Electron–Phonon Interaction as a Mechanism of Phase Transition in the CuInP$_2$S$_6$ Crystal

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Studies on the phases of CuInP$_2$S$_6$ crystal exhibiting phase transitions of the order-disorder type are performed. A possibility for the cooperative Jahn–Teller effect to occur in this crystal is analyzed. For this purpose, 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 $\Gamma_5 - \Gamma_5$ vibronic coupling for the proto- and paraelectric phases of CuInP$_2$S$_6$. The structure of the obtained potentials is analyzed together with the discussion on the appearance of spontaneous polarization in this crystal.

1. Introduction

It has been demonstrated in the literature (see e.g. [1–3]) that the interaction of electrons with the transverse optical phonons in a narrow band-gap semiconductor can cause an instability of the phonon mode and it can lead to the ferroelectric phase transition. This interaction is called the vibronic interaction. Similarly, the vibronic coupling is a mechanism of the ferroelectric order-disorder phase transition in wide band-gap crystals with Jahn–Teller's centers. However, in this case one deals with a cooperative Jahn–Teller effect, in contrast to the Jahn–Teller effect in molecules [4]. The interaction in wide band-gap crystals, like in narrow band-gap ones, is observed mainly between the nearby electron states, or degenerate states which form the top of the valence band. As a result, electrons from these states participating in the Jahn–Teller effect can exchange energy with the crystal lattice (phonons), provided that it is allowed by the selection rules. The electron states forming the valence band top should be therefore only partially filled. This condition can be fulfilled when the valence band top is formed by the d-states of Jahn–Teller's crystal centers. The layered CuInP$_2$S$_6$ crystals satisfy this condition. It has been shown [5] that the ferroelectric phase transition in CuInP$_2$S$_6$ crystals is of the order-disorder type and, that it is accompanied by the change of Cu atoms position in the unit cell which leads to the change in symmetry of the system, from C_{2h}^6 (para-phase) to C_s^4 (ferro-phase). The top of the crystal valence band is formed by d-states of Cu atoms, which play important role in this order-disorder transition. The crystal lattice parameters are not affected in this process. Copper atoms exhibit unfilled d-levels. Unoccupied nature of these states make an energy

interchange easier in narrow-gap semiconductors. Since the symmetry of CuInP$_2$S$_6$ is low (monoclinic system), merely the nearby lying d-bands formed from these levels can be the subject of studies and, correspondingly, the cooperative Jahn–Teller pseudoeffect [4].

The purpose of these studies is to investigate the origin of nearby lying bands and their evolution during the phase transition in CuInP$_2$S$_6$ crystals. In our study, based on the group theory, we elaborate a new method to construct the adiabatic potential and we take into account the full symmetry of the crystal. To our knowledge, such approach is used for the first time.

2. The model of CuInP$_2$S$_6$ protostructure and the construction of adiabatic potential

A single atomic layer of the CuInP$_2$S$_6$ crystal is composed of the octahedral sulfur framework in which Cu, In, and P–P atom pairs fill the octahedral voids [6]. A peculiarity of this layered crystal structure is the presence of three types of copper atoms sites which are partially occupied, i.e., (i) quasitrigonal Cu1, shifted from the centers of the octahedra, (ii) octahedral Cu2, located in the centers of the octahedra, and (iii) nearly tetrahedral Cu3, which penetrates into the interlayer space. The occupancy of these positions varies significantly with temperature [6]. Furthermore, there are two types of Cu1 positions: Cu^u which is shifted upward from the middle of the layer, and Cu^d, shifted downwards from it. At low temperatures ($T < 153$ K) copper atoms occupy fully positions Cu^u [5]. Upon heating the occupancy of Cu^u position decreases in favor of the Cu^d one. In the region of the phase transition from the ferroelectric to paraelectric phase (T$_c$ = 315 K) the positions Cu^u and Cu^d are filled with equal probability and the polarity of both copper sublattices disappears. This phase transition is accompanied by the space symmetry group change, within the monoclinic system, from C_s^4 (ferrophase) to C_{2h}^6 (paraphase).

