

The role of conduction band states in forming of electron negative-*U* centers

M. I. Klinger

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

S. N. Taraskin

Moscow Engineering Physics Institute, 115409 Moscow, Russia

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Strong electron self-trapping of a bare state with energy located within the conduction band is investigated. Interaction of the “self-trapping” state with both conduction and valence band states are taken into account. These interactions are shown to give rise to variations of the self-trapping level occupation and can result in double-well and even triple-well adiabatic potentials of the system in question. The dependence of the correlation energy on the “rigidity” of the atomic configuration is found to be nonmonotonic, resulting in a minimum of the correlation energy of the gap width.

1. Introduction. A theory of strong electron (electron pair) self-trapping at soft atomic configurations characteristic of glasses has recently been developed.^{1,2} According to this theory, a strong self-trapping occurs when a bare state, which is located in the mobility gap close to the “parent” band mobility edge,³ rather strongly localized at a soft configuration, is occupied by an electron (hole) or a singlet electron (hole) pair. The electron state is called a “bare” state if the electron-lattice and the interaction of this state with the “parent” and “nonparent” band states are ignored. For definiteness, self-trapping of electrons is explicitly analyzed. In this case, the conduction and valence bands are the parent and nonparent bands, respectively, while the situation for holes is quite similar. The strong self-trapping in question is due to strong interaction of electrons exclusively with the soft local atomic configurations. The self-trapping electron generally interacts with the parent and nonparent band, mainly with the extended states (the “interstate” interactions).² In what follows, a “self-trapping” electron state, by definition, is an electron state under self-trapping, where the interstate interactions are ignored, while a true (renormalized) electron gap state takes into account the electron-soft configuration and the interstate interactions.

In this paper we analyze the strong self-trapping, where the electron energy level of the bare-site state (localized on a soft configuration) lies within the conduction band or in its nearest tail (below the mobility edge) which consists of macroscopically localized states. Interaction of the bare-site state with extended states of the conduction band gives rise to the spreading out of the bare state, i.e., to the dispersion of the site's wave packet. Therefore, self-trapping of this state on a soft configuration of interatomic separation scale seems, at first glance, to be weak, in contrast with the strong self-trapping of a bare state which is strongly localized in the mobility gap. On the other hand, realization of strong self-trapping does not seem to depend on whether

the bare-site level lies above or below the mobility edge, or at least close to it. Therefore, the problem considered below is whether strong self-trapping in a soft configuration can be realized even when the bare-site state lies in the energy range corresponding to large-size or extended stationary states.

The answer is that strong self-trapping can be realized, even if the bare-state level $\tilde{E}_{d\sigma}^{(0)}$ lies within the conduction (parent) band at a strong enough electron–lattice coupling. The key parameter here is the value of the standard single-particle self-trapping energy, W , which characterizes the electron–lattice coupling in a soft configuration. The reason is as follows. Let the bare state lie within the energy range of the extended band states. The energy level of the “self-trapping” state, $E_{d\sigma}^{(0)}(z)$, which is strongly coupled with the soft atomic configuration, can move through the conduction band at atomic coordinate variations, so in the standard linear approximation

$$E_{d\sigma}^{(0)}(z) = \tilde{E}_{d\sigma}^{(0)} - Qx = \tilde{E}_{d\sigma}^{(0)} - 2Wz. \quad (1)$$

Here $W = Q^2/2k$, the soft-configuration low spring constants are $k \leq 3 \text{ eV}/\text{\AA}^2$ ($\leq 0.1 k_0$, with the standard spring-constant scale $k_0 \sim 30 \text{ eV}/\text{\AA}^2$), and the essential mode coordinate is x , or dimensionless $z = kx/Q$; the typical electron–atom coupling parameter is $Q \sim 3 \text{ eV}$. The subsequent analysis takes into account the difference between $\tilde{E}_{d\sigma}^{(0)}$ and $E_{d\sigma}^{(0)}(z)$. If $z \leq z^* = (\tilde{E}_{d\sigma}^{(0)} - E_g)/2W$, i.e., if the level $E_{d\sigma}^{(0)}(z)$ lies within the conduction band, the interstate (intraband) interactions strongly disperse the wave packet related to the bare state, so that self-trapping is greatly suppressed. However, at $z \geq z^*$ the level $E_{d\sigma}^{(0)}(z)$ leaves the band of extended states and the wave function related to the true state becomes generally localized. This means that self-trapping increases with increasing z resulting in the energy gain of the system. As usual, the increase in the elastic energy competes with the decrease in the electron level in the self-trapping. This competition can lead to the appearance of an extra minimum of the adiabatic potential of the system. This extra minimum at $z > 0$ is a signature of the self-trapping state. Moreover, at the appropriate values of W this extra minimum corresponds to the lowest energy state of the system.

