ELECTRONIC STRUCTURE OF THE β-MODIFICATION $LiNH_4SO_4$ CRYSTAL WITH A Cu^{2+} IMPURITY

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The work investigates the band-energy structure of the $LiNH_4SO_4$ crystal in β-modification with Cu^{2+} impurity. For this purpose, electronic structure modeling within the framework of density functional theory was used. Before calculations, geometric optimization of the crystal structure was carried out using the BFGS method. The features of the crystal structure of the $LiNH_4SO_4$ crystal in β-modification with Cu^{2+} impurity were clarified. It is shown that the addition of a copper impurity leads to the appearance of additional d-electron levels in the band gap of the crystal. These levels are located at an energy of 1.96 eV above the top of the valence band of the pure crystal. The location of the copper levels is close to that previously obtained for the K_2SO_4:Cu^{2+} crystal. It is shown that the levels of the copper d-states are higher than the levels for manganese atoms in the studied crystal.

Key words: lithium ammonium sulfate, dielectric, electronic structure, impurity, density of states.

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I. INTRODUCTION

Lithium ammonium sulfate, $LiNH_4SO_4$, is a well-known dielectric crystal belonging to the A_2BX_4 group of materials. This crystal is an interesting object of study due to its polytypism and polymorphism. It can be obtained by using the method of slow evaporation of the solvent from aqueous solutions at different constant temperatures [1]. Two modifications of the crystal are known. The α-modification of the crystal is formed during crystal growth under normal conditions at room temperature. The crystal belongs to the space group symmetry $Pca2_1$ with lattice parameters $a = 10.196$ Å, $b = 4.96$ Å, and $c = 17.100$ Å [2]. In the α-modification, coexistence of three polytypes within one sample is observed [3]. This modification undergoes a phase transition to the β-modification upon heating to $T = 462$ K, at which irreversible structural changes occur [4]. In the β-modification, the crystal belongs to the space symmetry group $Pc2_1n$ with lattice parameters $a = 9.140$ Å, $b = 5.280$ Å, and $c = 8.786$ Å [4]. In this modification, the crystal is at the temperature of liquid helium, undergoing phase transitions with decreasing temperature into the ferroelastic and low-temperature phases [5].

The study of the electrophysical, mechanical and optical properties of the pure $LiNH_4SO_4$ in β-modification is described in [6, 7]. Temperature-spectral-baric changes in refractive parameters were studied in [8, 9]. Theoretical studies of the band-energy structure of the $LiNH_4SO_4$ crystal are also discussed in [8, 9].

Important from the point of view of modifying the physical properties of the crystal is the study of the introduction of impurities into its structure. Changing the composition of the material through the introduction of impurities allows tuning its characteristics, particularly the structure, optical, mechanical, electrical properties, etc. Of particular interest is the introduction of impurities to obtain luminescent materials with different types of relaxation processes. In [10], the effect of impurities on the optical-spectral properties of the crystal with an admixture of Mn^{2+} is studied. The electronic structure of the $LiNH_4SO_4$ crystal with an admixture of Mn^{2+} was also studied in [10]. An important and relevant task is to clarify the effect of the Cu^{2+} impurity on the electronic structure of the crystal, which is related to its other properties. The proposed study aims to determine the effect of adding Cu^{2+} ions on the band-energy structure of the $LiNH_4SO_4$ crystal in the β-modification by performing self-consistent calculations from first principles using the density functional theory method.

II. CALCULATION METHODOLOGY

The calculations of the band energy structure and dielectric function were performed within the framework of density functional theory (DFT). For this purpose, the CASTEP program [11] was used, which is commonly used in the study of semiconductor and dielectric crystals. The initial data for the calculation is information about the crystal structure of the material. The calculations were performed by self-consistently solving the Kohn–Sham equation [12]. The calculations were performed for the ground state of the system using the Born–Oppenheimer approximation [13]. To describe the exchange-correlation interaction, the generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) parameterization was used [14]. The valence electrons were described using plane waves of the Bloch type. The electronic configuration of the valence electrons was used for the calculation: H $1s^1$;