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To investigate the evolution of nearby lying bands in $CuInP_2S_6$, we model first a protostructure of this crystal which is described by the D_{3d}^2 space symmetry group from the trigonal system with a hexagonal Bravais lattice. This is the symmetry group of the $CuInP_2Se_6$ crystal which is related to the $CuInP_2S_6$ one, and thus the Brillouin zones (BZs) that correspond to the hexagonal and base-centered monoclinic systems should be taken into account [7]. The basis vectors of the primitive base-centered lattice can be expressed by the basis vectors of the conventional unit cell as follows: $\boldsymbol{a}_1 = \boldsymbol{c}$, $\boldsymbol{a}_2 = (\boldsymbol{a}-\boldsymbol{b})/2$, $\boldsymbol{a}_3 = (\boldsymbol{a}+\boldsymbol{b})/2$. The symmetry group of para-phase is chosen in such a way that the twofold symmetry axis coincides with the $\boldsymbol{b}$ vector. The crystal lattice parameters of para-phase are as follows: $a = 6.0955$ Å, $b = 10.6230$ Å, $c = 13.6230$ Å, $\alpha = \beta = 107.1011°$ [8]. As can be seen, their values are close to those ones which are necessary to construct the basis vectors of the model crystal with hexagonal lattice. In our model hexagonal lattice crystal which represents the protostructure, the leading threefold axis is directed along $\boldsymbol{a}_1 = \boldsymbol{c}$ vector, while the angle between $\boldsymbol{a}_2$ and $\boldsymbol{a}_3$ vectors is close to 120°. By applying a small deformation one can transform the angles β (between vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_3$) and γ (between $\boldsymbol{a}_1$, $\boldsymbol{a}_2$) into the right ones. Hence, the $\boldsymbol{a}_1 = \boldsymbol{c}$ axis of the monoclinic crystal becomes the $\boldsymbol{c}$ hexagonal axis of the model crystal. There are two basis vectors in the plane that is perpendicular to $\boldsymbol{c}$ axis, and the angle between them is equal to 120°. Additionally, we change slightly the atomic positions in the para-phase of $CuInP_2S_6$, so as the model of crystal protostructure is obtained, with the symmetry described by the D_{3d}^2 space group. The coordinates of atoms in para- and ferroelectric phases of $CuInP_2S_6$ can be found in [5]. Next, we perform the DFT-based *ab initio* band structure calculations of all $CuInP_2S_6$ phases, based upon the above discussed crystal lattice parameters. Figure 1 shows a fragment of the band structures and the density of states functions of the proto- and para-phases of $CuInP_2S_6$ crystal.

As can be seen from Fig. 1 the valence band top of $CuInP_2S_6$ consists of a set of four nearby lying in energy bands (the so-called elementary energy bands), formed mainly by d-states of Cu. We have established the symmetry of these bands in the center of the BZ, which are described by the irreducible representations (IRs) of the wave vector group [9]. The following sequence of double degenerate states was obtained: $\Gamma_5(2)$, $\Gamma_6(2)$. The number in parentheses indicates the dimension of representation. Let us note that these representations can be induced from the IRs of the site symmetry group D_{3d} of the rays of the Wyckoff positions $d_1(1/3,2/3,1/4)$ and $d_2(2/3,1/3,1/4)$. These coordinates coincide with the localization of the Jahn–Teller center (Cu atoms). As was demonstrated in literature, the symmetry of the Wyckoff position determines the symmetry of the irreducible band representation, describing the elementary energy band [10, 11]. Hence, in order to determine the symmetry of the normal vibration (phonon) which is active
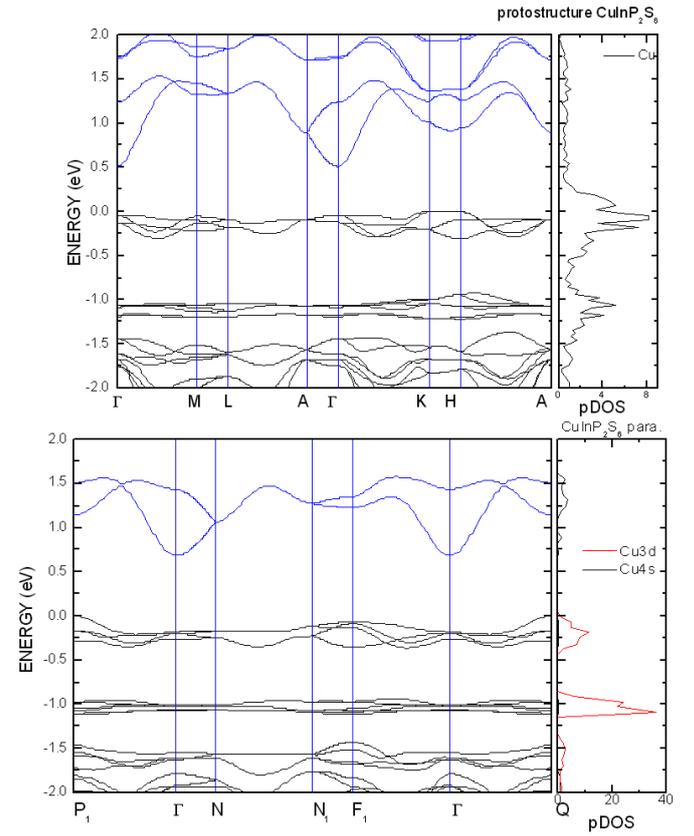

Fig. 1. Band structures and density of states of the $CuInP_2S_6$ protostructure and para-phase.

