Jahn-Teller symmetry breaking of an autolocalized barrier

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It is shown that a strong Jahn-Teller deformation is developed in crystals with a degenerate energy spectrum in the states corresponding to an autolocalized barrier and that the barrier height always has a scale that is determined by the heavy mass.

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Autolocalization (*AL*) of excitons is associated with the surmounting of an autolocalized barrier formed as a result of an increase of the kinetic energy of an exciton during its *AL*. An *AL* barrier has been observed experimentally in alkali-metal iodides, in solid noble gases and in other materials. It is also formed for the current carriers as a result of nonpolar interaction with phonons. Previously, the height of an *AL* barrier was calculated[1–4] only for the models in which the state of the barrier conserves the total symmetry of the point group of a crystal. The symmetry of the barrier states, however, can be broken because of the Jahn-Teller (JT) effect, which reduces the barrier.

Symmetry breaking can be easily investigated on the basis of the continuous model in terms of which the J-T effect occurs for particles with a degenerate spectrum. The continuous approximation can be used if the coupling with phonons is sufficiently strong[4]; according to Ref. 5, for example, it can be used for light noble gases. The degeneration of a spectrum, however, occurs almost without an exception when *AL* is observed.[6] It should be emphasized that symmetry breaking at the surmounting stage of the *AL* barrier is crucial, since it determines to a large extent the subsequent stages of relaxation of the *AL* states and establishes advantageous conditions for the forma-

tion of states with a reduced symmetry.

We shall examine below the particles with the momentum $J = 1$ ("excitons") and $J = 3/2$ ("holes") in a spherical approximation. These particles have two branches of the spectrum - one with a light mass and the other with a heavy mass (m_l and m_h). We shall limit ourselves to the model with a single deformation potential C and a single elastic modulus K.

The barrier height W for excitons (the band with $J = 1$) is determined by the steady-state functional

$$J[\Psi] = \int \left\{ \frac{1}{2m_l} (\mathrm{div}\,\Psi)^2 + \frac{1}{2m_h} (\mathrm{rot}\,\Psi)^2 - \frac{C^2}{2K} (\Psi^2)^2 \right\} d\mathbf{r}, \tag{1}$$

that corresponds to its lower track point: $\Psi(\mathbf{r})$ is a three-component function. At $m_l = m_h$ the equations have the same form as in the nondegenerate spectrum, and the J-T effect is missing. We analyze the limiting case $m_l/m_h \to 0$ below. In this case, we set div $\Psi = 0$, i.e., $\Psi = \mathrm{rot}\,\mathbf{A}(\mathbf{r})$. Thus, the Schrödinger equation, which corresponds to Eq. (1), has the form

$$-\frac{1}{2m_h} \Delta \Psi - \frac{C^2}{K} \{\Psi^2 \Psi\}_h = E\,\Psi. \tag{2}$$

The subscript h of the second term shows that only the contribution of the heavy holes is retained in it; at $J = 1$ this corresponds to elimination of the longitudinal part of the function in accordance with the definition

$$\Phi_h(\mathbf{r}) = \Phi(\mathbf{r}) + \frac{1}{4\pi} \nabla \otimes \nabla \int \frac{\Phi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}'. \tag{3}$$

We can assume that the lower saddle corresponds to the Ψ function, which is transformed along one of the lines of the vector representation, for example, z; therefore, $\mathbf{A}(\mathbf{r}) = \phi(\rho,z)[\mathbf{z}^0 \times \mathbf{r}]$, where ϕ is an arbitrary, axially symmetric function and the deformation is axially symmetric.[1] In this case, a decrease of $\Psi(\mathbf{r})$ as $\mathbf{r} \to \infty$, according to Eqs. (2) and (3), is determined by the formula $\Psi \sim \nabla \partial (r^{-1})/\partial z$, i.e., it obeys the power law. After a simple, one-parameter approximation of $\phi(\mathbf{r}) \sim (r^2 + a^2)^{-3/2}$, which behaves normally when $\mathbf{r} \to 0$ and $\mathbf{r} \to \infty$, we obtain from Eq. (1)

$$W = J[\Psi_{extr}] \approx 174\, K^2/C^4 m_h^3 . \tag{4}$$

Thus, W is determined by the heavy mass m_h. The numerical coefficient in Eq. (4) is approximately fourfold larger than that for the nondegenerate band [in which it is equal to ≈ 44 (Ref. 2); it has the same value for $m_l = m_h$]. If the oscillator strength of the excitonic transition is large and the longitudinally transverse splitting Δ_0 in the spectrum is large ($\Delta_0 >> W$), then Eq. (4) must be valid for an arbitrary m_l/m_h.

