Causes of hole localization on two halogen ions in alkali-halide crystals

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It is shown that within the framework of ordinary small-radius polaron theory the localization of an electron (or hole) on one crystal-lattice site is always energywise favored over localization on two neighboring sites occupied by ions of the same kind. A hypothesis is advanced that this theory does not hold for holes in alkali-halide crystals because the resonance integral J for two halide ions depends strongly on the distance R between them even at small deviations of R from the equilibrium value R_0. The "two-site" localization of a hole can be the result of the joint action of the strong $J(R)$ dependence and of the strong polaron effect.

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1. In 1957, Castner and Känzig,[1] in an investigation of electron spin resonance in a number of alkali-halide crystals (AHC) at low temperatures, have established that the resonance lines are due to a hole localized on two neighboring halide ions. A molecular ion X_2^- is produced, oriented in one of the six [110] directions of the crystal (see also[2]). Interest in the causes of the localization of the hole on two lattice sites arose in connection with theoretical investigations of the exciton mechanism of defect production in AHC.[3–12] Excitons in AHC, whose nonradiative annihilation can lead to the formation of F and H centers are also localized on two sites, and it is precisely the two-site localization that makes possible the exciton mechanism of defect production.

It is well known that electrons and holes in any polar crystal form polarons of large or small radius (see, e.g., [13, 14], where a detailed bibliography is given). The motion of large-radius polarons over the crystal is described by the band theory, in analogy with the motion of free electrons and holes. It was shown theoretically that small-radius polarons can be autolocalized. This means that the corresponding polaron band can be so narrow, that any small perturbations of the periodic potential in the crystal excludes the band motion. Since the large-radius polaron picture is patently inapplicable to holes in AHC [13,14] (in contrast, for example, to electrons in the same crystals), the hole autolocalization observed in experiment[1,2] is, generally speaking, not surprising.

What does call for an explanation, however, is the experimental fact that a hole in the AHC is localized not on one but on two neighboring halide ions. It will be shown in Sec. 2 that from the point of view of ordinary small-radius polarons (SRP) theory, the localization of a hole on two lattice sites is always energywise less favored than localization on one site. This leads to the conclusion that a hole localized on two sites is an entirely special state, different from both the large and small radius polarons. The qualitative difference of this state, which we shall call quasimolecular, from the ordinary polaron will be shown in Sec. 3. The fact that the quasimolecular state is energywise favored over the ordinary polaron follows from experiment.[1,2] In principle, quasimolecular and polaron states could coexist, being separated by a potential barrier, i.e., the polaron could be metastable. In this case, polaron theory would be applicable to the description of the metastable state. However, in so far as we know, no potential barrier has been experimentally observed to date in the formation of molecular ions in AHC.1) In Sec. 3 we propose a hypothesis that explains the absence of a potential barrier when a quasimolecular state is produced. If this hypothesis is correct, then the ordinary SRP theory, based on the harmonic approximation, does not hold for holes in AHC.

2. It can be shown that the energy E_a of activation of hopping conduction, which enters in the SRP theory, constitutes a gain in the polaron energy on going from the two-site to the single-site state. Since $E_a>0$ always, and furthermore, in the theory it is assumed that

$$J<E_a, \tag{1}$$

where J is the two-center resonance integral, the ordinary theory leads to the statement that single-site localization is always energywise favored over two-site localization.

To prove this, the Hamiltonian of a system consisting of an electron part H_e, a phonon part H_{ph}, and an electron-phonon interaction H_{int}, written, according to Peierls,[17] in the linear approximation in the displacements of the atoms from the lattice sites, will be expressed in the representation of certain orthonormal electronic functions φ_l, which depend, generally speaking, on the coordinates of all the electrons contained in this system. These, in particular, can be functions localized on one site, and then the subscript l should include the site number m and the numbers of the different states (ground and excited) on one site. The subscript l was previously[18] used to label simply the site number m. We shall also use below functions φ_l symmetrically localized on two neighboring lattice sites.

