Reports of the Academy of Sciences of the USSR

PHYSICS

1965

Fig. 1

Figure 1: Fig. 1

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1965, Volume 165, No. 3

UDC 548.0:535+535.343

PHYSICS

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LOW-TEMPERATURE SPECTROPHOTOMETRIC STUDIES IN THE REGION OF THE LONG-WAVELENGTH EDGE OF INTRINSIC ABSORPTION OF CADMIUM SELENIDE AND CADMIUM SULFIDE SINGLE CRYSTALS

(Presented by Academician B. P. Konstantinov, 12 IV 1965)

At low temperatures, in the region of the long-wavelength edge of fundamental absorption of CdS and CdSe crystals, complex line structures were discovered ([1,2]). Later, the line exciton spectra of edge absorption of CdSe and CdS were explained on the basis of the triplet structure of the valence band of hexagonal crystals of the $A^{II}B^{VI}$ group ([3–6]): the entire spectrum in each crystal is clearly divided into a strongly polarized series A and partially polarized series B and C (in CdS, in addition, "variable" lines of exciton-impurity nature are also observed). After qualitative agreement between experiment and theory had been established, the further development of a broad range of problems in solid-state theory made it necessary to carry out quantitative studies of the contour of exciton absorption bands ([7–11]).

At T equal to 4.2° and 160° K, in polarized light we studied the spectral distribution of the absorption coefficient of "pure" ([5]), very perfect thin (d = 0.2—20 μ) single-crystal hexagonal plates of CdSe (λ 7000—5300 Å) and CdS (λ 7000—4790 Å) ([4,12,13]). The studies were carried out on diffraction ($D \approx 3.2$ Å/mm in the second order) and prism ($D \approx 50$ Å/mm in the region of λ 5000 Å) spectrometers in special cryostats ([14]); the light receiver was an FEU-17 photomultiplier cooled with liquid nitrogen.

Figure 2

Figure 2: Figure 2

Fig. 1. Spectral distribution of the absorption coefficient of a cadmium selenide crystal at $T = 160^\circ$ K

In the spectral distribution of the optical density kd of CdSe ($d \approx 0.3$ μ) at $T = 160^\circ$ K, it is possible to reveal the leading members of three exciton series: λ 6960 Å (A_1), 6878 Å (B_1), and 5600 Å (C_1) (Fig. 1; $D = 50$ Å/mm in the region of λ 5000 Å), and at $T = 4.2^\circ$ K, besides A_1, B_1, and C_1, also the most intense lines of the fine structure A_1, A_2, and B_2 (Fig. 2, $D = 3.2$ Å/mm).

According to our measurements on a spectrometer with dispersion $D \approx 6.4$ Å/mm at $T = 160^\circ$ K, the values of the absorption coefficient at the band maximum $K_{\max}$, the half-width $\Delta\nu$, and the oscillator strength f were as follows: $0.77 \cdot 10^5$ cm^{-1}, 55 cm^{-1}, and 0.0022 (λ 6960 Å); $0.7 \cdot 10^5$ cm^{-1}, 52 cm^{-1}, and 0.0018 (λ 6878 Å, $\mathbf{E} \parallel c$); $0.23 \cdot 10^5$ cm^{-1}, 38 cm^{-1}, and 0.0004 (λ 6878 Å, $\mathbf{E} \perp c$); the half-

about λ5600 Å, very broad, with $K_{\max} \approx 0.2 \times 10^5$ cm^{-1}. Lowering the temperature leads to substantial changes in the spectrum (see Fig. 2 and Table 1).

A careful comparison of the experimental data we obtained with theory makes it possible to draw the following conclusions. 1) Judging from the magnitude of the absorption, most of the lines of the line-like edge absorption of CdSe must indeed have an excitonic origin. 2) In terms of absorption magnitude, polarization, and position in the spectrum, all the line-like and continuous absorption of CdSe is clearly divided into three nonoverlapping exciton series and three edges of intrinsic absorption, in accordance with the triplet structure of the valence band ([4],[5],[12]). 3) Indirect transitions are observed in a very narrow frequency region near the edges of the direct transitions (see, for example, Fig. 2). This indicates that the extrema of the bands (valence and conduction) are located at the same point of k-space. 4) The contour of the lines apparently indicates strong exciton-phonon interaction at $T = 160^\circ$K and weak interaction at $T = 4.2^\circ$K.*

