
Band energy structure of K_2ZnCl_4 crystals under uniaxial pressures

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Abstract

We have studied the energy band structure of uniaxially compressed single crystals K_2ZnCl_4 . The smallest direct energy-gap for the stress-free crystal is 4.55 eV and corresponds to the Γ -point of the Brillouin zone. The pressure coefficients for the energy positions of the valence and conduction band states and the band gap are determined. The pressure-induced decrease in the band gap found by us correlates well with the increase of the refractive indices known from the earlier experiments.

Key words: energy band structure, refractive indices, uniaxial pressure, potassium tetrachlorozincate

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1. Introduction

Potassium tetrachlorozincate crystals, K_2ZnCl_4 , are typical representatives of one-dimensionally modulated incommensurate compounds of A_2BX_4 type. They undergo a sequence of phase transitions: a second-order one at $T_i = 553$ K from a paraelectric phase with the space group $Pnam$ ($Z = 4$) into incommensurate phase with the modulation wave vector directed along the c axis, a first-order one at 402 K from the incommensurate phase into a ferroelectric commensurate phase with the space group Pna_12 , and a low-temperature first-order one into a ferroelastic phase (the space group $P2_111$) [1–4].

Optical studies of K_2ZnCl_4 dealing with the temperature and spectral changes of the refractive indices n_i and the birefringence Δn_i have revealed clear anomalies at the phase transitions [5]. It has also been found that the uniaxial stresses do not change the temperature behaviour of Δn_i and n_i in its essence, i.e. the profiles of the curves $\Delta n_i(T)$ and $n_i(T)$ are reproducible in every phase. On the contrary, specific Δn_i and n_i values, the phase transition points, and the jumps $\delta \Delta n_i$ and δn_i at the phase transitions have been revealed to be substantially affected [6, 7].

In principle, *ab initio* calculations of the electronic and structural properties of solids permit one to obtain information on the crystal structure, lattice parameters, elastic constants (such as bulk elastic modulus and shear modulus), binding energies, phonon spectra, etc. All these quantities can be determined from the total energy of the system under investigation. Any in-depth investigations of the phase transitions in crystals by optical and luminescence techniques and analysis and interpretation of their optical spectra are impossible without understanding of the energy band structure. The band-structure calculations for the stress-free K_2ZnCl_4 crystals have already been reported in the literature [8, 9]. Basing on these *ab initio* studies of the band electronic structure, the density of states (DOS) and the optical functions of K_2ZnCl_4 crystal have been obtained for the simplest case of their orthorhombic space symmetry group $Pna2_1$ (twelve formula units).

This paper reports on theoretical *ab initio* calculations of the energy band structure for uniaxially compressed K_2ZnCl_4 single crystals in the ferroelectric phase. Besides, we have established quantitative correlation between the changes in the energy band structure and the pressure dependences of the refractive indices n_i .

2. Calculation techniques

The first-principles calculations of the energy band structure of K_2ZnCl_4 single crystals were performed within the framework of density functional theory (DFT) using plane-wave basis. The electron-ion interactions were described by Vanderbilt ultrasoft pseudopotentials [10], while the electron exchange and the correlation energies were calculated with the Perdew, Burke and Ernzerhof (PBE) formulation of generalized gradient approximation (GGA) [11]. The Kohn-Sham wave functions of valence electrons were expanded over a basis of plane waves, with the kinetic cut-off energy of 310 eV. The inequality $\Delta E < 1 \times 10^{-6}$ eV for the electron energy difference between the consequent iterations was selected as a criterion of convergence for the self-consistent procedure. Integrations over the Brillouin zone were performed using a $2 \times 4 \times 7$ grid of special k -points as suggested by Monkhorst and Pack [12]. In all the calculations on the stressed crystals, one of the lattice parameters was fixed at a specific value, and the optimal values of other lattice parameters were determined, which corresponded to each of the fixed values. The calculations involved optimisation of the atomic positions such that each component of the force acting on every atom should become less than 0.05 eV/Å.

3. Results and discussion

The lattice parameters of K_2ZnCl_4 calculated for the ferroelectric phase are listed in Table 1. The theoretical lattice parameters obtained here are in reasonable agreement with the experimental data available and the results of calculations performed in the work [13].

