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## **Band electronic structure and dielectric functions of (C<sub>3</sub>N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>SbF<sub>5</sub> crystals**

**Key words:** crystals, first principles calculations, electronic structure, optical properties

### **1. Introduction**

The bis(imidazolium) pentafluoroantimonate(III) crystal (C<sub>3</sub>N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>SbF<sub>5</sub> is one of the known crystal of the general chemical formula A<sub>2</sub>SbX<sub>5</sub>, where A = NH<sub>4</sub><sup>+</sup> and C<sub>3</sub>N<sub>2</sub>H<sub>5</sub><sup>+</sup> and X = F and Cl. In the case of the (NH<sub>4</sub>)<sub>2</sub>SbF<sub>5</sub> a sequence of phase transition was found and ferroelastic properties below 292 K [1 - 5]. In the case of (C<sub>3</sub>N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>SbCl<sub>5</sub> the para- ferroelectric phase transition was revealed at 180 K [6]. The (C<sub>3</sub>N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>SbF<sub>5</sub> was found to exhibit first order structural phase transition from orthorhombic room temperature phase (space group *Pnma*) to monoclinic one (space group *P2<sub>1</sub>/c*) at about 220 K [7]. Structural studies revealed strong disorder of imdazolium cations at room temperature (phase I). Below phase transitions temperature (phase II) imidazolium cations are completely ordered. Disorder of cations is seen well in phase I, where enhanced values of permittivity (45 - 55) were observed along the a- and c-axes. At the phase transition temperature an abrupt decrease of permittivity connected with freezing of imdazolium cations was observed. Reorientational motion of imdazolium cations were confirmed and described in dielectric dispersion studies in the frequency range 10 kHz – 1 MHz [8]. Above room temperature the crystal reveals the properties, which permit to treat one as the ionic conductor [8].

Until now, no theoretical *ab initio* based studies of the materials properties of (C<sub>3</sub>N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>SbF<sub>5</sub> are known. Such investigations could however deliver information,

necessary for the better understanding of phase transition observed in  $(\text{C}_3\text{N}_2\text{H}_5)_2\text{SbF}_5$  on the basis of peculiarities of interatomic interactions in the crystal studied. We present results of the first principles calculations of electronic band structure of  $(\text{C}_3\text{N}_2\text{H}_5)_2\text{SbF}_5$  obtained for the first time.

## 2. Methods of investigations

First principles calculations of the band electronic structure and optical properties of  $(\text{C}_3\text{N}_2\text{H}_5)_2\text{SbF}_5$  were carried out using the CASTEP code (CAmbridge Serial Total Energy Package) [9] based on the density functional theory (DFT) and the plane-wave basis set. The generalized gradient approximation with the Perdew–Burke–Ernzerhof functional (GGA-PBE) for the exchange and correlation effects [10] together with ultrasoft pseudopotentials [11] were used for the calculations. A cutoff energy of 340 eV was assumed in the plane-wave basis set. During the self-consistent electronic minimization, the eigen-energy convergence tolerance was chosen to be  $2.4 \times 10^{-7}$  eV and the tolerance for the electronic total energy convergence during optimization was  $1.0 \times 10^{-5}$  eV. The corresponding maximum ionic force tolerance was  $3 \cdot 10^{-2}$  eV/Å and the maximum stress component tolerance was  $5 \cdot 10^{-2}$  GPa. Subsequently, the electronic properties, such as the band dispersion  $E(k)$ , partial density of states (PDOS), and dielectric functions  $\epsilon(E)$  were computed at the respective optimized geometry. In view of relatively large unit cell dimensions of the crystal studied ( $a = 7.50$  Å,  $b = 21.00$  Å,  $c = 7.56$  Å,  $\beta = 91^\circ 45'$  [7]) five  $k$ -points in the irreducible Brillouin zone were used (corresponds to the fine  $k$ -points setting), as well as a smearing of 0.1 eV. The calculations were performed at the ultrasoft and norm conserving pseudopotentials. The latter one was used for the calculations of phonons using density functional perturbation theory (DFPT).

