Double inversion of band spectrum in $TlBi_{1-x}Sb_x$-VI_2 solid solutions

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It is predicted that a change in the band structure of $TlBi_{1-x}Sb_x$-VI_2 solid solutions will be accompanied by a double inversion of the spectrum, and these alloys will be semimetals in an intermediate composition range. The possible realization of a semimetallic state at an inversion contact of such materials is discussed.

The active search for new narrow-gap semiconductors which has been carried out in recent years has revealed a new group of materials of this class: anisotropic solid solutions of III-V-VI_2 compounds,[1–3] which are ternary isoelectronic analogs of semimetals of the bismuth group and of IV–VI semiconductors. In $TlBi_{1-x}Sb_x$-VI_2 solid solutions, the group V atoms of one type are replaced by another element from the same group. They are reminiscent of IV–VI solid solutions of the $Pb_{1-x}Sn_xTe$ type, with the one difference that the substitution occurs in one of the two cationic sublattices. This circumstance, combined with the pronounced anisotropy of the crystal lattice (symmetry D_{3d}^5), can cause markedly different physical properties. The possibility of a healing of defects in these alloys because of their localization in different sublattices makes them promising for applications.

In this letter we use a model for the electronic band structure of rhombohedral III-V-VI_2 compounds[4] based on a p-type model for IV–VI semiconductors[5] and the approximation of a virtual crystal to study the changes in the band spectrum of $TlBi_{1-x}Sb_x$-VI_2 solid solutions.

In a disordered cubic phase with the NaCl structure (fcc phase) the band extrema of III-V-VI_2 semiconductors, like those of IV–VI compounds, lie at the L points.[4] After a doubling of the lattice period due to the ordering of the cations and the corresponding shift of the anionic layers and the rhombohedral deformation, the four L points of the fcc phase break up into two groups. One of the L points, on the preferred C_3 axis, coincides with the center of the Brillouin zone; the corresponding energy terms, along with the levels of the Γ point of the fcc phase, generate a first group of actual energy extrema at the Γ point of the Brillouin zone of the rhombohedral lattice. The second group of three L points of the fcc phase coincides with the X points, and their energy terms form band extrema at a L point of the Brillouin zone, According to the results of a theoretical analysis, the band structure of the Tl-V-VI_2 narrow-gap semiconductors is either normal or inverted, depending on whether the Bi or the Sb forms one of the cationic sublattices. Both groups of actual band extrema are inverted in TlSb-VI_2. As a result, there is a twofold inversion of the band structure in the $TlBi_{1-x}Sb_x$-IV_2 solid solutions: a new phenomenon in this class of narrow-gap semiconductors.

The secular equation determining the energy spectrum of the III-V-VI_2 rhombohedral semiconductors is[4]

$$\begin{vmatrix} \hat{\mathscr{H}}^{\text{fcc}}(\mathbf{k}|\epsilon) - E\hat{I} & \hat{\Sigma}(k) \\ \hat{\Sigma}^{+}(k) & \hat{\mathscr{H}}^{\text{fcc}}(\mathbf{k}-\mathbf{Q}/2|\epsilon) - E\hat{I} \end{vmatrix} = 0, \tag{1}$$

where $\hat{I}$ is the unit matrix of the twelfth rank, $\hat{\mathscr{H}}^{\text{fcc}}(\mathbf{k}|\epsilon)$ is the matrix of the Hamiltonian of the deformed fcc lattice, and $\hat{\Sigma}(\mathbf{k})$ is a nondiagonal block which stems from the period-doubling potential of the fcc lattice and which relates states separated by the vector $\mathbf{Q}/2 = \pi/2\pi(1,1,1)$ (α is the period of the simple cubic lattice).

The energy spectrum of III-V-VI_2 rhombohedral compounds described by (1) is determined by a set of phenomenological parameters. The parameters which are common to the cubic and rhombohedral phases are amenable to interpolation[6] on the basis of the data for IV–VI compounds.[5] Yet another set of parameters arises in the rhombohedral phase; the most important of these parameters can be determined by using data on the crystal lattice and atomic characteristics of the constituent elements.[4]

The possibility of a linear interpolation based on the composition of the basic parameters in the approximation of a virtual crystal makes it possible to use the model of the III-V-VI_2 spectrum to study changes in the band structure of $TlBi_{1-x}Sb_x$-VI_2 solid solutions.

Figure 1 is a qualitative picture of the composition-dependent changes in the band spectrum of $TlBi_{1-x}Sb_x$-VI_2 solid solutions. Near Tl-V-VI_2, the alloys are semiconductors with an indirect gap. With increasing x, the Γ conduction band and the L valence band close on each other, and at $x = x_L^{\Gamma}$ the indirect gap between them disappears. At $x > x_L^{\Gamma}$, these bands begin to overlap, and a semimetallic state arises. It persists up to $x = x_{\Gamma}^{L}$, where the extrema of the L conduction band and of the Γ valence band coincide. As in semimetals such as bismuth, there is an overlap of bands

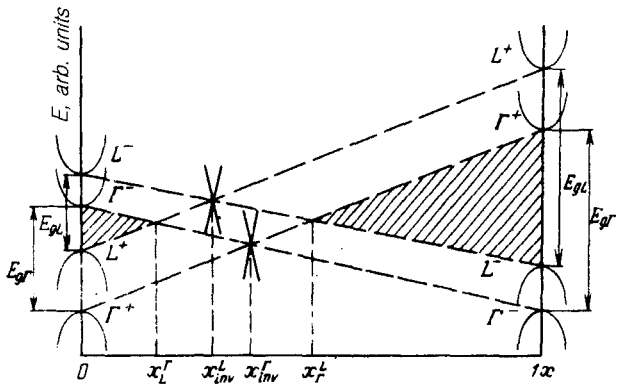

FIG. 1. Qualitative picture of the change in the energy spectrum as a function of the composition of the $TlBi_{1-x}Sb_x$-VI_2 rhombohedral solid solutions.