Li $1s^2\,2s^1$; N $2s^2\,2p^3$; O $2s^2\,2p^4$; S $3s^2\,3p^4$; Cu $3d^{10}\,4s^1$. The limiting kinetic energy of plane waves was determined by the cutoff energy, which was $E_{\text{cut}} = 450$ eV. The core electrons were described by the ultrasoft Vanderbilt pseudopotential [15], which requires a low cutoff energy and describes most systems well. Integration was performed over the first Brillouin zone along the lines connecting the following points: $\Gamma \to F \to Q \to Z$. For this purpose, a $3 \times 2 \times 4$ k-grid was used, selected according to the Monkhorst–Pack scheme [16]. The crystal structure was optimized by using the BFGS method [17]. The convergence parameters used in the geometric optimization process were as follows: total energy convergence 5×10^{-6} eV/atom, maximum force 1×10^{-2} eV/Å, maximum pressure 3×10^{-2} GPa, and maximum displacement 3×10^{-4} Å. The impurity simulation was performed using the supercell method. A $2 \times 2 \times 1$ supercell was used in the calculation, which allowed us to simulate an impurity concentration of 0.6 at.%. The supercell was pre-optimized at fixed lattice parameter values.

III. RESULTS AND DISCUSSION

For calculations of the band-energy structure, the initial data were the experimental results of the study of the crystal structure by using X-ray diffraction methods carried out in [18]. The experimentally obtained crystallographic data for the $LiNH_4SO_4$ crystal in the β-modification with an impurity of Cu^{2+} are collected in Tables 1 and 2. These data were obtained at room temperature for the grown $LiNH_4SO_4$ crystal with an impurity of copper, and analyzed using the Rietveld method [18]. The $LiNH_4SO_4$:Cu^{2+} crystal crystallizes in the space group $Pna2_1$ (No. 33), the number of formula units per unit cell $Z = 4$ and the volume of the unit cell $V = 422.45(2)$ Å^3. If we compare the results for the crystal with an impurity of Cu with the parameters of the pure crystal, we can notice a decrease in the volume of the crystal's unit cell. This is due to the fact that the atomic radii of lithium ions (0.73 Å) are larger than those of copper (0.71 Å). Accordingly, in the crystal structure, Cu atoms with a smaller atomic radius replace part of the Li atoms in the structure, which leads to a decrease in the unit cell volume $V = 422.45(2)$ Å^3.

The crystal cell of β-$LiNH_4SO_4$ consists of NH_4^+ and SO_4^{2-} tetrahedra, which form the "skeleton" of the crystal. The corresponding tetrahedral groups are relatively isolated. Inside the SO_4 and NH_4 tetrahedra, the atoms are covalently bonded, while the complexes interact via an ionic type of chemical bond. In the cavities between these tetrahedra, there are Li^+ cations.

Parameter	Experiment	Optimization
a, Å	8.7736(2)	8.08755
b, Å	9.1242(3)	9.5105
c, Å	5.27716(16)	4.511355
V, Å^3	422.45(2)	346.998

Table 1. Experimental [18] and optimized parameters of the crystal lattice of β-$LiNH_4SO_4$

	Experiment			Optimization		
Atom	x/a	y/b	z/c	x/a	y/b	z/c
N	0.00010	0.28570	0.49580	0.00205	0.25470	0.49010
S	0.20198	0.08349	0.00070	0.21420	0.07951	0.00069
O1	0.03830	0.09560	0.00070	0.04010	0.09820	0.00890
O2	0.22940	0.71960	0.40840	0.24132	0.75670	0.39891
O3	0.25670	0.05410	0.26030	0.23971	0.06213	0.28458
O4	0.24980	0.46180	0.33560	0.25672	0.45241	0.37640
Li	0.32310	0.41290	0.00000	0.323400	0.411700	0.008400
H1	0.00600	0.17700	0.41570	0.007619	0.192406	0.390509
H2	0.03400	0.70500	0.11670	0.02800	0.69500	0.11432
H3	0.10200	0.34000	0.46270	0.11320	0.34000	0.46270
H4	0.42400	0.17100	0.40670	0.41800	0.16150	0.41270

Table 2. Experimental [18] and optimized atomic coordinates in the lattice of β-$LiNH_4SO_4$

