V. V. SOBOLEV

1963

Fig. 1. Reflection spectra of selenium and tellurium

Figure 1: Fig. 1. Reflection spectra of selenium and tellurium

Abstract

Full Text

V. V. SOBOLEV

EXPERIMENTAL STUDIES OF THE BAND STRUCTURE OF HEXAGONAL CRYSTALS OF SELENIUM AND TELLURIUM

(Presented by Academician B. P. Konstantinov, 29 III 1963)

The crystal lattices of gray selenium and tellurium have one and the same hexagonal structure and consist of parallel helical chains of atoms; the atoms in each chain are bound by covalent forces, while the chains are bound to one another by forces somewhat greater than van der Waals forces*. Therefore Se and Te crystals possess a strong anisotropy of optical, electrical, and other properties ([3–8]): both crystals have two edges of intrinsic absorption (a strongly polarized long-wavelength edge for $\mathbf{E} \perp c$ and a partially polarized short-wavelength edge); in tellurium a hole absorption band has been found with $\lambda_{\max} = 11\,\mu$ for $\mathbf{E} \parallel c$ (a similar band is not known in selenium); the galvanomagnetic properties of tellurium also indicate a complex structure of the valence band of the crystals. From the absorption of soft x-rays in hexagonal Se and Te crystals, doublet structures have been found: the doublet separation is 1.2 eV in Se and 1.6 eV in Te ([10]), which are explained by the structure of the d-subbands of the conduction bands of the crystals.

Fig. 1. Reflection spectra of selenium and tellurium

Theoretically, the band structure of the crystals has been considered in a number of works ([11–16]). Cullen ([11]), on the basis of a highly simplified tetragonal model of the Te crystal, came to the conclusion that the conduction band arises as a result of doublet splitting of the atomic d-level, and the valence band as a result of splitting of the p-level. Later works confirmed this origin of the bands. Reitz ([12]), in the tight-binding approximation and taking into account only the nearest neighboring atoms in a chain (the interaction of the chains with one another was not taken into account), established that the p-levels of the atoms split into three triplet groups; moreover, it is assumed that the upper valence band is formed from the middle p-group, and the lower conduction band from the lower d-levels or from the upper p-group. Gaspar ([13]), consistently taking into account the symmetry of the lattice of real Se and Te crystals and the interaction not only of atoms in each chain but also between chains, obtained,

Fig. 2. Band scheme according to Gaspar

Figure 2: Fig. 2. Band scheme according to Gaspar

apparently, the most correct scheme of the band structure of hexagonal crystals (Fig. 2). The upper valence band consists of two overlapping bands formed from the p-levels of the atoms: a narrow subband np_z and a broad subband Api, with the ceiling of the first subband located above the ceiling of the second subband. Lower in the valence band there is an ns subband formed from the ns-levels of the atoms. The lower conduction band consists of a broad subband $nd\gamma_2$ and very narrow subbands $nd\varepsilon_1$, Ad, Bd, and $nd\gamma_1$, formed from the d-levels of the atoms; among all the subbands, the lowest is the $nd\gamma_2$ subband. A fundamentally important new result of work ([13]) is the possible existence of an empty, very narrow subband Bpi, which may lie in the forbidden band or in the conduction band. Finally, in works ([14,16]), on the basis of

* Muser and Pearson ([9]) proposed an explanation of the bonds between atoms of one and the same chain, as well as between chains, on the basis of valence-bond theory.

group theory, without resorting to the weak- or strong-bond approximations, the possibility of band joining along certain directions in k-space has been shown. Although in some works ([12,15]) it is established that the band extrema are at $k_z = \pi/c$, the question of the location of the band extrema in k-space remains unresolved.

Comparison of experiment and theory is carried out in works ([5–7,9,11–13]) in a contradictory way: in some works ([11]) the dichroism of the fundamental absorption is associated with the doublet character of the conduction band, in others ([5,13]) with that of the valence band; the hole absorption band of tellurium ($E = 0.11$ eV) is explained as the result of transitions between two upper valence bands having a gap of ≈ 0.05 eV and determining the dichroism of the fundamental absorption of the crystals*. In this connection we have carried out a study of some optical properties of Se and Te crystals over a much broader wavelength interval than had been done previously ([1,2]): reflection spectra of hexagonal single crystals of tellurium and polycrystals of selenium** have been studied in the range 1–6 eV (Fig. 1).

Fig. 2. Band scheme according to Gaspar

On the basis of a careful analysis of the experimental results obtained by us, of the known optical experimental data on fundamental and i.-k. absorption (in Se in the region 2.0 eV; in Te in the region 0.4 eV; i.-k. data on the hole absorption band with $E_{\max} = 0.11$ eV), of data on x-ray absorption, and of theoretical calculations, we have proposed the following band and transition schemes for Se and Te (Figs. 3 and 4; arrows indicate electron transitions upon absorption of light from the valence bands into the conduction bands; numbers give the magnitudes of the optical transitions of electrons or the distances between

Fig. 3. Band scheme of selenium

Figure 3: Fig. 3. Band scheme of selenium

subbands in the bands, in electron-volts; $\perp, \parallel$ denote the polarization of optical transitions).

