Spectra of IV–VI semiconductors

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Assuming that the electronic properties of SnTe are close to those of antimony, expressions for the electronic spectra are obtained on the basis of a model [2] for semimetals of the fifth group. The experimental consequences and the possibility of comparing the properties of SnTe and Sb are discussed.

The authors have previously attempted[1] to develop a microscopic theory of the electronic spectrum of semimetals of the fifth group (As, Sb, Bi). We have started from the picture proposed in[2] for the spectrum, it being assumed that in the primitive cubic lattice which is close to the Bi lattice the Fermi surfaces of the carriers are superimposed on each other when shifted by an amount equal to half the diagonal of the initial cubic Brillouin zone (the vector $\mathbf{q}_0$). It was noted in[1] that this picture of congruent Fermi surfaces conforms to the model of the dielectric transition.[3,4] Accordingly, the feasibility of such a model as mechanism causing the appearance of small carrier groups in As, Sb, and Bi was analyzed qualitatively in[1].

Semiconductors of the IV—VI type, as noted in the literature (see, e.g.,[5]) are similar in many respects to semimetals of the fifth group. They crystallize in a cubic lattice of the NaCl type, their electronic spectrum has common features, and some of them (GeTe) undergo a structural transition connected with a shift of the face-centered sublattices and rhombohedral deformation. From this point of view, greatest interest seems to attach to SnTe, which should be comparable in its properties with Sb. The difference can be described by means of a small additional contribution to the crystal potential, $\Delta_0(\mathbf{x}) = \Delta_0 u(\mathbf{x})$ for the electrons in SnTe. In all other respects, the electron spectra of SnTe and Sb coincide and are described in the primitive cubic phase by the model of[2]. It is assumed that the value of Δ_0 is sufficient to prevent a transition to the rhombohedral phase.

If the symmetry center is located at the site of the initial primitive cubic lattice, then $\Delta_0(\mathbf{x})$ corresponds to the representation of the space group $\Gamma_1(\mathbf{q}_0)$, i.e., it corresponds to the star $\mathbf{q}_0$ (doubling the period along the diagonal of the primitive cell) and to a unit representation of the crystal class O_h. The new translational asymmetry leads to a splitting of the electron terms of the initial primitive cubic lattice. The spectrum at an arbitrary point near the Fermi surface has the usual form typical of the model of[3,4]

$$\epsilon(\mathbf{p}) = \pm\sqrt{\xi^2(\mathbf{p}) + |\Delta_0(\mathbf{p})|^2}. \qquad (1)$$

where

$$\Delta_0(\mathbf{p}) = \int \phi^*_{1\mathbf{p}}(\mathbf{x})\Delta_0(\mathbf{x})\phi_{2\mathbf{p}-\mathbf{q}_0}(\mathbf{x})\,d^3x,$$

and $\phi_{1b}(\mathbf{x})$ and $\phi_{2b}(\mathbf{x})$ are the Bloch functions of the electrons in the first and second bands.

The equal-energy surfaces observed experimentally in SnTe lie near the points L. The points L in the SnTe lattice correspond to the points $\mathbf{k}_i = (\pm\frac{1}{4}, \pm\frac{1}{4}, \pm\frac{1}{4})$ in the primitive cubic lattice. It is necessary to take into account degeneracy near $\mathbf{k}_i$, and this leads to the matrix $D_{ss'}$ of[2], except that $\Delta_0(\mathbf{x})$ corresponds to the representation $\Gamma_1(\mathbf{q}_0)$ (instead of $\Gamma_{15}(\mathbf{q}_0)$). In view of the double degeneracy and the doubling of the period (the star $\mathbf{q}_0$), $\mathbf{D}_{ss'}$ is a 4×4 matrix

$$D_{ss'} = \begin{Vmatrix} p & q & \gamma & \delta \\ q^* & p & \delta^* & \gamma \\ \gamma & \delta & -p & -q \\ \delta^* & \gamma & -q^* & -p \end{Vmatrix} \qquad (2)$$

Here $p = a\kappa_z$; $q = b(\kappa_x + i\kappa_y)$; $\gamma = \gamma_0 + \mu\gamma_0(p^2 + \nu|q|^2)$; $\delta = \lambda\gamma_0(pq + \zeta q^{*2})$; $\gamma_0 \sim \Delta_0$; μ, ν, λ, $\zeta \approx 1$. The z axis is directed along a three fold axis, y along a twofold axis, and x lies in the reflection plane. The sign of γ_0 can be chosen positive. The signs of μ, ν, λ, and ζ are arbitrary.

