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The band energy structure of $RbKSO_4$ crystals

O.V.Bovgyra, V.Yo.Stadnyk, A.V.Franiv, M.R.Tuzyak, O.Z.Chyzh

Franko Lviv National University, 8 Kyrylo and Mefodij Str., Lviv, 79005 Ukraine

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The energy band structure of mechanically free and compressed $RbKSO_4$ single crystals is investigated. It is established that the top of the valence band is located at the D point of the Brillouin zone [$k = (0.5, 0.5, 0)$], the bottom of the conduction band lies at the Γ point, and the minimum direct band gap E_g is equal to 5.80 eV. The bottom of the conduction band is predominantly formed by the K s, Li p, Rb s, and Rb p states hybridized with the S p and O p antibonding states. The pressure coefficients of the energy position of the valence and conduction band states and the band gap E_g are determined.

Key words: *uniaxial pressure, energy band, structure, valence band, conduction band*

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1. Introduction

Crystals of potassium rubidium sulfate RbKSO4 have a pseudohexagonal lattice structure similar to the structure of ammonium lithium sulfate $LiRbSO_4$ [1–3]. At room temperature they possess the mmm point symmetry with the unit cell parameters $a = 7.552$, $b = 5.805$ and $c = 10.116$ Å [4]. The first order phase transition (PT) at 116 K was observed. It is accompanied by jump-like changes of the refractive indices n_i and birefringence Δn_i. It was found that an application of uniaxial mechanical stresses along the principal crystallographic axes results in PT displacements towards both lower and higher temperatures [4].

Investigations of phase transitions in crystals by optical and luminescence spectroscopy, as well as the analysis and interpretation of the optical and luminescence spectra of the compounds studied, are impossible without a clear understanding of the energy band structure of the crystals. Band-structure calculations of $RbKSO_4$ crystals have not been performed so far.

This paper reports on the results of *ab initio* theoretical calculations of the energy band structure and the imaginary part ε_2 of the complex permittivity for mechanically free single crystals of the $RbKSO_4$ compound at room temperature.

2. Experiments

$RbKSO_4$ crystals were grown by a slow evaporation of an aqueous stoichiometric solution of K_2SO_4 and Rb_2SO_4 substances at stable temperature. The crystals grown were of a good optical quality and were of a pseudo-hexagonal shape. They comprised three well-defined blocks, the pseudo-orthorombic axes a of which were oriented at 120° one to another.

The first-principles calculations of the energy band structure of $RbKSO_4$ single crystals were performed using the nonlocal norm-conserving pseudopotential method. The computational technique was described in detail in [5,6]. The theoretical details and basic approximations can be summarized as follows.

1. The total electron energies of the single crystals were self-consistently calculated in the local-density functional approximation with the use of a plane-wave basis set.

2. The electron energies and electron densities of states were determined from the Kohn-Sham equations.

3. The ion potentials were represented by the Bachelet-Hamann-Schlüter norm-conserving pseudopotentials [7]. The correlation potential was determined according to the Ceperley-Alder relationship for $r_s = (3/4\pi\rho)^{1/3}$ and the Gell-Mann-Brueckner relationship in the high-density limit. The charge density distribution was calculated by the special-point method [8,9] with the charge damping algorithm.

4. Relaxation of ion positions was simulated by calculating the atomic forces and by determining the total stress of the unit cell for each crystal structure.

The calculations were carried out in a basis set consisting of 9196 plane waves (the cutoff kinetic energy was $E_{\mathrm{cut}} = \frac{1}{2}G^2_{\mathrm{max}} = 450$ eV). The self-consistent potential was determined using 12 iterative cycles.

3. Results and discussion

Figure 1 presents the results of the calculations of the energy band structure along the high-symmetry lines of the Brillouin zone. It can be seen in this figure that, on the whole, the two bands forming the band gap are characterized by a relatively weak dispersion in the k space. An exception is provided by the lines at the center of the Brillouin zone in the vicinity of the Γ point.

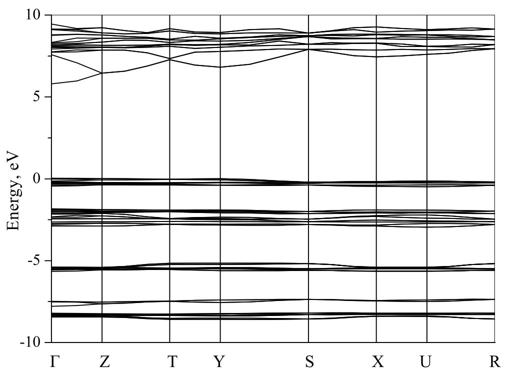
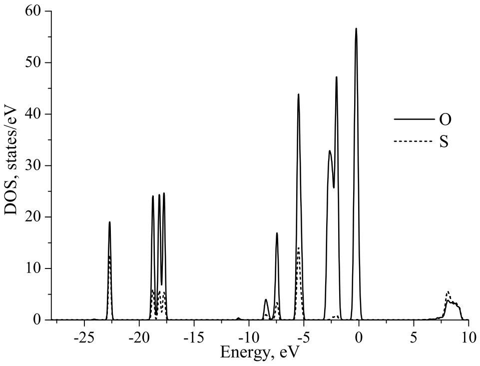


Figure 1. Energy band structure of $RbKSO_4$ crystals at room temperature.

