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Electronic properties of narrow gap IV – VI semiconductors

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1. Tight binding approximation to band spectrum model of IV – VI semiconductors

IV – VI semiconductors constitute compounds of elements of group IV (Pb, Sn, and Ge metals) and chalcogenides (Te, Se, S) [1]. They crystallize into an NaCl type structure. The important point, conceptually, is that the electronic spectra and crystal structures of IV – VI compounds are close to those of the bismuth-group semimetals. As in the crystals of group V elements, in IV – VI semiconductors there are, on average, three p-electrons per atom. Two s-electrons form deep narrow bands and do not participate in the actual valence bonds that exist in the crystal. Therefore, the valence and conduction bands should be constructed from p-orbitals (p_x, p_y, p_z) whose cubic symmetry reflects the cubic structure of bonds in IV – VI compounds. If the metal and chalcogene atoms were made chemically identical, their FCC lattice would become a simple cubic lattice with an odd number of (three) electrons per unit cell. According to Luttinger theorem, such a structure must be a metal. It is this praphase which Abrikosov and Fal'kovskiĭ [6] employed to explain the semimetal character of the spectrum of bismuth whose rhombohedral lattice can be considered as a slightly distorted simple cubic one.

A similar approach can conveniently be employed in constructing the electronic spectrum of IV – VI semiconductors by introducing the potential of ionicity into the praphase Hamiltonian — the potential which accounts for the difference between the metal and chalcogene atoms. This potential doubles the period of the simple cubic lattice, with the result that the new (FCC) cell has an even number of electrons ($3 \times 2 = 6$) and its spectrum becomes an insulating one. By order of magnitude, the potential of ionicity is close to the difference between the ionization potentials of the atoms of the metal and chalcogene.

In order to determine the spectrum of the praphase, it is convenient to employ the tight binding approximation by making allowance for the overlap integral taken between the nearest neighboring atoms only. Then, because of the symmetry, this integral will be nonzero only for like atomic p-orbitals, and the spectrum of the praphase will consist of three one-dimensional branches. Each of these will be only half-filled, in which case the Fermi surface of the praphase takes on the appearance of a three-dimensional cross. The symmetry-unrelated degeneracy of the one-dimensional spectrum of the praphase is removed by its interaction with deep s-orbitals and by the intraatomic spin – orbit coupling. This gives rise to a complex Fermi surface consisting of three parts. A nearly-cube-shaped hole surface resides in the center of the praphase's Brillouin zone, whereas at the vertices there are electronic pockets whose total volume is equal to that of the hole surface. In addition, there is also an open Fermi surface. The three surfaces never intersect. As a result of the introduction of ionicity, the whole of the Fermi surface is covered by the gap, giving rise to a real spectrum of semiconducting IV – VI compounds. The above picture of the genesis of the electronic spectrum of IV – VI semiconductors explains, by the way, why it is near the L-points of the Brillouin zone of an FCC lattice that the gap in a IV – VI spectrum is the narrowest. The reason is simply that all Fermi surfaces of the praphase come closest there to one another.

In concluding this section it should be noted that the spectrum of the praphase is not the only point of similarity between the group V semimetals and IV – VI semiconductors. Another is that in some IV – VI semiconductors (GeTe, SnTe) one observes structural transformations from the cubic phase to the rhombohedral (ferroelectric) phase completely similar to the bismuth structure. This occurs when the potential of ionicity is sufficiently small to prevent the deformation of the lattice along the trigonal axis.

2. Dielectric and magnetic properties of IV – VI semiconductors

It is well known that semiconducting IV – VI compounds possess anomalously large values of both the high-frequency (ε_∞) and static (ε_0) dielectric constants. By ε_∞ here is meant the dielectric constant at frequencies higher than all phonon frequencies but much lower than the average ionicity gap. The presence of the narrow gap between the L-points can be ignored because the phase volume corresponding to them is small, whereas that corresponding to transitions across the average ionicity gap is equal to the volume of the Brillouin zone itself. The calculations in Ref. [7] were performed including the local field effects and the exchange correction to vertices.

