Proc. of the XXVII Intern. School on Physics of Semiconducting Compounds, Jaszowiec 1998

THE In_4Se_3 CRYSTAL AS A THREE-DIMENSIONAL IMITATIVE MODEL OF PHENOMENA IN ONE-DIMENSIONAL CRYSTALS

D.M. BERCHA, M. SZNAJDER

Institute of Physics, Pedagogical University of Rzeszów
Rejtana 16a, 35-310 Rzeszów, Poland

A.I. BERCHA, L.YU. KHARKHALIS AND K. RUSHCHANSKII

Institute of Physics and Chemistry of Solid State, Uzhgorod State University, Ukraine

For three-dimensional charge carriers described by the dispersion law with quartic terms of the wave vector, the density of states function similar as in the one-dimensional case was determined. This similarity allows the Pekar and Dejgen condenson states in the continuum approximation to exist. The calculated phonon spectrum reveals optical vibrations of a very low frequency, which favours the electron–phonon interaction and creation of the condenson states.

PACS numbers: 71.20.Nr, 71.45.–d, 63.20.Dj, 63.20.Kr, 63.22.+m

1. Introduction

In the density of states function the dimension of space is revealed in the most direct way. For the first time it was found in the temperature dependence of the specific heat: $C_v \sim T^d$, where d is the dimension of space. With the change of the dimension from 3 to 1 the density of states function changes rapidly and assumes a form of an infinite asymmetric peak. In magnetic fields it may lead to significant changes of electron properties, because one-dimensional Landau subbands are created and hence the density of states takes the one-dimensional form. The peak-like density of states is one of the most important parameters which appear in theoretical models of superconductivity and in models of phase transitions induced by the electron–phonon interaction.

In our paper we will show that the similar asymmetric peak of the density of states appears for 3D space, in case when the dispersion law differs essentially from the parabolic form and contains additional quartic terms of the wave vector of significant magnitude. Such dispersion law was obtained for the In_4Se_3 crystal [1]. We will show that this peculiarity of the density of states allows the polarons (condensons), generalized for covalent crystals, to exist in 3D crystals in the deformation potential approximation. We will also present the calculation of the phonon spectrum for the In_4Se_3 crystal.

2. The model of the dispersion law and the condenson states in the In_4Se_3 crystal

The In_4Se_3 crystal belongs to the selenide group; it has the layered structure and is utilized in the solar energetics. The crystal consists of 28 atoms in the unit cell, crystallizes in the orthorhombic structure of space group P_{nnm}. The dimensions of the unit cell are: $a_1 = 15.297$ Å, $a_2 = 12.308$ Å, $a_3 = 4.085$ Å. The energy gap lies in the range from 0.6 to 0.8 eV. Our investigations based on the semi-empirical pseudopotential method showed that the direct energy gap is localized in the $\boldsymbol{k} = 0$ point of the Brillouin zone and equals 0.67 eV [2].

Let us consider the band structure of the In_4Se_3 crystal in the vicinity of the extremal point Γ. The detailed calculation of the energy spectrum near the centre of the Brillouin zone led us to the unusual dependence of the energy on the wave vector in k_x, k_y, k_z directions (see Fig. 2) [3]

$$E(\boldsymbol{k}) = -A_1k_x^2 - A_2k_y^2 - A_3k_z^2 + B_1k_x^4 + B_2k_y^4 + B_3k_z^4, \tag{1}$$

where k_x, k_y, k_z are dimensionless quantities. The energy eigenstates in the Γ point are non-degenerate due to their low symmetry (they are described by one-dimensional representations). The dispersion law is ellipsoidal in the vicinity of Γ point, in the approximation of one subband, which neglects fourth powers of the wave vector components. In our case, the values of parameters of Eq. (1) are significantly large: $A_1 = 5.7$ eV, $A_2 = 13.0$ eV, $A_3 = 3.1$ eV, $B_1 = 479.8$ eV, $B_2 = 888.0$ eV, $B_3 = 2957.0$ eV, therefore it is not correct to neglect the fourth power terms in the $E(\boldsymbol{k})$ decomposition.

In the following we will introduce the functional with a minimum, which will indicate the possibility of the condenson states to exist in the continuum approximation.