The problem in question is analyzed by the Green’s function method for Haldane-Anderson-like Hamiltonian,⁴ using the mean-field approximation for Hubbard repulsion at localized states. We derived the analytic expressions for adiabatic potentials of the system at different initial occupations of the localized state and calculated the correlation energy of the self-trapped state¹ as a function of the bare level energy position and standard single-particle self-trapping energy (or atomic spring constant). The self-trapping is shown to be efficient only at large enough standard self-trapping energies and at an intermediate position of the bare level with respect to the bottom of the conduction band.

2. The model. We consider a two-band system consisting of the valence $|v_{i\sigma}\rangle$ and conduction $|c_{i\sigma}\rangle$ band states and a bare state $|d\rangle$ localized at a soft atomic configuration. The $|d\rangle$ state is assumed to be coupled with a soft atomic configuration and to interact with the band states. The total Hamiltonian of the system can then be written in the form

$$\hat{H} = Wz^2 + \sum_{i,\sigma}^{N_v} \varepsilon_{i\sigma} v_{i\sigma}^+ v_{i\sigma} + \sum_{i,\sigma}^{N_c} \varepsilon_{i\sigma} c_{i\sigma}^+ c_{i\sigma} + \sum_{\sigma} E_{d\sigma}^{(0)}(z) d_{\sigma}^+ d_{\sigma} + \frac{1}{2} U_c \sum_{\sigma \neq \sigma'} d_{\sigma}^+ d_{\sigma} d_{\sigma'}^+ d_{\sigma'} + \sum_{i,\sigma}^{N_v} (V_{i\sigma}^v v_{i\sigma}^+ d_{\sigma} + \text{h.c.}) + \sum_{i,\sigma}^{N_c} (V_{i\sigma}^c c_{i\sigma}^+ d_{\sigma} + \text{h.c.}) \quad (2)$$

The first term in Eq. (2) describes an elastic atomic energy and the next two terms are the bare ($V=0$ and $Q=0$) band energies. The Hubbard repulsion at the $|d\rangle$ state is characterized by the energy U_c (≤ 0.3 eV; Ref. 1). The last two terms are related to the interband ($\sim V_{i\sigma}^v$) and the intraband ($\sim V_{i\sigma}^c$) interactions ($|V_{i\sigma}^v| \sim |V_{i\sigma}^c| \sim |V_1|/\sqrt{N}$; $N_v \sim N_c \sim N$, $|V_1| \sim 1$ eV; Ref. 5).

The band energy spectrum is approximated, as in Ref. 4, by rectangular distributions: $\rho_{v\sigma}(\varepsilon) = N_v/\Delta E_v$ at $-\Delta E_v < \varepsilon < 0$ and $\rho_{c\sigma}(\varepsilon) = N_c/\Delta E_c$ at $E_g < \varepsilon < E_g + \Delta E_c$, where ΔE_v , ΔE_c , and E_g are the band and the gap widths ($\Delta E_v \sim \Delta E_c \sim 10$ eV, $E_g \sim 1$ eV), respectively. The bare energy level $\tilde{E}_{d\sigma}^{(0)}$ is assumed to be located in the conduction band $E_g < \tilde{E}_{d\sigma}^{(0)} < E_g + \Delta E_c$.