For the proper reflection of the observable physical properties the considering of the van-der-Waals (vdW) and hydrogen types interactions in theoretical calculations could be indispensable. Therefore, the vdW interaction has been taken into account at presented *ab initio* calculations of  $(\text{C}_3\text{N}_2\text{H}_5)_2\text{SbF}_5$  using CASTEP package [12, 13].

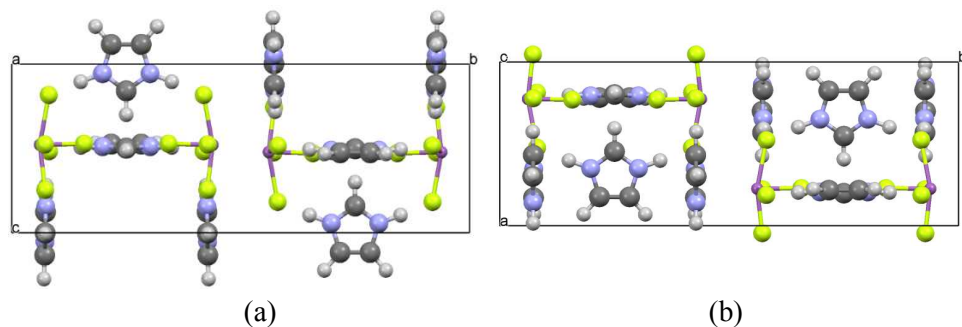
## 3. Results and discussion

The experimental [7] and computationally optimized crystal unit cell parameters of  $(\text{C}_3\text{N}_2\text{H}_5)_2\text{SbF}_5$  at the space group of symmetry  $P2_1/m$  (no. 11) are presented in Table 1.

**Table 1.** Unit cell parameters of  $(C_3N_2H_5)_2SbF_5$  crystal at the space group of symmetry  $P2_1/m$ 

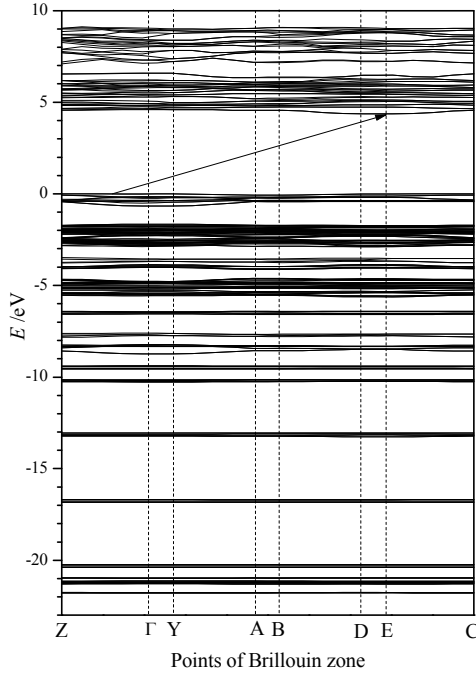
Unit cell parameters Source	$a / \text{\AA}$	$b / \text{\AA}$	$c / \text{\AA}$	$\beta$ /degree	$V / \text{\AA}^3$
Experiment [7] at $T = 85 \text{ K}$	7.50	21.0	7.56	91.45	1190
Calculations without vdW interactions	7.99	25.6	8.10	97.1	1644
Calculations with vdW interactions	7.58	20.9	7.62	92.4	1207

The vdW interaction of the Grimme's form has been taken into account at calculations using CASTEP code. In the case without taking into account the vdW interaction, the optimized structure of the crystal was obtained after 88 iterations, whereas, in case with taking into account the vdW interaction, the necessary number of iterations steps was almost twice smaller (45). The structural data obtained (Table 1) indicate that the consideration of vdW interaction in the *ab initio* structure optimization is rather indispensable to obtain reliable results for  $(C_3N_2H_5)_2SbF_5$ , that was observed also at studies of similar molecular type crystals [14]. Two views of  $(C_3N_2H_5)_2SbF_5$  structure are presented in figure 1, which show clear difference between cuts, perpendicular to  $a$ - and  $c$ -axes.