Fig. 3. Band scheme of selenium

Let us note the common properties of the band structures of Se and Te crystals proposed by us (Figs. 3 and 4): 1) the forbidden bands of the crystals are formed by the top of the P_z subbands and the bottom of the $d\gamma_2$ subbands; 2) the two absorption edges are due to transitions from two valence subbands (p_z and p_i) into the lower conduction band (in the region of 1.9 eV ([6,7]) and 0.33 eV ([4,5]), respectively, for Se and Te); 3) the two lower conduction bands (in very good agreement with the x-ray absorption data ([10])) are separated from each other by 1.1 eV (Se) and 1.6 eV (Te); 4) besides the two upper valence p-subbands, which determine

* The three-band model proposed by Muser and Pearson ([9]) also cannot explain the energy difference between the relative position of the two polarized edges of the fundamental absorption and the value of the maximum of the hole absorption band of Te.

** The author expresses gratitude to A. M. Potarskii and T. P. Kozarev for kindly providing Te ([8]) and Se ([17]) crystals.

crystals exhibiting dichroism, there are s-subbands located above the upper p_z-subband at a distance of 1.7 eV for Se and 0.6 eV for Te (according to Gaspar' s calculations [13], the distances between the $3p_z$ and $3s$ subbands in Se should be much larger than the analogous gap in Te).

The four reflection peaks of the Se crystal that we have found (2.07; 2.95; 3.65; 4.6 eV) and the two reflection peaks of the tellurium crystal (2.0 and 2.58 eV) are in good agreement with the predictions of the band schemes of the crystals proposed by us: 1) in the Se crystal, transitions between the two lower valence bands, which have a narrow gap of 0.15 eV [(6,7)], and the two upper conduction bands should occur at absorbed-light energies of 1.9–2.05 eV [(6,7)] and 3.0–3.15 eV, respectively, while in the Te crystal they should occur at 0.33–0.38 eV [(4,5)] and 1.93–1.98 eV, respectively, with a gap between the two valence subbands of 0.05 eV [(4,5)]; 2) in the Se crystal, transitions between the lower ($3s$) valence subband and the two lower conduction bands ($3d_{\gamma 2}$ and $3d'$) should occur upon absorption of light with energies 3.6 and 4.7 eV, respectively, while in the Te crystal—with energies 1 and 2.6 eV (the reflection peak in Te at 1 eV was not found by us, apparently because of its comparatively large half-width; according to the absorption of films [(3)], it is indeed possible to detect a very broad band near 1 μ).

Fig. 4. Band scheme of tellurium

Fig. 4. Band scheme of tellurium

Figure 4: Fig. 4. Band scheme of tellurium

The good agreement between the experimental data found by us and the semiempirical schemes of the band structures of the crystals proposed by us makes it possible to suggest that all five subbands of Se and Te crystals have extrema at identical values of the wave vector.

It seems to us that the hole absorption band of tellurium at $\lambda 11\,\mu$ found in [5] (and the band at $\lambda 7\,\mu$, not noted by the authors of [5]) can be explained as the result of electron transitions from the two upper filled valence subbands ($4p_z$ and Ap_i) into the empty narrow Bp_i subband, located at a distance of 0.11 eV from the top of the $4p_z$ subband.

Institute of Physics and Mathematics
Academy of Sciences of the MSSR

Received
21 III 1963

CITED LITERATURE

1. V. V. Sobolev, Author' s abstract of Candidate' s dissertation, L., 1962.
2. E. F. Gross, V. V. Sobolev, Abstracts of reports, II All-Union Conference on Photoelectric and Optical Phenomena in Semiconductors, Lviv, October 1961.
3. T. S. Moss, *Optical Properties of Semiconductors*, 1961.
4. J. J. Loferski, *Phys. Rev.*, **93**, 707 (1954).
5. R. S. Caldwell, H. J. Fan, *Phys. Rev.*, **114**, 664 (1959).
6. V. Prosser, *Czechoslovak Journal of Physics*, vol. 10, 306 (1960).
7. H. Gobrecht, A. Tausend, *Zs. Phys.*, **161**, 205 (1961).
8. S. S. Shalyt, P. V. Parfen' ev et al., *Fiz. Tverd. Tela*, **4**, 3596 (1962).
9. E. Mooser, W. C. Pearson, *J. Phys. Chem. Solids*, **7**, 65 (1958).
10. M. P. Givens, Ch. J. Koester, W. L. Goffe, *Phys. Rev.*, **100**, 1112 (1955).
11. H. B. Callen, *J. Chem. Phys.*, **22**, 518 (1954).

12. J. R. Reitz, *Phys. Rev.*, **105**, 1233 (1957).

13. R. Gaspar, *Acta Phys. Hungarica*, **27**, 289 (1957).

14. I. I. Korovin, Ya. A. Firsov, *ZhTF*, **28**, 2417 (1958).

15. A. P. Caryalno, *C. R.*, **248**, 778 (1959).

16. Ya. A. Firsov, *ZhTF*, **32** (6), 1350 (1957); **34** (1), 240 (1958).

17. P. T. Kozyrev, *ZhTF*, **28**, 500 (1958).

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