To study the self-trapping of the $|d\rangle$ state, we must determine the adiabatic potential $\Phi_n(z)$ of the system with totally filled valence band and various initial (before spreading due to the interaction) occupations of the $|d\rangle$ state ($n=0,1,2$) at zero temperature. We solved the problem and found $\Phi_n(z)$ in the mean-field approximation (detailed calculations will be presented in another paper; see also Ref. 2):

$$\Phi_n(x) = Wz^2 - \frac{1}{\pi} \sum_{\sigma} \int_{-\Delta E_v}^0 \left[\frac{\pi}{2} + \arctan \frac{\omega - E_{d\sigma}^{\text{eff}}(z) - \Sigma_2(\omega)}{\pi \Delta_v} \right] \times d\omega + \sum_{\text{occupied}} D_{d\sigma} - U_c \langle \tilde{n}_{\sigma+} \rangle \langle \tilde{n}_{\sigma-} \rangle. \quad (3)$$

Here the second term describes the repulsion of the valence band states from the state $|d\rangle$, and the third term is the true energy of the self-trapping state which can be calculated from the equation

$$E_{d\sigma} - E_{d\sigma}^{\text{eff}} = \Sigma_3(E_{d\sigma}). \quad (4)$$

The effective energies $E_{d\sigma}^{\text{eff}}$ can be found in a self-consistent way from the following set of equations:

$$\begin{cases} E_{d\sigma+}^{\text{eff}} = E_d^{(0)}(z) + U_c \langle \hat{n}_{d\sigma-} \rangle; \\ E_{d\sigma-}^{\text{eff}} = E_d^{(0)}(z) + U_c \langle \hat{n}_{d\sigma+} \rangle, \end{cases} \quad (5a)$$

$$\quad (5b)$$

where $\langle \hat{n}_{d\sigma} \rangle$ is an average of the number operator for the $|d\rangle$ state with the spin projection σ ;

$$\langle \hat{n}_{d\sigma} \rangle = \Delta_v \int_{-\Delta E_v}^0 \frac{d\omega}{[\omega - E_{d\sigma}^{\text{eff}}(z) - \Sigma_2(\omega)]^2 + (\pi \Delta_v)^2} + \left(1 - \frac{d\Sigma_3}{d\omega} \right)_{E_{d\sigma, \text{occupied}}}^{-1}, \quad (6)$$

where

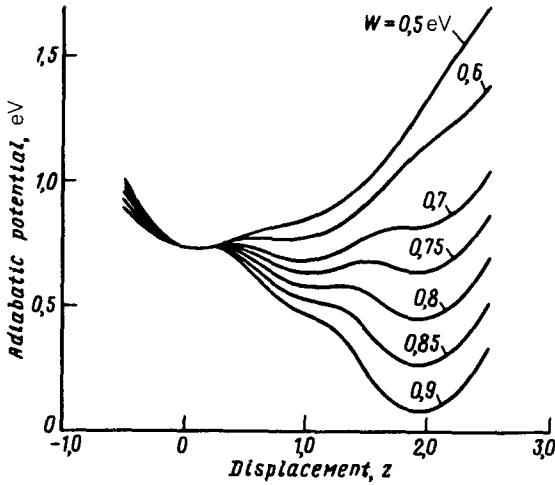


FIG. 1. Evolution of the adiabatic potential $\Phi_1(z)$ with W at $\tilde{E}_{d\sigma}^{(0)} = 1.8$ eV, $E_g = 1.0$ eV, $\Delta E_c = \Delta E_v = 5$ eV, $\Delta = 0.1$ eV, and $U_c = 0.3$ eV.

$$\Sigma_2(\omega) = \Delta_v \ln \frac{\omega + \Delta E_v}{-\omega} + \Delta_c \ln \frac{E_g - \omega}{E_g + \Delta E_c - \omega}, \quad (7a)$$

$$\Sigma_3(\omega) = \Delta_v \ln \frac{\omega + \Delta E_v}{\omega} + \Delta_c \ln \frac{E_g - \omega}{E_g + \Delta E_c - \omega}. \quad (7b)$$

The self-energy part of the Green's function and $\Delta_{v(c)} = \rho_{v(c)} |V^{v(c)}|^2$ are the effective interaction parameters ($\Delta_v \sim \Delta_c \sim \Delta \sim 0.1$ eV).

