
B. A. Volkov and O. A. Pankratov. *Electronic structure of quasicubic crystals: energy bands, dielectric properties, and defects in narrow-gap semiconductors.* Though completely different, at first glance, crystal materials—group V semimetals, group VI semiconductors—chalcogenides, semicon-

ductor compounds of elements from IV and VI groups, and a number of complex ternary and quaternary compounds are similar to each other in the origin of their electronic and crystal structure.¹⁻³ The lattices of these materials, i.e., quasicubic crystals, are similar to simple cubic lattices and differ

from them only by small structural distortions or by the weak nonequivalency of composing atoms. The energy bands close to the Fermi energy are formed mainly from the atomic states of p -symmetry. For this reason the electron spectra of quasicubic crystals can be obtained from the universal spectrum of a so-called "parent phase"—a hypothetical metal with a simple cubic lattice and three overlapping p -type energy bands. The degree of filling of these bands is determined by the average number of valence p -electrons per atom for the particular material under consideration. The perturbations that characterize the difference between the crystal lattice and a simple cubic lattice transform the hypothetical spectrum into a real spectrum.

Although the "parent phase" is a metal, all quasicubic crystals are dielectrics (or semimetals). This means that the distortion of a simple cubic structure is always such that the initial Fermi surface becomes "covered" by a dielectric gap. The only exception, i.e., metallic polonium, supports this rule, because polonium is stable in a simple cubic modification.

The concept of a "parent phase" was for the first time used by Abrikosov and Fal'kovskii⁴ in 1962 when they were developing a theory of electronic spectra of semimetals from the group of bismuth. However, at that time the spectrum of the "parent phase" itself was not known. This led Abrikosov and Fal'kovskii to make an assumption about the symmetry of the initial irreducible representation for electronic energy levels responsible for the formation of semimetallic properties of crystals from group V. It was later found that this assumption leads to a theoretical contradiction (the Luttinger theorem is not satisfied⁵) and does not allow a description of all available experimental data. An attempt to remove this contradiction with the Luttinger theorem by taking into account the Fermi-liquid effects⁵ had failed.⁶ The origin of the spectra of semimetals from the bismuth group of IV–VI group semiconductors and alloys based on them and of selenium and tellurium crystals has become completely clear only after the "parent phase" spectrum common to all these materials was constructed systematically from the atomic p -orbitals. As a result of this construction it was found that it is not sufficient to have one irreducible representation of the "parent phase" for a complete description of real spectra.²

Let us illustrate this on the example of the semiconductor material PbTe. The difference of its lattice geometry (of the NaCl type) from a simple cubic lattice is characterized by the ionicity potential $\Delta_{\text{ion}}(\mathbf{r})$ that has different values for the sub-lattices of lead and tellurium. $\Delta_{\text{ion}}(\mathbf{r})$ has the translational symmetry of a face-centered cubic-sublattice of the original cubic lattice. In the inverse k -space there appears the new transfer vector $\mathbf{q} = (\pi/a)(111)$ (a is the period of the simple cubic lattice). This is why the ionicity mixes the Bloch states of the "parent phase" $|n, \mathbf{k}, \sigma\rangle$ and $|n, \mathbf{k} + \mathbf{q}, \sigma\rangle$ (the index $n = x, y, z$ refers to p -bands, σ is the spin). As a result the spectrum

$$E_{n,\mathbf{k}} = \eta_{n,\mathbf{k}} \pm (\xi_{n,\mathbf{k}}^2 + \Delta_{n,\mathbf{k}}^2)^{1/2}, \quad (1)$$

is formed where $\xi_{n,\mathbf{k}+\mathbf{q}} = -\xi_{n,\mathbf{k}}$ and $\eta_{n,\mathbf{k}+\mathbf{q}} = \eta_{n,\mathbf{k}}$ are the

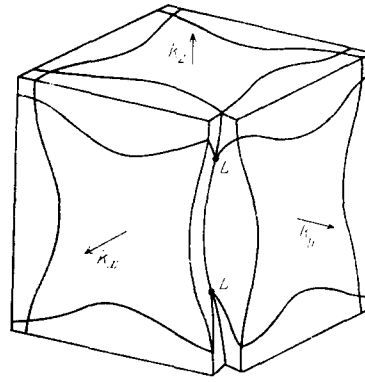


FIG. 1.

congruent and noncongruent parts of the parent phase spectrum $\varepsilon_{n,\mathbf{k}} = \xi_{n,\mathbf{k}} + \eta_{n,\mathbf{k}}$.

When the matrix element of the ionicity $\Delta_{n,\mathbf{k}}$ exceeds $\eta_{n,\mathbf{k}}$, the spectrum (1) corresponds to a dielectric. For all three noninteracting p -bands, the Fermi surface of the parent phase $\xi_{n,\mathbf{k}} = 0$ consists of three pairs of corrugated surfaces (Fig. 1). The ideal congruency of this surface is perturbed by the mixing of different energy bands and by the overlap integrals in the remote coordination spheres that contribute to the correction $\eta_{n,\mathbf{k}}$. It is obvious that the band mixing is the most significant near the intersection points (and lines) of Fermi-surfaces. It is exactly at these points which are called the L -points of a Brillouin zone that the smallest forbidden energy gap between bands is formed. The reason for this is the triple degeneracy of the original spectrum of a non-symmetric nature. Because of the ionicity, the opposite L -points related by an inversion transformation become equivalent. The corresponding levels are split and form the even L^+ and odd L^- levels (Fig. 2). The subsequent splitting (see Fig. 2) is caused by the mixing of bands by the crystal field and the spin-orbital interaction. The detailed theory developed in Ref. 2 made possible the description of the dispersion of six near bands with only five parameters, while a standard symmetry approach based on the $\mathbf{k}\mathbf{p}$ -method leads in this case to 18 independent parameters.⁷

The formulated model not only allows the description of the spectrum near the symmetrical points in binary compounds of elements of the IV–VI groups and alloys based on

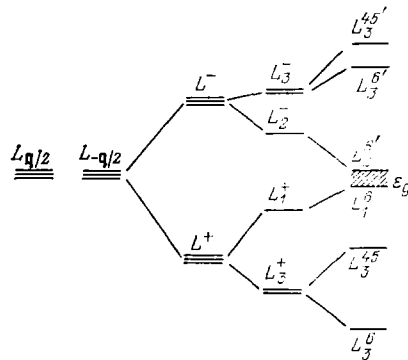


FIG. 2.

them⁸ and the calculation of g -factors,⁹ but also gives a qualitatively correct description of energy bands for wide energy intervals [formula (1)]. For these reasons it became possible to study analytically the deep localized states caused by impurities and defects,¹⁰ to understand the phenomenon of long-term relaxation,¹¹ dielectric properties¹²⁻¹⁴ and structural phase transitions.

In summary, we have developed a unified theory giving a practically complete description of the physical properties of a large group of real materials-the quasicubic crystals.

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