

a semiconductor under the influence of the dislocations), but in the surface layer. This indeed determines the form of the characteristic (curve 2, Fig. 2).

In investigations of screw dislocations in n-Si (curve 3, Fig. 1), and also of both types of dislocations in p-Si, no appreciable change in the characteristics of the metal-semiconductor microcontact was observed under the influence of the dislocations. In the latter case the contact was strongly rectifying also on the dislocation-free surface. A similar situation occurred in the first investigation [4] of the diode properties of dislocations in n-Ge, for which the inverse currents on the volt-ampere characteristics, of a contact mounted on either a dislocation-free surface or in etch pits on edge and screw dislocations, were the same.

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OBSERVATION OF EXCITED STATES AND EXPERIMENTAL DETERMINATION OF THE BINDING ENERGY OF AN INDIRECT EXCITON IN GERMANIUM

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We have investigated the exciton structure of the indirect-absorption edge in germanium by using the method of differentiating the spectrum with respect to the wavelength. As is well known, an analysis of the unusual indirect-absorption spectra calls for a numerical resolution of the experimental curve into components, and this naturally does not make it possible to separate reliably and to identify the weak singularities of the spectrum. In our case, the use of a highly-sensitive differential method has made it possible not only to observe the transition to the ground state of the exciton with participation of all four crystal phonons (TA, LA, LO, and TO), but also to observe transitions to the excited state with $n = 2$. As a result we have obtained, for the first time, the value of the exciton Rydberg constant and determined the binding energy of the lowest level of the indirect exciton in germanium, $E_{ex} = 0.0036 - 0.0003$ eV.

Indirect transitions to the exciton states with participation of phonons, as is well known, become manifest in the spectra in the form of absorption bands. For allowed transitions, the exciton band takes the form [1 - 3]

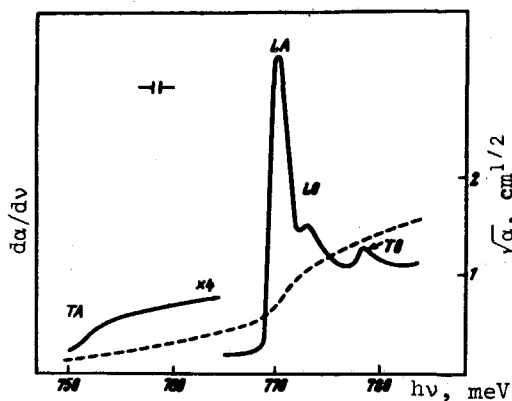


Fig. 1. $d\alpha/d\nu$ spectrum (solid curve) and ordinary absorption spectrum (dashed curve) of germanium single crystals in region of indirect transitions at 1.8°K .

$\alpha \sim (h\nu - E_{tr})^{1/2}$, where $E_{tr} = E_g - E_{ex} \pm E_{ph}$, with E_g the width of the forbidden band, E_{ex} the binding energy of the exciton state, and E_{ph} the energy of the phonon taking part in the transition. However, if one registers not the absorption coefficient α but its derivative with respect to the wavelength, then these bands become transformed in the $d\alpha/d\nu$ spectra into sharp maxima $d\alpha/d\nu \sim (h\nu - E_{tr})^{-1/2}$ ($d\alpha/d\nu \rightarrow \infty$ at $h\nu = E_{tr}$). For forbidden transitions [1] we have $\alpha \sim (h\nu - E_{tr})^{3/2}$, and only the "step" $d\alpha/d\nu \sim (h\nu - E_{tr})^{1/2}$ will appear in the spectrum of the first derivative, while the sharp maxima will occur only in the spectra of the second derivative $d^2\alpha/d\nu^2 \sim (h\nu - E_{tr})^{-1/2}$.

