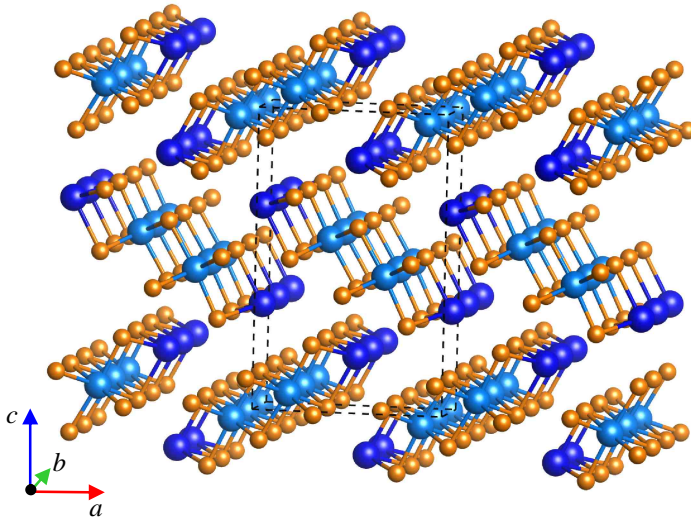


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 e-mail: crystal\_lab457@yahoo.com

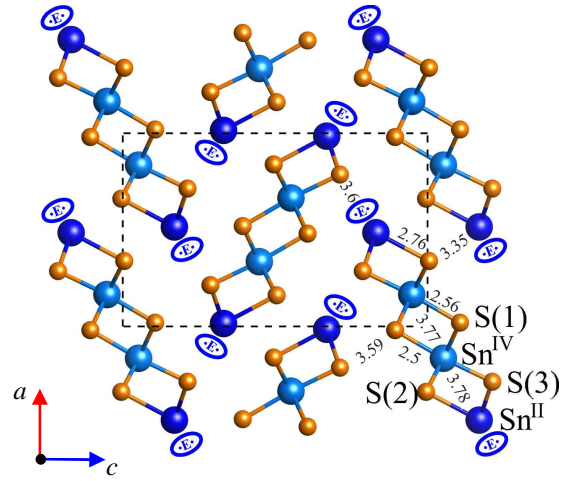
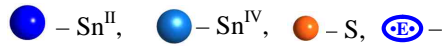
### Sn<sub>2</sub>S<sub>3</sub>

Sn<sub>2</sub>S<sub>3</sub>; ...  
 Sn<sub>2</sub>S<sub>3</sub> ...  
 $E_{gi} = 0.53$  ...  
 S3p- ...  
 S-Sn ...  
 Sn<sub>2</sub>S<sub>3</sub> ...  
 Sn-S ...  
 SnS, SnS<sub>2</sub>, ...  
**1.** ...  
 Sn<sub>2</sub>S<sub>3</sub> ...  
 β-, γ- δ- ...  
 [2]. ...  
 (Sn<sub>2</sub>S<sub>3</sub>) ...  
 [3], ...  
 [4, 5], ...  
 [6], ...  
 Sn<sub>2</sub>S<sub>3</sub> [7]. ...  
 Sn<sub>2</sub>S<sub>3</sub> ...  
 [8], ...  
 $E(\mathbf{k})$  ...  
 Sn<sup>II</sup>, ... Sn<sup>IV</sup>, ... S ( ... 2).  
 Sn<sup>II</sup> ... Sn<sup>II</sup> Sn<sup>IV</sup>, ...  
 S(1), S(2) S(3) ...  
 4 ...  
*ab initio* ...  
 Pnma ...  
 m ( ... 1, ...).



. 1.

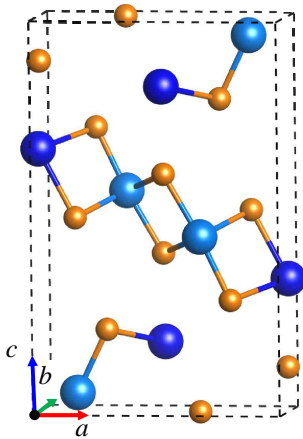
( )



XZ ( )

Sn<sub>2</sub>S<sub>3</sub>

2.