The essential point is that, as tight binding calculations of IV – VI spectra reveal, the wave functions near the upper and lower edges of the average ionicity gap are of opposite symmetry. States near the upper edge are formed from the atomic functions of the metal and therefore are odd, whereas those near the lower edge are constructed from the atomic functions of the chalcogene, i.e., they are even. The calculations showed that in the cubic phase corrections for the local field are absent, whereas in the rhombohedral phase they are nonzero and proportional to the square of the parameter of rhombohedrality, leading to a drop in the value of ε_∞ with a kink at the phase transition point.

In Ref. [8], the static dielectric constant and effective charge Z^* were calculated. The basic idea was first to determine the polarization of the crystal at fixed displacements of the metal and chalcogene sublattices by taking into account changes in the electron wave functions, and then to use the polarization for finding the static dielectric constant and the effective charge Z^*. It turned out that the effective charge grows as the degree of ionicity decreases. This

[1] The results of my work with the colleagues, both theoreticians and experimenters, can be found in reviews [1 – 5] where they are discussed in detail, and in a number of separate original papers on the dielectric and magnetic properties of IV – VI semiconductors [6 – 10].

phenomenon is due to the increase in the arm of the dipole that arises in the electron system of the crystal, when the crystal sublattices become displaced. It is shown that for $Z^* \geqslant 8$ the crystal is rendered structurally unstable towards the transition to the rhombohedral phase.

The investigation into the magnetic properties of IV – VI semiconductors has shown that all of them are diamagnetic and that their diamagnetism is comparable to that of bismuth. In Ref. [9], the magnetic susceptibility of IV – VI semiconductors was calculated using the gauge-invariant linear response theory without invoking the concept of Landau levels. It turned out that the main diamagnetic contribution forms in the vicinity of the narrow gap at L-points and is due only to interband transitions. This contribution displays a logarithmic divergence as the width of the narrow gap tends to zero. The presence of free carriers leads to a weakening of diamagnetism because it cuts off the logarithmic divergence at the Fermi level of these carriers, as measured from the edges of the narrow band at the L-point. The temperature dependence of this susceptibility was also determined.

3. Spectra and electrical activity of point defects in IV – VI semiconductors

The tight-binding model of the electronic spectrum of IV – VI semiconductors makes it possible to easily find the electronic spectrum and charge states of site point defects in these compounds. This is true, in particular, of metal and chalcogene vacancies. The main idea of the method is to modify the Hamiltonian of the perfect crystal at a given lattice site by first adding the potential of the defect and then subtracting the potential of the main atom that occupied the site before. For a vacancy this means that we simply subtract the potential of the atom which resided there before, thus creating a repulsion potential at the site. Another simplification of the problem derives from the fact that this potential is a short-range one and thus contains the entire set of Fourier components — i.e., covers the entire Brillouin zone. But then, as was the case with calculating the electronic dielectric constant, we can neglect the narrow gap near the L-point (because the corresponding phase volume is small) and go over to a quasi-one-dimensional Hamiltonian with an average ionicity gap. The only thing to remember is that if a local level of the defect falls into the allowed spectral region near the L-points, the level becomes a resonance one.

It is now an easy matter to determine the position of the vacancy levels if we recall the above discussion about the symmetry of the states at the bottom and of those at the top of the average ionicity gap — the fact, namely, that the latter are built from the atomic orbitals of the metal, and the former from those of the chalcogene. Therefore, the appearance of a metal vacancy cannot split out a level from the top of the filled band into the ionicity gap, whereas a chalcogene vacancy splits out three such levels (ignoring spin). It is this fact that explains the electrical activity of the vacancies. Because during the formation of a metal vacancy the metal atom takes with itself two p-electrons when leaving the system, and because the number of filled states remains unchanged, two holes appear in the system. Hence, the metal vacancy turns out to be a doubly charged acceptor. For a chalcogene vacancy, the situation is different. A chalcogene atom leaves the system in company with four p-electrons, but (taking into account spin) there are six levels which split out from the filled states. As a result, two orphaned electrons remain in the system, which are forced to occupy states in the previously empty bands. This makes the chalcogene vacancy a doubly charged donor.