The differential spectra were obtained experimentally with the aid of a special spectrometer: a rotating mirror mounted ahead of the output slit inside the monochromator was made to oscillate at a frequency $\omega = 73$ Hz, as a result of which the light emerging from the instrument was wavelength-modulated at a frequency 73 Hz. Since the transmission of the crystal depends on the wavelength of the incident light, the light flux passing through the crystal was already intensity-modulated. As a result, an alternating signal was produced in a photoreceiver installed past the crystal. To separate the first and second derivatives $d\alpha/d\nu$ and $d^2\alpha/d\nu^2$ of the absorption coefficient, the signal from the receiver was detected at frequencies ω and 2ω , respectively.

Figure 1 shows the differential spectrum $d\alpha/d\nu$ and the ordinary absorption spectrum of germanium at 1.8°K in the indirect transition region. We see that the differential spectrum reveals a number of sharp singularities (a "step" and maxima) corresponding only to weak changes in the slope of the absorption curve in the ordinary spectrum. These singularities of the $d\alpha/d\nu$ spectrum are due to transitions to the ground exciton state with simultaneous production of different crystal phonons. In addition to the transition with participation of TA and LA phonons, previously observed also in the ordinary absorption spectra [1], one can see clearly in the $d\alpha/d\nu$ spectra also transitions with participation of the LO and TO phonons (with energies 30.3 and 35.8 meV, respectively). The identification of these transitions agrees with observations by other authors [5, 6] and with data on the phonon spectrum of germanium [4].

The form of the observed singularities of the $d\alpha/d\nu$ spectrum shows directly that, as already noted earlier [1], the transition with participation of the TA phonon is a forbidden one (it produces a "step" in the $d\alpha/d\nu$ spectrum), and the transition with the LA phonon is allowed (it produces a sharp maximum). Obviously, the transitions with participation of the LO and TO phonons should also be regarded as allowed.

The structure of the absorption in the region of the transitions with participation of the TA phonon was investigated by us most thoroughly with the aid of the second-derivative spectra, in which the exciton indirect forbidden transitions should appear already in the form of maxima. The obtained $d^2\alpha/d\nu^2$ spectrum (Fig. 2) revealed, besides the intense maximum coinciding in position with the "step" in the $d\alpha/d\nu$ spectrum and corresponding to the transition to

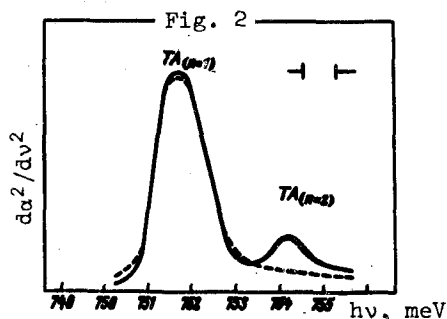


Fig. 2. Spectrum of second derivative of absorption coefficient with respect to the wavelength, of germanium crystals in the region of forbidden exciton transitions with participation of the TA phonon at $T = 1.8^\circ\text{K}$. The dashed curve corresponds to the spectrum of the crystal when an external constant electric field of intensity ~ 300 V/cm is applied.

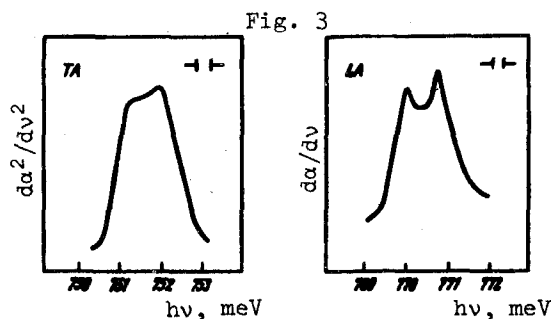


Fig. 3. Fine structure of transitions to the ground state of an exciton with participation of TA and LA phonons. $T = 1.8^\circ\text{K}$.

the ground state, also a weaker peak on the short-wave side. A number of observations have shown that this peak is due to transitions to the excited state of the exciton, a state characterized by a lower binding energy than the ground state.

First, when the temperature was increased, the short-wave maximum decreased rapidly in intensity, and was practically invisible in the spectrum at 78°K . On the other hand, the amplitude of the long-wave maximum, due to transitions to the ground state, changed little with changing temperature from 1.8 to 78°K .