. 2.

Sn<sub>2</sub>S<sub>3</sub>.

Sn<sup>II</sup> 5p-

5s-

(ABINIT),

(SIESTA),

[12–15],

[16, 17].

[18]

Sn – [Kr] 5s<sup>2</sup>5p<sup>2</sup>,  
[Ne] 3s<sup>2</sup>3p<sup>4</sup>.

:

S –

, [Kr], [Ne] –

[19].

3.

3.1.

ψ- [SnS<sub>3</sub>•E•], •E• –

Sn<sub>2</sub>S<sub>3</sub>  
[Sn<sup>IV</sup>S<sub>6</sub>],

b.

ψ- [SnS<sub>3</sub>•E•].

( . 3).  
Sn<sub>2</sub>S<sub>3</sub>

. 4,

E(k)

52

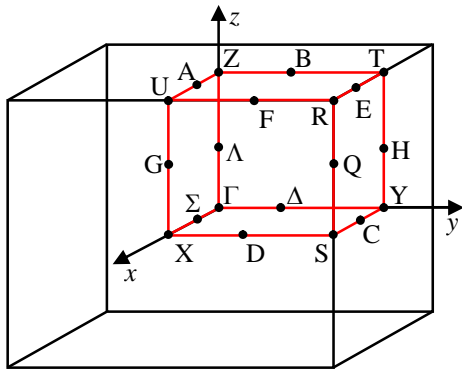


Fig. 3. Crystal structure of  $\text{Sn}_2\text{S}_3$ .

5s-, 5p-  
 U.  
 $E_{gi} = 0.53$  ( →U).

Z ( $E_{gd} = 0.54$ ).

**3.2.**

( . 5) ,  
 s-, - d-  
 d-  
 s- - ,

[20].

$\text{Sn}_2\text{S}_3$  ( . 5).  
 $\text{Sn}_2\text{S}_3$   $S3s$ -

$\text{Sn}_2\text{S}_3$ , [7],

$\text{Sn}$  S ( . 5) -  
 s-, p-, d-  
 s- p-

$h\nu = 1253.6$

$S3$  -  
 . 6  
 $S3p$

5s- 5 -  
 3 -

[7].

