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Abstract

Full Text

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V. V. SOBOLEV

COMPLEX STRUCTURE OF BANDS AND EXCITONS IN CADMIUM SELENIDE CRYSTALS

(Presented by Academician A. N. Terenin on 23 IV 1963)

I. A group-theoretical consideration of the band structure of crystals of the group $A^{\mathrm{II}}B^{\mathrm{VI}}$ has been carried out in a number of works ($^{1-7}$). The presence of spin-orbit interaction and of an inhomogeneous crystal field in hexagonal crystals leads to the complete lifting of the degeneracy of the upper valence P-band —its splitting into three subbands. In some works (^{1,6}) the spin-orbit interaction is taken into account under the assumption that the spin-orbit splitting energy Δ_{co} is considerably smaller than the energy of splitting of the valence bands due to the presence of the crystal field Δ_{k}: $\Delta_{\mathrm{co}} \ll \Delta_{\mathrm{k}}$; in other works (^{2}), on the contrary, it is assumed that $\Delta_{\mathrm{co}} \gg \Delta_{\mathrm{k}}$ (see Fig. 1).

Fig. 1. Scheme of the CdSe valence bands: *a*—according to Birman, *b*—according to Hopfield

One may hope that consideration of the influence of deformations on the positions of the upper valence bands, analysis of data on the structure of the valence bands for two modifications of one and the same crystal (cubic and hexagonal), and comparison of the values of the level-splitting energy due to spin-orbit interaction in atoms and in crystals will make it possible to choose one of the two proposed (Fig. 1) models for the structure of the valence bands of the crystals.

Pikus (^{13}) considered the change in the energy spectrum for the case of volume deformation of semiconductors with a wurtzite lattice for both models under consideration. We have calculated the positions of the two upper valence bands of a CdSe crystal on the basis of equations (17) and (22) of work (^{13}) for the case of deformations in the plane containing the hexagonal axis of the crystals. It turned out that the two upper valence bands (and therefore the two corresponding intrinsic-absorption edges and both exciton series of lines) behave differently in this case: in the case $\Delta_{\mathrm{k}} \gg \Delta_{\mathrm{co}}$ both bands are displaced equally, whereas in the case $\Delta_{\mathrm{k}} \ll \Delta_{\mathrm{co}}$ they are displaced sharply unequally (the upper band may be displaced much more strongly than the second band).

Rashba (^{5}), Casella (^{4}), Balkanskii and Klyazo (^{6}) theoretically showed that in crystals with the wurtzite structure, for bands with symmetry Γ_7, the double degeneracy can be lifted for the directions $k_x = 0$ and $k_y = 0$, which can lead to the realization of toroidal energy surfaces (“loops of extrema”) (Fig. 2).

From Hopfield's calculations (^{7}) it follows that the realization of loops of extrema in hexagonal crystals of the wurtzite type should be manifested experimentally in the splitting of the exciton state with $n = 2$ into four levels with doublet splitting of the $2P_{xy}$ level.

In the theory of exciton states of hexagonal crystals, in accordance with the complex structure of the valence bands, each of the three valence bands and

in the conduction band there corresponds, respectively, a system of exciton hydrogen-like states. Experimentally, in a number of crystals (ZnO (^{12}), ZnS (^{11}), ZnSe (^{11}, ^{14}), CdS (^{10}, ^{2}), CdSe (^{8}, ^{9}), etc.) a complex exciton structure of the absorption spectra has been found. The experimental data known so far do not make it possible to verify the results of theoretical calculations on the complex structure of bands and excitons: to unambiguously determine the origin of the three upper valence bands of the crystals and to “recognize” the loop of extrema, or to carry out a sufficiently clear classification of the exciton series (the latter has been done only in CdS).

