

Role of hybridization in the polaron mechanism for the formation of U^- centers, soft potentials, and two-well potentials

K. D. Tséndin

A. F. Ioffe Physicotechnical Institute, 194021, St. Petersburg

(Submitted 14 April 1992)

Pis'ma Zh. Eksp. Teor. Fiz. **55**, No. 11, 635–638 (10 June 1992)

A new version of the polaron mechanism for the formation of U^- centers is discussed. This version is valid in the case of a pronounced hybridization of a localized state with band states. With hybridization, the electron–phonon coupling describes both the appearance of U^- centers and the formation of soft and two-well potentials

Many of the experimental facts which have been established on semiconductors can be explained well by assuming that these materials contain intrinsic defects with a negative effective correlation energy (U^- centers). The main distinguishing feature of U^- centers is that they are not neutral in their ground state, since the resultant energy of the charged states is lower than twice the energy of the neutral state:

$$E_0^0 + E_2^0 - 2E_1^0 \equiv U^- < 0. \tag{1}$$

The subscripts $n = 0, 1, 2$ correspond to the charge states D^+, D^0, D^- of the centers, since it is assumed that the center is neutral if there is one electron at it. The superscript specifies the equilibrium energy. Equation (1) determines the effective correlation energy U^- . Various mechanisms for the occurrence of U^- center were discussed in Refs. 1–8; in particular, a polaron mechanism has been discussed.^{4–8}

In this letter we show that hybridization plays a decisive role in the polaron mechanism for the formation of U^- centers. A second result of fundamental importance is that when hybridization is taken into account the electron-phonon interaction is itself capable of giving rise to soft and two-well potentials, whose configurations depend on the charge state of the center.

1. We consider a simple model in which the valence and conduction bands are replaced by a doubly occupied bonding orbital (Ψ_v, ϵ_v) and a vacant antibonding orbital (Ψ_c, ϵ_c). The Coulomb repulsion of the electrons (U) is considered only at the localized electron level of the center (Ψ_d, ϵ_d). The electron part of the Hamiltonian of the model is then the Anderson Hamiltonian⁹

$$H = \sum_{\substack{\sigma \\ i=v,c}} [\epsilon_i a_{i\sigma}^\dagger a_{i\sigma} + (V_i a_{i\sigma}^\dagger a_{d\sigma} + \text{c.c.})] + \sum_{\sigma' \neq \sigma} \left[\epsilon_d a_{d\sigma}^\dagger a_{d\sigma} + \frac{U}{2} a_{d\sigma}^\dagger a_{d\sigma} a_{d\sigma'}^\dagger a_{d\sigma'} \right], \tag{2}$$

where σ is the spin, and $V_{v,c}$ are parameters of the hybridization of the band states Ψ_v and Ψ_c with the localized state Ψ_d .

We write the phonon component of the total energy of the center in classical form:

$$H_{ph} = \frac{KX^2}{2}, \quad (3)$$

where K is a hardness coefficient, and X is a configuration coordinate.

We denote by $\Psi_{v,c,d}$ the eigenfunctions (wave functions) of Hamiltonian (2) for the case $n=0$, $X=0$. For $X \neq 0$ we expand (2), finding in the first approximation

$$\epsilon_d = \epsilon_0 - \langle d | (\partial H / \partial X)_{X=0} | d \rangle X \equiv \epsilon_0 - QX,$$

$$V_{v,c} = \langle d | (\partial H / \partial X)_{X=0} | v, c \rangle X \equiv \bar{v}_{v,c} X. \quad (4)$$

All energies are expressed in units of the band gap: $E_g = \epsilon_c - \epsilon_v = 1$, $\epsilon_c = 0$, $\epsilon_v = -1$. We ignore the diagonal polaron shift of the states $\epsilon_{v,c}$. We have solved the problem formulated by Eqs. (1)–(4) exactly in the adiabatic approximation. For this purpose, a complete set of many-electron wave functions was constructed from the functions $\Psi_{v,c,d}$. This set included 15, 18, and 15 wave functions for the charge states D^+ ($n=0$), D^0 ($n=1$) and D^- ($n=2$), respectively. For each X , the matrices $D^{0,\pm}$ were then diagonalized numerically. The minimum energy was found. Phonon energy (3) was added to it, and a term with a total energy $E_n(X)$ was constructed. The E_n^0 values corresponding to the minima of the terms $E_n(X)$ were then used to calculate U^- from Eq. (1). The results of this calculation are shown in Fig. 1, where $q = Q^2 / KE_g$ and $v = v_{v,c} = \bar{v}_{v,c} Q / KE_g$; X is expressed in units of Q/K . The increase in $|U^-|$ before the minimum stems from the hybridization of the ϵ_d and ϵ_c levels, which—

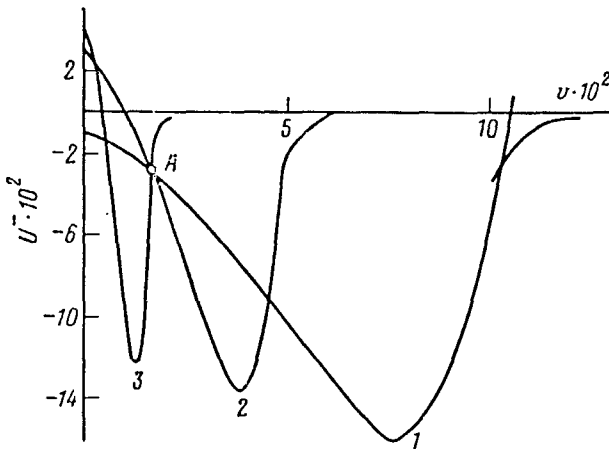


FIG. 1. U^- versus v . $\epsilon_0 = -0.02$, $U = 0.04$. 1–3— $q = 0.05$, 0.01 , and 0.001 , respectively.

