Properties of electron-impurity system in semiconductors with different types of troughs

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The possibility of formation of an electronic crystal in semiconductors is discussed.

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The conduction band in a number of semiconductors contains troughs of different types. This pertains, above all, to the A_3B_5 semiconductors and their alloys [see, for example, Refs. 1–4 (GaSb), Ref. 5 (GaAs), Ref. 6 (InP) and Ref. 7 (Ge)]. We are interested in the placement of troughs shown in the figure below (solid line) which is characteristic for the A_3B_5 compounds. The following is significant: (1) the effective mass of the central trough m_1 is considerably smaller than the effective mass of the lateral trough m_2; (2) the energy gap Δ decreases under pressure[1–7] (and in the case of

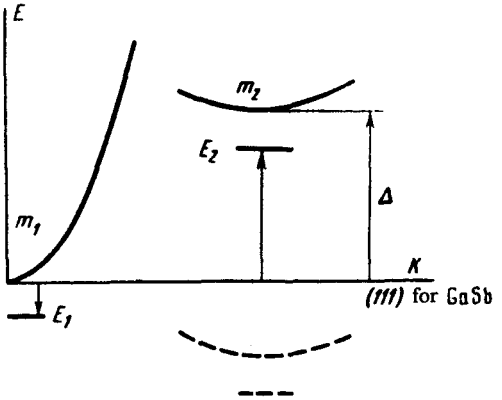

FIG. 1.

uniaxial compression) such that an inversion of the energy spectrum occurs at certain pressures (dotted line in Fig. 1).

The electron-impurity system of such semiconductors may undergo a number of phase transformations as the pressure is varied. At given donor concentrations and sufficiently-low temperatures certain of these phases will be characterized by spatial periodicity (3-*D* lattice). We shall demonstrate this.

As is known, in addition to a hydrogen-like level E_1 that is associated with the central trough, a single donor also exhibits a resonance E_2 level associated with a secondary trough; the E_2 level becomes primary when the spectrum is inverted. We shall first consider small concentrations $n_D \ll 1$ (as a unit length we shall consider the effective Bohr radius $\hbar^2\epsilon/m_1e^2$, and energy—the effective Rydberg $\mathrm{Ry} = m_1e^4/2\hbar^2\epsilon^2$). In this case we have a unique transition—if we may call it that—which occurs at $E_1 = E_2$ (zero temperature $T = 0$ is implied); moreover, the impurity electron wave function changes.

Let us now consider high concentrations $n_D \gg 1$ which, however, are sufficiently small such that the E_2 levels retain their individuality (i.e., in the inverted case the donors are non-overlapping). This is in principle possible for a relatively large ratio m_2/m_1. We shall begin with the case $E_2 < E_1$. At first, all the electrons are at the E_2 level ($T = 0$). The E_1 levels become filled when $E_1 - E_2$ is comparable to the binding energy of a hydrogen molecule, i.e., at $E_1 - E_2 \approx 1/3$. Actually, due to $n_D \gg 1$ a separate "hydrogen atom" (donor in state E_1) may shift practically continuously, and two such atoms may converge to an optimal distance—equal to 1.4—to form a molecule. In addition to this, a macroscopic number of these molecules occur at once to form a molecular crystal (as a result of this the threshold value of $E_1 - E_2$ is slightly higher than molecular binding energy). The density of this crystal at the transition point, i.e., the electron concentration in the central trough n, may be determined using the known density of molecular hydrogen crystal that has not been subjected to any external effects; it turns out that $n \approx 0.7 \times 10^{-2}$ (data for hydrogen were taken from Ref. 8). We should emphasize that the periodic structure in a system of disordered donors is obtained from the condition $n_D \gg 1$.

With subsequent increases in E_2 the molecular crystal density grows until such

time as the molecular crystal is converted to metal. According to calculations,[9] this occurs at $r_s \approx 1.3$ ($4\pi/3\ r_s^{\ 3} n \equiv 1$) which yields $n \approx 0.11$ (for conventional hydrogen this corresponds to pressures of approximately 3 Mbn). Finally, the periodic structure vanishes at $n \sim n_D$. Thus, at $0.11 < n \ll n_D$, a metal exists with a periodic distribution of ionized donors at suffuciently low temperatures. The melting temperature for the metallic hydrogen is $T_m = 0.016\ r_s^{-1}$.[10] The value of T_m cited in other works is two–three times higher.[11]

We should note that the melting temperature of a molecular crystal of extremely low density is negligible; therefore, the following occurs as E_2 increases at any reasonable temperature: disordered system (electrons at the E_2 level)—molecular liquid—molecular crystal-metal-amorphous metal. Evidently, the two latter transitions may be observed directly from conductivity.

Heretofore, we have considered an idealized situation. Actually, there exists, for instance, a certain dispersion of the E_2 levels which should be sufficiently small—less than Ry. This is a rigid constraint which, clearly, will be most difficult to satisfy concurrently with $n_D \gg 1$. We shall cite certain calculations for GaSb(Se). Gallium antimonide is interesting because the Δ is small ($\Delta \approx 80$ MeV [1]) and only several kilobar pressure is sufficient to invert the spectrum. The binding energy $\Delta - E_2 \approx 14$ MeV for Te[3] and 50 MeV for Se.[1] Critical Te concentrations at which the impurity levels E_2 remain relatively undispersed, are $(1\text{–}2) \times 10^{17}$ cm^{-3}.[3] The corresponding numbers for Se are unknown. We shall attempt to calculate them. Radius of the bound state is of the order $\hbar\,[m_2(\Delta - E_2)]^{-1/2}$ and, therefore, the critical Se concentrations should be $(50/14)^{3/2} = 6.75$-fold higher than those given above for Te. Thus, it may be expected that, for example, $n_D = 4$ (which for $m_1 = 0.047\ m_e$ and $\epsilon = 15.7$ corresponds to concentration 7.2×10^{17} cm^{-3}). This value (instead of $n_D \gg 1$) may be considered satisfactory. Thus, in a spherical layer, 1.4 ± 0.14 for $n_D = 4$, 28 impurities are contained on the average, such that a possibility exists for a formation of molecules with different orientations, a fact important for molecular crystals. Melting temperature $T_m \simeq 0.5$ K at $r_s = 1$ (calculation based on Ref. 10).

As regards the E_1 levels, interaction (with compensation) with donor-acceptor dipoles is the central problem. Therefore, a unique requirement that is possible here, is the smallness of compensation: not simply $n_A \ll n_D$, but $n_A \ll n$.

In GaSb(Se) there also exists a resonance E_3 that is associated with a series of higher troughs (100); at zero pressure $\Delta > E_3 > E_2$.[1] At high doping levels at which an impurity region E_2 and the Fermi level become "glued" to E_3, identical formation of an electronic crystal is possible in principle, although in this case basically in connection with a pair of E_3–E_2 levels and, therefore, with higher characteristic energies and melting temperature. However, the situation involving heavy doping remains unclear.[1]

In conclusion, we note that the subject electron-impurity system tends to imitate to a certain degree at low temperatures and moderate pressures (several kilobar in the case of GaSb) the behavior of crystalline hydrogen at high pressures (several megabar).

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