We therefore undertook a comprehensive study of the optical properties of one of the poorly studied hexagonal crystals—cadmium selenide—over a wide spectral region (1-6 eV), over a wide temperature range (290-4° K), with high dispersion of the spectral instruments (5-10 Å/mm), on a very large number of “pure” and “impurity” crystals. From the absorption and reflection spectra of CdSe single crystals we found a coarse structure (3 edges of continuous absorption in the region of the long-wavelength edge of fundamental absorption; one broad u.-v. absorption band, resolved in reflection into 3 peaks) and a complex line structure (16 very narrow lines and one broad line having a triplet structure) (see Table 1). In addition, in order to resolve the question of the nature of the complex structure of the CdSe valence band, using Pikus' s calculations (^{13}), we performed experiments to determine the influence of deformations on the positions of the two upper valence bands (the edge for $E \perp c$ and for $E \parallel c$) and the corresponding two exciton states ($\lambda\lambda$ 6739 and 6833 Å—the principal absorption lines at $T = 77.3°$ K of two exciton series) of CdSe. The deformations were produced by cooling to 77.3° K single crystals partially glued to substrates having a different coefficient of linear expansion (NaCl). The displacement (relative to a free crystal) for the edge with $E \perp c$ and the line

Fig. 2. Band scheme of CdSe according to Kleuzot

Figure 2: Fig. 2. Band scheme of CdSe according to Kleuzot

$\lambda 6833$ Å proved to be ~ 48 Å, and for the edge with $E \parallel c$ and the line $\lambda 6729$ Å only ~ 21 Å (Fig. 3).

Fig. 2. Band scheme of CdSe according to Kleuzot

II. Good agreement of our experimental data (Table 1) with theoretical calculations (^{1}–^{7}) (in polarization, magnitude of absorption, and position in the spectrum) gives us grounds to identify the energies of direct electron transitions upon absorption of light from the three upper valence bands into the conduction band of the CdSe crystal with the energy values of the corresponding three edges of continuous absorption, and to calculate with high accuracy the main parameters of the CdSe band structure at the center of the Brillouin zone: the band-gap energy $E_g = 1.84$ eV, the distances between the first (upper) and second, and also between the second and third valence bands, respectively 0.024 and 0.41 eV.

The u.-v. absorption band and the 3 u.-v. reflection peaks of CdSe that we found may be due, as it seems to us: 1) to transitions between the 4th valence band and the conduction band; 2) to transitions between the valence bands and the conduction band not at the center of the Brillouin zone; 3) to trans-

Table 1

List of CdSe absorption lines at $T = 4.2$°K

	λ, Å	ν, cm^{-1}	E, eV	N
1st group	6804	14697	1.8217	$1'$
1st group	6798	14710	1.8233	$2'$
1st group	6792	14723	1.8249	$3'$
1st group	6789	14730	1.8258	$4'$
1st group	6759	14795	1.8338	$5'$
1st group	6752	14810	1.8357	$6'$
1st group	6746	14821	1.8371	$7'$
1st group	6738	14841	1.8395	$8'$
Edge of continuous absorption $E \perp c$	6735	14849	1.8405	
2nd group	6714	14894	1.8461	1
2nd group	6705	14914	1.8486	2
2nd group	6698	14930	1.8506	3
2nd group	6682	14966	1.8550	4
2nd group	6671	14990	1.8580	5

	λ, Å	ν, cm^{-1}	E, eV	N
2nd group	6661	15013	1.8609	6
2nd group	6657	15022	1.8620	7
2nd group	6646	15047	1.8651	8
Edge of continuous absorption $E \parallel c$	6644	18052	1.8657	
3rd group	5494	18202	2.255	
3rd edge of continuous absorption	5440	18382	2.280	
Structure in u.-v. light	Absorption of polycrystalline films	2600	38460	4.77
Structure in u.-v. light	Reflection of a single crystal	2550	39220	4.865
Structure in u.-v. light	Reflection of a single crystal	2850	35090	4.355
Structure in u.-v. light	Reflection of a single crystal	3000	33330	4.135

transitions between the valence bands and the upper conduction bands, or by the corresponding exciton transitions*.