3. Results and discussion. The adiabatic potentials in Eq. (3) were calculated by computer simulations. The results for $\Phi_1(z)$, the most interesting example, are shown in Fig. 1. The minima coordinates (equilibrium displacements) $z_{nj} = z_{1j}$ are shown to be close to $z_{11} = 0$, $z_{12} = 1$, or $z_{13} = 2$, where j is the minimum number. In the case of zero and double initial occupation of the $|d\rangle$ state, similar equilibrium displacements can be obtained for a sufficiently wide range of parameters ($\tilde{E}_{d\sigma}^{(0)}$, E_g , and W) of the system under investigation. This result allows us to use very simple approximations for the lowest-energy state of the system at different site occupations n and to obtain simple analytic expressions; here the pair correlation energy is an important characteristic of self-trapping.¹

To determine the shape of the adiabatic potentials and its transformation with variation of the parameters of the system (W and $\tilde{E}_{d\sigma}^{(0)}$), we derivate Eq. (3) and obtain the following equation for equilibrium displacements:

$$z - \sum_{\sigma} \langle \hat{n}_{d\sigma}(z) \rangle = 0. \quad (8)$$

It follows from Eq. (8) that both the roots and the number of the roots essentially depend on the average occupation of the $|d\rangle$ state and on its variation with the position of $E_{d\sigma}^{(0)}(z)$ [see Eq. (1)]. As was mentioned above, if the atomic displacement is not very large ($z < z_*$), so that $E_{d\sigma}^{(0)}(z)$ does not split off the conduction band, the intraband interactions are essential and result in the mixing of the $|d\rangle$ state with the

conduction band states. The occupation of the $|d\rangle$ state is thus negligible at any initial occupation. This means that for small z (< 1) the adiabatic potentials have a single minimum only at $z_{01} \approx z_{11} \approx z_{21} \approx 0$.

For larger atomic displacements the level $E_{d\sigma}^{(0)}(z)$ splits off the conduction band and the role of the intraband interactions decreases. This leads to an increase in the occupation of the state $|d\rangle$ to $\Sigma_{\sigma} \langle \hat{n}_{d\sigma}(z) \rangle \approx 1$ for a single initial occupation or to $\Sigma_{\sigma} \langle \hat{n}_{d\sigma}(z) \rangle \approx 2$ for a double initial occupation. The appearance of an additional minimum of $\Phi_1(z)$ and $\Phi_2(z)$ at $z_{12} \approx 1$ and $z_{22} \approx 2$ can accompany this process.

When the level $E_{d\sigma}^{(0)}(z)$ reaches the valence band with a further increase in z , the interband interactions become essential and give rise to double occupation of the initially free or singly occupied state $|d\rangle$ (see also Ref. 2). This process can also lead to the appearance of an additional minimum at $z_{02} \approx z_{13}(z_{12}) \approx 2$.

The appearance of the additional minima of $\Phi_n(z)$ strongly depends on the value of the system parameters such as W and $\tilde{E}_{d\sigma}^{(0)}$. This is clearly demonstrated in Fig. 1 which shows the evolution of a single-well potential to a double-well and triple-well potential and back to a double-well and single-well potential as the standard self-trapping energy is increased.

The relative energies of the different minima also depend on $\tilde{E}_{d\sigma}^{(0)}$, E_g , and W . Therefore, the lowest-energy state of the system can be associated with one of the minima of the adiabatic potential and can go from one minimum to another as the system's parameters are varied. Such a transformation can be clearly demonstrated in the analysis of the dependence of the correlation energy on the standard self-trapping energy at different positions of the bare-site state level (see Fig. 2).

The correlation energy, U , defined in the usual way,¹

$$U = \Phi_2(z_2) - 2\Phi_1(z_1) + \Phi_0(z_0), \quad (9)$$

is negative. The negative- U centers therefore form the ground state of the electron system, while the single-particle states are the excited states of the negative- U centers. In other words, the lowest-energy state is the ground state only for double initial occupation. The values of z_i in Eq. (9) denote the equilibrium atomic displacements at the ground state. It is shown in Fig. 2 that the shape of the curve $U(W)$ depends on the $E_{d\sigma}^{(0)}$ position.