in the Jahn–Teller effect, it is enough to analyze a decomposition of the symmetrized square of the representation induced from the site symmetry group of the Wyckoff position $d(1/3,2/3,1/4)$ [12], i.e., the decomposition of characters of the wave vector group in $\boldsymbol{k} = 0$ which describe the degenerate (Γ_5, Γ_6) states. The decomposition of the symmetrized squares of representations Γ_5 and Γ_6 of the D_{3d}^2 group leads to the representations Γ_1 and Γ_5 of this group. Γ_1 corresponds to the normal vibration which does not change the configuration of cells in the crystal, and hence it must be discarded. Next, we construct the matrix of vibronic potential energy for the Γ_5 active normal mode by means of the Pikus' invariants method [7]. As a result, the following adiabatic potential with six minima is obtained:

$$\varepsilon_{1,2}(\rho,\varphi) = \frac{\omega^2\rho^4}{2} \pm [V\rho^4 + 2VW\rho^6\sin 6\varphi + W^2\rho^8]^{1/2}, (1)$$

which depends on the polar coordinates ρ and ϕ. This adiabatic potential provides a transition of the system from the protostructure both to the monoclinic centrosymmetric paraelectric and to the ferroelectric phases. A near energy distance between the Γ_5 and Γ_6 states in the energy spectrum of the $CuInP_2S_6$ protostructure leads to four Γ_{1M}, Γ_{2M}, Γ_{3M}, Γ_{4M} nearby energy states, at the transition to the monoclinic paraphase of the crystal (where M denotes an IR belonging to the monoclinic

C$_{2h}^6$ space group [8]). The adiabatic potential $\varepsilon(Q)$ takes in this case the form

$$\varepsilon(Q) = \frac{1}{2}Q^2 \pm \sqrt{\Delta^2 + V^2 Q^2}, \qquad (2)$$

where Q denotes a normal coordinate, while D and V are parameters of the linear vibronic interaction.

3. Discussion and conclusions

Due to the presence of pairs of states Γ_{1M} and Γ_{2M} as well as Γ_{3M} and Γ_{4M} with the opposite parity the Jahn–Teller pseudoeffect [5] can take place in the system. States with the opposite parity are connected by a phonon with odd parity. This leads to the appearance of the dipole moments in the CuInP$_2$S$_6$ crystal. As a consequence of the vibronic interaction of the quasi-degenerate electronic state with a polar phonon the levels nearby-in-energy become apart from one another, a connection between them is lost, and the adiabatic potential becomes a single minimum one. In the case of double minimum adiabatic potential related to the CuInP$_2$S$_6$ para-phase two possible atomic sites of Cu in the unit cell are filled with equal probability. When the transition to the single minimum adiabatic potential take place, the ordering of dipoles occurs with the appearance of spontaneous polarization. To summarize, it is worth to note that in classical papers (e.g. [4]) the cooperative Jahn–Teller pseudoeffect is explained as a result of ordering of local distortions of the dipole-unstable unit cells. This part of the theory is described with accounting of the site symmetry of the Jahn–Teller centers, while the interaction between these centers is modeled without taking into account the crystal symmetry. Meanwhile, in our approach we take into account the full crystal symmetry. Additionally, the method of invariants is used for the first time for the construction of the adiabatic potential.

References

[1] K.D. Tovstyuk, *Solid Materials*, Naukova Dumka, Kiev 1984, p. 263.
[2] N. Kristoffel, P. Konsin, *Phys. Status Solidi* **21**, K39 (1967).
[3] V.I. Litvinov, V.L. Volkov, V.K. Dugaev, *Sov. Phys.-Solid State Phys.* **22**, 32 (1980).
[4] I.B. Bersuker, B.G. Vekhter, *Sov. Phys.-Solid State Phys.* **9**, 2087 (1969).
[5] Yu.M. Vysochanskii, V.A. Stephanovich, A.A. Molnar, V.B. Cajipe, X. Bourdon, *Phys. Rev. B* **58**, 9119 (1998).
[6] V. Maisonneuve, V.B. Cajipe, A. Simon, R. Von Der Muhll, J. Ravez, *Phys. Rev. B* **56**, 10860 (1997).
[7] G.L. Bir, G.E. Pikus, *Symmetry and Strain-Induced Effect in Semiconductors*, Wiley, New York 1974, p. 484.
[8] V. Maisonneuve, M. Evain, C. Payen, V.B. Gajipe, P. Molinie, *J. Alloys Comp.* **218**, 157 (1995).
[9] O.V. Kovalev, *Representations of the Crystallographic Space Groups. Irreducible Representations. Induced Representations and Corepresentations*, Brigman Yung University, Provo 1993.
[10] J. Zak, *Phys. Rev. Lett.* **45**, 1025 (1980).
[11] J. Zak, *Phys. Rev. B* **25**, 1344 (1982).
[12] L.D. Landau, E.M. Lifshitz, *Quantum Mechanics (Non-relativistic Theory)*, Pergamon Press, Oxford 1977, p. 677.