OPTICAL REFLECTION SPECTRA OF SINGLE CRYSTALS OF ZnSiP$_{2}$

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OPTICAL REFLECTION SPECTRA OF SINGLE CRYSTALS OF $ZnSiP_2$

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In recent years there has been great interest in semiconductor compounds of the type $A^2B^4C_2^5$. This is due, on the one hand, to the need to search for semiconductor substances with new combinations of properties important for practical purposes, and, on the other, to the fact that a certain similarity of these substances to $A^{III}B^V$ compounds may, when studied, provide new data on the influence of the chemical nature of these substances on their physical properties. A major contribution to the preparation and study of compounds of the type $A^2B^4C_2^5$ belongs to N. A. Goryunova and her collaborators.

The group of substances $A^2B^4C_2^5$ also includes $ZnSiP_2$ crystals, obtained by one of the authors in the laboratory of N. A. Goryunova, which were the object of our investigations. For these crystals a number of physical properties, photoconductivity ([1–3]), and the absorption coefficient ([4]) have already been investigated. In the present work we studied the reflection spectra of $ZnSiP_2$ single crystals beyond the edge of their fundamental absorption, with the aim of obtaining data on the band structure of these crystals.

Experimental part. Owing to the sufficiently high quality of the surface of the $ZnSiP_2$ crystals, no additional grinding, polishing, or etching was required, and the reflection spectra were observed from the natural crystal surfaces. The single optical reflection was measured on an apparatus consisting of a DMR-4 double monochromator with a quartz prism and a dispersion of 35 Å/mm in the region of 3000 Å, an FEU-18a photomultiplier, an FEP-1 photoelectric setup, and a hydrogen lamp as the light source. The reflection spectra were recorded at small angles of incidence $\approx 10^\circ$ and temperature $T = 300^\circ$K. To investigate the dependence of the reflection spectrum on the direction of polarization of the light, we used a Glan polarizing prism with an air gap.

The reflection spectrum of $ZnSiP_2$ single crystals in the region 2800–3700 Å with unpolarized incident radiation has three maxima (Fig. 1a). The values of the reflection peaks E_1, E_2, and E_3 are as follows: $E_1 = 3.70 \pm 0.05$ eV; $E_2 = 4.05 \pm 0.05$ eV; $E_3 = 4.40 \pm 0.02$ eV.

Figure 1. Spectra of single reflection of ZnSiP2 with unpolarized (a) and polarized (b) incident radiation, T = 300 K.

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To obtain a clearer picture of the reflection spectrum ([5]), the crystals were recorded with polarized incident radiation. In the case when the light vector is perpendicular to the plane of incidence and parallel to the c axis of the crystal (S component), only the reflection peak E_3 appears distinctly (Fig. 1b), while the peaks E_1 and E_2 are barely noticeable. When the light vector is parallel to the plane of incidence and perpendicular to the c axis of the crystal (P component), the peak E_2 appears distinctly. Thus, the preliminary results of the polarization study show that the reflection peak E_3 is polarized parallel to the c axis of the crystal, the reflection peak E_2 perpendicular to the c axis of the crystal, and the reflection peak E_1, apparently, is not polarized.

Discussion of results. The great analogy in the nature of the chemical bond in semiconductor compounds with sphalerite structures, on the one hand, and chalcopyrite structures, on the other, gives grounds for making a pre-

the proposition concerning the similarity of the structures of their energy bands ([6–8]). On the basis of the similarity to semiconductors of the A^3B^5 type, it may be assumed that the observed reflection peaks correspond to electronic transitions at high-symmetry points of K-space on the surface of the Brillouin zone of the $ZnSiP_2$ crystal. This assumption is in agreement with the invariance of the valence bands in various semiconductor compounds, noted in Ref. ([9]), according to which the first reflection maxima in semiconductor crystals of the $A^2B^4C_2^5$ type with the chalcopyrite structure should be expected in the energy region $E = E_g + \Delta$, where E_g is the forbidden-band width and $\Delta = 1 \div 3$ eV. For $ZnSiP_2$, $E_g = 2.0$ eV, and therefore E should lie in the energy interval $3 \div 5$ eV, where the observed reflection maxima of $ZnSiP_2$ are indeed located.