If the bare level lies in the conduction band sufficiently close to the band (mobility) edge, i.e., if $\tilde{E}_{d\sigma}^{(0)} < E_* \approx 3E_g/2 + U_c/2$, then the situation can be described as follows. For small values of W , $W < W_1 \approx \tilde{E}_{d\sigma}^{(0)}/2 - E_g/2 + U_c/4$, the equilibrium displacements $z_0 \approx z_1 \approx z_2 \approx 0$ and the state $|d\rangle$ is basically not occupied for any initial occupation. Accordingly, $U(z_0, z_1, z_2) \approx U(0, 0, 0) = 0$.

For larger standard self-trapping energies, $W_1 < W < W_2 = \tilde{E}_{d\sigma}^{(0)} - E_g$, where the level $E_{d\sigma}^{(0)}(z)$ enters the gap, the second minimum of $\Phi_2(z)$ corresponds to the lowest-energy state, so $z_2 \approx 2$. The respective true level of the self-trapped state is located near (above) the valence band top, and the state $|d\rangle$ is easily occupied by two electrons because of very small admixing of the conduction band states (at $\Delta_c \ll E_g$). At the same time, the positions of the minima of the potentials $\Phi_1(z)$ and $\Phi_0(z)$ are, as before, close to $z_0 \approx z_1 \approx 0$. Then

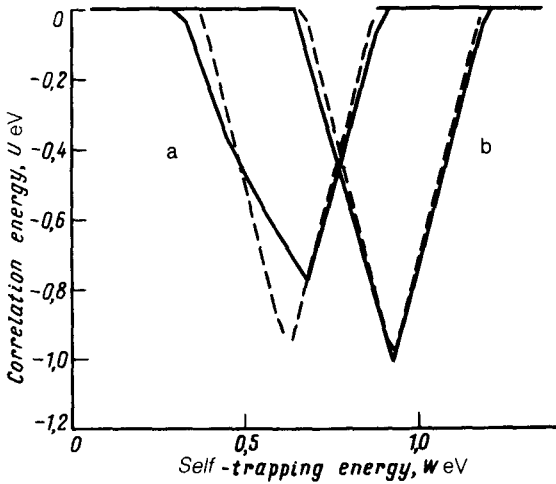


FIG. 2. Dependence of the correlation energy U on the standard self-trapping energy W at different positions $\tilde{E}_{d\sigma}^{(0)}$ of the bare level within the conduction band: (a) sufficiently close to the band edge, $E_g < \tilde{E}_{d\sigma}^{(0)} < E^*$, $\tilde{E}_{d\sigma}^{(0)} = 1.6$ eV; (b) sufficiently far from the band edge, $E_{d\sigma}^{(0)} > E^*$, $\tilde{E}_{d\sigma}^{(0)} = 2.2$ eV [solid curves—numerical solution according to Eqs. (9) and (3); dashed curves—approximate dependence according to Eqs. (10), (11), and (12)]; $E_g = 1.0$ eV, $\Delta E_c = \Delta E_v = 5$ eV, $\Delta = 0.1$ eV, and $U_c = 0.3$ eV.

$$U \simeq U(0,0,2) \simeq 2\tilde{E}_{d\sigma}^{(0)} - 2E_g - 4W + U_c. \quad (10)$$

This expression can be derived from Eq. (2) if the unessential interactions of the $|d\rangle$ state with the conduction-band states at double initial occupation and with the valence-band states at single or zero initial occupation of the $|d\rangle$ state are ignored.

If $W_2 < W < W_3 = \tilde{E}_{d\sigma}^{(0)}/3 + U_c/3$, we see a change in the equilibrium position of z_1 , with $z_1 \simeq 1$, instead of $z_1 \simeq 0$. The true level for such W and single initial occupation lies in the neighborhood of the midgap and its occupation is close to unity. However, at zero initial occupation the true level lies within the conduction band, as before, so that

$$U \simeq U(0,1,2) \simeq -2W + U_c. \quad (11)$$

This is the well-known expression for the correlation energy in the common negative- U center theory.¹ Indeed, this follows from Eq. (2) when the interactions of the $|d\rangle$ state with extended band states are ignored.