The anisotropy of $\Psi^2(\mathbf{r})$ is large – the function, which is extended along the $0z$ axis, is small in the plane $z = 0$; for example, at $r^2 = a^2$ the ratio of the values of Ψ^2 on the axis and in the plane is equal to 16. Therefore, the system must have a tendency to

"role down" to the extended (for example, quasi-molecular binodal) AL states after surmounting the AL barrier. The role of the J-T effect can also be determined by comparing Eq. (4) with the barrier in the $\Psi = \mathbf{r}g(r)$ functions, which belong to a completely symmetrical representation and give a spherically symmetric deformation. Since $div\ \Psi \neq 0$ (in the normalizable functions), then $W \sim m_l^{-3}$, i.e., the barrier heights differ in the parameter $(m_l/m_h)^3 << 1$.

The $\Psi(\mathbf{r})$ function for the holes (the band with $J = 3/2$) is a four-component function and

$$J[\Psi] = \int \left\{ \left(\Psi, \left[-\frac{1}{4m_l}\left(\frac{9}{4}\Delta - (\mathbf{J}\nabla)^2\right) - \frac{1}{4m_h}\left((\mathbf{J}\nabla)^2 - \frac{1}{4}\Delta\right)\right]\Psi\right) - \frac{C^2}{2K}(\Psi^2)^2 \right\} d\mathbf{r}. \tag{5}$$

We again obtain Eq. (2) in the limit $m_l/m_h \to 0$, but in this case by substituting the following expression for Eq. (3):

$$\Phi_h(\mathbf{r}) = \frac{1}{8\pi}\left\{\frac{1}{4}\Delta - (\mathbf{J}\nabla')^2\right\}\int \frac{\Phi(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|}\, d\mathbf{r}'. \tag{6}$$

This function automatically satisfies the condition $\left[\frac{9}{4}\Delta - (\mathbf{J}\nabla)^2\right]\Phi_h = 0$. We shall again assume that we have an axially symmetric deformation and that the lower saddle corresponds to the states with the original symmetry corresponding to the band symmetry, i.e., with the momentum 3/2. This gives rise to two Kramers doublets of the Ψ states: with projections of the momentum $M = \pm 1/2$ and $\pm 3/2$. The $\Psi_{1/2}$ and $\Psi_{3/2}$ functions, which were dropped here, depend on two axially symmetric functions ϕ_1 and ϕ_2 that are defined by the condition $\delta J[\Psi] = 0$. Limiting ourselves to a one-parameter approximation analogous to that used above, we obtain

$$W_{1/2} \approx W_{3/2} \approx 473K^2/C^4 m_h^3. \tag{7}$$

Therefore, W in this case is determined by the mass m_h, but the numerical coefficient increases further.

Although the barrier height for $\Psi_{1/2}$ is the same as that for $\Psi_{3/2}$ in the approximation used by us, the shape of their Ψ^2 cloud [and hence the spatial distribution of the deformation $\epsilon(\mathbf{r}) \sim \Psi^2(\mathbf{r})$] is markedly different: the cloud is extended along the z asis in the states with $M = \pm 1/2$ and it is flattened and concentrated near the plane $z = 0$ in the states with $M = \pm 3/2$. The use of more flexible variational functions will presumably diminish both quantities $W_{1/2}$ and $W_{3/2}$ and destroy their equality, although they will apparently remain similar. This means that at temperatures $T \gtrsim |W_{1/2} - W_{3/2}|$ the relaxation proceeds through two channels to the different AL states which can be observed simultaneously (for example, in the hot-fluorescence spectra).

In conclusion, we note that the tunneling AL also proceeds through the states with a broken symmetry.

Thus, as m_l decreases, the barrier height W increases, although it preserves its order of magnitude which is determined by the mass m_h; at the same time, the J-T lattice deformation increases.

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[1)]This means that the maximum symmetry (axis + center of symmetry) is preserved, consistent with the elimination of triple degeneracy of the band.

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