Fig. 1. Spectra of single reflection of $ZnSiP_2$ with unpolarized (a) and polarized (b) incident radiation, $T = 300^{\circ}$K.

Comparison of the Brillouin zones of sphalerite and chalcopyrite shows that the points L and X of sphalerite, to which the most distinct reflection maxima correspond, can be matched in the Brillouin zone of chalcopyrite only with points of type X of two kinds, with coordinates $X_a[\pi/a, 0, 0]$ and $X_c[0, 0, \pi/c]$. This gives, without taking into account other points of the Brillouin zone, two main possibilities for interpreting the observed reflection peaks if these peaks are associated with transitions at the points X_a and X_c.

The first of these is that all three reflection maxima correspond to transitions from different closely spaced valence bands to the nearest conduction bands at one of these points of K-space. The second and most probable possibility of explanation is that the appearance of the reflection peaks is due to transitions

from the same valence bands, but from states belonging both to the points X_a and to the points X_c.

In semiconductors of the $A^2B^4C_2^5$ type, at an arbitrary point of the Brillouin zone possessing the lowest symmetry, without taking degeneracy into account, the number of valence bands alone that are not degenerate can be 32, whereas in semiconductors A^4 and A^3B^5 there are 4 valence bands. Such a considerable number of valence bands (not even counting the numerous conduction bands) in a narrow energy interval should lead to a complex structure of absorption and reflection spectra.

A large number of bands can produce a reflection spectrum rich in peaks and lead to an increase in the observed width of the reflection peaks due to

overlap of reflection maxima associated with different bands. Indeed, as is seen from Fig. 1, the reflection maxima of $ZnSiP_2$ are broader than in the case of A^3B^5 compounds.

The presence of three maxima in the reflection spectrum of $ZnSiP_2$ may be connected with spin-orbit interaction, although its estimate for $ZnSiP_2$ at $k = 0$ from the magnitudes of the spin-orbit splitting of the p-states of the isolated atoms gives a value of 0.09 eV, i.e., somewhat smaller than the experimental data.

It is not possible to make any definitive judgments about the polarization state of the observed reflection maxima of $ZnSiP_2$ before a more detailed theoretical study of the band structure of this compound has been carried out.

It should be noted that our reflection data do not agree with the data of work ([10]), where only two reflection maxima were observed. In our opinion, this discrepancy is connected with the less accurate measurement technique in work ([10]). In addition, our interpretation of the results obtained and the interpretation of the data by the authors of work [10] also differ.

In conclusion, the authors express their gratitude to Prof. N. A. Goryunova for her constant interest in the work, to Corresponding Member of the Academy of Sciences of the USSR E. F. Gross for discussion of the results of the work, and to V. E. Khartsiev for calculating the spin-orbit interaction and for consultations.

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REFERENCES

1. N. A. Goryunova, Yu. A. Valov, L. B. Zlatkin, Reports of the XXIII Scientific Conference, Leningrad Civil Engineering Institute, collection *Physics*, L., 1965, p. 18.

2. N. A. Goryunova, F. P. Kesamanly et al., *FTT*, 7, No. 5, 1312 (1965).

3. M. P. Belits, Yu. A. Valov et al., *DAN*, 163, No. 3 (1965).

4. L. B. Zlatkin, B. V. Novikov, IV All-Union Conference on Photoelectric Phenomena in Semiconductors. Abstracts of Reports. Odessa, 1965, p. 46.

5. Chzhan Guan-in, *Optics and Spectroscopy*, 13, 536 (1962).

6. V. E. Khartsiev, Author' s abstract of dissertation, Physico-Technical Institute named after A. F. Ioffe, Academy of Sciences of the USSR, 1962.

7. F. M. Gashimzade, *FTT*, 5, 1199 (1963); *Izv. AN AzerbSSR*, series of physico-mathematical sciences, 3, 67 (1963).

8. A. A. Vaypolin, F. M. Gashimzade et al., *Izv. AN SSSR*, series physics, 28, Proceedings of the III All-Union Conference on Semiconductor Compounds, Kishinev, 1964.

9. C. Hilsum, *Physic of Semiconductors*, Paris, 1964, p. 1127.

10. F. P. Kesamanly, S. T. Kroitor et al., *DAN*, 163, No. 4, 868 (1965).

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