The properties of the ground state of our crystals have been calculated from the total energy, using the equation of state. Our calculations have been performed with the most frequently employed equation of state $E(V)$, the third-order Birch–Murnaghan equation [14]:

$$E(V) = E_0 + \frac{9}{8} B_0 V_0 \left(\left(\frac{V_0}{V} \right)^{2/3} - 1 \right)^2 \times \left(1 + \left(\frac{4 - B'}{2} \right) \left(1 - \left(\frac{V_0}{V} \right)^{2/3} \right) \right), \quad (1)$$

where E_0 is the minimum total energy, V_0 the equilibrium volume (i.e., the unit cell volume for which the total energy is minimal), B_0 the bulk modulus, and B' the derivative of the bulk modulus. As a result of calculations, we have obtained the following equilibrium parameters for the single crystals of K_2ZnCl_4 : the minimum total energy $E_0 = -58967.38$ eV, the equilibrium unit cell volume $V_0 = 2483.32 \text{ \AA}^3$, the hydrostatic bulk modulus $B_0 = 108.6$ GPa, and the first derivative of the hydrostatic bulk modulus $B'_0 = 6.34$.

Table 1. Theoretical and experimental structural parameters of K_2ZnCl_4 crystals in the ferroelectric phase (the unit cell parameters a, b, c are in \AA and the volume of unit cell V_0 in \AA^3).

| Parameter | a | b | c | V_0 |
|-------------------|--------|--------|-------|---------|
| Experimental data | 26.789 | 12.418 | 7.259 | 2414.82 |
| Theoretical data | 27.232 | 12.592 | 7.242 | 2483.32 |

Fig. 1 and Fig. 2 show the results of calculations of the energy band structure along the high-symmetry lines of the Brillouin zone obtained using the equilibrium lattice parameters as a result of optimization process. It can be seen from Fig. 1 and Fig. 2 that, on the whole, the two bands forming the band gap are characterised by relatively weak dispersion in the k space. An exception is the lines located in the centre of the Brillouin zone in the vicinity of the Γ -point. It is also evident that the uniaxial pressures lead to decrease in the band gap.

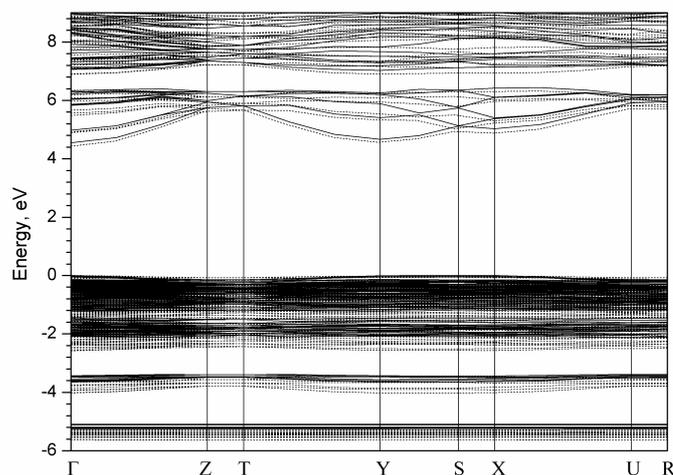


Fig. 1. Band energy dispersion $E(k)$ for K_2ZnCl_4 crystals in the ferroelectric phase: solid lines correspond to stress-free crystals and dashed ones to those stressed along the X direction.

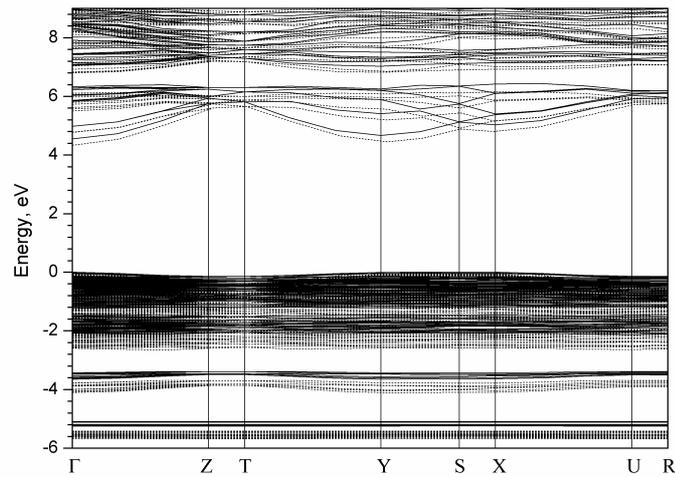
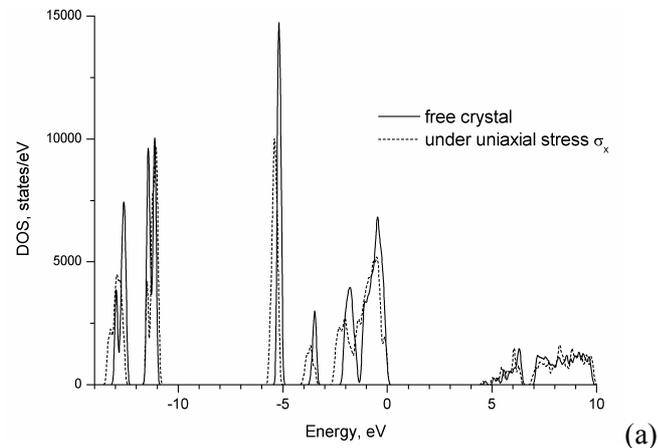
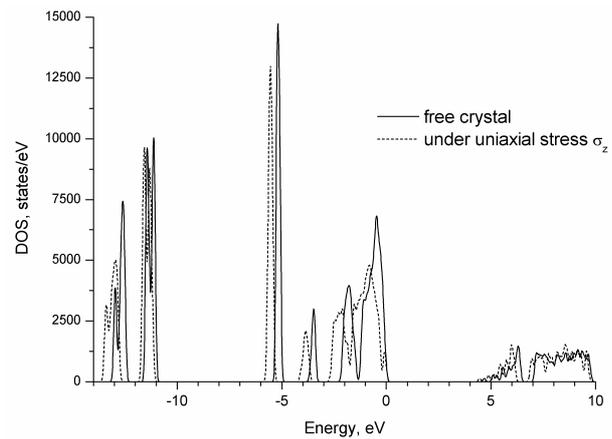