4. Properties of group III impurities (Ga, In, Te) in IV – VI semiconductors

The site impurities of group III elements demonstrate even more original behavior in semiconducting IV – VI compounds. Depending on the position of the Fermi level in the semiconductor crystal, these impurities can exhibit either donor or acceptor properties. If the Fermi level lies low enough, then they are donors, if high, acceptors. The p-states of group III elements are now not enough to explain this phenomenon: their s-states should also be considered. In an isolated atomic configuration, group III elements always have two electrons in the s-shell, and one in the p-shell. But it has long been known from chemistry that when in a compound, group III elements can be not only monovalent but bi- or trivalent as well. For example, there exist three compounds of indium: InCl, $InCl_2$, and $InCl_3$, of which the $InCl_2$ compound is unstable towards the decay into monovalent ICl and trivalent $InCl_3$. This behavior can be explained qualitatively as follows. In the monovalent state, the s-shell is completely filled and does not participate in the chemical bonding. In bi- and trivalent states, this shell must be depaired, that is to say, one or two electrons should make a transition into p-like states. But if only one electron leaves the s-shell and participate in chemical bonding, then the remaining electron will turn out to be unpaired (possibly, will exhibit paramagnetic behavior) — which is, in principle, unfavorable from the binding energy viewpoint. Therefore, all three electrons must participate in the formation of chemical bonds.

In order to extend these arguments to the case of indium impurity in IV – VI semiconductors — where indium atoms occupy metal sites — consideration must be given to the possibility for electrons to make transitions from the indium filled s-shell to band p-states. This process is favorable from the point of view of the total crystal energy if the Fermi energy of the band electrons is sufficiently small; note that because the density of states at the Fermi level is always sufficient, both of s-electrons must go to the Fermi level simultaneously. Thus, at 'low-lying' Fermi levels the indium impurity supplies the p-bands with three electrons at once, as compared to only two supplied by the metal. In other words, indium will behave in this case as a singly charged donor.

But all good things end. As the number of such donors increases, the Fermi level is also elevated, making it unfavorable for the impurity to make the transition to the trivalent state. Some of the electrons must remain in the s-shell of the impurity, and in such a configuration there will be only one p-electron in the bands, whereas the metal always supplied two p-electrons to the bands. Thus, when a certain critical value of the Fermi energy is reached, indium will exhibit the properties of a singly charged acceptor. This phenomenon leads to the stabilization (pinning) of the Fermi level as the concentration of the indium impurity is increased. Another important point to note is that an actual donor – acceptor transition must necessarily occur through an intermediate state, because there are no fields in nature which enable two-electron transitions to be made directly. Such an intermediate state is a bivalent state of indium impurity, which can occur only as an excited state. For this reason, a 'potential' barrier appears in the system, leading to the long-time relaxation of nonequilibrium carriers at sufficiently low temperatures.

5. Spectra of inverse heterojunctions between IV – VI semiconductors of different chemical composition

A few words now about so-called inverse junctions. Experiment and band calculations show that as the chemical composition is changed or under pressure, the inversion of band terms may occur in the vicinity of the narrow gap near the L-points. This comes about when the band gap passes through zero at L-points, having the effect that the electronic terms near the tops and bottoms of the bands reverse symmetry (namely, the even states become odd at the bottom of the conduction band, and vice versa). If two such semiconductors of opposite parity are brought together to form a junction, it can be shown that independent of whether the junction is smooth or sharp, bound electron states appear at the interface. The only requirement is that the work function values on the right and on the left of the junction be less than the gap widths involved. Mathematically, this phenomenon is due to the supersymmetry of the problem and manifests itself in the appearance of the zero mode. The spectrum of the bound states is nondegenerate with respect to 'spin' in the plane of the junction and is similar to that of the Weyl equation for neutrino.

