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ENERGY SPECTRUM OF GROUP A^V CRYSTALS IN THE 1–12 eV RANGE

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The reflection spectra of Bi, Sb, As, and P crystals were investigated in the energy range 1–12.5 eV. A complex structure was observed instead of the previously reported relatively simple spectra. The energies of the interband transitions were determined. A general (and in some cases detailed) similarity was found in the structure of the interband transitions and, possibly, of the energy bands of Bi, Sb, and As, as well as of those of Bi and P. The experimental data were in good agreement with the published theoretical calculations of the band structure of Sb crystals.

BISMUTH, antimony, and arsenic crystallize in rhombohedral lattices (D_{3d}^5) with two atoms per unit cell. Black phosphorus has a complex orthorhombic lattice (D_{2h}^{18}) with eight atoms per cell. The lattice of red phosphorus is monoclinic and similar to that of black phosphorus.[1-3] The first three elements are semimetals with overlapping allowed bands, very complex Fermi surfaces, narrow forbidden bands (E_g is 0.015 eV for Bi, 0.1 eV for Sb, and 0.15 eV for As), and complex fine structures of the energy bands near E_g.[4-10] Red and black phosphorus are semiconductors and their forbidden band widths, E_g, are respectively, ~ 0.3 and ~ 1.6 eV.[3]

The energy bands of As and Sb crystals are calculated in detail in[11-14] by the OPW and pseudopotential methods. These calculations are carried out for many important directions of the Brillouin zone, taking into account the relativistic effects. The results reported in[11-14] not only agree with the results of other investigations[4-7,10] in respect of the complex band structure near E_g, but they also predict an exceptionally complex nature of the band structure and of the direct optical transitions in the energy range $E > E_g$.

The published experimental investigations of the reflection spectra of Bi, As, and Sb crystals have indicated three to five optical interband transitions.[15] On the other hand, the theoretical calculations for Sb[16] and, obviously, for other group A^V crystals predict a much larger number of transitions. Therefore, experimental investigations which would yield a larger number of interband transitions than that reported in[15], together with a comparison of such transitions with the band theory[11-14,16] would be of great interest from the point of view of solid-state theory.

We used the reflection spectra[15] as an effective method for investigating the band structure of group A^V crystals in a wide range of energies. An automatic spectroscopic unit (Fig. 1) was used in the precision recording of the reflection spectra in the 1.5–5 eV range. The main advantage of our apparatus over other known methods was the direct recording of the reflection coefficient by an electronic potentiometer with an

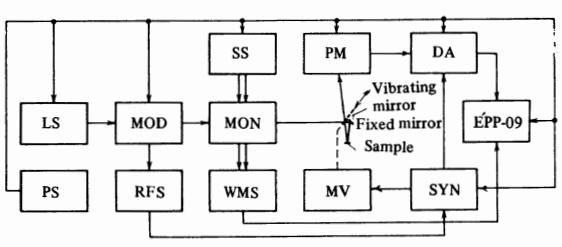

FIG. 1. Block diagram of the apparatus used in the measurements in the 1.5-5.5 eV energy range: LS is the source of light; MOD–modulator; RFS–reference frequency source; SS–spectral scanning device; MON–monochromator of the SPM-2 type; WMS–wavelength-mark source; PM–photomultiplier; DA–detector-amplifier unit; SYN–synchronizer; MV–mirror vibrator (the double-pointed arrow indicates the directions of the vibrations of the movable mirror); PS–power source.

error of the order of 0.03% (compared with the usual error of 0.2%[15]). In the 5–12.5 eV range, the spectra were recorded using a VMR-2 spectrometer. The samples were in the form of a large specularly reflecting cleaved samples (Bi, Sb), specularly reflecting plates (As, red and black P), or polished crystals (black P). The measurements were carried out at 77 and 293°K in 10^{-4}–10^{-5} mm Hg vacuum.

Typical spectra obtained in our investigation are presented in Fig. 2. The spectrum of each crystal consisted of a large number of strongly overlapping reflection bands. When the temperature was lowered from 293 to 77°K, a redistribution of the intensities between the bands in the 1–5 eV range was observed, as well as a narrowing of all the peaks and a slight shift of their positions in the direction of lower energies. This allowed us to use only the results obtained at T = 77°K (to avoid overcrowding Fig. 2 we have not shown the results obtained at T = 293°K in the energy range 1–5 eV). Table I gives our results (denoted by OR) obtained at T = 77°K, and the results of Cardona and Greenaway[15] obtained at T = 293°K.

Before analyzing the actual nature of individual bands, it is often useful to consider the positions of the bands (on the eV scale) of a series of similar compounds plotted graphically as a function of the lattice parameter.[15] In this way, it is possible to establish general empirical relationships governing changes in the energies of interband transitions of the same type in a family of isomorphous crystals. A similar analysis was carried out in our investigation for Bi, Sb, and As. As a result, we were able to identify bands (interband transitions) of similar origin (Table I). Our results for Bi-Sb alloys, obtained in the 1–12.5 eV range, confirmed the band classification given in Table I. It was found that the positions of many bands in the Bi-Sb system was practically independent of decomposition and that the E_5' and E_5'' bands approached the E_5 band when the concentration of Bi was increased.