Fig. 2. Band energy dispersion $E(k)$ for K_2ZnCl_4 crystals in the ferroelectric phase: solid lines correspond to stress-free crystals and dashed ones to those stressed along the Z direction.



(a)



(b)

Fig. 3. Comparison of total DOS for stress-free K_2ZnCl_4 crystals in the ferroelectric phase and the same crystals stressed along the X (a) and Z (b) directions.

The top of the valence band is located at the Γ -point which is taken as zero energy (0 eV). The bottom of the conduction band is also located at the Γ -point, so that the minimum direct band gap is equal to 4.55 eV. We have $E_g = 4.33$ eV for the uniaxial pressure $\sigma_z \sim 10$ kbar and $E_g = 4.43$ eV for $\sigma_x \sim 10$ kbar. However, we remind that our values of the band gap are underestimated. Such a situation is typical of the majority of calculations performed in the framework of local-density formalism.

Fig. 3 shows the results of DOS calculations for the electronic states in the K_2ZnCl_4 crystals. The valence band of K_2ZnCl_4 consists of narrow energy bands separated by gaps. When analysing partial contributions of individual orbitals to the function of total DOS (Fig. 4) and partial contributions of individual bands to the electron density, we have determined genesis of the valence bands and the bottom of the conduction band of K_2ZnCl_4 crystals. The two top valence bands in the energy range of 0–2 eV originate mainly from the p -states of chlorine atoms. Only small pd -hybridisation of the states of chlorine and zinc atoms takes place here, whereas the hybridisation with the s -orbitals is very small. The uniaxial pressures σ_x and σ_z shift all the DOS maxima in the valence region towards the shortwave spectral region but do not change the degree of hybridisation. The next two narrow valence bands at –3.5 and –4.6 eV are also formed mainly by the states of chlorine and zinc atoms. The band at –3.5 eV is characterised by a high degree of sp -hybridisation. The band located at –4.6 eV is mainly formed by the d -states of zinc atoms and a small pd -hybridisation with chlorines takes place here as well. The fifth and the sixth valence bands at –11 and –13 eV are formed respectively by the states of potassium and chlorine atoms. They are characterised by very small hybridisation. Again, the uniaxial pressures do not change the corresponding degree of hybridisation.

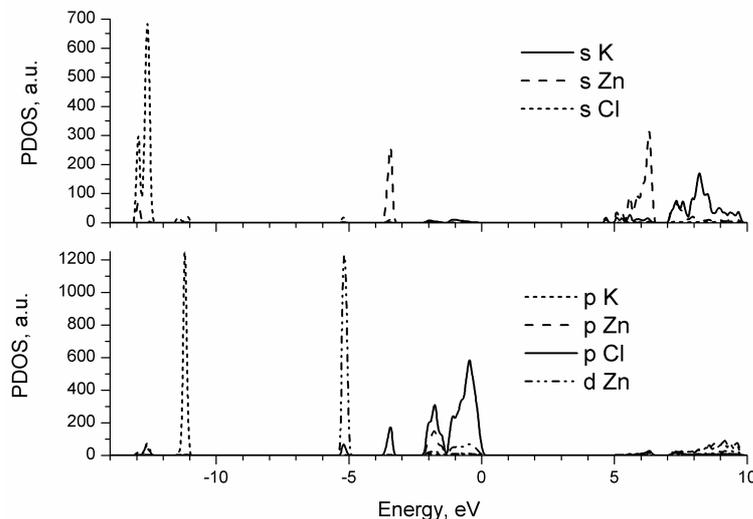


Fig. 4. Partial DOS of s -, p - and d -orbitals of K, Zn, and Cl atoms for stress-free K_2ZnCl_4 crystals in the ferroelectric phase.