Since the experimental coordinates of copper atoms are not available to us, to simulate the impurity crystal while maintaining the condition of electroneutrality of the crystal, two Li^+ atoms were replaced with Cu^{2+} ions. The supercell method was used to simulate the impurity (Fig. 1). A similar method is often used to simulate defects of various types in crystalline materials [19–21]. The generated supercell had a size of $2 \times 2 \times 1$. As a result, the concentration of the copper impurity was 0.6 at. %. Previously, the electronic structure of impurity crystals

of the A_2BX_4 group was studied for K_2SO_4 with an impurity of Cu^{2+}, and for $LiNH_4SO_4$ with an impurity of Mn^{2+} [18, 21]. Also, Tables 1 and 2 present the theoretical crystallographic parameters of the $LiNH_4SO_4$ crystal in β-modification, which show good agreement with the experimental results.

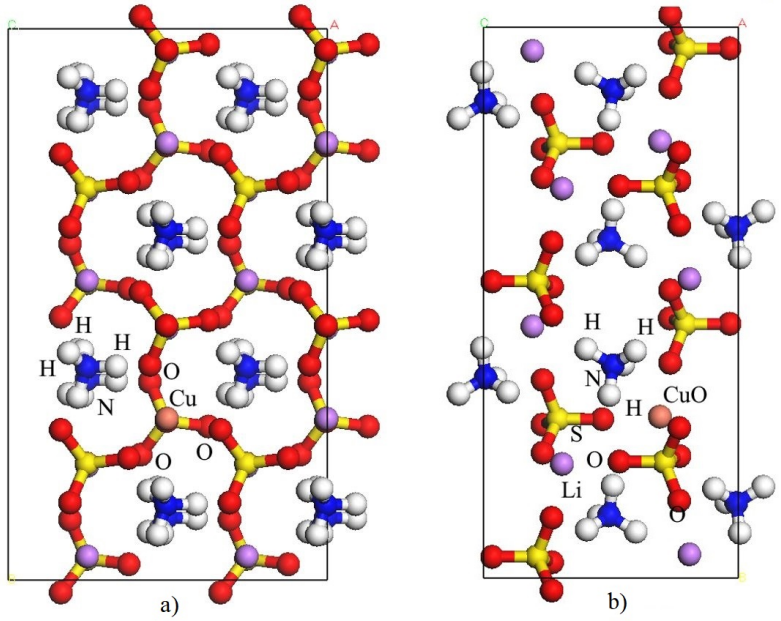

Fig. 1. Appearance of the supercell of the $LiNH_4SO_4$ crystal in β-modification with Cu^{2+} impurity: a) xy-plane; b) yz-plane

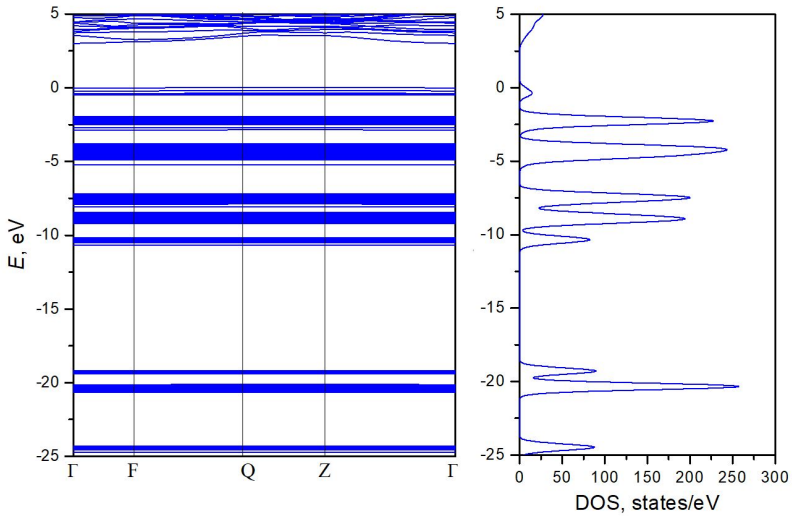

Fig. 2. Band-energy structure of the $LiNH_4SO_4$ crystal in β-modification with Cu^{2+} impurity. The coordinates of the high symmetry points are as follows: $\Gamma(0,0,0)$; $F(0,0.5,0)$; $Q(0,0.5,0.5)$; $Z(0,0,0.5)$