$\text{Sn}_2\text{S}_3$ ,

-14.58 -12.07 ,  
 3s-  
 5s- Sn 5p- 5d-

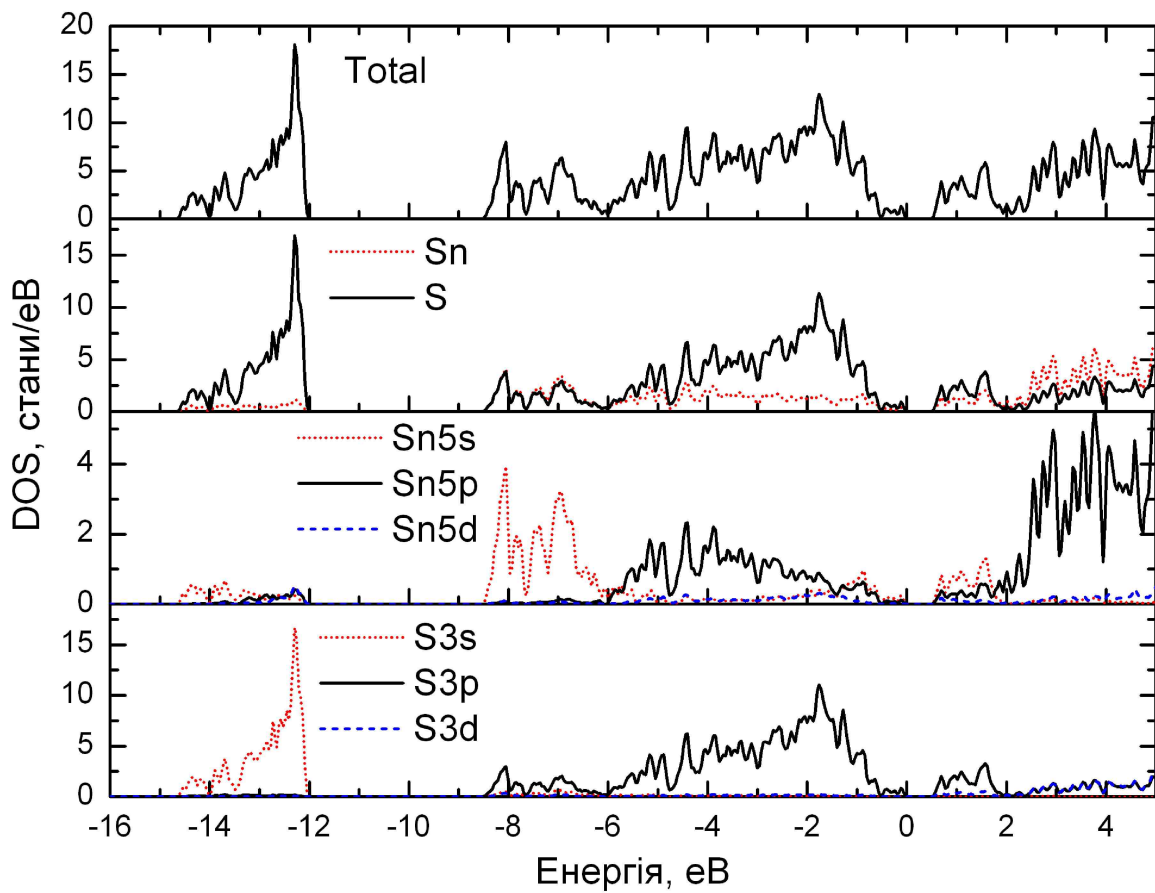
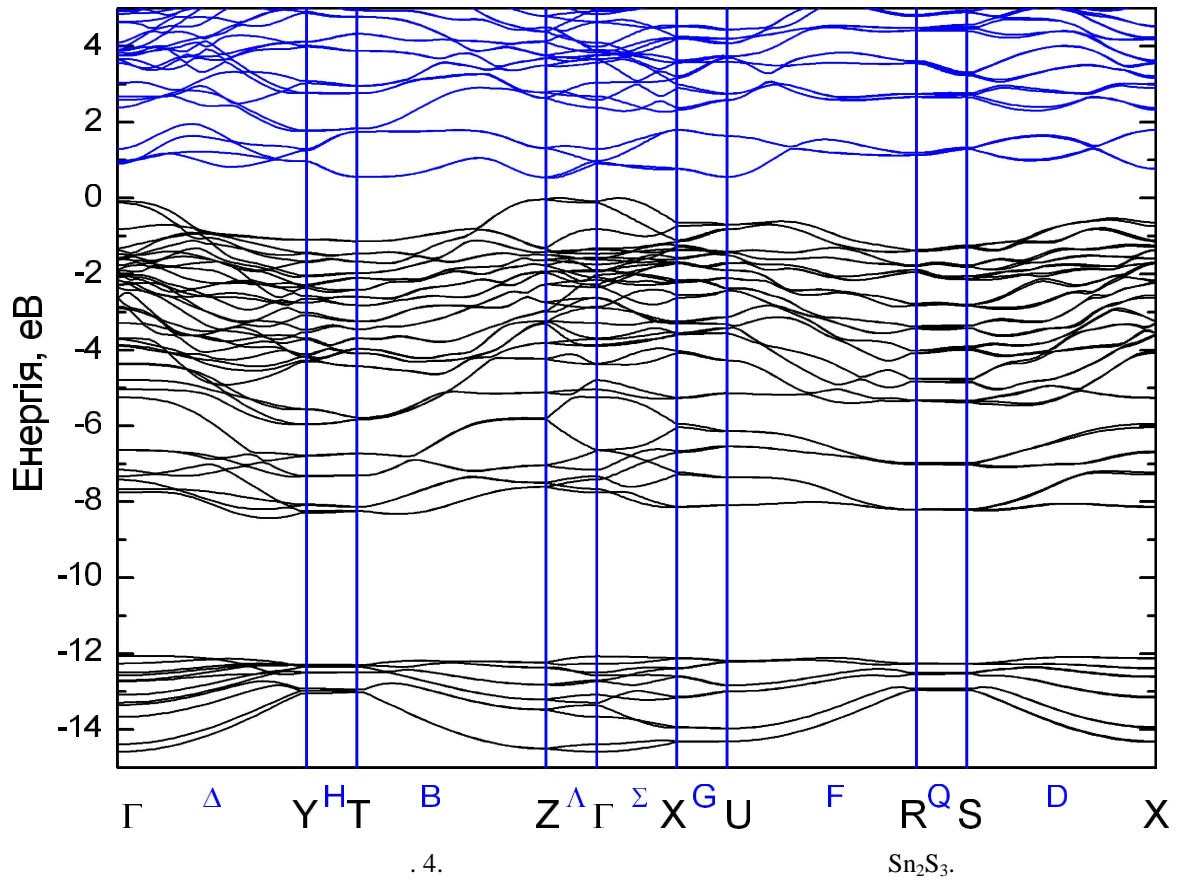
(-8.43 ÷ -5.24 ) 3s-  
 3.64 3 -  
 5s-

