Dynamic model of quasimolecular hole of the V_K-center type and of its diffusion in nonmetals

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An essentially dynamic model, connected with barriers of fluctuation origin, is considered for a quasimolecular hole of the V_K-center type. The consequences of the model are compared with the experimental data.

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The question of the nature of quasimolecular holes (QMH) and excitons in alkali-halide crystals (AHC),[1] inert gases,[2] and others (SiO_2[3]), which determine a number of radiative and optical effects, has been discussed in a number of papers.[3–6] However, the mechanisms proposed in [4] and [6] for the QMH formation do not lead to a consistent qualitative description of QMH diffusion, and the mechanism of [3] seems to pertain more readily to crystals of the molecular type (see [7]).

In this communication, an attempt is made at a new approach to the nature of the QMH and at a qualitative description of the main features of diffusion and conductivity of QMH, assuming[5] that the hole dynamics is strongly influenced by the fluctuation-induced barrier "preparation" (FBP[8]). The latter is realized when the quantity $B(R)$, which determines the carrier tunneling amplitude $J(R) \equiv \Omega_0 \exp[-B(R)]$ for any specified atomic configuration R ($\equiv \{R_{ij}\}$; $i, j = 1,2,...$), changes substantially in comparison with the case ($B(R^0)$) of an ideal configuration $R^0 \equiv \{R_{ij} = a\}$, for which $J \equiv J(R^0) \ll \Omega_0$ at $B(R^0) \gg 1$ (the characteristic energy scale $\Omega_0 \sim 1$ eV corresponds to band widths $D_0 = 2z\Omega_0 \sim 10$ eV). In the FBP,[8] the tunneling takes place mainly at a certain external lattice configuration $R^* \equiv \{R^*_{12} = a + u^*_{12}, ...$, for certain nearest atoms, or $R_{ij} = a$ for the remaining i and $j\}$, with an optimally lowered barrier. This configuration R^* is the result of the competition between the growth of $J(R)$ and the decrease of the probability $C_0 \exp[-Q_{fl}(R,T)]$ of the configuration R with increasing displacements (u) of the appropritate (close to the hole) atoms, i.e., R^* is the solution of the extremal problem for the function $F(R) \equiv \exp\{-B(R) - Q_{fl}(R,T)\}$, which describes the contribution of $J(R)$ to the real carrier-tunneling amplitude determined by the sum of these contributions for all possible R. The effect of the FBP, naturally, should greatly enhance the carrier tunneling in comparison with the ideal (undeformed) lattice, so that it can be substantial when $J \equiv J(R_0)$ is small enough ($D \approx 2zJ \ll D_0 \sim 10$ eV). The situation for a hole (exciton) can differ greatly from the situation for atomic particles (for the latter $\Omega_0 \sim 10^{-2}$ eV and the harmonic approximation[8,5] is used for the analysis: the extremal displacements (u^*) for a hole correspond mainly to the mutual approach of atoms (ions) of like type, between which tunneling takes place (chlorine ons in NaCl, etc.), and $|u^*| = |u^*_{12}|$ can be so appreciable ($\sim a$) that the anharmonicities of the lattice become significant (but $a - |u^*_{12}| \gtrsim 2\rho_0$ in the sense of the atomic or ionic 'radius" ρ_0). At such large $|u^*_{12}| a^{-1} (\lesssim 1)$ the hole diffusion has the appearance of being

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produced by a sequence of tunnel transitions between atoms (ions) that are very close together. The gist of the QMH model is precisely the fact that the very close pair of atoms (ions) on which a hole is localized is likened to the QMH; such a local structure should exist in the course of the unique motion of the "narrow-band" hole (for example at $D \approx 2zJ \sim 0.3$ eV, which is much less than D_0, for a hole in an AHC[1]) during the characteristic times τ of the existence (and formation) of the "prepared" barrier ($\tau \sim \omega_{ph}^{-1}$; ω_{ph} is the frequency of the significant phonons, see [8,5]). In this case the FBP effect, which can exist both in the presence of a weak ($\Phi_0 < 1$) and a strong ($\Phi_0 > 1$) polaron effect, prevails over the latter, since the contribution of the polaron effect (u_p) to $|u^*_{12}|$ is small, $u_p \ll |u^*_{12}|$ (usually $u_p \ll a$ [9]).

Just as atomic quantum diffusion,[8,5] the diffusion of QMH in this model is different in the case of low concentration of QMH $c_p < c_p^{(cr)}$ and defects $c_d < c_d^{(cr)}$ or high concentration $c_d > c_d^{(cr)}$ (for example, $c^{(cr)} \sim \Delta^*/|V_0|$ if elastic interaction $\sim V_0 (a/r)^3$ predominates). Accordingly, at $c_{d,p} < c_{d,p}^{(cr)}$ or $c_d > c_d^{(cr)}$ the diffusion coefficient is $D = D_c + D_h$ or $D = D_h$.