2. Contour of the exciton absorption lines of a cadmium selenide crystal at $T = 4.2^\circ$K: a–$\mathbf{E} \perp \mathbf{c}$; b–$\mathbf{E} \parallel \mathbf{c}$

The spectral distribution of the absorption coefficient of a CdS single crystal was studied by photographic photometry ([15–17]) and by reflection ([3]). It is known, however, that structural reflection depends strongly on the state of the crystal surface ([12]), and the use of the photometric method ([15–17]) entails a number of difficulties. We investigated transmission curves (with reflection taken into account) at $D = 3.2$ Å/mm for various "pure" CdS crystals and determined the values of $K_{\max}$ and $\Delta\nu$ for A_1, A_2, B_1 (Fig. 3, crystal No. 12) and for certain "variable" lines. It should be noted that the dependence $K = K(\lambda)$

Fig. 3. Contour of exciton absorption lines of a cadmium sulfide crystal at $T = 4.2^{\circ}$K

Figure 3: Fig. 3. Contour of exciton absorption lines of a cadmium sulfide crystal at $T = 4.2^{\circ}$K

may vary appreciably from crystal to crystal. Changes in $K(\lambda)$ are especially substantial in the region A_1: for $\mathbf{E} \perp \mathbf{c}$ and $T = 4.2^{\circ}$K, the value of $K_{\max}$ for the long-wavelength component of the doublet structure $A_1(A_{1d})$ may be either greater,

* In work ([6]), because of insufficient spectrometer dispersion, only the continuous absorption of CdSe was studied.

than $K_{\max}$ of the short-wavelength component (A_{1k}) (crystal No. 12), or equal to $K_{\max}$ for A_{1k} (crystal No. 18), or less than $K_{\max}$ for A_{1k} (crystal No. 7); for $E \parallel c$, $K_{\max}(A_{1k})$ is always considerably greater than $K_{\max}(A_{1d})$. In addition, we have for the first time quantitatively detected the phenomenon of weak polarization of the absorption lines of the exciton series A with $n \geq 2$ (according to theory

Fig. 3. Contour of exciton absorption lines of a cadmium sulfide crystal at $T = 4.2^{\circ}$K

one would expect, as in the case of CdSe (3), sharp polarization of the lines of series A). According to our data, on crystal No. 7 the values of $K_{\max}$ at $T = 4.2^{\circ}$K for the "variable" lines λ 4870.2–4868.9 Å and λ 4888; 4866.4; 4862.4 Å proved to be equal to $1.6 \cdot 10^5$ and $\sim 0.4 \cdot 10^5$ cm^{-1}, respectively. This indicates that the absorption of exciton-impurity complexes (18) can, in magnitude, be comparable with exciton absorption. The symmetry of the contours of the lines $A_1(E \parallel c)$, $B_1(E \parallel c,\ E \perp c)$, and $A_2(E \perp c,\ E \parallel c)$ apparently indicates the strong character of the exciton-phonon interaction in CdS at $T = 4.2^{\circ}$K. Our experimental data for CdS are not consistent with the results of recalculations of reflection curves (3), nor with theoretical calculations of the dependence of the intensity of exciton lines on the quantum number n (11).

Table 1

Values of several parameters of the absorption lines of a CdSe crystal at $T = 4.2^{\circ}$K

λ, Å	ν, cm^{-1}	Polarization	$K_{\max} \cdot 10^5$, cm^{-1}	$\Delta\nu$, cm^{-1}	$f \cdot 10^4$
6804	14 697	$E \perp c$	0.2	35	3.07
6798	14 710	$E \perp c$	0.27	12	1.18
6788	14 731	$E \perp c$	0.97	19	10
6752	14 810	$E \perp c$	0.06	8.3	0.12
6746	14 821	$E \perp c$	0.22	12	1.07

λ, Å	ν, cm^{-1}	Polarization	$K_{\max} \cdot 10^5$, cm^{-1}	$\Delta\nu$, cm^{-1}	$f \cdot 10^4$
6698	14 930	$E \parallel c$	1.33	27	23
6698	14 930	$E \perp c$	1.05	20	13
6657	15 022	$E \parallel c$	0.17	15	0.7
6657	15 022	$E \perp c$	0.07	10	0.4
5494	18 202	$E \parallel c$	0.22	310	19
5494	18 202	$E \perp c$	0.14	310	13

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Received
8 III 1965

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Note: Figure translations are in progress. See original paper for figures.