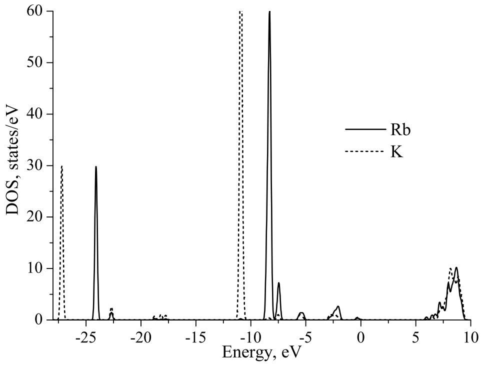
The top of the valence band is located at the D point [$k = (0.5, 0.5, 0)$], which is taken as zero energy (0 eV). The bottom of the conduction band is located at the Γ point ($E = 5.16$ eV). The minimum direct band gap (at the Γ point) is equal to 5.80 eV. However, it should be remembered that the given value of the band gap is underestimated. This situation is typical of the majority of the calculations performed within the framework of the local-density formalism.

The spectral dependences of the total density of states and the partial densities of states for atoms with the appropriate orbital moments are shown in figure 2. The valence band of the $RbKSO_4$ single crystal consists of narrow energy bands separated by band gaps. The density of states in the range of binding energies close to -27 eV is determined by the K $2s$ bound states. The valence bands in the energy range between -22.5 and -24.5 eV are predominantly formed by the Rb $5s$ and O $2p$ states with an admixture of the S $2p$ states. The bands of the O $2p$ states are separated into three wide subbands in the energy ranges from -1.5 to -3.5 eV, from -5 to -8 eV, and from -18 to -19 eV. In other ranges, the S $2p$ states are admixed to a large extent. The Rb p orbitals make the main contribution to the density of states in the range of -8.5 eV.

The top of the valence band is formed by the S p bounding orbitals. The bottom of the conduction band is predominantly formed by the K s, K p, Rb s, and Rb p states hybridized with the S p and O p antibonding states. In other words, the fundamental optical absorption is primarily associated with the intra-anion transitions.



(a)



(b)

Figure 2. Partial density of states of $RbKSO_4$ crystals.

The relation between the interband transitions and their optical response can be best analysed in terms of the spectral dependences of the imaginary part of the permittivity ϵ_2. However, it should be noted that optical spectra have often been identified using the calculated reduced densities of states.

Ab initio calculations of the electronic and structural properties of simple solids permit one to obtain information on the crystal structure, lattice parameters, elastic constants (such as the bulk elastic modulus and the shear modulus), binding energies, phonon spectra, etc. Moreover, the derivatives of the direct and indirect band gaps with respect to the pressure, as well as the x-ray structure factors, can also be obtained by analysing the electronic properties. All these quantities can be determined from the total energy of the system under investigation.

The properties of the ground state of a crystal can be calculated from the total energy with the use of the equation of state for $p = 0$ and $T = 0$; that is,

$$\left(\frac{\partial E}{\partial V}\right)_S = 0, \tag{1}$$

where S is the entropy. Our calculations were performed with the most frequently employed equation of state, namely, the third-order Birch-Murnaghan equation of state [9,10]

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

where E_0 is the minimum total energy and V_0 is the equilibrium volume. The equilibrium volume V_0 (the unit cell volume for which the total energy is minimum), the bulk modulus B_0, and the derivative of the bulk modulus B_0' with respect to the pressure were determined by least-squares fitting of the equation of state (2) to the calculated total energies.

When optimizing the structural parameters, the equilibrium unit cell volume was determined for fixed experimental values of the ratios a/b and c/b [4]. Then, the theoretically obtained unit cell volume was used to optimize the ratios of the lattice parameters a/b and c/b.

Table 2 presents the first and second pressure derivatives of the difference between the energies of the states of the upper (valence) and lower (conduction) bands, which are responsible for the optical transitions in the vicinity of the fundamental absorption edge.

As a result, we obtained the following equilibrium parameters of the $RbKSO_4$ single crystal: the minimum total energy $E_0 = -11\ 513.58$ eV, the equilibrium unit cell volume $V_0 = 442.69 \text{Å}^3$, the hydrostatic bulk modulus $B_0 = 98.6$ GPa, and the first derivative of the hydrostatic bulk modulus $B_0' = 4.45$.

