

form of the function  $\phi(x)$  will differ from the form indicated in [1], and this leads to the observed discrepancy between the values of  $a_n$  obtained at various frequencies. This reasoning is confirmed by the fact that in more contaminated samples the deviations of the curves from the value of  $\eta$  is much smaller and the saturation state is reached at higher frequencies.

Since the values of  $a_n$  obtained from the data at 70 and 110 MHz coincide, it can be concluded that these values are close to the true thickness of the normal layers in the interior of the sample at the given sample geometry. It should be noted that the obtained values of  $a_n$  are smaller on the average by a factor of four than those obtained by calculations for a plane-parallel plate, and they change less than predicted by the theory in the region  $0.1 < \eta < 0.8$ .

It was impossible to observe the oscillations of the sound-absorption coefficient in these experiments probably because the thickness of the normal layers was small compared with the Larmor radius of the electrons at  $H = H_c$ .

In conclusion, we are grateful to V. P. Galaiko for interesting discussions and to V. F. Gorodinskii for help with the measurements.

- [1] A. F. Andreev, Zh. Eksp. Teor. Fiz. 53, 680 (1967) [Sov. Phys.-JETP 26, 428 (1968).
- [2] A. F. Andreev, *ibid.* 51, 1510 (1966) [24, 1019 (1967)].
- [3] Yu. V. Sharvin, *ibid.* 38, 295 (1969) [11, 214 (1960)].
- [4] A. L. Schawlow and G. E. Devlin, Phys. Rev. 110, 1011 (1958).
- [5] D. Shoenberg, Proc. Camb. Phil. Soc. 33, 260 (1937).
- [6] I. R. Leibowitz, Phys. Rev. 133, A 84 (1964).

#### FINE STRUCTURE OF EXCITON BANDS AND BAND EXTREMA LOOP OF CdS AND CdSe CRYSTALS

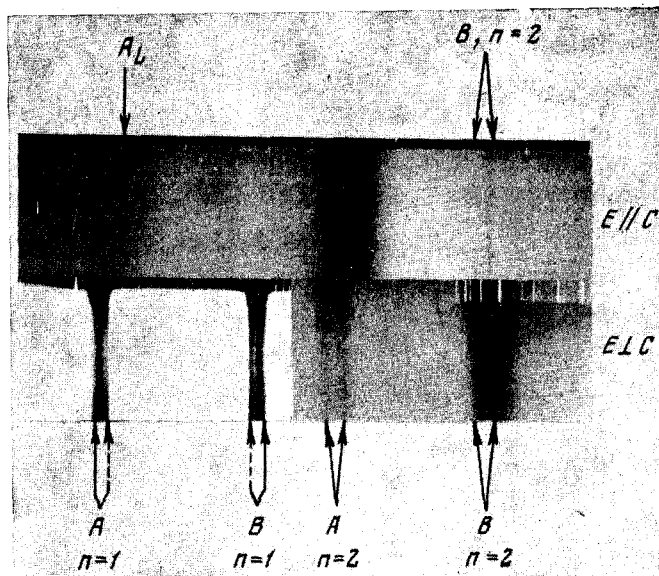
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Rashba and Sheka [1] have shown theoretically that a so called band extrema loop can appear in wurtzite crystals without inversion centers because the expansion of  $E(\vec{k})$  contains a term linear in the quasimomentum  $\vec{k}$ . This can cause splitting of the bands into individual components. We report here observation and measurement of such a splitting in the spectra of CdS and CdSe crystals.

A spectrograph with large dispersion ( $4 \text{ \AA}/\text{mm}$ ) was used to obtain at  $T = 4.2^\circ\text{K}$  the absorption spectra of thin ( $d \sim 0.15 \mu$ ) single-crystal CdS films and the reflection spectra of bulky CdS and CdSe single crystals. Unlike the earlier measurements [2], in our case the single crystals were not secured through an optical contact to transparent substrate, a practice that inevitably leads at low temperatures to stresses of the sample and to a distortion of its spectrum, but were in a "free" state. The measurements were made in polarized light with the electric vector  $\vec{E}$  of the wave parallel and perpendicular to the optical C axis of the crystal. Figure 1 shows the absorption spectra of the crystal at  $\vec{E}$  perpendicular and parallel to C, covering the section of the exciton lines A and B,  $n = 1$  and  $n = 2$ , connected with the transitions  $\Gamma_9 - \Gamma_7$ , respectively. It is seen from these spectra that the states  $n = 1$  have a fine

Fig. 1. Absorption spectrum of CdS crystal 0.18  $\mu$  thick,  $T = 4.2^\circ\text{K}$ . The spectrum of the component  $E \perp C$  in the region of the state  $n = 1$  was obtained with a longer exposure than in the remaining cases, in order to reveal the fine structure.