5s- 3s-  $\text{Sn}_2\text{S}_3$  3p-

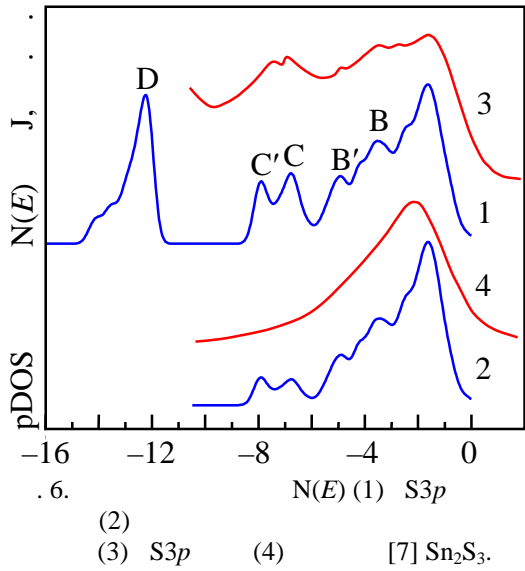
0 ) 3 -  
 5p-

3p- 5 -

3p-  
 5s-



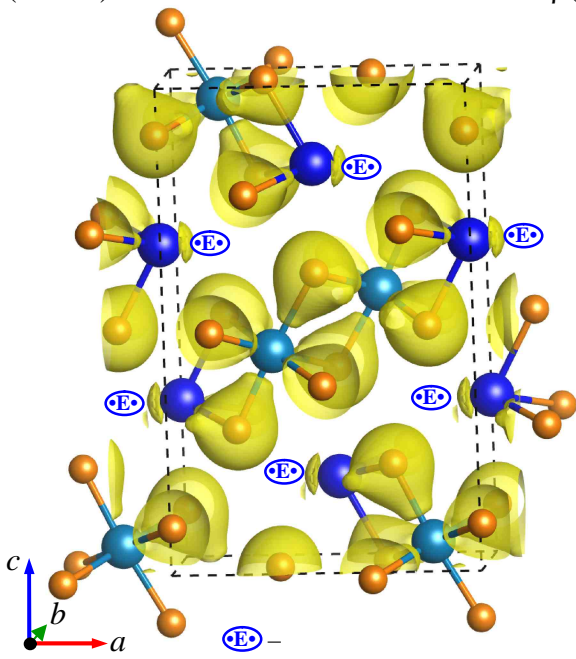
. 5.