On the basis of a careful analysis of the large amount of experimental material obtained by us, it may be asserted that the characteristic and important features of the line edge absorption of a CdSe crystal are as follows: 1) according to its position in the spectrum, all line absorption is clearly divided into 3 groups, and each group closely adjoins one of the 3 edges of continuous absorption—respectively, by 8 narrow lines to the first two edges for $E \perp c$ and $E \parallel c$, and by one broad triplet line to the third edge; 2) the polarization of the line absorption in each of the 3 groups of lines coincides with the polarization of the corresponding edge of continuous absorption; 3) the absorption lines are unchanged in their position in the spectrum, polarization, number of lines, and intensity; 4) according to quantitative measurements, the intensity of many absorption lines is of the same order as the intrinsic absorption of the crystal lattice ($\sim 10^5$ cm^{-1}). According to the theory of exciton states of uniaxial crystals, precisely such distinctive properties are inherent in the excited states of the crystal lattice itself—excitons; moreover, the quantum number $n = 1$ can be assigned to the long-wavelength quartets of lines, and $n = 2$ to the short-wavelength quartets.

* A complex triplet structure of u.-v. reflection spectra has also been found by us in cadmium telluride single crystals (^{8}).

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Fig. 3. Reflection spectra at $T = 77.3$°K of CdSe single crystals, free and deformed

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Fig. 2. Microphotographs of crystals in samples of the Sc_2O_3—Al_2O_3 system, reflected light, 240×. *a*—composition $Sc_2O_3 \cdot Al_2O_3$, *b*—composition 55 mol. % Sc_2O_3, 40 mol. % Al_2O_3, and 5 mol. % SiO_2, *v*—composition 25 mol. % Sc_2O_3 and 75 mol. % Al_2O_3, *g*—composition 25 mol. % Sc_2O_3, 70 mol. % Al_2O_3, and 5 mol. % SiO_2

III. The experimental data we have obtained on the influence of deformations on the reflection spectra of CdSe single crystals indicate a strong difference in the relative shift of the exciton reflection lines (and hence of the corresponding two upper valence bands): upon compression of a CdSe crystal the shift of the upper valence band is twice as large as that of the second. This direct experimental test of the two band models (Fig. 1) makes it possible to choose unambiguously Hopfield' s scheme. Thus, in CdSe crystals (and, apparently, in other crystals of the $A^{II}B^{VI}$ group) the splitting of the valence band into the two upper bands is caused by the crystal field, while the third band is due to spin-orbit splitting. Indirectly, Hopfield' s band scheme is also confirmed by work (^{15}) on the band structure of cubic and hexagonal ZnS.

IV. In good agreement with Hopfield' s theory, we have found that the exciton state with $n = 2$ of the first exciton series of CdSe consists of 4 sublevels (Table 1, absorption lines λλ 6759; 6752; 6746 and 6738 Å). Using the known formulas for hydrogen-like states (^{12}), we have determined the values m_z, m_g, a_1, and k: $m_z \simeq 0.1\, m_0$, $m_g \simeq m_0$, $a_1 = 50$ Å, $k = 2.8 \cdot 10^5$ cm^{-1}. Further, from the experimentally determined splitting of the $2P_{xy}$ level ($\simeq 2 \cdot 10^{-3}$ eV) and the calculated values a_1, m_z, m_g, and k, we obtain for the finite slope of the conduction band at $k = 0$ the value $C = 3 \cdot 10^{-9}$ eV · cm. Since the quantity C is directly proportional to Δ_{co}, it becomes clear why in oxides and sulfides of the $A^{II}B^{VI}$ group the loop of extrema has not yet been observed: $C(\mathrm{CdSe}) : C(\mathrm{CdS}) \simeq 6$, i.e., the splitting of the $2P_{xy}$ level in CdS should be $\ll 1$ Å, and it is experimentally difficult to resolve it. Using formulas (^{5}) and assuming that $A(\mathrm{CdSe}) = A(\mathrm{CdS})$ (^{7}), we have calculated the main parameters (along with C) of the loop of extrema in CdSe: the depth of the loop is $\varepsilon = 2 \cdot 10^{-3}$ eV and the radius of the loop is $k_0 = 1.5 \cdot 10^6$ cm^{-1}.

Institute of Physics and Mathematics
Academy of Sciences of the MSSR

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