A further increase in W results in a change of z_0 from $z_0 \simeq 1$ to $z_0 \simeq 2$ for $W_3 < W < W_4 = \tilde{E}_{d\sigma}^{(0)}/2 + U_c/4$. This change is the result of a strong admixing of the valence band states to the state $|d\rangle$, which leads to an almost double occupation of the state $|d\rangle$ at its single initial occupation. The true level of the self-trapped state at single initial occupation (like that at double occupation) lies now near (above) the top of the valence band, while the true level at zero initial occupation is located near the conduction band bottom, so that

$$U \simeq U(0,2,2) \simeq 4W - 2\tilde{E}_{d\sigma}^{(0)} - U_c \quad (12)$$

We clearly see from Eq. (12) that this correlation energy increases with the standard self-trapping energy, in contrast with Eqs. (10) and (11). This means that U reaches the minimum value at $W = W_3$,

$$U_{\min} = U(W_3) \simeq -\frac{2}{3}\tilde{E}_{d\sigma}^{(0)} + \frac{1}{3}U_c \quad (13)$$

(see also Ref. 2, where such effects in unessential intraband interactions are studied).

At $W > W_4$, the second minimum of $\Phi_0(z)$ at $z \simeq 2$ becomes the lowest-energy-state minimum, so an initially unoccupied $|d\rangle$ state becomes doubly occupied, because of strong admixing of the valence band electrons. The correlation energy in this case obviously is zero, $U(2,2,2) \simeq 0$.

When the bare energy lies within the conduction band sufficiently far from its bottom, $\tilde{E}_{d\sigma}^{(0)} > E_*$, the shape of $U(W)$ is changed (see Fig. 2): The region $W_2 < W < W_3$ disappears and W_2 should be replaced by $W_2^* = E_{d\sigma}^{(0)}/2 - E_g/4 + U_c/4$. This results in a change of U_{\min} from Eq. (13) to $U_{\min} \simeq U(W_2^*) \simeq E_g$.

We have presented above several approximate expressions for $U(W)$, which agree rather well with the exact solution calculated by computer simulations (see Fig. 2).

4. Conclusions. We studied the self-trapping of a bare-site state of energy $\tilde{E}_{d\sigma}^{(0)}$ lying within the conduction band, and we took into account the interaction of this state with the states of the parent and nonparent bands.

Self-trapping takes place if the standard self-trapping energy W is large enough for the level $\tilde{E}_{d\sigma}^{(0)}(z)$ to reach the neighborhood of the band (mobility) edge. The wave function related to this state then becomes localized and a strong electron-atom interaction at the $|d\rangle$ state can be realized. The related atomic adiabatic potentials, in particular, double-well and even triple-well potentials, of the system seem to become anharmonic, although the original bare adiabatic potential is a standard harmonic single-well potential Wz^2 in Eq. (3). In this connection, the interactions of the state $|d\rangle$ with the extended states can be considered as an additional source of atomic double-well potentials and related two-level systems which determine the universal properties of glasses at very low temperatures (see, e.g., Ref. 1). The origin of atomic, anharmonic, in particular, double-well potentials in glasses cannot be reduced to the influence of the hybridization effects under discussion, since the well-known low-temperature properties characteristic of glasses are universal, while the hybridization effects and negative- U centers are essential largely in glassy semiconductors. It is worth noting in this connection that a model,⁶ which is different from the present model in some essential respects, has recently been proposed for studying the role of hybridization effects in forming negative- U centers. Despite the basic differences, some similar features appear in the behavior of the adiabatic potentials $\Phi_n(z)$ and the negative correlation energy U .

The negative correlation energy, $U(\tilde{E}_{d\sigma}^{(0)}, W)$, is shown to depend on the bare level ($\tilde{E}_{d\sigma}^{(0)}$) position in the conduction band, or close to the band (mobility) edge, and to

be a nonmonotonic function of the standard single-particle self-trapping energy (W), where the minimal value of the correlation energy is $U_{\min} \sim -E_g$

The effects which we analyzed can be essential for self-trapping in condensed systems with atomic soft configurations (e.g., in glassy semiconductors¹). It should be noted that such effects can be observed at a high pressure when the bare level can enter the band of the extended states.

The results of a detailed study of the electron and atomic-dynamical properties of the systems under discussion will be reported elsewhere.

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