Electron-Phonon Interaction as a Mechanism of Phase Transition in a Layered $CuInP_2S_6$ Crystal

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A $CuInP_2S_6$ crystal belongs to the class materials in which the order-disorder type phase transitions [1] take place. Some authors [2] relate the mechanism of such transitions to the cooperative Jahn-Teller effect. The theory of this effect described in literature [3] is based on the partially model approach. Namely the effect of vibronic interaction is considered inside the so-called Jahn-Teler's center (a unit cell), and next, an interaction between these centers is modeled based upon some empirical parameters. In this approach the real symmetry of crystal and, in consequence, its real one-electron band structure is neglected. As oppose to molecules, where in the vibronic process involves consideration of the degenerate or pseudodegenerate local electronic states, in crystals the energy spectrum E(***k***) over the whole Brillouin zone should be taken into account. This circumstance encourages the search of new approaches to solve the problem of the Jahn-Teller's effect in crystals. In the $CuInP_2S_6$ crystals, a spontaneous change in the Cu atom position along the hexagonal axis with respect to the six surrounding S atoms is accompanied by a phase transition of the order-disorder type. As a consequence, a change in symmetry from C_{2h}^5 (paraelectric phase) to C_s^4 (ferroelectric phase) without the change in the lattice periodicity occurs. A possible reason of this phase transition is considered to be the vibronic interaction (the cooperative Jahn-Teller's pseudoeffect).

In this work, a simulation of the hexagonal pra-structure of $CuInP_2S_6$ crystal by means of a slight change in the lattice parameters of the paraelectric phase is performed. Next, the *ab inito* band structure calculations of all $CuInP_2S_6$ phases accompanied by the group-theoretical studies enable to relate the Cu atom *d*-states with certain energy ranges of valence band, located near the energy bandgap. The procedure of constructing the potential energy matrix is generalized for the case of crystal and it is illustrated by the construction of the adiabatic potentials for Γ_5 - Γ_5 vibronic coupling for the pra- and paraelectric phases of the $CuInP_2S_6$ crystal. The structure of the obtained potentials is analyzed and some conclusions concerning their transformation during the phase transitions are drawn, together with the discussion on the appearance of the spontaneous polarization in this crystal.

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