

Tunnel impurity autolocalization in semiconductors. Anomalous properties of the $\text{Pb}_{1-x}\text{Sn}_x\text{Te}$ compounds with In impurity

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It is shown that the appearance of autolocalized impurity states associated with the capture of an electron by an intrinsic impurity well as a result of deformation, leads to the appearance of subbarrier kinetics that account for the anomalous properties of the $\text{Pb}_{1-x}\text{Sn}_x\text{Te}(\text{In})$ compound.

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1. Recently two experimental groups^{1,2} discovered highly unusual kinetics in $\text{Pb}_{1-x}\text{Sn}_x\text{Te}(\text{In})$ semiconductors. If the nontrivial, nonequilibrium characteristics of these compounds are taken into account,³⁻⁵ a number of properties, which set this system sharply apart from others, can be identified. a) Introduction of In into the alloys with $x < 0.2$ produces a level $\epsilon_0(x)$ in the conduction band, which determines the Fermi energy ϵ_F , if the concentration of In exceeds that of the other defects.^{3,4} b) ϵ_0 decreases linearly with x , crosses the energy gap, and enters the valence band; the crossing of $\epsilon_c(x)$ and $\epsilon_v(x)$ with the edges of the bands is not accompanied by peculiarities in the $\epsilon_0(x)$ dependence—the level moves without sensing the band structure.⁵ c) If ϵ_F is varied in a pulsed manner by violating the condition $\epsilon_0 = \epsilon_F$, we can observe an anomalously slow flow of electrons from this level to the conduction band ($\epsilon_0 > \epsilon_F$) or vice versa ($\epsilon_0 < \epsilon_F$), which at helium temperatures can continue for hours.¹ This time decreases sharply at $T \approx 20$ K. d) In the dielectric state these compounds have a unique photosensitivity at low T —for illumination of very low intensity the resistance ρ decreases by many orders of magnitude.² As T increases ρ increases, and only at $T \approx 20$ K the activation drop of $\rho(T)$ is restored.

The ideas developed below about the tunnel impurity state of an autolocalized nature enable us to explain uniquely all these anomalous properties.

2. Let us examine a semiconductor doped with donor, substitutional impurities. As a result of departure of an electron from the impurity, a deeper “potential funnel”

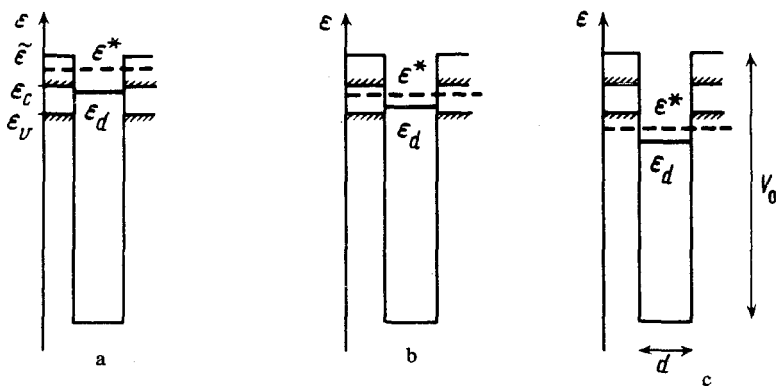


FIG. 1.

is produced in its place in the charge pattern. Because of the influence of the surrounding medium, it appears to be narrower and lower in height than the free-ion potential, because of which it does not contain a discrete level. If, however, the lattice is deformed around the impurity atom, then the broadening of the well and increase of its height will lead to the appearance of a level in it, whose depth will increase with increasing deformation. When this level ϵ_d is lower than the chemical potential μ , a localized state appears in the system. As a result of further increase of deformation, the level will cross the gap and enter the valence band. If ϵ_d decreases faster with increasing deformation than the elastic energy increases, then an impurity, autolocalized state (IAS) corresponding to the final deformation (for autolocalization in ideal crystals see review article⁶) will appear in the system. The appearance of a IAS, which is separated by a potential barrier from the state of the crystal without a deformation, gives rise to low-temperature anomalies such as those mentioned above.