Figure 2,a shows the calculated band-energy structure of the $LiNH_4SO_4$ crystal in the β-modification with Cu^{2+} impurity. The $E(k)$ dependence was constructed along the lines connecting the following points of the first Brillouin zone: $\Gamma(0,0,0) \to F(0,0.5,0) \to Q(0,0.5,0.5) \to Z(0,0,0.5) \to \Gamma(0,0,0)$. In the figure, the energy mark 0 eV coincides with the highest levels of valence electrons. The Fermi level in calculations for the impurity crystal is also at the energy level of 0 eV. At the same time, the Fermi level of the pure crystal coincides with the top of the band of $2p$ states of oxygen. As can be seen from the figure, all levels of the valence band of the $LiNH_4SO_4$:Cu crystal reveal extremely weak dispersion. This feature is inherent in a number of materials with an ionic-covalent type of chemical bonding, in which the structure contains isolated structural complexes (for example, tetrahedral, octahedral complexes, etc.). In the $LiNH_4SO_4$ crystal, such complexes are cationic and anionic tetrahedra NH_4 and SO_4. A similar feature was previously obtained in other crystals of the A_2BX_4 group, such as K_2SO_4, $NaNH_4SO_4$, $LiNH_4SO_4$, $(NH_4)_2BeF_4$, $LiRbSO_4$, $RbNH_4SO_4$ etc. [9, 21–24]. The highest levels of the valence band originate from $2p$ states of the oxygen atoms, which correspond to the pure $LiNH_4SO_4$ crystal [25].

The structure of the valence states of the impurity crystal corresponds to the structure of the crystal without impurity and is formed by a set of narrow sublevels of the electronic level bindings. The two upper bands of the valence band of the impurity crystal, located at energies of approximately −2.5 and −4.6 eV, correspond to the oxygen states of the SO_4 tetrahedra. Near the 0 eV mark are the Cu^{2+} impurity levels. These levels correspond to the *d*-electrons of copper atoms located in the band gap of the pure $LiNH_4SO_4$ crystal. As can be seen from the figure, the *d*-states of copper are represented by a set of four sublevels. It is known that in the tetrahedral environment, the *d*-electron levels of copper are split into doubly degenerate *e* levels and triply degenerate t_2 levels. Thus, the splitting into four components indicates a low symmetry of the ligand field, which leads to a greater degree of degeneracy of the *d*-states of copper. As can be seen from the figure, the copper *d*-state levels are located in the band gap approximately 1.9 eV above the valence band top of the pure crystal. This energy agrees well with the location of the copper levels in the K_2SO_4 crystal, which are 1.1–1.8 eV above the valence band top of the crystal [21].

The conduction band has a larger dispersion of energy levels compared to the states of the valence band of the $LiNH_4SO_4$:Cu crystal. The bottom of the conduction band of the crystal is located in the center of the Brillouin zone, which indicates that the introduction of the Cu impurity does not lead to a change in the type of band gap. The calculated value of the band gap width is 4.95 eV. This value is slightly smaller than that obtained for the pure $LiNH_4SO_4$ crystal in [25]. Such a decrease in E_g can either be caused by the shortcomings of the DFT approach, which usually underestimates the value of the band gap width, or be the result of the influence of the impurity on the electronic subsystem of the crystal. To clarify the nature of the influence of the impurity on the band structure, additional studies of the absorption spectra in the ultraviolet region of the spectrum are necessary. Figure 2,b shows the full density of electronic states of the $LiNH_4SO_4$:Cu crystal in the β-modification with a copper impurity. The total density of states indicates the described characteristics of the band-energy structure of the crystal, which are expressed in the presence of narrow localized bands of the valence band, separated by forbidden energy gaps.