**Figure 1.** View of the optimized crystal structure of monoclinic  $(C_3N_2H_5)_2SbF_5$  along  $a$ -axis (a) and  $c$ -axis (b) (space group no. 11). Hydrogen - white, carbon - grey, nitrogen - blue, fluorine - green, antimony - violet.

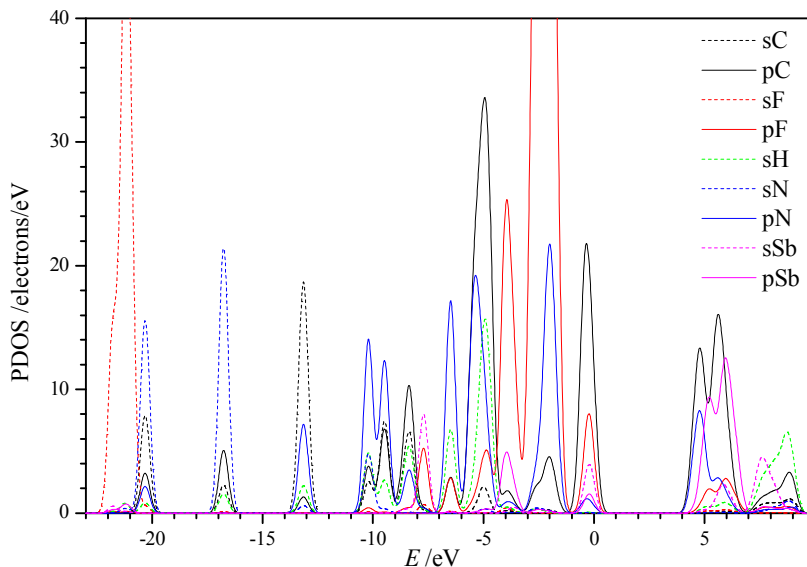
Band electronic structure of  $(C_3N_2H_5)_2SbF_5$  consists of a number of narrow valence bands that indicates low 'band energy - wave vector' dispersion  $E(K)$  (Fig. 2). The

corresponding valence - to - conduction band gap  $E_g = 4.362$  eV is found to be indirect, taking place between  $Z\Gamma$  and E points of Brillouin zone (Fig. 2).



**Figure 2.** Band structure of  $(C_3N_2H_5)_2SbF_5$  at monoclinic symmetry group no. 11. Arrow indicates the electronic transition from the highest valence to the lowest conduction band.

The partial density of electronic states (PDOS) of  $(C_3N_2H_5)_2SbF_5$  consists of 14 narrow valence bands of the width 1 – 2 eV (Fig. 3). On the other hand, the degree of hybridization of these bands is relatively high. These narrow bands and their clear hybridization are the main characteristic features of the electronic structure of the crystal.



**Figure 3.** Partial density of electronic states of  $(C_3N_2H_5)_2SbF_5$  at the monoclinic symmetry group no. 11 for all chemical elements (H, C, N, F, Sb) and different orbital moments ( $s, p$ ).