Second, the external electric field caused also attenuation of the short-wave maximum. A complete vanishing of this peak was observed in very weak fields, (~ 300 V/cm¹). Ionization of the ground state of the exciton, as is well known [7], occurs at much higher external-field intensities, ~ 3700 V/cm.

In addition, both maxima had approximately the same shape, and the ratio of their amplitudes was approximately 7 : 1. According to Elliot [3], the intensity of the exciton lines decreases in proportion to n^{-3} , and the intensity ratio of the lines with $n = 1$ and $n = 2$ should be 8 : 1.

Thus, the maxima observed in the $d^2\alpha/d\nu^2$ spectrum should be set in correspondence with indirect forbidden transitions to exciton states with $n = 1$ and $n = 2$, with simultaneous emission of a TA phonon²). The distance between maxima is 2.4 meV, which gives in the hydrogenlike approximation a value $R = 3.2 \pm 0.3$ meV for the Rydberg constant of the indirect exciton in germanium.

The ground state of the indirect exciton in germanium, as is well known [2, 8], splits into a doublet, this being due to the complicated structure

¹) High-resistance crystals compensated with radiation defects (γ irradiation) were used in these experiments. At a dc electric field intensity 300 V/cm, the power released in the crystal was 0.3 W. The sample surface area was ~ 16 cm².

²) The observation of the state with $n = 2$ in the region of the LA transition is made difficult by the close proximity of the transitions with participation of the LO phonon.

of the valence band and the anisotropy of the effective mass of the electron. At the increased resolution, we succeeded in observing the doublet structure of the ground-state maxima for transitions with participation of TA and LA phonons (Fig. 3). The splitting was the same in both cases and amounted to 0.8 ± 0.1 meV. The obtained value of the splitting, although smaller than the value 1.1 meV obtained in [1, 2] still exceeds somewhat the theoretical value 0.6 meV [8]. Taking into account the observed splitting, the binding energy of the two components of the ground state of the indirect exciton amounts in accordance with our data to 3.6 ± 0.3 meV and 2.8 ± 0.3 meV. The obtained quantities are in good agreement with the theoretical values 3.5 and 2.9 meV obtained by McLean and London [8] in the effective-mass approximation.

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OBSERVATION OF VECTOR SYNCHRONISM IN GENERATION OF THE SECOND HARMONIC OF A NEODYMIUM LASER WITH SINGLE CRYSTALS OF METANITROANILINE

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We have shown in earlier papers [1, 2] that the efficiency of generating the second harmonic of neodymium-laser radiation in powders of metanitroaniline is not lower than the efficiency for lithium-niobate powders. It was of interest to investigate the second-harmonic generation in single crystals of this compound. The single crystals were obtained by evaporating a saturated solution of metanitroaniline in acetone at room temperature. Under free-surface conditions, the crystals grow mainly in the form of elongated prisms {120}, with average dimension $3 \times 2 \times 10$ mm. The dimensions of individual single crystals were of the order of $5 \times 10 \times 15$ mm. As is well known, metanitroaniline crystals belong to rhombic syngony and space group $C_{2v}^5 = P_{ca}2_1$ [3]. The crystals have a (010) cleavage plane. When cleaved along this plane, the crystals could be used without additional polishing, but erosion due to exposure for 2 - 3 days in air made the surface of the crystal dull.

The metanitroaniline crystals are biaxial and their refractive indices n for the sodium D line are [4] $n_x = 1.687$, $n_y = 1.72 - 1.74$, and $n_z > 1.78$. We measured the dispersion of the refractive indices of the obtained crystals in the visible region of the spectrum. The measurements were made by the prism method (n_x and n_y) and by the immersion method (n_z). The accuracy of the measurements by the prism method was 0.0005 for n_x and 0.02 for n_y (owing to the inaccuracy with which the prism was cut) and 0.01 for the immersion method. The values of n for the infrared region of the spectrum were obtained by linear extrapolation of the plot of $(n - 1)v^2$ vs. $n - 1$, where v is the radiation frequency. The extrapolation accuracy is ~ 0.03 . The obtained data are listed in