The matrix elements of the operators H_e and H_{int} will be written in the form

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$$\langle l|H_e|l'\rangle=\varepsilon_l\delta_{ll'}+\varepsilon_{ll'}, \tag{2}$$

$$\langle l|H_{int}|l'\rangle=\sum_{j,\mathbf{q}}\hbar\omega_{j\mathbf{q}}(C_{j\mathbf{q}l}b_{j\mathbf{q}}+C^{*}_{j\mathbf{q}l}b_{j\mathbf{q}}{}^{+})\delta_{ll'}+\sum_{j,\mathbf{q}}\hbar\omega_{j\mathbf{q}}(C_{j\mathbf{q}ll'}b_{j\mathbf{q}}+C^{*}_{j\mathbf{q}ll'}b_{j\mathbf{q}}{}^{+}), \tag{3}$$

where $\omega_{j\mathbf{q}}$ is the frequency of the lattice oscillations of the branch j with wave vector $\mathbf{q}$, and $b_{j\mathbf{q}}(b^{+}_{j\mathbf{q}})$ is the phonon annihilation (creation) operator. It is understood that $\varepsilon_{ll'}$ and $C_{j\mathbf{q}ll'}$ are equal to zero at $l=l'$.

We note that a Hamiltonian of the form (2) and (3) describes exactly all the exciton states of the crystal in the linear (harmonic) approximation in the displacement of the atoms from the lattice sites. By exciton state we mean here electronic excitations and, particularly, the hole state. If we consider an exciton of the type of electron-hole bound pair in AHC, then H_e must include the Coulomb interaction between the electrons, and the number l of the different states must include the ground state of the crystal, for which it can be shown that $C_{j\mathbf{q}l}=0$. The wave function φ_m describes in this case a hole localized on the site, to which an electron is bound by Coulomb forces (the resonance integral $\varepsilon_{mm'}$ is small because of the small overlap of the hole functions on the neighboring sites).

For simplicity we shall henceforth omit the index j, with the implication that the strong polaron effect is due to the interaction of an electron (or hole) with longitudinal optical vibrations of the lattice.

We carry out an exact canonical transformation of the Hamiltonian, which eliminates completely those electron-phonon interaction matrix elements which are diagonal in l (see also[18]). The physical meaning of the transformation consists in the fact that for each electronic state l we consider the vibrations of the atoms relative to the new equilibrium positions, shifted away from the lattice sites as a result of the polaron effect. The canonically transformed Hamiltonian $\tilde{H}$ is defined by the expression

$$\tilde{H}=e^{-S}He^{S},\qquad \langle l|S|l'\rangle=\sum_{\mathbf{q}}(C_{\mathbf{q}l}b_{\mathbf{q}}-C_{\mathbf{q}l}{}^{*}b_{\mathbf{q}}{}^{+})\delta_{ll'}. \tag{4}$$

We have then $\tilde{H}=H'+H_{\mathrm{ph}}$, with

$$\langle l|H'|l\rangle=\varepsilon_l-E_{pl}, \tag{5}$$

where

$$E_{pl}=\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}|C_{\mathbf{q}l}|^2 \tag{6}$$

is the polaron energy shift

$$\begin{aligned}\langle l|H'|l'\rangle=\varepsilon_{ll'}\Phi_{ll'}-\frac{1}{2}\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}[C_{\mathbf{q}ll'}(C_{\mathbf{q}l}{}^{*}+C^{*}_{\mathbf{q}l'})+C^{*}_{\mathbf{q}ll'}(C_{\mathbf{q}l}+C_{\mathbf{q}l'})]\Phi_{ll'}\\+\frac{1}{2}\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}[C_{\mathbf{q}ll'}\{b_{\mathbf{q}},\Phi_{ll'}\}+C^{*}_{\mathbf{q}ll'}\{b_{\mathbf{q}}{}^{+},\Phi_{ll'}\}],\end{aligned} \tag{7}$$

where

$$\Phi_{ll'}=\exp\sum_{\mathbf{q}}[(C_{\mathbf{q}l}-C_{\mathbf{q}l'})b_{\mathbf{q}}-(C_{\mathbf{q}l}{}^{*}-C^{*}_{\mathbf{q}l'})b_{\mathbf{q}}{}^{+}], \tag{8}$$

and { } denotes the anticommutator.