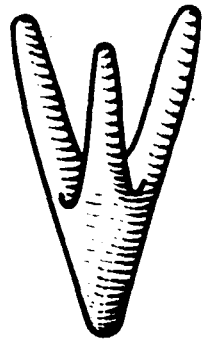

FIG. 1.

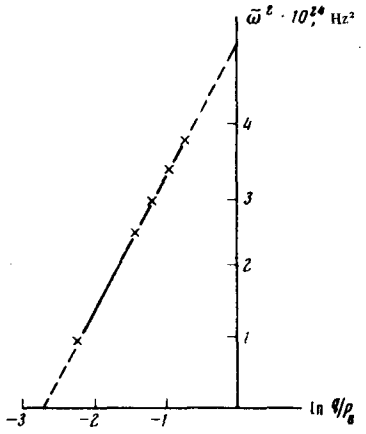

FIG. 2.

The energy gap at the point $\mathbf{k}_i$ is equal to γ_0. Assuming that the Fermi level of the electrons (holes), which is determined by the degree of doping, coincides approximately with γ_0, i.e., $(\omega-\gamma_0)/\gamma_0 \ll 1$, it is necessary to take into account the dependence of $\Delta_0(\mathbf{k}_i+\kappa)$ on κ. This is manifest in the presence of the terms δ and of the increments to γ.

The equations for the equal-energy surfaces are $(\epsilon=\omega-\gamma_0 \ll \gamma_0)$:

$$p=|q|\pm\left[2\gamma_0\epsilon-2\gamma_0^2|q|^2(\mu\nu-\lambda\zeta\cos 3\phi)\right]^{1/2},$$
$$p=-|q|\pm\left[2\gamma_0\epsilon-2\gamma_0^2|q|^2(\mu\nu+\lambda\zeta\cos 3\phi)\right]^{1/2}. \qquad (3)$$

The general symmetry of the surface is D_{3d} ($\tan\phi=\kappa_x/\kappa_y$). The form of the surface is Fig. 1. The "whiskers" lie in the reflection planes. The experimental results for SbTe[6] lead to Fermi surfaces of the form shown in Fig. 1, and in particular, they are not bodies of revolution and are strongly elongated along the C_3 axis. The ratio a/b is therefore found to range from 1/5 to 1/10. We recall that a similar aperture of the cone $p=|q|$ should be obtained in Sb. The electron ellipsoids in Sb lie in bisector planes. Within the framework of the model assumed above, they are strongly elongated along the cone $p=|q|$. The estimate for the ratio a/b in SnTe agrees fully with the fact that the electron ellipsoids in Sb are inclined 5—10° to the basal plane. A more detailed reduction of the results[6] is made difficult by the uncertainty in the doping.

SnTe has one more singularity, namely a soft optical mode.[7] Under the assumptions made, the interaction of the electrons with the representation $\Gamma_{15}(q_0)$ leads to a softening of the corresponding phonon frequency and would cause a shift of the sublattices in Sb. In SnTe, this softening is limited by the value of Δ_0. It is easy to determine, by calculating the polarization operators on the new Green's function, that

$$\tilde{\omega}^2_{SnTe}(q=0)=g^2\omega_0^2\left(\ln\frac{\Delta_0}{\Delta_{Sb}}+1\right). \qquad (4)$$

The phonon spectra of SnTe and Sb should concide in the wave-vector region $E_F \gg vq \gg \Delta_0,\ \Delta_{Sb}$:

$$\tilde{\omega}^2(q)=g^2\omega_0^2\ln\frac{vq}{\Delta_{Sb}}. \qquad (5)$$

In (4) and (5), g^2 is the dimensionless constant of the interaction with the phonons in the cubic phase, $\omega_0=\omega(\mathbf{q}_0)$, v is the average velocity on the Fermi surface, and $\Delta_{Sb}=2E_F\exp(-1/g^2)$ is the shift of the lattices in Sb in energy units.

Figure 2 shows the data of[7] in a logarithmic scale in accordance with expression (5). Hence using (4) and (5), we obtain $g=0.7$, $\Delta_0/\Delta_{Sb}=0.44$, $E_F/\Delta_{Sb}=20$, and $g\omega_0=1.35\times10^{12}$ Hz. There are no data on the phonon spectra of Sb. Within the framework of our model, however, it can be indicated accurately that $\tilde{\omega}_{Sb}(\mathbf{q}=0)=1.35\times10^{12}$ Hz. The relatively large value of g indicates that the softening of the optical mode in Sb should be relatively small.

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