Figure 3 shows the partial density of electronic states calculated for the $LiNH_4SO_4$ crystal of β-modification with an impurity of Cu^{2+}. The states of lithium atoms are represented by the *s*-electron peak at energy −43 eV in the valence band and a weak peak in the conduction band. For the NH_4 structural complex, significant hybridization of the electronic *s*-states of hydrogen and *p*-states of nitrogen is observed. The main peak of the *p*-states of nitrogen is at −8 eV, and the *s*-states of nitrogen at −19.3 eV. In the conduction band, NH_4 complexes are represented by the *s*-states of hydrogen.

The top of the valence band of the β-$LiNH_4SO_4$:Cu^{2+} crystal, similar to the pure crystal [25], is formed by the *p*-states of oxygen, while at energy −20.3 eV, the *s*-electron levels of oxygen are hybridized with the *p*-states of sulfur. The copper impurity, as can be seen from the consideration of the band structure, contributes to the density of electronic states mainly for the levels located in the forbidden band. Here, the *d*-states of the impurity atom, which are split by the crystal field, form four closely spaced localized sublevels. The *p*-states of the Cu atoms are in the conduction band, and the *s*-electron levels form a local sublevel near the bottom of the conduction band. Since the bottom of the conduction band is formed by the *s*-states of copper, the insignificant decrease in the band gap of the $LiNH_4SO_4$:Cu crystal compared to the pure $LiNH_4SO_4$ crystal can be associated with a decrease in the bottom of the conduction band due to the *s*- and *p*-states of the impurity copper atoms.

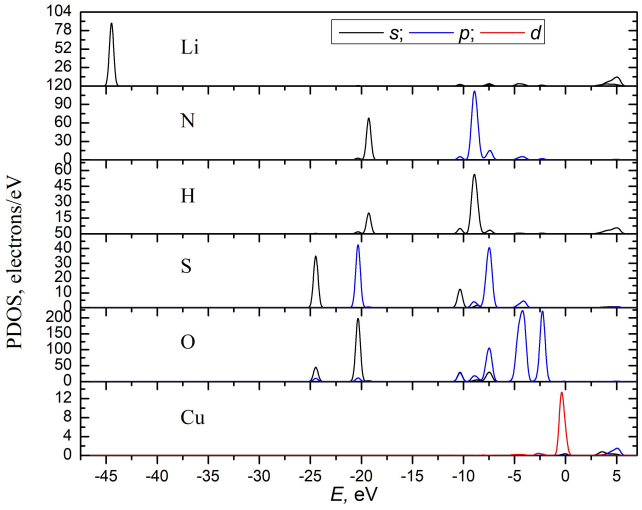

Fig. 3. Partial density of states of the $LiNH_4SO_4$ crystal in β-modification with Cu^{2+} impurity

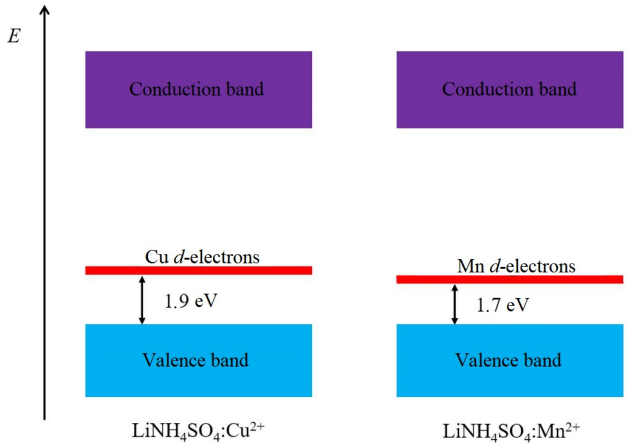

Fig. 4. Diagram of the location of electronic levels of copper and manganese impurities in the band gap of the $LiNH_4SO_4$ crystal in β-modification

Figure 4 shows a schematic diagram depicting the location of the *d*-electron levels of the Cu impurity and the Mn impurity in the $LiNH_4SO_4$ crystal. For comparison

with the impurity crystal containing manganese atoms, data from [10] was used. It is worth considering that the lack of experimental data on the value of the crystal band gap leaves open the question of the choice of the functional and the clarification of the exact positions of the electronic levels, in particular, the impurity. Thus, the position of the *d*-states of copper atoms requires a separate experimental study.