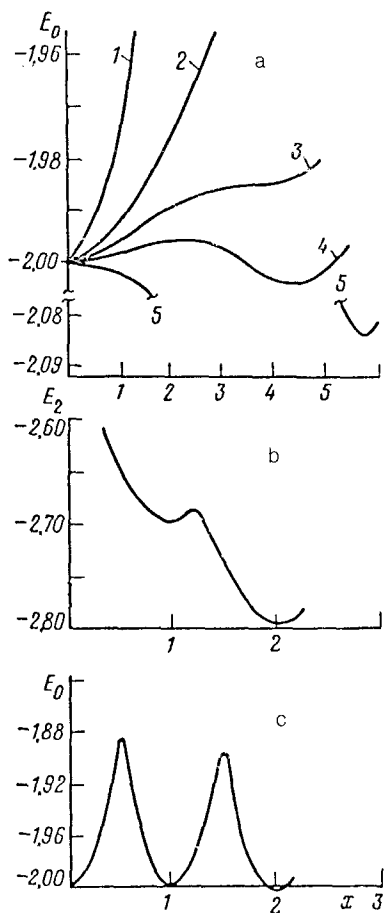


FIG. 2. Profiles of the terms $E_n(x)$ along the coordinate. a: $n=0$, $\epsilon_0 = -0.02$, $U=0.04$, $q=0.05$. 1-5— $v=0, 0.09, 0.1, 0.103$, and 0.11 , respectively. b: $n=2$, $\epsilon_0 = -0.5$, $U=1.0$, $q=0.4$, $v=0.005$. c: $n=0$, $\epsilon_0 = -0.5$, $U=1.0$, $q=1.0$, $v=0.01$.

because of the repulsion of these levels—increases the polaron shift of level ϵ_d , and thus $|U^-|$, by a factor of $\sim B^2 = (1 + \sqrt{1 + v^2/q^2})^2/4$. The hybridization of the levels ϵ_d and ϵ_v prevents a polaron shift of ϵ_d and reduces $|U^-|$ after the minimum. The retardation of the polaron shift was examined for some more-complex models in Refs. 7 and 10. As $v \rightarrow \infty$, $U^- \rightarrow 0$, since the relative weight of the Ψ_d state in the wave function of the localized state decreases.

2. Figure 2 shows results calculated on the term $E_0(X)$ for the same values of ϵ_0 , U , and q as in Fig. 1. We see that incorporating hybridization makes it possible to explain the appearance of intrinsic defects of the soft- and two-well-potential types in a natural way. In this case, these defects are associated with a competition between diagonal ($\propto qx$) and nondiagonal ($\propto vx$) contributions to the polaron shift.

A second reason for the appearance of two-well potentials (or, more generally, multiwell potentials) is the joint operation of Coulomb repulsion at the ϵ_d level and hybridization. For example, when ϵ_d lies below ϵ_c and is not far from it, so that the upper Hubbard level is above ϵ_c , the term $E_2(X)$ is similar to the term $E_1(X)$ (the minimum on the left in Fig. 2b), since the second electron is in the ϵ_c level, not in the upper Hubbard level. As X increases, the upper Hubbard level then crosses ϵ_c , and the term $E_2(X)$ (the minimum on the right in Fig. 2b) is no longer similar to the term $E_1(X)$. The hybridization mixes the terms and can put their minima at about the same depth, as is demonstrated in Fig. 2c for the case of a three-well potential.

3. Incorporating hybridization radically changes the relationship between the value of U^- and the softness of the potential which was found in Refs. 6 and 7 for $v = 0$. Thus $|U^-|$ increases to the left of the minimum in Fig. 1, while the potential undergoes essentially no softening. To the right of the minimum, in contrast, the potentials become progressively softer as q increases (Fig. 2a), but $|U^-|$ decreases instead of increasing.