Let us begin from shortly reviewing some results of the phenomenological theory of condenson states for the quadratic dispersion law. The condenson is an electron, localized near the deformation potential well in the region of the crystal deformation induced by this electron itself [4]. Utilizing the quadratic dispersion law, the stable condenson state in the continuum approximation can be determined from the minimization of the functional

$$E(\mu) = c_1\mu^2 - c_2\mu^d, \tag{2}$$

where $c_1 = (\hbar^2/2m^*)\int|\nabla\Psi_0|^2\mathrm{d}^3r > 0$ and $c_2 = [3b^2/2(\lambda_{11}+\lambda_{12})]\int|\Psi_0|^4\mathrm{d}^3r > 0$. Here b is the deformation potential constant, λ_{11}, λ_{12} are the isotropic elastic moduli, μ is the variational parameter and d is the dimension of space. As follows from Eq. (2) the autolocalized electron states of a large radius do not exist in the continuum approximation in the 3D case, however they form in the 1D case. We should note that polarons in ionic crystals in the 3D case are described by the functional (2) with parameter $d = 1$.

Let us consider the interaction between the charge carriers and the acoustic phonons, taking into account the dispersion law (1), to solve the problem of formation of the condenson states. The variational procedure proposed by Dejgen and Pekar in Ref. [4], utilized by us [5], led to the following functional:

$$E(\mu) = -\pi(A_1\mu_1^2 + A_2\mu_2^2 + A_3\mu_3^2) + 3\pi^2(B_1\mu_1^4 + B_2\mu_2^4 + B_3\mu_3^4) - \widetilde{A}\mu_1\mu_2\mu_3, \tag{3}$$

where $\widetilde{A}$ is the electron–phonon interaction component. To analyse the formation of the condenson states we assumed the isotropic case

$$E(\mu) = -3\pi A\mu^2 + 9\pi^2 B\mu^4 - \widetilde{A}\mu^3. \tag{4}$$

Utilizing the average parameters of the In_4Se_3 crystal we calculated $\mu_{min} = 0.06$ and the radius of the condenson state to be approximately 100 Å, with binding energy $E_b \approx 4 \times 10^{-2}$ eV [5]. In Eq. (4) the exponent 3 is the dimension of 3D space.

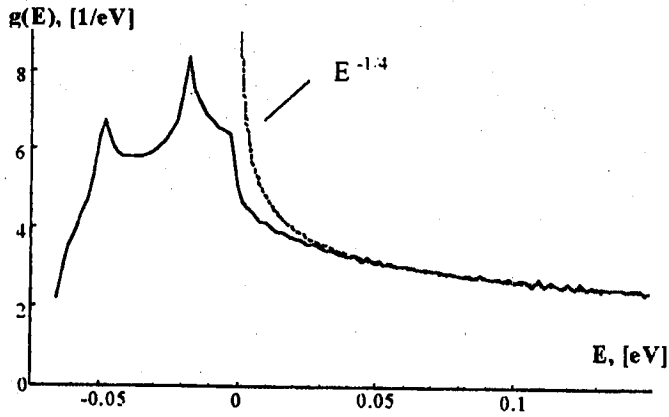

Fig. 1. Density of states function for the dispersion law (1).

For the dispersion law (1) the isoenergetic surfaces differ from these of usual quadratic dispersion law. Their topology described by Euler's characteristic is subjected to frequent changes. Figure 1 presents the density of states function for the dispersion law (1) with parameters of the In_4Se_3 crystal. This function consists of a peak with a distinct fine structure in a low energy interval. The presence of the peak testifies the increase in the effective mass and possibility of an instability of the system, if the Fermi level occurs in the vicinity of the peak. Such conditions contribute to creation of an inhomogeneous phase [5, 6]. Therefore, we see that the presence of the fourth power terms in the dispersion law leads to the imitation of "one-dimensionality" in a 3D system. As follows from Fig. 1 the shape of the right part of the density of states may be described by $E^{-1/4}$ function (for the 1D case the approximation function is $E^{-1/2}$). We obtained the minimum of the functional for the dispersion law (1) and, simultaneously, the similar shape of the density of states function.

3. The phonon spectrum of the In_4Se_3 crystal

The investigation of the phonon spectrum is important due to the large role of the electron–phonon interaction in the creation of the polaron states, and in particular, condenson states. The model we proposed is based on the simplest and the most common approximations concerning the force constants, which yet preserve peculiarities of the In_4Se_3 crystal formation.