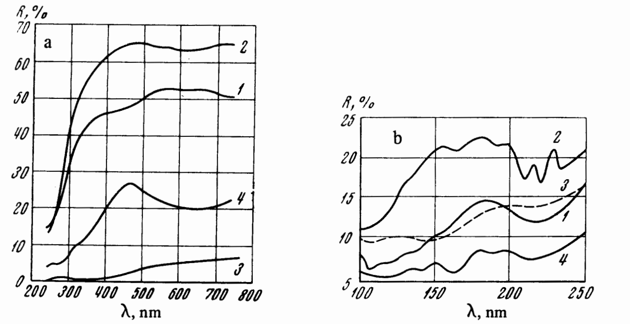

FIG. 2. Reflection spectra of single crystals of Bi (curves denoted by 1), Sb (2), As (3), and black P (4): a) at T = 77°K in the energy range 1.5-5.5 eV; b) at T = 293°K in the energy range 5-12.5 eV.

It was interesting to note that, in spite of considerable differences between the lattices of black and red P, on the one hand, and of Bi, Sb, and As, on the other, their spectra were so similar that we were able to identify the bands of black and red phosphorus which were related to the bands of bismuth, antimony, and arsenic. Unfortunately, the lack of theoretical data on the energy structure of P prevented us from pursuing more thoroughly the analogies in the structure of the reflection spectra of P and Bi, and from determining the actual nature of the bands of P.

We considered carefully the theoretical energy band schemes[14] and calculations of the imaginary component of the permittivity $\epsilon_2(\omega)$[16] of Sb. An analysis of the results reported in[14,16] was used to estimate the energies of the possible direct interband transitions responsible for the observed optical reflection bands of Sb crystals (Table I, column denoted by "theory"). The agreement between the theory[14,16] and our results for Sb crystals was good and it justified the theoretical predictions given in[14] that the optical spectra should be more complex than those reported in[15].

Our experimental results indicated that, in a wide range of transition energies, the energy band schemes of three similar crystals of group A^V—Sb, Bi, and As—should be similar. However, the results of theoretical calculations of the energy band structures of As[12,13] and Sb[14,16] indicate that there could be considerable differences in the nature of those transitions which were found experimentally to be similar. The origin of this disagreement between the experiment and theory was not clear. It was predicted theoretically in[12] that the spin-orbit splitting of the upper valence band should be ~ 1.5 eV for Bi, 0.6 eV for Sb, and 0.3 eV for As, i.e., there should be a fivefold difference between the split-

Table I. Positions of reflection band maxima (eV), nature and energies of interband transitions (eV) of group A^V crystals*

	Bi		Sb				As		P, OR	
	[15]	OR	[15]	OR	theory	[14, 16]	[15]	OR	black	red
E_1'	—	1,3	—	1.4	$\Sigma_{2'} \to \Sigma_2$	1.4	—	(1.7)	1.4?	2?
E_1	1.2	1,8	—	1,7	$\gamma_2 \to \gamma_1$, $L_{2,4} \to L_1, \sigma_{3'} \to \to \sigma_{2,3}$	1.6—1.7	2.2	2.2	3	3.1
E_1''	—	2,2	—	2.2	$L_{2,4} \to L_3$	~2.3	—	(2.5)	—	—
E_1'''	—	—	—	2,5			—	—	—	—
E_2	1,7	3	2.5	3	$\Sigma_1 \to \Sigma_2$	3.1	3.5	3.45	5,0	4,6
E_3'	3.1	4	3.9?	4	$S_2 \to S_1$, $\sigma_{3,4} \to \sigma_1$	~5	5.1?	5.0	6.3	6,1
E_3''									6.9	6,1
E_4	5?	(5,4)	5.7	5.4	$V_{3,4} \to V_{1,2}$	5—6	6.9	6,2	8,2	(7,4)
E_5'	—	(6,4)	—	6.2	$\Gamma_{1,3} \to \Gamma_{2'}, _{3'}$	6.2	—	—	—	—
E_5	7	6.7	7,6	6,7	$\Lambda_1 \to \Lambda_{2'}$	6—7	10,6	(7,4)	9.4	8.8
E_5''	—	(7,2)	—	7.7	$V_1 \to V_2$	6,6—7,7	—	—	—	—
E_6	8,6	9.2	9.4?	9,5	$\Lambda_{2'} \to \Lambda_{3'}$, $\sigma_{2'} \to \sigma_{3'}$	9—10	13,6	10	—	—

*Parentheses are used for the estimates obtained from the dependences of the positions of the band maxima on the lattice parameter; question marks are used for the results obtained for very weak bands; OR denotes our results.

ting in Bi and As. However, our experimental data on the structure of optical interband transitions in group A^V crystals indicated no spin-orbit effects.

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