Table 1. Eqilibrium structural parameters of $RbKSO_4$ single crystal (the unit cell parameters a, b, and c are given in Å, the unit cell volume, Å^3).

	a	b	c	a/b	c/b	V
Theory	7.549	5.801	10.109	1.301	1.742	442.69
Experiment	7.552	5.805	10.113	1.301	1.742	443.35

Table 2. Pressure coefficients of the energy position E of the valence (subscript ν) and conduction (subscipt c) band states with respect to the top of the valence band of $RbKSO_4$ crystals.

	Γ	Γ	Y_ν	Y_c	B_ν	B_c	D_c
E,eV	–0.09	5.0	–0.14	5.86	–0.08	5.83	6.86
$\mathrm{d}E/\mathrm{d}p$, meV/GPa	–58.2	–206.2	–49.9	–121.5	–96.9	–211.2	–146.1

The energy band structure of the $RbKSO_4$ single crystal was calculated from the theoretically obtained structural parameters. The energy band structure of the $RbKSO_4$ single crystal under compression was also calculated by simulating the relaxation of the ion positions.

The pressure coefficient of the minimum direct band gap between the states located at the Γ point in the Brillouin zone is determined to be $\mathrm{d}E_\mathrm{g}/\mathrm{d}p \sim -1.48 \cdot 10^{-5}$ eV/bar. This indicates that the direct band gap in the structure of the $RbKSO_4$ single crystal decreases with increasing pressure.

The equilibrium unit cell volume was determined for the fixed experiment values of ratios a/b and c/d by optimizing the structural parameters. Then, the unit cell volume obtained theoretically was used to optimize the ratios of lattice parameters a/b and c/d (table 1).

4. Conclusions

Thus, the energy band structure of $RbKSO_4$ single crystals was determined by the pseudopotential method with the use of the Bachelet-Hamann-Schlüter pseudo-potentials. It was revealed that the top of the valence band is located at the D point $[k = (0.5,\ 0.5,\ 0)]$ and the bottom of the conduction band lies at the Γ point ($E = 5.16$ eV) of the Brillouin zone. The minimum direct band gap is 5.80 eV. The top of the valence band is formed by the S p bounding orbitals. The bottom of the conduction band is predominantly formed by the K s, K p, Rb s, and Rb p states hybridized with the S p and O p antibonding states. The pressure coefficients of the energy position E of the valence and conduction band states were 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 $\sim 1.48 \cdot 10^{-5}$ eV/bar.

References

1. Aleksandrov K.S., Beznosikov B.V. Structural Phase Transitions in Crystals (A Family of Potassium-Sulfate). Nauka, Novosibirsk, 1993 (in Russian).
2. Steurer W., Wittmann H., Jagodzinski H. Acta Crystallogr., Sect. B: Struct. Sci., 1986, **42**, 11.
3. Kunishge H., Mashiyama H.J. J. Phys. Soc. Jpn.,1987, **56** (9), 3189.
4. Stadnyk V.Yo., Romanyuk N.A., Brezvin R.S. Kristallografiya, 2005, **50** (6), 1038 (in Russian).
5. Hasebe K., Asahi T. Phys. Rev. B: Condens. Matter, 1990, **41** (10), 6794.
6. Kolinko M.I. J. Phys.: Condens. Matter, 1994, **6** (1), 167.
7. Bachelet B., Hamann D.R., Schlüter M. Phys. Rev. B, 1982, **26** (8), 4199.
8. Chadi D.J., Cohen M.L. Phys. Rev. B: Solid State, 1973, **8** (5), 5747.
9. Cohen R.E., Gulseren O., Hemley R.J. Am. Mineral, 2000, **85**, 338.
10. Ravindran P., Subramoniam G., Asokamani R. Phys. Rev. B, 1996, **53** (3), 1129.

Зонно-енергетична структура кристалів $RbKSO_4$

О.В.Бовгира, В.Й.Стадник, А.В.Франів, М.Р.Тузяк, О.З.Чиж

Львівський національний університет ім.І.Франка, фізичний факультет,
79005 Львів, вул.Кирила і Мефодія 8

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Досліджено енергетичну структуру механічно вільних і затиснених одновісним тиском монокристалів $RbKSO_4$. Встановлено, що вершина валентної зони локалізована в точці D зони Бріллюена $[k = (0.5, 0.5, 0)]$, дно зони провідності знаходиться в точці Γ, а найменша ширина прямої забороненої щілини E_g рівна 5,80 еВ. Дно зони провідності сформовано в основному K s, Li p, Rb s і Rb p станами, гібридизованими з антизв'язуючими S p і O p станами. Визначені баричні коефіцієнти енергетичної зміни валентної зони, зони провідності та ширини забороненої зони E_g.

Ключові слова: *одновісний тиск, енергетичні зони, структура, валентна зона, зона провідності*

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