The model of the central two-body interaction is useful to carry out the elementary calculations of the phonon spectrum, since the small number of unknown parameters is involved. In this model the force constants are described by the equation with two parameters A and B

$$\Phi_{\alpha\beta}(lk, l'k') = \frac{-R_\alpha R_\beta}{R^2}(A - B) - \delta_{\alpha\beta}B, \tag{5}$$

where $\boldsymbol{R} = r(l) + r(k) - r(l') - r(k')$ is the radius vector of interacting particles, l is the index of the cell, k is the index of the atom in the cell and R_α, R_β are components of the $\boldsymbol{R}$ vector. A and B are the radial and the tangential force constants, respectively. In our calculations we assumed that the dependence of the parameter A on the chemical kind of the atom and on the distance between interacting atoms is the following: $A_i = A_{\text{In-Se}} \exp[-\alpha_{\text{In-Se}}(r_i - r_1)]$, $i = 1 \ldots 10$, $A_i = A_{\text{In-In}} \exp[-\alpha_{\text{In-In}}(r_i - r_{11})]$, for $i = 11 \ldots 15$, where i is the index of the pair of interacting atoms. The distances between atoms are presented in Ref. [7]. The equilibrium conditions $\sum_{l,k} r_\alpha(l, kk')B(l, kk') = 0$ impose 14 restrictions on the 15 parameters B_i. We consider only first 10 In–Se bonds within the distance $|r(l, kk')| < 3.8$ Å and first 5 In–In bonds within the distance less than 3.9 Å. As a result, the dynamical matrix determining the normal vibrational frequencies depends on 5 unknown parameters: $A_{\text{In-Se}}$, $\alpha_{\text{In-Se}}$, $A_{\text{In-In}}$, $\alpha_{\text{In-In}}$, and B_{13}. To determine parameters of our model we utilized the known experimental data: elastic moduli and the range of frequencies observed in the long-wave infrared reflection spectra [8].

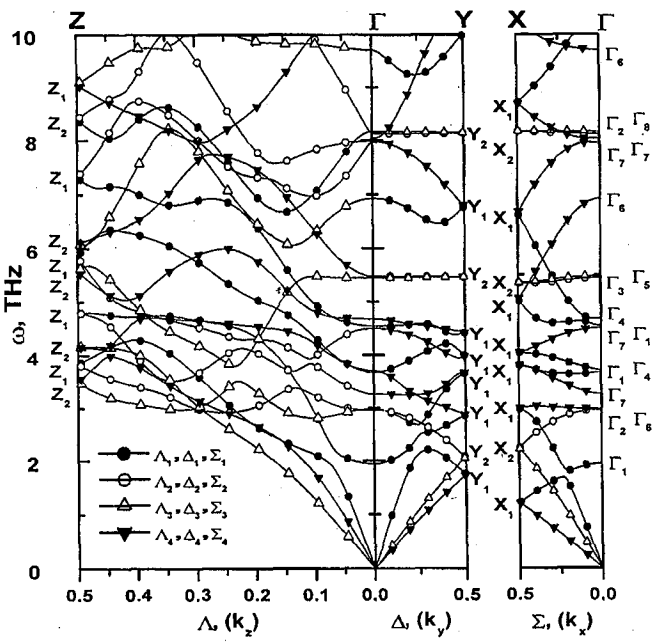

Fig. 2. Low-vibrations branches for the In_4Se_3 crystal.

Figure 2 presents the results of the low-frequency phonon spectrum calculation. Acoustic vibrations are repeatedly deformed by the interaction with the low-frequency optical ones.

The lowest low-frequency mode in the vicinity of the Γ point is characterised by an interesting dispersion law similar to the dispersion law for electrons and containing fourth power terms.

References

[1] M. Sznajder, D.M. Bercha, L.Yu. Kharkhalis, *Opto-Electr. Rev.* **5**, 123 (1997).

[2] D.M. Bercha, O.B. Mitin, I.M. Rarenko, L.Yu. Kharkhalis, A.I. Bercha, *Fiz. Tekh. Poluprovodn.* **28**, 1249 (1994).

[3] D.M. Bercha, O.B. Mitin, L.Yu. Kharkhalis, A.I. Bercha, *Fiz. Tverd. Tela* **37**, 3233 (1995).

[4] M.F. Dejgen, S.I. Pekar, *Zh. Exp. Teor. Fiz.* **21**, 803 (1951).

[5] D.M. Bercha, L.Yu. Kharkhalis, A.I. Bercha, M. Sznajder, *Phys. Status Solidi B* **203**, 427 (1997).

[6] V.A. Kochelap, V.N. Sokolov, *Zh. Eksp. Teor. Fiz.* **65**, 823 (1973).

[7] R. Walter, Ph.D. Thesis, University of Siegen, Siegen 1995, p. 274.

[8] V.J. Kuriachii, V.Yu. Bogachev, V.P. Mihalechenko, I.M. Stakhira, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **22**, 855 (1986).