3. To analyze this picture, we shall use a model description, after selecting an impurity potential in the form of a square well (Fig. 1) and assuming for definiteness that displacement of the surrounding atoms increases its diameter d . Let us assume that the strongest deformation is attributable to a symmetrical broadening of the nearest coordination sphere, which is described by one parameter u . Assuming that $\epsilon_d(u)$ varies little compared with the depth of the level in the free well, we can write approximately

$$\epsilon_d(u) \approx \tilde{\epsilon} - \frac{\pi^2}{4} V_0 \delta^2 + \frac{\pi^4}{16} V_0 \delta^3, \quad \delta = [d(u) - d_c] / d_c. \quad (1)$$

Here $\tilde{\epsilon}$ is the location of the "barrier" of the potential well (see Fig. 1) (we assume that $\tilde{\epsilon} > \mu$).

Let us examine a n -type semiconductor with the number of electrons N_e in the band. Adiabatic variation of the crystal's energy due to deformation is

$$\Delta E(u) = E(N_e, u) - E(N_e, 0), \quad (2)$$

Before the displacement $u \sim u_c$, for which $\epsilon_d \sim \mu$, ΔE is determined solely by the elastic strain

$$\Delta E(u) = \frac{1}{2} a u^2, \quad u < u_c. \quad (3)$$

At $u > u_c$

$$\Delta E(u) = E(N_e - 1, u) + \epsilon_d(u) - E(N_e, 0) \approx \epsilon_d(u) - \mu,$$

$$\epsilon(u) = \frac{1}{2} \alpha u^2 + \epsilon_d(u). \quad (4)$$

In fact, at $u \sim u_c$ Eq. (3) goes over smoothly to Eq. (4).

Assuming that the relation between the well diameter and the displacement is linear, $d = d_0 + \gamma u$, we determine from the condition $d(\Delta E)/du = 0$ the displacements $u_{1,2}$ corresponding to the maximum and the minimum of the curve $\Delta E(u)$. The barrier height $\Delta E_{\max}(u_1)$ is

$$\Delta E_{\max}(u_1) \approx \frac{\pi^2}{4} V_0 \eta \left[\delta_0 + \frac{2}{\pi} \left(\frac{\tilde{\epsilon} - \mu}{V_0} \right)^{1/2} \right]^2 \quad \eta = \hbar^2 \alpha / 4 \gamma^2 m_0 V_0^2, \\ \delta_0 = |\delta(u=0)|. \quad (5)$$

The value $\Delta E(u)$ [Eq. (4)] with $u = u_2$ determines the energy level of the IAS

$$\epsilon^* \equiv \epsilon(u_2) \approx \tilde{\epsilon} - \frac{16 V_0}{27 \pi^2} (1 - \eta)^3 + \frac{4}{3} V_0 \eta (1 - \eta) \delta_0. \quad (6)$$

The minimum on the curve $\Delta E(u)$ exists under the conditions

$$\eta < 1, (1 - \eta)^2 > \frac{3 \pi^2}{2} \eta \delta_0, \quad (1 - \eta)^2 > \frac{9 \pi^2}{16} \frac{\tilde{\epsilon} - \mu}{V_0}, \quad (7)$$

which are compatible at $\eta \ll 1$ and $\delta_0 \ll 1$. It can be seen from Eq. (6) that the relative position of ϵ^* and ϵ_c in principle is arbitrary. If $\epsilon^* > \epsilon_c$, then ϵ^* is the stabilization level of ϵ_F at $N_e < N_{\text{imp}}$, which immediately follows from the vanishing of ΔE if

$$\mu = \epsilon^* \quad (8)$$

(see curve 2 in Fig. 2a). If the equilibrium condition (8) is violated for a specified N_e , then at $\mu < \epsilon^*$ (curve 1 in Fig. 2a) the electrons will flow from the autolocalized states until μ again is equal to ϵ^* . At $\epsilon^* < \mu$ (curve 3 in Fig. 2a) we see the opposite picture.