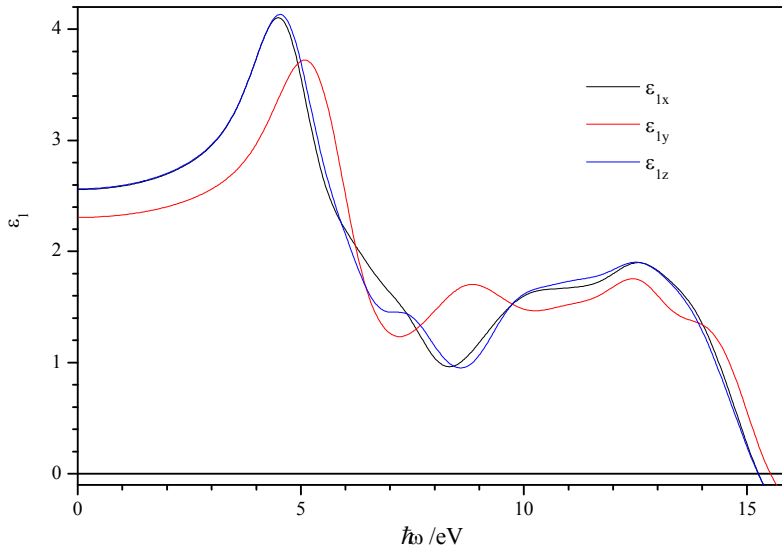
The calculated dielectric function  $\epsilon(\eta\omega)$  in the range of electronic excitations of  $(C_3N_2H_5)_2SbF_5$  reveals significant anisotropy (Figs. 4, 5). Namely, the real part of dielectric function  $\epsilon_1$  polarized along the  $b$ -axis ( $\epsilon_{1y}$ ) is clearly smaller than the components  $\epsilon_{1x}$  and  $\epsilon_{1z}$  polarized along the perpendicular axes  $a$  and  $c$  (Fig. 4). Also, the low photon energy shoulder of the imaginary part of dielectric function  $\epsilon_{2y}(\eta\omega)$  is shifted near 1 eV into the higher photon energies  $\hbar\omega$  (Fig. 5). Thus,  $(C_3N_2H_5)_2SbF_5$  reveals peculiarities of the layer structure crystal. In the ranges of the crystal unit cell close to the fractional coordinates  $y=0$  and  $y=0.5$ , the smallest distances between the negative fluorine ions of the  $SbF_5$  group and the positive carbon ions of pentagon of the  $C_3N_2H_5$  group is equal to 3.26 Å, that is too big to form the relatively strong bond. The total electronic charges of atoms in the crystal  $(C_3N_2H_5)_2SbF_5$  are presented in Table 2.

**Table 2.** The total electronic charges of atoms in the crystal  $(C_3N_2H_5)_2SbF_5$  obtained using CASTEP code

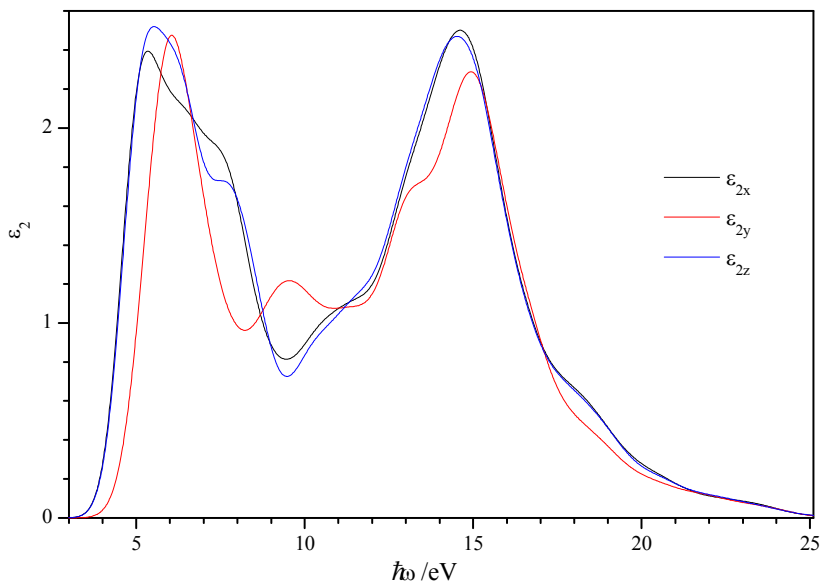
Atom	H	C	N	F	Sb
Charge /e	0.57 - 0.71	3.92 - 4.17	5.47	7.64 - 7.67	2.17

