Hybridization of *s*, *p*, and *d* states in quasicubic materials

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It is suggested that the effect of unfilled *d* states on the electronic structure of group V semimetals and IV–VI semiconductors be taken into account. Comparison with the experimental data available on the carrier characteristics yields the constants for *s–p* and *p–d* hybridization in antimony and bismuth.

A developing theory is making it possible to describe IV–VI semiconductors[1] and group V semimetals[2] by a common approach, based on the Peierls idea of the instability of a simple cubic lattice along with the strong-coupling approximation. The initial basis here consists of atomic *p* states. Parameters of various magnitudes arise in this theory. The most important among them characterize a cubic regular phase. These characteristics are the overlap integrals of nearest neighbors in the simple cubic lattice. They are on the order of 3.5 eV. Quantities of the next order of magnitude (0.5 eV) in the group V semimetals arise because of the small difference between their spatial lattice and a simple cubic lattice. In IV–VI semiconductors, the corresponding quantities are a result of the difference between the group IV atom and the group VI atom. The spin-orbit interaction, which is important in heavy atoms, is also taken into account.

These quantities by themselves, however, are not sufficient for an adequate de-

scription of these materials. For example, the random degeneracy of electron terms at certain points in the Brillouin zone is not lifted. Furthermore, the high accuracy required by an experiment is not achieved because of the pronounced anisotropy of the effective masses in certain directions. For this reason, overlap integrals in the second and even third coordination spheres are taken into consideration. For bismuth, for example, all the available experimental information on the electrons and holes and also optical data have been described within an error no greater than 10%. An attempt to implement the same program for antimony, however, ran into a fundamental difficulty: A hole extremum appeared in the ΓX direction above the Fermi level. This hole is not seen experimentally.

We took into account the circumstance that pseudopotential calculations of the electronic structure of semimetals (see Ref. 3, for example), although not accurate enough to satisfy the experimentalists, do give a qualitatively correct picture. It is easy to see that the pseudopotential method, in contrast with the approximation which we use, incorporates in a hidden form all of the atomic states. Accordingly, the first step in the correct direction is to supplement the p states with the closest-lying other atomic terms. The one attempt which has been made in this direction was that by Vogl et al.[4] They were concerned with semiconductors having the zinc blende and diamond structures; in addition to filled states, they considered a higher-lying state, which was spherically symmetric (apparently for simplicity).

We begin by taking into account a filled s state which lies 7 eV deeper than the p term, according to atomic calculations.[5] In the strong-coupling approximation, its dispersion is described by the following expression, which takes account of Peierls doubling:

$$\epsilon_s = \epsilon_{0s} \pm (\xi_s^2 + u_s^2)^{1/2} \, ,$$

where $\xi_s = \xi_{0s} (\cos k_x + \cos k_y + \cos k_z)$ and $u_s = u_{0s} (\sin k_x + \sin k_y + \sin k_z)$. We are using coordinates associated with a simple cubic lattice with lattice constants $a = 1$. The overlap integral of the s functions with nearest neighbors, ξ_{0s}, and the change in this integral due to Peierls doubling, u_{0s}, can be estimated by working from pseudopotential calculations[3] and by treating the two deepest zones as arising from an atomic s term. For bismuth at the point $L = \pi(1,1,\bar{1})$, for example, the corresponding splitting $2u_{0s}$ of the lower valence levels leads to the value $u_{0s} = 0.226$ eV, while the splitting at $X = \pi(1,0,0)$ gives us $\xi_{0s} = 0.639$ eV. Comparing these values with those ($u_{0s} = 0.219$ eV, $\xi_{0s} = 0.693$ eV) given by the points $T = \pi(1,1,1)$ and $\Gamma = (0,0,0)$, where the splittings are three times larger, we see that the interpretation of the pseudopotential results with the help of the strong-coupling approximation is noncontradictory.

The hybridization of the s and p states is described by the matrix element

$$V_{sp} = \langle s(0,0,0) | V | p_x(1,0,0) \rangle ,$$

where V is the crystal potential, and the numbers in parentheses are the coordinates of the nearest atoms. In second-order perturbation theory we find the contribution of s–p hybridization to the matrix element of the effective Hamiltonian constructed in the

basis of p states:

$$h_{xy} = \eta_{sp} \sin k_x \sin k_y ,$$

where

$$\eta_{sp} = 4V_{sp}^2 / (\epsilon_{0p} - \epsilon_{0s}). \tag{1}$$

If we restrict the analysis to exclusively p states, we could find a matrix element of the same symmetry[1] in only the second coordination sphere; it is denoted by w in Ref. 1 and η_0 in Ref. 2 (however, the corresponding diagonal element h_{xx} vanishes).