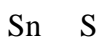
3.3.



(. 7).



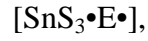
. 7.



. 7



$\psi^-$



$\rho(r)$

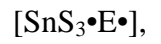
Sn-S.



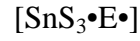
. 8



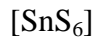
$\psi^-$



$\psi^-$



Sn-S



(. 7, 8).

S Sn -



Sn

+2 +4, S - +6,

*ab initio*



$E_{gi} = 0.53$

(  $\rightarrow U$ ).

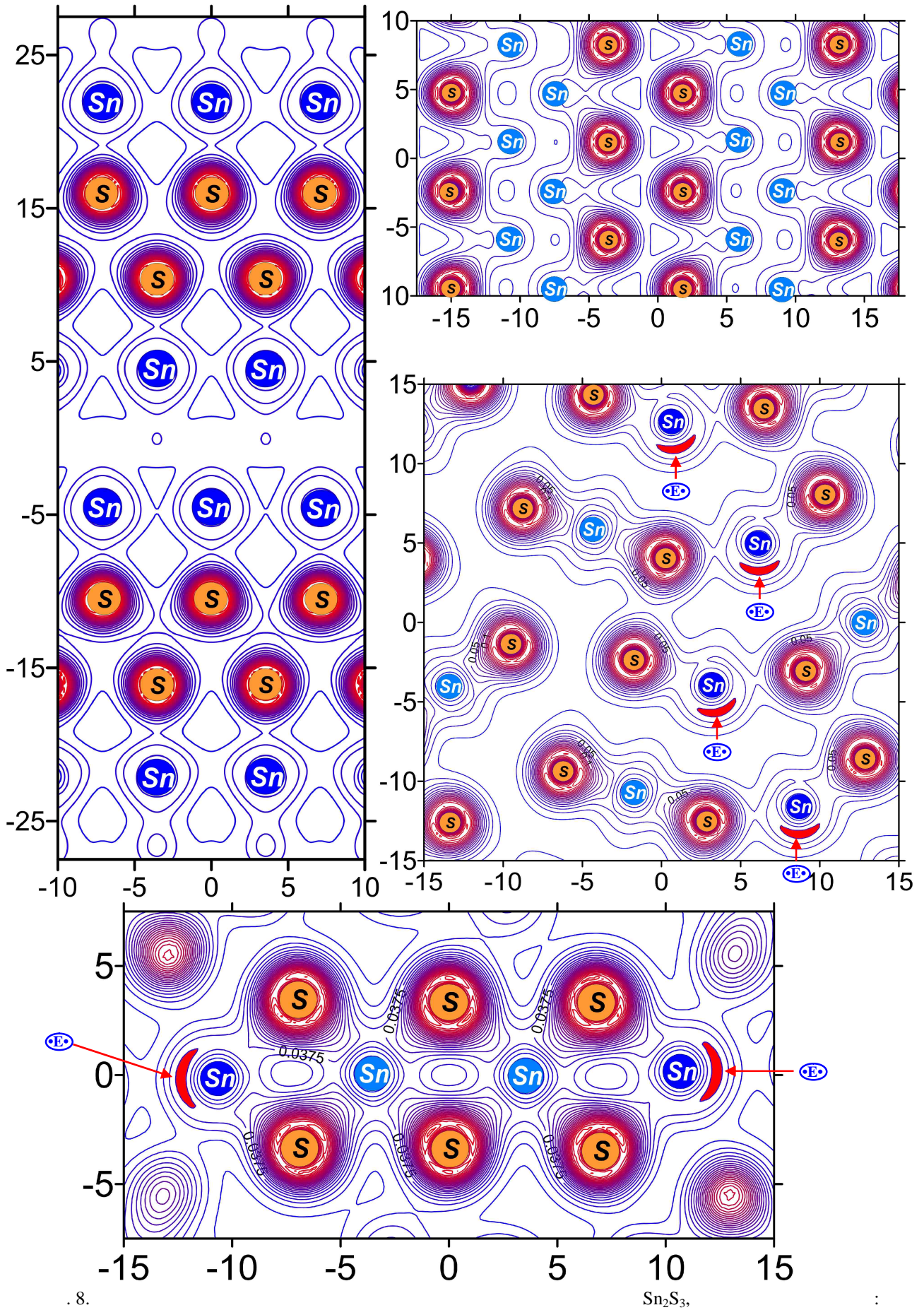
$N(E)$

S3p-



2D 3D





. 8.