Two approaches take us to the same value of U^- (point A in Fig. 1). First, we can assume that q is large (curve 1), so that incorporating v does no more than increase $|U^-|$ slightly, leaving the result fundamentally the same as in Refs. 6 and 7. Second, we can assume that q is small (curves 2 and 3), so that U^- would be positive if we ignored hybridization. We see that in this case the incorporation of v makes U^- negative and comparable in absolute value to the value of U^- found by the first approach. It was suggested in Refs. 4–8 that the anomalous large polaron shift $W \sim |U^-|/2 \sim 1$ eV (typical values are ~ 0.1 eV) in glassy chalcogenide semiconductors stems from a local softness of the potential, $W \sim q/2$ at $U, v \sim 0$. In our case ($v > q$), on the other hand, the polaron shift is anomalously large: $W \sim qB^2/2$ (see, for example, point A and curves 1 and 2), even for $K \sim K_0$. Incorporating hybridization thus makes it possible to describe the anomalously large values of W in regions with an intermediate lattice hardness, in which the energy scale has increased by a factor $\sim B^2$ because of hybridization. The shift of the equilibrium positions of the terms at $v = 0$ for $Q \sim 3$ eV/Å, $K \sim 0.1K_0 \sim 3$ eV/Å² is^{7,8} $\Delta X \sim Q/K \sim 1$ Å. In contrast with such large shifts—on the order of the bond length itself—in our case ($v \neq 0$) we have $\Delta X \sim BQ/K_0$. This value is about an order of magnitude smaller (at comparable values of U^-), since the increase in the energy scales is proportional to B^2 , while the length scales vary linearly with B . An important point is that the length scale Q/K_0 contains average hardness coefficient of the lattice rather than $K \ll K_0$. The scale of the displacements found when v is taken into account agrees with the scale of the lattice distortions due to the Jahn–Teller effect, since, when ϵ_d is equal to $\epsilon_{v,c}$ or approximately so, this model describes the Jahn–Teller effect or the pseudo-Jahn–Teller effect, respectively, as special cases.¹¹

The formation of U^- centers in glassy chalcogenide semiconductors was attributed in Refs. 2 and 3 to the existence of electrons of unshared pairs, and a large W was postulated. In Refs. 4–8, U^- centers and a large W were described from a common standpoint, under the assumption that an electron–phonon coupling and soft potentials exist independently.

The results of the present study show that in the case $v \sim q$ the last two sugges-

tions are not independent and that the electron-phonon coupling, with hybridization, describes both the appearance of U^- centers and the existence of soft and two-well potentials.

A spectrum of U^- centers found for a doped chalcogenide glass in Ref. 12 consisted of a peak near the ϵ_a acceptor level. A spectrum of this shape can be explained in terms of a hybridization of the states of U^- centers and the acceptor state ϵ_a . Because of repulsion, this hybridization reduces the density of states of U^- centers above the ϵ_a level (displacing them upward) and also below it (displacing them downward). The mechanism discussed here for the formation of soft and two-well potentials with a configuration which depends on the charge state may also be pertinent to several photoinduced effects—absorption, anisotropy and bistability—which have been seen experimentally in glassy chalcogenide semiconductors.^{13,14} At $v \sim q$, these effects may be linked with small atomic displacements, $\sim BQ/K_0$.

I wish to thank B. L. Gel'mont for useful advice and V. A. Khartsiev, L. D. Tséndin, and V. Kh. Shnunt for useful discussions.

¹For $\epsilon_0 \leq 0$.

¹P. W. Anderson, Phys. Rev. Lett. **34**, 953 (1975).

²R. A. Street and N. F. Mott, Phys. Rev. Lett. **35**, 1293 (1975).

³M. Kastner, D. Adler, and H. Fritzsche, Phys. Rev. Lett. **37**, 1504 (1976).

⁴M. I. Klinger, in *Problems of Modern Physics*, Nauka, Moscow, 1980, p. 293.

⁵M. I. Klinger and V. G. Karpov, Pis'ma Zh. Tekh. Fiz. **6**, 1473 (1980) [Sov. Tech. Phys. Lett. **6**, 634 (1980)].

⁶M. I. Klinger and V. G. Karpov, Zh. Eksp. Teor. Fiz. **82**, 1687 (1982) [Sov. Phys. JETP **55**, 976 (1982)].

⁷V. G. Karpov, Zh. Eksp. Teor. Fiz. **85**, 1017 (1983) [Sov. Phys. JETP **58**, 592 (1983)].

⁸S. D. Baranovskii and V. G. Karpov, Fiz. Tekh. Poluprovodn. **21**, 3 (1987) [Sov. Phys. Semicond. **21**, 1 (1987)].

⁹F. D. Haldane and P. W. Anderson, Phys. Rev. B **13**, 2553 (1976).

¹⁰M. I. Klinger and S. N. Taraskin, in *Proceedings of the Second All-Union Conference on the Physics of Glassy Solids*, Riga-Lielupe, 1991, p. 25.

¹¹A. M. Stoneham and M. Lamhoo, J. Phys. Chem. Solids **30**, 1769 (1969).

¹²K. D. Tséndin, Fiz. Tekh. Poluprovodn. **25**, 617 (1991) [Sov. Phys. Semicond. **25**, 374 (1991)].

¹³V. M. Lyubin and V. K. Tikhomirov, J. Non-Cryst. Solids **114**, 133 (1989).

¹⁴V. M. Lyubin and V. K. Tikhomirov, Pis'ma Zh. Eksp. Teor. Fiz. **55**(1), 25 (1992) [JETP Lett. **55**, 23 (1992)].

Translated by D. Parsons