What is the effect of the nearest d states? In group V elements, these states are not filled, and for this reason they were ignored in the atomic calculations of Ref. 5. Their presence is seen in pseudopotential calculations,[3] where higher-lying states are visible. Because of the fivefold degeneracy, however, an analysis like the s-term analysis becomes quite complicated here. We accordingly restrict the analysis to p–d hybridization. In a cubic field, the quintet of d states is known to split into a triplet, which transforms as the products xy, yz, zx, and a doublet x^2–y^2, $3z^2$–r^2. The matrix element of the crystal potential between the d function of the triplet and the p function of the nearest neighbors is

$$V_{xy,\,x} = \langle xy\,(0,0,0) \mid V \mid p_x\,(0,1,0) \rangle.$$

The matrix element

$$V_{x^2-y^2,\,x} = \langle (x^2-y^2)\,(0,0,0) \mid V \mid p_x\,(1,0,0) \rangle ,$$

$$V_{3z^2-r^2,\,x} = \langle (3z^2-r^2)(0,0,0) \mid V \mid p_x\,(1,0,0) \rangle ,$$

$$V_{3z^2-r^2,\,z} = \langle (3z^2-r^2)\,(0,0,0) \mid V \mid p_z\,(0,0,1) \rangle$$

are related by

$$V_{3z^2-r^2,\,x} = -\frac{\sqrt{3}}{2}\,V_{x^2-y^2,\,x} - \frac{1}{2}\,V_{3z^2-r^2,\,x} ,$$

$$V_{3z^2-r^2,\,z} = \frac{\sqrt{3}}{2}\,V_{x^2-y^2,\,x} - \frac{1}{2}\,V_{3z^2-r^2,\,x} ,$$

which can be found if their left sides are transformed by the rotations $y \to z$, $z \to -y$ and $x \to y \to z \to x$. The hybridization of the doublet with p states in the nearest-neighbor approximation can thus be described by a single constant, e.g., $V_{3z^2-r^2,z}$ in terms of which the others are expressed:

$$V_{3z^2-r^2,\,x} = -\frac{1}{2}\,V_{3z^2-r^2,\,z} , \qquad V_{x^2-y^2,\,x} = \frac{\sqrt{3}}{2}\,V_{3z^2-r^2,\,z} .$$

The matrix elements of the effective Hamiltonian, which incorporate the hybridization of the p states with the s and d terms, are found in second-order perturbation

theory to be

$$h_{xx} = (\eta_{sp} + \eta_{dp}^{(2)}) \sin^2 k_x + \eta_{dp}^{(1)} (\sin^2 k_y + \sin^2 k_z),$$

$$h_{xy} = (\eta_{sp} + \eta_{dp}^{(1)} - \frac{1}{2}\eta_{dp}^{(2)}) \sin k_x \sin k_y$$

where

$$\eta_{dp}^{(1)} = 4V^2_{xy,\,x} / (\epsilon_{0p} - \epsilon_{0d}), \qquad \eta_{dp}^{(2)} = 4V^2_{3z^2 - r^2,\,z} / (\epsilon_{0p} - \epsilon_{0d}) \qquad (2)$$

and ϵ_{0s}, ϵ_{0p} and ϵ_{0d} are the energies of the atomic s, p, and d terms.

The values of the constants η_{sp}, $\eta_{dp}^{(1)}$ and $\eta_{dp}^{(2)}$ have been found numerically through a comparison with the available experimental characteristics of electrons and holes in semimetals. They turn out to be 0.041, -0.095, and -0.123 eV, respectively, for bismuth, and 0.283, -0.364, and -0.365 eV, respectively, for antimony (the details of this study will be published separately). These numbers have the appropriate sign [see Eqs. (1) and (2)], and they are also of the correct order of magnitude: The matrix elements of the crystal potential are on the order of 1 eV. We note in conclusion that incorporating the hybridization of the s, p, and d terms has made it possible to restrict the analysis to simply the nearest neighbors, without a loss of accuracy in the description of the electron characteristics (the number of parameters in the effective Hamiltonian decreases). This approach has also eliminated the difficulty regarding antimony, which we mentioned earlier.

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