In the ordinary SRP theory,[18] where φ_l is chosen to be the function φ_m localized on site number m, we have

$$\varepsilon_m=\varepsilon,\qquad C_{\mathbf{q}m}=\frac{\gamma_{\mathbf{q}}}{(2N)^{1/2}}e^{i\mathbf{q}\mathbf{R}_m}, \tag{9}$$

where N is the number of cells in the crystal and $\mathbf{R}_m$ is the radius vector that determines the position cell m. From (6) we obtain the polaron energy shift

$$E_{pm}=E_p=\frac{1}{2N}\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}|\gamma_{\mathbf{q}}|^2 \tag{10}$$

following localization of the polaron on one site.

The off-diagonal matrix elements (7) make it possible for the polaron to go over to other lattice sites, and it is understood that the polaron moves over ions of the same kind (for example, in an AHC the hole moves over sites occupied by the halide ions). The H_{int} matrix elements that are off-diagonal in the sites were previously[18] described as small (we shall return to this question later), i.e., it was assumed that $C_{\mathbf{q}mm'}=0$. The right-hand side of (7) is therefore left only with the first term, which contains the resonant integral $\varepsilon_{mm'}=J(\mathbf{G})$, where $\mathbf{G}=\mathbf{R}_{m'}-\mathbf{R}_m$.

To determine the energy shift of a polaron when localized on two sites, we confine our analysis to two neighboring sites occupied by ions of one kind, and introduce for them the function

$$\psi_1=2^{-1/2}(\varphi_m+\varphi_{m+g}),\ \psi_2=2^{-1/2}(\varphi_m-\varphi_{m+g}), \tag{11}$$

where the subscript $m+g$ denotes a site characterized by the vector $\mathbf{R}_m+\mathbf{g}$.

We shall assume that the subscript l takes on only two values, 1 and 2, in accordance with (11). Then, calculating the matrix elements for the functions (11), we obtain

$$\varepsilon_1=\varepsilon+J,\ \varepsilon_2=\varepsilon-J,\ \varepsilon_{12}=\varepsilon_{21}=0, \tag{12}$$

where $J=J(\mathbf{g})$, and also

$$C_{\mathbf{q}1}=C_{\mathbf{q}2}=\frac{\gamma_{\mathbf{q}}}{(2^3N)^{1/2}}e^{i\mathbf{q}\mathbf{R}_m}(1+e^{i\mathbf{q}\mathbf{g}}), \tag{13}$$

$$C_{\mathbf{q}12}=C_{\mathbf{q}21}=\frac{\gamma_{\mathbf{q}}}{(2^3N)^{1/2}}e^{i\mathbf{q}\mathbf{R}_m}(1-e^{i\mathbf{q}\mathbf{g}}). \tag{14}$$

Substituting (13) in (6), we find that the polaron energy shift E_p' for two-site localization is equal to

$$E_p'=E_{p1}=E_{p2}=\frac{1}{4N}\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}|\gamma_{\mathbf{q}}|^2(1+\cos\mathbf{q}\mathbf{g}), \tag{15}$$

i.e., it is smaller than the polaron shift E_p for one-site localizations by an amount

$$E_a=E_p-E_p'=\frac{1}{4N}\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}|\gamma_{\mathbf{q}}|^2(1-\cos\mathbf{q}\mathbf{g}). \tag{16}$$

It is well known[19,18] that E_a is the hop activation energy in hopping conduction produced by small-radius polarons. The physical meaning of (16) is that for a

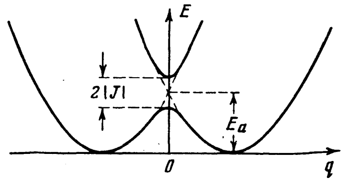

FIG. 1. Adiabatic terms, the motion over which described the jump of a small-radius polaron over to the neighboring lattice site.

transition of the electron (or hole) to the neighboring site it must of necessity go through a stage of localization on two sites, so that the activation energy is equal to the difference between the polaron energy shifts for one-site and two-site localization.

It was shown earlier[19–21] that the jump of a polaron from one site to another can be described as motion over adiabatic terms (see Fig. 1) that intersect at a height E_a and are separated at the intersection point by an amount $2|J|$. In light of our reasoning, it becomes clear that the polaron is localized on two sites at the instant when it passes the term-intersection point, and the separation of the terms correspond to the level splitting described by (12). When moving over the term towards the intersection point, the electron (hole) state φ_m acquires an ever increasing admixture of the state φ_{m+g} on the neighboring site (accordingly, the true terms deviate more and more from the terms designated by the dashed lines, obtained in the limit as $J\to 0$). Thus, each activated jump of the polaron from site to site constitutes a sequence of transitions: single-site polaron—two-site polaron—single-site polaron, etc.

