Charge Centers and Small Polarons in the Molecular Cryocrystals

Victor A.Lykah [a,1], Eugenii S.Syrkin [b,2],

[a] *National Technical University -Kharkov Polytechnic Institute, Kharkov, 61002, Ukraine*
[b] *Institute for Low Temperature Physics and Engineering, Kharkov, 61103, Ukraine*

Abstract

The conditions of formation of the static polaron and quasipolaron states due to the rotational degrees of freedom in molecular cryocrystals are theoretically investigated. It is shown the two types of behavior are realized for the nearest to the carrier molecules in dependence on the parameter G (the ratio of amplitudes of the anisotropic parts of interaction energy of the molecule with the carrier electric field and the molecular field): free rotation or kicking of the molecules. The small polaron energy are evaluated for the cryocrystals H_2 and compared to the experimental data.

Key words: cryocrystal, rotation degrees of freedom, polaron, localization

The quantum molecular cryocrystals have new for polaron theory the rotational degrees of freedom [1], [2]. Last experiments dealing with electron and muon mobility in different cryocrystals show strong particle localization into a small polaron[3]. In the present paper the small polaron states of charged carrier (electron, hole, muon), localized on one molecule in oriental ordered solid ortho-H_2 phase is considered.

Hamiltonian of the system under consideration includes H_e the kinetic energy of carrier, H_l the energy of interaction between molecules, H_{el} the energy of carrier-lattice interaction. Let us represent intermolecular interaction in the solid H_2 in the following manner: $H_l = \sum(U_{Hi} - U_{Ha}(\theta))$, where U_{Hi} is isotropic part of interaction, U_{Ha} is amplitude of anisotropic one; sum is for different neighbors. The main anisotropic contribution gives electric quadrupol-quadrupol interaction [2]. Note, H_2 crystal with high concentration of ortho-hydrogen at T $\leq$ 2.9 K has FCC structure with molecular axes frozen along space diagonals ($\theta = 0$) of cubic cell (Pa3) [2]. We use the experimental value of the barrier for rotation only (7.49K in case of interaction with one molecule [2] and 89.4K for 12 neighbors). The carrier-lattice interaction $H_{el} = \sum W_{el}$ is sum for the neighbors of interaction of the charge with induced dipole moment and intrinsic quadruple moment Q of the molecule [4]. It can be written as sum of isotropic and anisotropic contributions:

$$W_{el} = V_i - V_a cos^2\Theta;$$
$$V_i = -\frac{\alpha_2 q^2}{2R^4} - \frac{Qq}{4R^3};\ V_a = \frac{(\alpha_1 - \alpha_2)q^2}{2R^4} - \frac{3Qq}{4R^3}. \quad (1)$$

Here components of the polarizability tensor are α_1 along and α_2 normal to molecule axe; $q = \pm e$ is charge of the carrier; R is distance between molecules, Θ is angle between $\mathbf{E}$ and molecular axe.

The main parameter of the considered problem: $G \equiv \frac{1}{g} = \frac{V_a}{U_a}$. Using crystal H_2 parameters ($\alpha_1 - \alpha_2 = 0.316A^3$, $\alpha_2 = 0.701A^3$, $Q = -0.6*10^{-26}CGS$, $R = 3.80A$ [2]) one can obtain $g = 0.113$ (positive q); g = - 0.165 (negative q). It means the main influence onto behavior of the nearest neighbors has the carrier electric field. The sign of V_a depends on the sign of q: for positive q (hole, muon) V_a is positive; for negative q (electron) V_a is negative. Therefore positive q yields equilibrium molecular orientation along $\mathbf{E}$; negative q

[1] Corresponding author. Present address:Inst. Low Temp. Phys. Eng., Lenin ave.,47, Kharkov, 61103 Ukraine. E-mail: lykah@ilt.kharkov.ua
[2] Present address: E-mail: syrkin@ilt.kharkov.ua

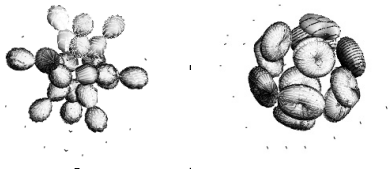

Fig. 1. The space dependence of the orientation energy of molecules. The maximum energy (zero level) is in the center of each molecule figure. Negative values of the energy are more remote from the center. (Left panel) positive q (hole, muon). (Right panel) negative q (electron).

yields the indifferent equilibrium state with molecular axe normal to **E** (see Fig.1). The last situation means the free rotation of the molecule is realized.

The Schrodinger equation for each molecular rigid rotator orientation in main approximation has axial symmetry. The wave function can be represented in form $\Psi(\theta,\phi) = \Theta(\theta) * \Phi(\phi)$ where $\Phi_m(\phi) = (2\pi)^{-1/2} exp(im\phi), m = 0, \pm 1, \pm 2, ..., \theta$ for each molecule is counted from polar axe oriented along **E**. Then for $\Theta(\theta)$ we obtain equation well known in special function theory [5] with rotational constant $B = \hbar^2/2J = 85.25$K of H_2 molecule [2]. We evaluate the energies as classic ground state value plus energy W_0 of the zero-point vibration:

$$\begin{aligned} W_{elp} &= -V_{ap} - V_{ip} + W_{0p}; \\ W_{eln} &= 0 - V_{in} + W_{0n}; \end{aligned} \tag{2}$$

where index p or n means positive or negative carrier. The different classic ground state leads in quantum case to the qualitatively different eigenfunctions and eigenvalues of the Schrodinger equation. Anyway classic relation $W_{elp} < W_{eln}$ (ground state of the positive carrier is deeper) is keeping in quantum case in spite of $W_{0p} \approx 2W_{0n} > 0$. The last draft relation is due to the fact of free rotation of the molecule around one local axe **E** in main approximation for negative carrier.

The polaron energy is:

$$W_{polq} = Z_1 W_{elq} + Z_2 W_{elq2} + W_q; \tag{3}$$

where index q means index p or n, $Z_1 = 12$, W_{elq} and $Z_2 = 6, W_{elq2}$ are the number and energy of the nearest and next to the nearest neighbors respectively, $W_q > 0$ is the change of eigenenergy of the ground state of particle in the autolocalization potential.

Calculations give the best localization conditions in the case of the heavy and positive muon. The localization condition for more light hole is worse. The localization condition for light and negative electron is on the edge of the small polaron existence and need more accurate investigation, the experimental data [3] show relatively low electron mobility (stronger localization) in the solid hydrogen.

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