IV. CONCLUSIONS

Within the framework of the theoretical approach, a study of the band-energy structure of the $LiNH_4SO_4$ crystal in β-modification with an admixture of Cu^{2+} ions was carried out. For this purpose quantum-chemical calculations from first principles were carried out using the density functional theory. Crystallographic data from X-ray studies were used as input parameters for modeling. The experimental crystal structure was optimized using the BFGS method. The optimized crystal structure was close to the experimental one. A slight deviation of the crystal lattice parameters from the experimental values is observed, which is typical when using the GGA functional to describe the exchange-correlation interaction of electrons.

The supercell method was used to simulate the $LiNH_4SO_4$ crystal in the β-modification with an admixture of Cu^{2+} ions by replacing two Li^+ ions with one Cu^{2+} ion. It was shown that the calculated band-energy structure is similar to that obtained for the pure crystal. The valence band is formed by a set of narrow bands containing bundles of electronic states corresponding to individual chemical elements. These levels have weak dispersion. The conduction band levels are characterized by greater dispersion. The bottom of the conduction band is located in the center of the Brillouin zone (point Γ), which corresponds to the direct type of the band gap of the crystal. The calculated value of the band gap width is 4.95 eV. Inside the band gap, a narrow band of electronic levels is observed, formed by four sublevels of *d*-electrons of copper ions. This splitting of levels is due to the low symmetry of the ligand field surrounding the copper atoms in the crystal. These levels are located at energies 1.9 eV higher than the top of the valence band of the $LiNH_4SO_4$ crystal without impurities. It is shown that the levels of the copper *d*-states are located higher than the levels for manganese ions in the $LiNH_4SO_4$:Mn^{2+} compound studied earlier (located 1.7 eV above the top of the valence band).

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ЕЛЕКТРОННА БУДОВА КРИСТАЛА $LiNH_4SO_4$ У β-МОДИФІКАЦІЇ З ДОМІШКОЮ Cu^{2+}

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Літій амоній сульфат, $LiNH_4SO_4$, є відомим діелектричним кристалом, що належить до групи матеріалів A_2BX_4. Цей кристал — цікавий об'єкт дослідження через його політипізм і поліморфізм.

У цій статті в межах теоретичного підходу досліджено зонно-енергетичну структуру кристала $LiNH_4SO_4$ у β-модифікації з домішкою йонів Cu^{2+}. Для цього проведено квантово-хімічні розрахунки з перших принципів за допомогою теорії функціонала густини. Для моделювання як вхідні параметри використано кристалографічні дані Х-променевого дослідження. Експериментальну структуру кристала оптимізовували BFGS-методом. Оптимізована кристалічна структура виявилася близькою до експериментальної. Помітно незначне відхилення параметрів кристалічної ґратки кристала від експериментальних значень, що типово для використання GGA-функціонала в описі обмінно-кореляційної взаємодії електронів.

Методом суперкомірки проведено моделювання кристала $LiNH_4SO_4$ у β-модифікації з домішкою йонів Cu^{2+} заміною двох йонів Li^+ на один йон Cu^{2+}. Показано, що розрахована зонно-енергетична структура подібна до отриманої для чистого кристала. Валентна зона формується набором вузьких смуг, що містять в'язки електронних станів, які відповідають окремим хімічним елементам. Ці рівні мають слабку дисперсію. Рівні зони провідності характеризуються більшою дисперсією. Дно зони провідності розташоване в центрі зони Бріллюена (точка Г), що відповідає прямому типу забороненої зони кристала. Розрахункове значення ширини забороненої зони становить 4.95 еВ. Усередині забороненої зони спостерігаємо вузьку смугу електронних рівнів, утворену чотирма підрівнями d-електронів йонів міді. Таке розщеплення рівнів зумовлене низькою симетрією поля лігандів оточення атомів міді в кристалі. Ці рівні розташовані за енергій вищих від вершини валентної зони кристала $LiNH_4SO_4$ без домішок на 1.9 еВ. Показано, що рівні d-станів міді розташовані вище за рівні для йонів мангану сполуки $LiNH_4SO_4$:Mn^{2+}, дослідженої раніше (на 1.7 еВ вище від вершини валентної зони).

Ключові слова: літій-амоній сульфат, діелектрик, електронна структура, домішка, густина станів.