We note that in the motion over the upper term (see the figure) the two-site state of the polaron is an equilibrium state, but one that lies, of course, higher than the equilibrium single-site state corresponding to the lower term. As to the matrix elements of (7) that are off-diagonal in the states 1 and 2, we can show by using (13) that they are equal to

$$\langle 1|H'|2\rangle=\langle 2|H'|1\rangle=\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}(C_{\mathbf{q}12}b_{\mathbf{q}}+C^{*}_{\mathbf{q}12}b_{\mathbf{q}}^{+}). \tag{17}$$

It can be shown that the off-diagonal matrix elements (17) lead to a transition of the polaron from a two-site to a single-site state. For the proof, we subject the Hamiltonian (12)–(17) to one more canonical transformation, which eliminates completely the elements (17). The new operator S' (see (4)) is defined by

$$\begin{gathered}\langle 1|S'|1\rangle=\langle 2|S'|2\rangle=0,\\ \langle 1|S'|2\rangle=\langle 2|S'|1\rangle=\sum_{\mathbf{q}}(C_{\mathbf{q}12}b_{\mathbf{q}}-C^{*}_{\mathbf{q}12}b_{\mathbf{q}}^{+}).\end{gathered} \tag{18}$$

As a result of the transformation, which can be carried out exactly, we again obtain for the polaron energy shift the value (10) corresponding to the single-site polaron. The results of the transformation for part of the Hamiltonian (12) will not be written out here, we indicate only that this result corresponds to a symmetrical distribution of single-site polarons over two sites. Physically this means simply that a two-site polaron localized on the pair of sites m and $m+g$ can go over to single-site states on the sites m and $m+g$ with equal probability.

If there were no off-diagonal matrix elements (17), then a two-site polaron produced in the crystal at $T\approx 0$ could not go over to a single-site state (see also the description given below for the successive stages of localization of an electron or a hole produced by irradiation of the crystal), since there would be no coupling of the two-site polaron with phonons to which it could transfer its excess energy E_a.

We have thus shown that the SRP theory based on the harmonic approximation cannot lead to localization of a hole on two halogen ions. Large-radius polarons, whose theory is also constructed in the harmonic approximation, are not localized at all. It can therefore be concluded that the experimentally observed localization of holes on two sites in AHC demonstrates that the harmonic approximation cannot be used. We shall explain below why this is so.

3. We assume that the localization of a hole on two halogen ions in AHC is the result of the joint action of a strong polaron effect and a strong dependence of the resonance integral J on the distance R between the ions. It is assumed that the resonance integral is small when the atoms are located at the lattice sites (see (1)). It is precisely this value $J=J(R_0)$ which is used in the SRP theory. However, when the distance between the atoms decreases to a critical value R_{cr} the value of $J(R)$ begins to increase strongly. If $R-R_{\mathrm{cr}}$ is comparable with the polaron displacements, then the mutual approach of atoms of the same type, due to the polaron effect, leads to a sharp increase of the resonance integral and to a transition of the hole to a two-site state.

It is clear that this is patently a two-site effect. Indeed, three atoms or more atoms of the same sort in a lattice of the NaCl type cannot be so disposed that all the distances between them are $R\leqslant R_{\mathrm{cr}}$. The second sum of the right-hand side of (3) was previously[18] discarded on the basis of the following estimates:

$$\langle m|H_{\mathrm{int}}|m\rangle\approx\varepsilon u_p/a,\ \langle m|H_e|m+g\rangle\approx J,\ \langle m|H_{\mathrm{int}}|m+g\rangle\approx Ju_p/a, \tag{19}$$

where ε is an energy on the order of atomic, u_p is the polaron displacements of the atoms from the lattice sites, and a is the lattice constant. Since the conditions

$$J/\varepsilon\ll 1,\ u_p/a\ll 1, \tag{20}$$

are satisfied, the quantity $\langle m|H_{\mathrm{int}}|m+g\rangle$ turned out to be the smallest and was discarded. However, the last of the estimates in (19) can be incorrect in some cases. Assume, for example, that the resonance integral has an exponential dependence on the distance R between the atoms