structure in the form of additional extrema, marked by the dashed arrows. The states  $n = 2$  comprise distinctly separated doublets with comparable intensity of the components. In the case of the  $n = 1$  A-band, an additional maximum  $A'$  ( $\nu = 20589.9 \text{ cm}^{-1}$ ) is located on the short-wave side of the main maximum  $A$  ( $\nu = 20594.1 \text{ cm}^{-1}$ ), and in the case of the B-band with  $E$  perpendicular to  $C$  the additional maximum is on the long-wave side ( $\nu = 20706.7$  and  $\nu = 20713.2 \text{ cm}^{-1}$  for  $B'$  and  $B$ , respectively). In the component of the spectrum with  $E$  parallel to  $C$ , the B-band remains structureless ( $\nu = 20713.2 \text{ cm}^{-1}$ ), and in the A-band region one can see a narrow weak line  $A_L$  ( $\nu = 20599.7 \text{ cm}^{-1}$ ) corresponding to the position of the longitudinal exciton and shifted towards the short-wave side away from both components of the doublet.

The reflection spectra of the "thick" CdS crystal, the fine structure of which has already been noted earlier [3 - 5], correlate with the described absorption spectrum of the thin crystal.

Figure 2 shows the reflection spectrum of single-crystal CdSe, obtained at  $4.2^\circ\text{K}$ . We see that the A-band for states  $n = 1$  and  $n = 2$  reveals a clearly pronounced doublet structure, more distinct than in the case of CdS. The doublet components are  $\nu_1 = 14736.2$  and  $\nu_2 = 14739.1 \text{ cm}^{-1}$  for  $n = 1$ , and  $\nu_1 = 14824.1$  and  $\nu_2 = 14828.3 \text{ cm}^{-1}$  for  $n = 2$ . The B-band, which falls in the region of the ionization continuum of series A, is not split in the presented spectrum, although in some cases a weak separation into a doublet can be seen. Not having enough thin CdSe crystals, we were unable to obtain their exciton absorption spectra, but it can be assumed that the picture of the reflection spectrum, just as in the case of CdS, is determined by the structure of the absorption spectrum and thus points to a doublet splitting of the A-band.

The observed splitting of the A-band of CdS and CdSe crystals can be attributed to the presence of an extremum loop in the conduction band  $\Gamma_7$ , which leads to the presence of two  $E(k)$  branches in the exciton band. The fine structure of the B-band is the consequence of the

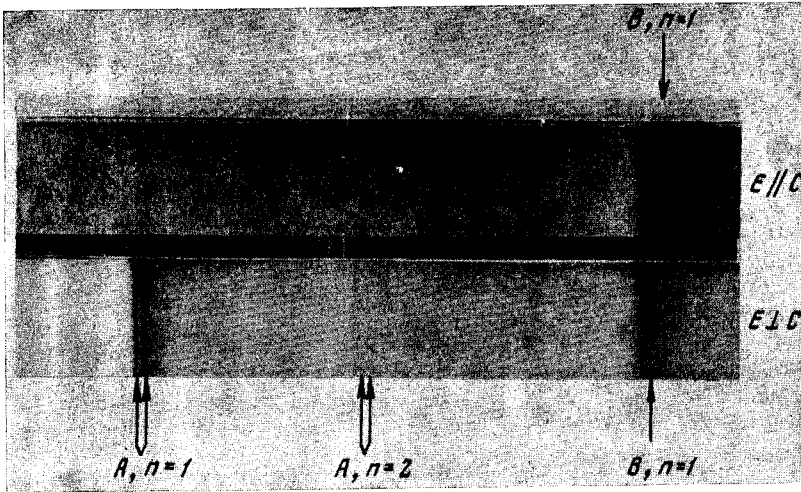


Fig. 2. Reflection spectra of CdS crystal,  $T = 4.2^\circ\text{K}$ .

extremum loop in the initial valence band and in the conduction band. In this case the exciton band constitutes four  $E(k)$  branches, two of which have minima. As shown in [6], the transition to one of the minima is allowed for both polarization of the light, and to the other only when  $E \parallel C$ .

Using the relations of [7], we can calculate from the magnitude of the splitting of the exciton A-band in CdS and CdSe the parameters of the extremum loop in the conduction band: the coefficient  $\alpha_e$  of the linear term in the expansion of  $E(k)$ , the shift  $k_{\min}$  of the extremum of the band from the point  $k = 0$ , and the depth  $E(k_{\min})$  of the loop. The calculations yield  $\alpha_e = 7 \times 10^{-10}$  eV-cm,  $k_{\min} = 1.63 \times 10^5$  cm $^{-1}$ , and  $E(k_{\min}) = -5.6 \times 10^{-5}$  eV for CdS. The respective values for CdSe are  $7 \times 10^{-10}$  eV-cm,  $0.9 \times 10^5$  cm $^{-1}$ , and  $-3.3 \times 10^{-5}$  eV.