The bottom of the conduction band originates mainly from the $ZnCl_4$ complexes and the second wide conduction band located above 6.7 eV is formed mainly by the p - and d -states of potassium atoms, with small hybridisation with the zinc and chlorine atoms.

Table 2 gathers the first pressure derivatives of the differences between the energies of the states in the upper valence and lower conduction bands, which are responsible for the transitions in the vicinity of the fundamental absorption edge.

Table 2. Baric coefficients of energy positions E of states in the valence (index v) and conduction (index c) bands with respect to the top of the valence band for the ferroelectric phase of K_2ZnCl_4 crystals.

| Parameter | Γ_v | Γ_c | Y_v | Y_c | S_v | S_c | X_v | X_c |
|--------------------------------------|------------|------------|-------|-------|-------|--------|-------|-------|
| E , eV | 0.0 | 4.55 | -0.01 | 4.67 | 5.03 | -0.005 | -0.04 | 5.17 |
| $dE/d\sigma_x$, 10^{-5} eV/bar | 0 | -1.21 | -0.24 | -1.04 | -0.13 | -1.58 | 0.17 | -1.57 |
| $dE/d\sigma_z$, 10^{-5} eV/bar | -0.08 | -2.21 | -0.04 | -2.17 | 0.02 | -2.27 | -0.55 | -2.09 |

The pressure coefficients of the minimum direct band gap between the states located at the Γ -point in the Brillouin zone are determined as $dE_g/d\sigma_x \sim -1.21 \times 10^{-5}$ eV bar $^{-1}$ and $dE_g/d\sigma_z \sim -2.13 \times 10^{-5}$ eV bar $^{-1}$. This indicates that the direct band gap in the crystalline structure of K_2ZnCl_4 decreases with increasing uniaxial pressure.

It should be noticed that the changes in the band gap of K_2ZnCl_4 single crystals occurring with pressure are in good agreement with the experimental pressure dependences of the refractive indices n_i . The latter have earlier been studied by analysing the effect of uniaxial mechanical pressure on the birefringence [5, 6]. It has been established that the refractive indices n_i of K_2ZnCl_4 increase with increasing pressure, with the average baric coefficient $dn/d\sigma \sim 2 \times 10^{-6}$ bar $^{-1}$ [6]. It is known [15] that the refractive indices n_i and the band gap E_g are related through the Moss relationship,

$$n^4 E_g = \text{const.} \quad (2)$$

After differentiating this expression with respect to the pressure σ , we obtain

$$\frac{dE_g}{d\sigma} = -\frac{4}{n} \frac{dn}{d\sigma} E_g. \quad (3)$$

It can be seen from Eq. (3) that decrease in the band gap E_g under pressure should be accompanied by increasing refractive indices n_i . Using the parameters $n_i \sim 1.55$, $E_g \sim 4.55$ eV, and $dn_i/d\sigma \sim 2 \times 10^{-6}$ bar $^{-1}$ obtained in the work [6], we find that the baric coefficient for the band gap is equal to $dE_g/d\sigma = 2.30 \times 10^{-5}$ eV bar $^{-1}$ on the average. This result agrees with our theoretical calculations for the baric shift of the band structure.

4. Conclusions

Hence, we have determined the energy band structure of K_2ZnCl_4 single crystals using the pseudopotential method and the Vanderbilt ultrasoft pseudopotentials. It is revealed that the minimum direct band gap is equal to 4.55 eV. The top of the valence band is formed by the p -states of chlorine atoms, with small pd -hybridisation of the states of chlorine and zinc atoms. The bottom of the conduction band mainly originates from the ZnCl_4 complexes. The second conduction band is due to the p - and d -states of potassium atoms, with small hybridisation with the states of zinc and chlorine atoms. The pressure coefficients of the energy positions E of the valence and conduction band states are determined. The pressure coefficient of the minimum direct band gap between the states located at the Γ -point of the Brillouin zone is equal to $1.90 \times 10^{-5} \text{ eV bar}^{-1}$. Finally, we have shown that the calculated decrease in the band gap E_g induced by the uniaxial pressure agrees well with the corresponding increase detected experimentally for the refractive indices ($dn_i/d\sigma \sim 10^{-6} \text{ bar}^{-1}$).

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***Анотація.** У роботі досліджено зонно-енергетичну структуру одновісно затиснутих монокристалів K_2ZnCl_4 . Найменша пряма енергетична щільність для незатиснутого кристала становить 4.55 eV і відповідає Γ -точці зони Бриллюена. Розраховано баричні коефіцієнти для енергетичних положень станів у валентній зоні та зоні провідності, а також для ширини забороненої зони E_g . Розрахована нами величина індукованого тисками звуження забороненої зони кількісно корелює зі зростанням показників заломлення, відомим з раніше виконаних експериментів*