$$J(R)=J\exp\left(\frac{R_0-R}{R_0-R_{\mathrm{cr}}}\right)\approx J\left[1+\frac{u}{u_{\mathrm{cr}}}+\frac{1}{2}\left(\frac{u}{u_{\mathrm{cr}}}\right)^2+\ldots\right], \tag{21}$$

where $u=R_0-R_1$ and $u_{\mathrm{cr}}=R_0-R_{\mathrm{cr}}$, which corresponds to a rapid growth of $J(R)$ at $R<R_{\mathrm{cr}}$. It is important that the condition

$$\exp\left(\frac{R_0}{R_0-R_{\mathrm{cr}}}\right)\gg 1,$$

which means that the maximum value (at $R=0$) of the resonance integral should be much larger than the equilibrium value (at $R=R_0$), leads to the inequality

$$u\ /R_0 \ll 1. \tag{22}$$

It follows from (21) that the last estimate in (19) should be replaced by

$$\langle m|H_{int}|m+g\rangle \approx J u_p/u_{cr}. \tag{23}$$

If

$$u_p/u_{cr} \gtrsim 1, \tag{24}$$

then the resonance integral $J(R)$ cannot be expanded in the series in the displacements. Thus, the harmonic approximation cannot be used to describe the behavior of a hole in an AHC, i.e., the usual SRP theory does not hold.

If the distance between the halogen ions has decreased to R_{cr} and the hole has gone over to the two-site state, the ions can approach each other further quite strongly, since the sharp decrease of the energy $\varepsilon - |J(R)|$ of the lower term with decreasing R offsets the energy of the repulsion between the ions if two electrons are situated on the two atoms X, i.e., if there is no hole. The mutual approach stops with certainty only if the deeper electron shells of the atoms come in contact, which leads to repulsion.

Castner and Känzig[1] have established that two halogen atoms with one electron on each exhibit properties similar to the properties of a molecule or a molecular ion. A molecular ion X_2^- with a covalent bond is produced. They have indicated[1] that the interatomic distances in the X_2^- ions are intermediate between the distances in the unperturbed crystals and in the free X_2 molecules. The very fact that molecular properties have been observed indicates that the displacements of the halide atoms from the lattice sites are large—they are comparable with the interatomic distances. We assume that the gain in energy due to the transition of the hole from the single-site to the two-site state can be determined from the value E_a' of the activation energy in the diffusion coefficient $D=D_0\exp(-E_a'/k_0T)$ of the holes. In fact, in order for a hole localized on two sites to go over into a position such that one of the two localization sites has changed, an intermediate localization on a single site is necessary on the very site which is common to the different two-site localizations). Just as in the case of ordinary SRP, a hole that diffuses as a result of oscillation jumps occupies alternately single-site and two-site positions.[2]

It would be of interest to trace the time variation of the localization of the holes if the holes are produced by irradiation at low temperatures. So far, only some quantitative considerations can be advanced. According to the Franck-Condon principle, at the instant when a hole is produced by irradiation, all the atoms are at the lattice sites (if we neglect the thermal vibrations, which we assume to be smaller than the polaron vibrations in accordance with the SRP theory).

The polaron displacements and the large displacements in the X_2^- ions can arise only after a time on the order of ω_{LO}^{-1}. The first to be produced is therefore a hole that moves freely over the crystal, since all the atoms are equivalent for it. This is followed by a gradual relaxation—localization of the hole, the excess energy being transferred to the photons. In the course of relaxation, the hole goes through successive stages of localization on an ever decreasing number of sites. If this were ordinary SRP, then the penultimate stage would include localization on two sites, corresponding to the upper term on the figure, while the last stage would consist of localization on a single site. It is probable that in the case when holes are produced in AHC, the stage of production of molecular ions X_2^- follows the stage of localization on one site. It is also possible that the stage of localization on one site can be bypassed if the localization of the hole on two sites leads to sufficiently large polarons displacements $u_p \gtrsim R - R_{cr}$.

There is no doubt that the molecular ion X_2^- is produced in an excited vibrational state, which relaxes only gradually to the equilibrium position, since, for example, a sudden transition from a single-site state to the equilibrium state of X_2^- with lower energy is impossible.