Hopfield [3], starting from the absence of splitting of the  $P_{xy}$  state of the exciton  $A, n = 2$  in a zero magnetic field, proposed that  $\alpha_e$  is smaller than  $5 \times 10^{-10}$  eV-cm. Sheka [7], however, has shown that the expected splitting should be quadratically dependent on  $\alpha_e$  (and not linearly as stated in [8]), and consequently  $\alpha_e$  can be larger.

The splitting of the B-band in CdS yielded the value of  $\alpha_h$  of the second valence sub-band  $\Gamma_7$ , viz.,  $\alpha_h = 1.1 \times 10^{-9}$  eV-cm; this is somewhat larger than the value obtained in [5].

The doublet splittings of the lines  $n = 2$ , observed under all polarization conditions ( $A_{\perp}$ ,  $B_{\perp}$ , and  $B_{\parallel}$ ), are apparently connected with the splitting of the conduction band that takes part in the optical transitions. The definite differences in the character of the splitting and in the intensity ratio of the splitting components for the states  $n = 1$  and  $n = 2$  call for a further, particularly theoretical, study.

The short-wave additional extremum  $A', n = 1$ , observed in the reflection spectrum of CdS, was previously treated by Hopfield and Thomas [3] as the result of a manifestation of specific boundary conditions in the presence of spatial dispersion, i.e., it was not connected with the volume properties of the crystal. Actually, however, as is seen from the absorption spectra obtained here, this extremum is a manifestation of the "volume" properties and a consequence of the corresponding structure of the energy bands of the crystal.

- [1] E. I. Rashba and V. I. Sheka, Fiz. Tverd. Tela 2, 157 (1959) [Sov. Phys.-Solid State 2, 145 (1959)].
- [2] M. S. Brodin and M. I. Strashnikova, ibid. 4, 2454 (1962) and 8, 684 (1966) [4, 1798 (1963) and 8, 549 (1966)].
- [3] J. J. Hopfield and D. G. Thomas, Phys. Rev. 132, 563 (1963).
- [4] M. S. Brodin and M. I. Strashnikova, Ukr. Fiz. Zh. 10, 410 (1965).
- [5] G. D. Mahan and J. J. Hopfield, Phys. Rev. 135, A428 (1964).
- [6] M. Balkanski and J. des Clizeaux, J. Physique Rad. 21, 825 (1960); 22, 41 (1961).
- [7] V. I. Sheka, Fiz. Tverd. Tela 7, 1783 (1965) [Sov. Phys.-Solid State 7, 1437 (1965)].
- [8] J. J. Hopfield, J. Appl. Phys. Suppl. 32, 2277 (1961).

#### LIFETIMES OF FREE AND BOUND EXCITONS IN $\text{Cu}_2\text{O}$ CRYSTALS

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The optical properties of an exciton in a cuprous oxide crystal have been investigated in great detail [1]. At low temperatures, two hydrogenlike series of exciton lines, yellow and green are seen on the long-wave edge of the main absorption. The yellow-series absorption line with  $n = 1$  was found in [2, 3] to be due to a quadrupole transition. According to [4], the radiative lifetime of the exciton with  $n = 1$  is of the order of 10 sec.

Following observation of resonance luminescence of the  $n = 1$  exciton in  $\text{Cu}_2\text{O}$  [5], it became possible to investigate the exciton radiative lifetime and to compare it with the calculated value.

The cuprous oxide crystals investigated by us were grown in the same manner as in [5]. The tests were made at temperatures 2 - 4.2°K. The luminescence damping time was determined from the afterglow spectra. The minimum damping time that could be determined in our experiments from the afterglow spectra was  $10^{-4}$  sec.

The edge luminescence of the purest  $\text{Cu}_2\text{O}$  crystals contains only the emission of the free exciton and its background repetitions, and was described by us earlier.

In the investigation of the afterglow spectra of such (purest)  $\text{Cu}_2\text{O}$  crystals, we observed no afterglow of the free electron with a lifetime  $10^{-4}$  sec or longer. From a comparison of this result with the calculated value of the radiative lifetime of the  $n = 1$  exciton ( $\tau_{\text{rad}} \sim 10$  sec), it follows that the probability of nonradiative transitions for the free electron is at least  $10^5$  times larger than the probability of radiative transitions.

An entirely different result was obtained with crystals with impurities, for which afterglow of a number of narrow lines and bands was noted. At the same time, all the lines belonging to the emission of a free exciton were missing from the afterglow spectrum. Figure 1 shows microphotographs of the luminescence spectrum of one of the  $\text{Cu}_2\text{O}$  crystals at a temperature  $T = 2^\circ\text{K}$ , obtained with continuous excitation (curve 1) and in the afterglow (curve 2).

The narrow lines observed in the luminescence spectra of the crystals with the impurities are due to the annihilation of the bound excitons. Luminescence of the bound excitons is observed, with simultaneous excitation of phonons, just as in the case of the emission of the free exciton. In the crystal whose spectrum is shown in Fig. 1, the frequencies of the