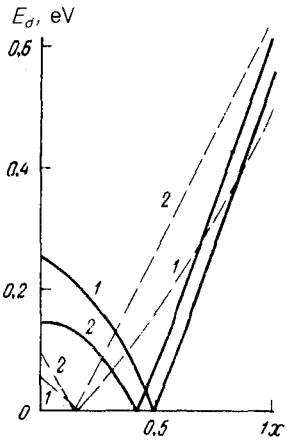

FIG. 2. Change in the energy gaps between the Γ bands (solid lines) and the L bands (dashed lines) in rhombohedral solid solutions (1) of the $TlBi_{1-x}Sb_xSe_2$ type and (2) of the $TlBi_{1-x}Sb_xTe_2$ type.

localized at different points in **k**-space. At compositions $x_L^\Gamma < x < x_\Gamma^L$, an inversion, of, first, the L bands occurs, at $x = x_{\text{inv}}^L$, and then, at $x = x_{\text{inv}}^\Gamma$ an inversion of the Γ bands occurs. At $x = x_L^\Gamma$ and $x = x_\Gamma^L$, the alloys are gapless semiconductors with finite effective masses in the bands because of the nonzero values of the direct gaps, $E_{g\Gamma}$ and E_{gL}. At $x > x_\Gamma^L$ the overlap of the L and Γ bands disappears, and the solid solutions become semiconductors again. The appearance of a semimetallic state in the intermediate region of compositions stems from the double inversion of the spectrum and the shift of the band L extrema with respect to the Γ extrema in the original Tl-V-VI_2 components.

In $TlBi_{1-x}Sb_x$-VI_2 solid solutions, there is accordingly a change in the band structure which is the opposite of that which occurs in $Bi_{1-x}Sb_x$ alloys. In the latter alloys, the solid solutions near Bi and Sb are semimetallic, while those at $0.07 < x < 0.22$ are semiconducting.

Figure 2 shows the energy gaps $E_{g\Gamma}$ and E_{gL} versus the composition for the $TlBi_{1-x}Sb_x$-VI_2 alloys (VI = Se, Te). We see that the changes in both of the gaps go through a gapless state. Since $E_{gL} < E_{g\Gamma}$ in TlBi-VI_2, the L bands invert first, and then the Γ bands invert.

The experimental results currently available provide indirect confirmation of the model proposed here for the changes in the spectra of these solid solutions. In particular, the curve of the magnetic susceptibility as a function of the composition of $TlBi_{1-x}Sb_xTe_2$ alloys has two maxima,[7] whose appearance can be attributed to a double inversion of the band spectrum. The same factor is apparently responsible for the observed features in the behavior of the resistivity as a function of the composition.[7]

In connection with the double inversion of the band spectrum in $TlBi_{1-x}Sb_x$-VI_2 solid solutions, it is interesting to study an inverted contact[8] based on these solid solutions. Since there are two groups of inverting bands, shifted with respect to each other along the energy scale, a semimetallic region of electron states will arise at a contact made from these alloys. In other words, a semimetallic two-dimensional layer

can appear at the interface between two narrow-gap semiconductors. The pronounced stratification of these materials is very advantageous for the fabrication of such contacts.

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[1]D. V. Gitsu, G. M. Dyntu, N. S. Popovich, *et al.*, Izv. Akad. Nauk SSSR. Ser. Neorg. Mater. **15**, 1479 (1979).
[2]D. V. Gitsu, I. N. Grincheshen, N. S. Popovich, *et al.*, Izv. Akad. Nauk SSSR. Ser. Neorg. Mater. **16**, 1111 (1980).
[3]R. Mazelsky and M. S. Lubell, J. Phys. Chem. Sol. **66**, 1408 (1962).
[4]D. V. Gitsu, V. G. Kantser, and N. M. Malkova, Preprint 85-3, Institute of Applied Physics, Academy of Sciences of the Moldavian SSR, Kishinev, 1985.
[5]B. A. Volkov, O. A. Pankrotov, and A. V. Sazonov, Zh. Eksp. Teor. Fiz. **85**, 1395 (1983) [Sov. Phys. JETP **58**, 809 (1983)].
[6]V. G. Kantser, N. M. Malkova, and A. S. Sidorenko, Fiz. Tekh. Poluprovodn. **19**, 1756 (1985) [Sov. Phys. Semicond. **19**, 1079 (1985)].
[7]V. K. Shura, Author's Abstract, Candidate's Dissertation, Kishinev, 1985.
[8]B. A. Volkov and O. A. Pankrotov, Pis'ma Zh. Eksp. Teor. Fiz. **42**, 145 (1985) [JETP Lett. **42**, 178 (1985)].

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