the fine structure of the spectrum and the interpretation of the corresponding lines. The vertical arrows show the theoretical positions of the photoexcitation lines.[4] The horizontal arrows indicate the scales for the corresponding curves.

width $E_g = E_{gx} + E_{ex}$. The exciton width E_{gx} of the forbidden band is known for GaP with high accuracy, [5,6] whereas the ionization energy $E_{ex} = 10$ meV of the free electron was determined indirectly in only one study.[5] If it is assumed that the exciton binding energy in GaP amounts to 18 ± 2 meV, then this explains the entire aggregate of the experimental data. We note that according to the theoretical calculation[7] the binding energy of the indirect exciton in GaP amounts to 17.65 meV.

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