The production of a molecular ion X_2^- in an excited vibrational state plays the decisive role in the action of the exciton mechanism[3-12] of defect production at low temperatures.

Thus, the molecular ion X_2^- can be produced if two neighboring ions X^-, on which (or on one of which) a hole is located, have come close enough together, $R \leqslant R_{cr}$. If the value $u_{cr}=R_0-R_{cr}$ were to exceed greatly the polaron and the average thermal displacements, then the critical oscillations of the ions could occur only as a result of fluctuations. In this case the molecular ions could not be produced without overcoming a potential barrier whose height would exceed the energy E_p of the polaron shift. This would mean that the polaron state is metastable.

TABLE I. Zero-point LO-vibration amplitudes u_0 which make it possible to estimate the lower bounds of the polaron displacements u_p and of the distance $R_0 - 2r_{X^-}$ between the neighboring halide ions in the hard-sphere model. These amplitudes give the upper bounds of the critical displacements u_{cr} in the case of four different AHC.

AHC	$u_0=\left(\frac{\hbar}{2M\omega_{LO}}\right)^{1/2}$, Å	R_0, Å	$R_0-2r_{X^-}$, Å
LiF	0.030	2.84	0.12
NaCl	0.033	3.98	0.36
KCl	0.033	4.44	0.82
KBr	0.030	4.51	0.59

Let us attempt to compare quantitatively the quantities $u_{cr}=R_0-R_{cr}$ and u_p. We can express u_p in the form

$$u_p=\left(\frac{\hbar}{2M\omega_{LO}}\right)^{1/2}\xi, \tag{25}$$

where M is the mass of the cell, ω_{LO} is the limiting frequency of the long-wave optical lattice vibrations, and ξ is a dimensionless parameter whose value depends on the binding force of the hole with the LO phonons, i.e., it is determined by the form of the function $\gamma_{\mathbf{q}}$ (see (9)) at all values of **q**. Table I lists the values of $u_0=(\hbar/2M\omega_{LO})^{1/2}$ for four AHC. The value of ξ should exceed unity if the polaron displacement exceeds the amplitude of the zero-point LO vibrations. The values of ξ are presently unknown, since the form of the function $\gamma_{\mathbf{q}}$ is unknown. The table gives also the values of R_0 and $R_0-2r_{X^-}$, where R_0 is the distance between the neighboring X^- ions, and R_{X^-} are the radii of the X^- ions according to[23]. It turns out that it suffices to move the ions through a distance $R_0-2r_{X^-}\ll R_0$ in order for them to "touch." However, an estimate of ξ as the ratio $(R_0-2r_{X^-})/u_0$ yields for ξ values that are too large. Thus, the absence of the potential barrier in the formation of quasimolecular states offers evidence that u_{cr} is much smaller than $R_0-2r_{X^-}$. This conclusion is not very strange if the following circumstances are taken into account: a) the concept of the ion radius is quite indeterminate, b) according to (21), when the distance between the ions decreases to $R_{cr}=R_0-u_{cr}$, the resonance integral increases only e times in comparison with the equilibrium value $J(R_0)$. If, for example, we estimate u_{cr} at $(R_0-2r_{X^-})/10$, then values $\xi\leqslant 3$ are sufficient to satisfy the condition $u_p\approx u_{cr}$ in the case of all the crystals in the table, and it turns out in the case of LiF that the critical approach of the halogen ions can be the result of the zero-point lattice vibrations, i.e., a strong polaron effect is not obligatory).

Even all the data in the table do not exclude the possibility of the inequality $u_p<u_{cr}$ for certain AHC. Therefore information on the absence of a potential barrier when the molecular ions X_2^- are produced and on the absence of metastable hole polaron states call for further experimental verification for different crystals.

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1) The existence in AHC of two types of excitons, mobile and localized, has recently been observed.[15] The transition from the mobile state to the localized state requires that a small potential barrier be surmounted (see also the theoretical investigation in [16]).

2) Tunneling of a quasimolecular state as a unit to neighboring sites does not play apparently any role whatever, because of the exceptional narrowness of the corresponding band. The narrowness of the band is due to the very large (on the order of the lattice constant) equilibrium displacements of the atoms in the ion X_2^-.

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