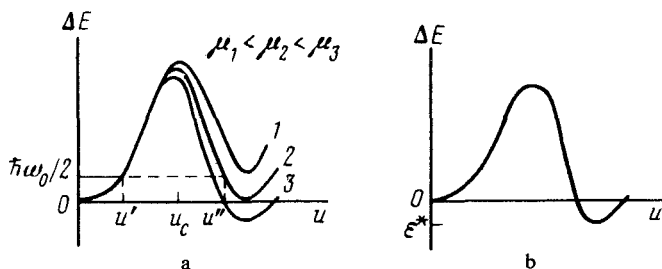


FIG. 2.

If ϵ^* enters the forbidden band (Fig. 1b), then the electrons are autolocalized with the thermal activation energy $\epsilon_c - \epsilon^*$ (dielectric state) and are separated from the band states by the potential barrier $\Delta E(u)$ [Eqs. (3) and (4)] (with the substitution $\mu \rightarrow \epsilon_c$)—see Figs. 1b and 2b. We emphasize that in all the cases the level in the well ϵ_d lies below ϵ^* (Fig. 1). At $\epsilon^* < \epsilon_v$ the valence electrons with $\epsilon_v < \epsilon < \epsilon^*$ go over to the IAS and ϵ^* stabilizes μ of the hole Fermi surface (Fig. 1c).

5. Because the IAS are separated from the band states by a potential barrier, as $T \rightarrow 0$ the kinetics of the transitions have a purely tunnel nature. To determine the probability of the subbarrier transition W , we introduce the kinetic energy operator \hat{T} which can be approximately related to the motion of only the nearest coordination sphere

$$\hat{T} = \sum_n \frac{1}{2} M u_n^2 = \frac{1}{2} Z M \dot{u}^2, \quad (9)$$

where M is the mass of the neighboring atoms and Z is the coordination number. The generalized momentum is $P_u = ZM\dot{u}$, and in the quasi-classical approximation

$$W \approx \omega_0 \exp \left\{ - \frac{2}{\hbar} \int_{u'}^{u''} (2 Z M [\Delta E(u) - \hbar \omega_0 / 2])^{1/2} du \right\} \quad (10)$$

(see Refs. 7 and 8). Here ω_0 is the frequency of the zero-point vibrations in the well corresponding to the initial state. On going from left to right (Fig. 2), it coincides with the characteristic phonon frequency. As a rule the transition time $\tau = W^{-1}$ is very large. As the temperature increases, τ begins to decrease at relatively small T , which is attributable to the shape of the barrier and to its small height (5).

The optical transitions from the IAS occur at a constant configuration of the surrounding medium with the threshold energy $\mu - \epsilon_d(u_2)$ [or $\epsilon_c - \epsilon_d(u_2)$ for the dielectric state], irrespective of the size of the potential barrier. At small T the time τ of the reverse transition to the IAS is exponentially large, and this predetermines the enormously large decrease of the resistance of the system in the dielectric state at a small light intensity. At constant illumination the fixed number of carriers and photoconductivity decrease with increasing T in proportion to decreasing τ , until this decrease is interrupted by an increase of the number of carriers due to thermal ionization of the IAS.

6. The developed ideas fully account for the anomalous properties of the $\text{Pb}_{1-x}\text{Sn}_x\text{Te(In)}$ system. The appearance of IAS in this system is not accidental. The main condition

$$\eta \approx \frac{Z}{4\gamma} \frac{M}{m_0} \left(\frac{\hbar \omega_0}{V_0} \right)^2 < 1$$

is realized here because the phonon spectrum is soft. This is facilitated by a unique softening of the modes due to a displacement-type phase transition at large x . A decrease of ϵ^* , and hence of the level at which μ is set, is evidently connected with a decrease of η as x increases. On the other hand, the enormous polarizability of Te ($\epsilon_\infty > 35$) is responsible for the increase of the effective diameter of the impurity well as the nearest coordination sphere expands.

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