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New semiconductor laser designs and the exploratory investigation of the terahertz frequency range

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Owing to advances in quantum and classical electronics and radio engineering, the efficient generation of coherent electromagnetic radiation has been realized in a wide frequency range — from petahertz (ultraviolet) to kilohertz (myriametric waves). The progress towards the hard ultraviolet and soft X-ray ranges (above 10^{16} Hz) is moderated by the short radiative lifetime of excited states participating in allowed transitions in atomic systems, which is inversely proportional to the cube of the transition frequency and falls into the pico- or femtosecond ranges. In this case, the excessive requisite pump power or the necessity of employing inefficient forbidden transitions turns out to be the inevitable limiting factor.

Such limitations are of no fundamental importance in the terahertz range, which corresponds to transition frequencies $\omega/2\pi$ ranging from 0.5 – 1 THz to 10 – 20 THz, i.e., to emission wavelengths λ from 600 – 300 μm to 30 – 15 μm. Nevertheless, it is precisely this range, being at the interface between microwave electronics and laser physics, that is mastered with great difficulty [1 – 4]. For various reasons, the techniques of vacuum and classical solid-state electronics, as well as the conventional schemes of quantum electronics, do not work well here. (In the former case, submillimeter travelling wave tubes (TWTs) and backward wave tubes (BWTs) [3] encounter the problems of low cathode efficiency, complications in e-beam matching with a slow-wave structure, and large losses in vacuum waveguides, while resorting to plasma instabilities in the ballistic transport in semiconductors requires the presently unattainable quality of submicrometer field-effect transistors [5]. In the latter case, molecular (beam) masers necessitate intense cooling and hardly realizable high-quality microresonators, while the inversion on rotational transitions in gas-discharge lasers, sufficient for lasing, is attained only for a limited number of lines [4].) Endeavors to excite terahertz oscillations in a cold plasma, including semiconductor plasmas, or in dipole photoconductor antennas by employing ultrashort (femtosecond) optical pulses are hampered by too low an efficiency ($< 10^{-4}$) of the corresponding 'optical rectification' [6 – 8]. By and large the available sources of coherent terahertz radiation are low-power (from nano- to microwatts, sometimes ranging into the watts), poorly tunable, and actually cover only narrow frequency bands. (Of course, we are not dealing with unique and expensive facilities and instruments relying, for instance, on synchrotrons and free-electron lasers [9] or powerful lasers with parametric mixers based on nonlinear optical crystals, including semiconductor crystals [10, 11].)

This situation is highly unfavorable for a broad range of potential applications of terahertz radiation, including radars, satellite and ground-based communication, security and guidance systems, three-dimensional tomography, diagnostics (biochemical and medical), molecular and solid-state spectroscopy, etc. [1 – 3]. In this connection strong hopes are pinned on semiconductor sources which have proven to be advantageous in the visible and near-infrared (IR) ranges and have recently come under the scrutiny of researchers as sources in the terahertz and far-IR ranges as well. Our work is concerned with precisely this direction of semiconductor laser physics, which potentially leads to the fabrication of compact, monolithic, efficient, and inexpensive laser sources ranging from ten to hundreds of micrometers in wavelength.

Conventional diode heterojunction lasers utilizing interband transitions in narrow-gap semiconductors based, for instance, on lead salts of the Pb(S, Se) or $Pb_{1-x}Sn_xTe(Se)$ type prove to be inefficient and unable to work in the far-IR range for $\lambda > 30$ μm. The achievement of the population inversion in them even in the middle-IR range is associated with cooling down to helium (4 K) or nitrogen (77 K) temperatures and a high threshold current density ranging, respectively, from a fraction of to tens of kiloamperes per square centimeter. Their stability, reliability, and output power (milliwatts) leaves much to be desired [12]. Here, lasers utilizing interband