$$D_c \sim za^2(\Delta^*)^2 \tau_{tr}/3\hbar, \qquad D_h \sim za^2(\Delta^*)^2 \exp[-2\phi^* + 2\chi]\Lambda/3\hbar^2\omega_{ph}, \quad (1)$$

where $\Lambda \approx \{10^5 e^{-2\Phi_0}\Phi_0^2(T/\hbar\omega_D)^7$ at $T \ll T_0 \equiv \frac{1}{2}\hbar\omega_{ph}$, but $\exp(-\mathcal{E}/T)(\omega_{ph}/T\Phi_0)^{\frac{1}{2}}$ at $\Phi_0 > 1$ and $T \gtrsim \frac{1}{2}T_0$, or $\Phi_0^2(T/T_0)^2$ at $\Phi_0 < 1$ and $T \gtrsim \frac{1}{2}T_0\}$; $\mathcal{E} \sim \hbar\omega_{ph}\Phi_0$. Here D_c and D_h are the contribution of the coherent (without emission or absorption of phonons) tunneling with amplitude Δ^* and with the noncoherent tunneling;

$$\Delta^* = A_0 \Omega_0 \exp\{-\phi^* + \chi - \Phi - B(R^*)\}, \qquad A_0 \approx \text{const}, \quad (2)$$

at $\phi^* \equiv \phi^*(T) \equiv Q_{fl}(R^*, T), B(R^0) - B(R^*) - \phi^* \gg 1$ and $\Delta^* \gg J$. In this case $\phi^* \approx \{\phi^*(0) \gg 1$ at $T \ll T_0$, or $Q/T \approx (u^*/u_0)^2(\hbar\omega_{ph}/T)$ at $T \gtrsim T_0/2\} \approx (u^*/u_T)^2$ and the polaron parameter is $\Phi \equiv \Phi(T) \approx \{\Phi_0 \equiv \Phi(0)$ at $T \ll T_0$ or $T\Phi_0(\hbar\omega_{ph})^{-1}$ at $T \gtrsim \frac{1}{2}T_0\} \approx (u_p u_T/u_0)^2$ (with $\phi^*(0) \gg \Phi_0$ and $Q \gg$ at $|u^*| \gg u_p$), and $\exp[\chi(t)]$ at $\chi(T) \approx \{\chi(0)$ and $T \ll T_0$ or $T\chi(0)/\hbar\omega_{ph}$ at $T \gtrsim \frac{1}{2}T_0\}$ ($\chi(0) \quad 1$) is due to the relatively small change of $B(R)$ at $|u| \sim u_T$ on the modes that are of no importance for the FBP; $\tau_{tr} \equiv \tau_{tr}(T)$ is the transport time corresponding to scattering by defects (and other carriers)[8,10] and by phonons;[8,5] u_T is the average thermal displacement of the atoms or ions, $u_T > u_0 \equiv u_{T=0}$. It follows from [1] and [2] that with increasing $T \ll T_0$ (at finite c_d and c_p) the value of D_c is initially practically constant, can then decrease (as a result of scattering by the phonons) like $\tau_{tr} \sim T^{-9}$, goes through a minimum (with not too low $T_{min} < \frac{1}{2}T_0$ at $\phi^*(0) \gg 1$), and then increases, particularly strongly at $T \gtrsim \frac{1}{2}T_0$. The qualitative behavior of $D(T)$ at $c < c^{(cr)}$ is similar: $D_h(T)$ increases with T, and prevails because of its stronger growth at sufficiently high $T(\gtrsim \frac{1}{2}T_0)$; at $c_d > c_d^{(cr)}$, as already noted, we have $D(T) = D_h(T)$, so that D is small at low T ($D_h \to 0$ as $T \to 0$). The growth of $\Delta^*(T)$ and D_c or D_h with increasing T at $T \gtrsim \frac{1}{2}T_0$ can, in general, be different at small $|u^*|a^{-1} \ll 1$ and at large $|u^*|a^{-1}(\lesssim 1)$. In the latter case, for QMH, owing to the strong anharmonicity, the growth can be noticeably stronger (say like

$\exp[-CT^{-\alpha}]$ with $\alpha > 1$, in which case $\phi^* \ll (u^*/u_T)^2$) than the activation-type growth $\sim \exp(-Q/T)$ in the former case.

If the considered dynamic model of the AMH corresponds to carriers of the V_K-center type, then the consequences of the foregoing arguments can be observed in appropriate experiments. In particular, since in AHC the effective mechanism of pair production of H and F centers is due to the "decay" of the excitons with QMH,[1] then we can expect a different change in the similar defect formation (as well as, probably, in the luminescence in which such excitons or QMH take part) with increasing T in the cases of low (a) and high (b) concentrations of the QMH (excitons) and defects. In case (b) at low $T(\ll T_0)$, the QMH have low mobility ($D = D_h \to 0$ as $T \to 0$) and the probability $q(T)$ of the competing "trapping" of the QMH and (or) "decay" of the exciton by the appropriate defect (impurity) is low, so that the defect formation is practically independent of the presence of impurities or defects; with increasing T, the situation should change, since $q(T)$, just like $D(T)$, should increase rapidly if $T > \frac{1}{2}T_0$). In case (a) (if c_d can be sufficient at $c_d < c_d^{(cr)}$ to make "trapping" QMH by similar defects effective), $q(T)$ could be noticeable at lower $T(\ll T_0)$. The case (a) (at $c < c^{(cr)}$) is quite difficult to realize in experiment (expecially for charge impurities or defects, see [5]). In fact, for AHC the behavior of $q(T)$ observed in experiment (see, e.g., [1]) agrees qualitatively with the behavior of $D(T)$ for case (b)–for different AHC on observes a correlation between the changes of the characteristic phonon frequencies (the Debye frequency ω_D and others) and the the temperature T_q above which a noticeable growth of $q(T)$ is observed (for example, $T_q = 210$ K and $\hbar\omega_D = 230$ K for KCl and $T_q \approx 175$ K and $\hbar\omega_D \approx 180$ K for KBr).

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