The interatomic distances Sb - F are equal to 2.29 Å (within one SbF<sub>5</sub> group) and 3.53 Å (for two neighboring SbF<sub>5</sub> groups). Because of the absence of more shorter interatomic distances between C<sub>3</sub>N<sub>2</sub>H<sub>5</sub> and SbF<sub>5</sub> groups in this region, the value 3.26 Å may be regarded as the interlayer distance. In the ranges [0 - 0.5] and [0.5 - 1.0] of the unit cell *y*-coordinates, the shortest interatomic distances F - H are changed between 1.61 Å and 2.35 Å. So, here the interatomic bonds between the groups C<sub>3</sub>N<sub>2</sub>H<sub>5</sub> and SbF<sub>5</sub> are stronger. The above remarks on the interatomic distances and corresponding bonding in the crystal (C<sub>3</sub>N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>SbF<sub>5</sub> permit to regard the half of the unit cell dimension  $b/2 \approx 10$  Å as the thickness of the layers mentioned.

When taking into account the above remarks on the crystal structure of (C<sub>3</sub>N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>SbF<sub>5</sub>, the characteristic features of PDOS of the crystal (Fig. 3), become understandable: (1) relatively large number of PDOS valence bands are caused by small interatomic interaction in the *b*-direction of the crystal, and (2) clear hybridization of the electronic states within separate PDOS band takes place due to the relatively high interatomic interaction within one structural *b*-layer of the crystal.

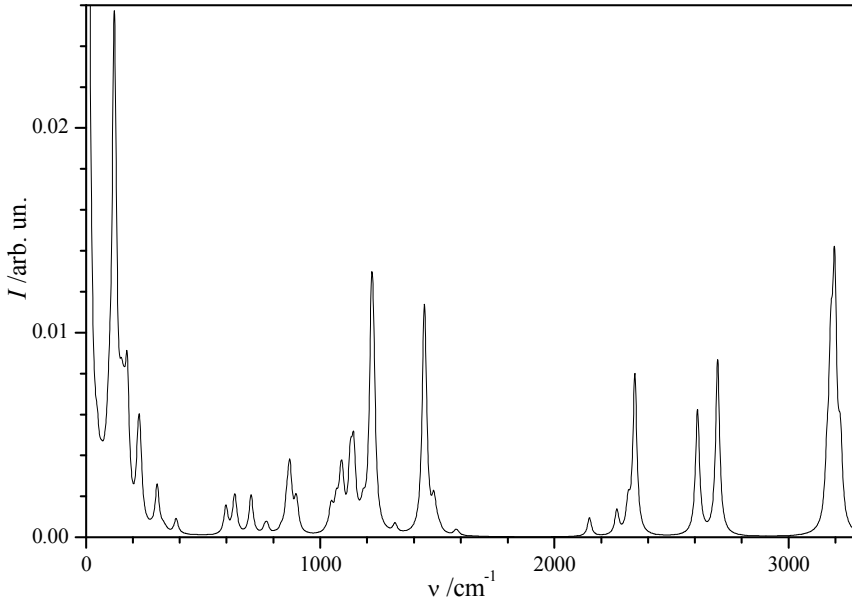


**Figure 4.** The Cartesian components  $\epsilon_{1x}$ ,  $\epsilon_{1y}$ , and  $\epsilon_{1z}$  of the real part of dielectric function  $\epsilon_1$  versus photon energy  $\hbar\omega$  for (C<sub>3</sub>N<sub>2</sub>H<sub>5</sub>)<sub>2</sub>SbF<sub>5</sub> at the monoclinic symmetry group no. 11.



**Figure 5.** The Cartesian components  $\epsilon_{2x}$ ,  $\epsilon_{2y}$ , and  $\epsilon_{2z}$  of the imaginary part of dielectric function  $\epsilon_2$  versus photon energy  $\hbar\omega$  for  $(C_3N_2H_5)_2SbF_5$  at the monoclinic symmetry group no. 11.

The vibration spectrum of  $(C_3N_2H_5)_2SbF_5$  has been calculated also using the CASTEP code of the Materials Studio 8.0 package [9] in the frequency range of  $0\text{ cm}^{-1}$  -  $3300\text{ cm}^{-1}$ . In the wavenumber range of  $1000\text{ cm}^{-1}$  -  $3300\text{ cm}^{-1}$ , the calculated partial DOS is associated mainly with the vibrations of H – C and H – N bonds. The calculated Raman spectrum of  $(C_3N_2H_5)_2SbF_5$  is presented in figure 6. Unfortunately, we have no possibility to compare the Raman spectrum obtained with the corresponding experimental data because of the absent of the reference experimental studies for  $(C_3N_2H_5)_2SbF_5$ .



**Figure 6.** Raman spectrum of  $(\text{C}_3\text{N}_2\text{H}_5)_2\text{SbF}_5$  at the space group of symmetry no. 11 computed in the framework of the DFPT using the CASTEP code of Materials Studio 8.0 package.

## Conclusions

1. The layer-type crystal structure of  $(\text{C}_3\text{N}_2\text{H}_5)_2\text{SbF}_5$  at the monoclinic symmetry (space group no. 11) has been revealed clearly in the characteristics of band electronic structure and optical functions of the crystal: (1) relatively large number of PDOS valence bands are caused by small interatomic interaction in the  $b$ -direction of the crystal; (2) clear hybridization of the electronic states within separate PDOS band takes place due to the relatively high interatomic interaction within one structural  $b$ -layer of the crystal.
2. The crystals  $(\text{C}_3\text{N}_2\text{H}_5)_2\text{SbF}_5$  are characterized by the relatively large anisotropy of the real part of dielectric function  $\epsilon_{li}$  ( $i = x, y, z$ ) due to the value  $\epsilon_{ly}$ , which is smaller than the values  $\epsilon_{lx}$  and  $\epsilon_{lz}$  by 0.3. The corresponding maximum birefringence  $\Delta n_{xy} \approx \Delta n_{zy} = 0.1$  is also relatively large, that makes this crystal perspective for practical use as an active material for the birefringence based optical polarizers.



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## Abstract

Structural and electronic properties of the ferroelastic crystal  $(C_3N_2H_5)_2SbF_5$  of the molecular type were studied by *ab initio* methods in the framework of the density functional theory. Band electronic structure, density of electronic states and dielectric functions in the range of valence electrons excitations of the crystal in the monoclinic phase (space group no. 11) have been obtained using the plane waves, ultrasoft pseudopotentials and van-der-Waals corrections. The electronic values obtained are discussed from the viewpoint of the layer-type crystal structure of  $(C_3N_2H_5)_2SbF_5$ .

## Streszczenie

Strukturalne i elektronowe właściwości ferroelektrycznego kryształu  $(\text{C}_3\text{N}_2\text{H}_5)_2\text{SbF}_5$  typu molekularnego zostały obliczone w ramach teorii funkcjonału gęstości (DFT) z wykorzystaniem odpowiedniej metody z pierwszych zasad (*ab initio*). Pasmowa struktura elektronowa, gęstość stanów elektronowych i funkcje dielektryczne w zakresie wzbudzenia elektronów walencyjnych kryształu zostały obliczone dla strukturalnej fazy jednoskośnej (grupa przestrzenna no. 11) z wykorzystaniem płaskich fal, super pseudopotencjałów miękkich i uwzględnienia poprawek na oddziaływania międzyatomowe typu van-der-Waalsa. Otrzymane wielkości elektronowe zostały omówione pod kątem warstwowej struktury krystalicznej  $(\text{C}_3\text{N}_2\text{H}_5)_2\text{SbF}_5$ .

**Słowa kluczowe:** kryształy, obliczenia z pierwszych zasad, struktura elektronowa, właściwości optyczne