$-(100), -(001), -(010), -$   
68

$\text{Sn}_2\text{S}_3,$

1. ... ..  
// ... ..  
– 1967. – .3, 11. . 1979–1983.
2. Moh G.H. The Tin-Sulfur system and related minerals // N. Jb. Miner. Abh. – 1969. – V.111, 3. – . 227–263.
3. Alpen U.V., Fenner J., Gmelin E. Semiconductors of the type  $\text{Me}^{\text{II}}\text{Me}^{\text{IV}}\text{S}_3$  // Mater. Res. Bull. – 1975. – V.10, 3. – .175–180.
4. Chandrasekhar H.R., Mead D.G. Long-wavelength phonons in mixed-valence semiconductor  $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}\text{S}_3$  // Phys. Rev. B. – 1979. – V.19, 2. – . 932–937.
5. Mead D.G., Chandrasekhar H.R. Far infrared optical properties of  $\text{Sn}^{\text{II}}\text{Sn}^{\text{IV}}\text{S}_3$  // Infrared Physics. – 1980. – V. 20, 4. – . 245–247.
6. Wiedemeier H., Csillag F.J. Decomposition and thermodynamic properties of  $\text{Sn}_2\text{S}_3$  // Z. anorg. allg. Chem. – 1980. – Bd. 469, 10. – .197–206.
7. De La Rocque A.G., Belin-Ferré E., Fontaine M.F., Senemaud C., Olivier-Fourcade J., Jumas J. C. X-ray spectroscopy investigation of the electronic  $\text{SnS}_x$  and  $\text{Li}_{0.57}\text{SnS}_2$  compounds // Phil. Mag. B. – V.80, 11. – .1933–1942.
8. Lefebvre I., Lannoo M., Olivier-Fourcade J., Jumas J.C. Tin oxidation number and the electronic structure of  $\text{SnS-In}_2\text{S}_3\text{-SnS}_2$  systems // Phys.Rev. B. – V.44, 3. – .1004–1011.
9. Mootz D., Puhl H. Die Kristallstruktur von  $\text{Sn}_2\text{S}_3$  // Acta. Cryst. – 1967. – V.23, 3. – .471–476.
10. Kniep R., Mootz D., Severin U., Wunderlich H. Structure of tin(II) tin(IV) trisulfide, a redetermination // Acta Cryst. B. – 1982. – V.38, 7. – . 2022–2023.
11. Robin M.B., Day P. Mixed Valence Chemistry-A Survey and Classification // Adv. Inorg. Chem. Radiochem. – 1968. – V.10. – P.247–422.
12. <http://www.abinit.org/>
13. Gonze X., Beuken J.-M., Caracas R., Detraux F., Fuchs M., Rignanese G.-M., Sindic L., Verstraete G., Zerah G., Jollet F., Torrent M., Roy A., Mikami M., Ghosez Ph., Raty J.-Y., Allan D.C. First-principle computation of material properties: the ABINIT software project // Comp. Mat. Sci. B. – 2002. – V. 25, 3. – P. 478– 492.
14. Soler J.M., Artacho E., Gale J.D., Garcia A., Junquera J., Ordejon P., Sanchez-Portal D. The SIESTA method for ab initio order-N materials simulation // J. Phys.: Condens. Matter. – 2002. – V. 14, 11. – P. 2745–2779.
15. <http://icmab.cat/leem/siesta/>
16. Hohenberg P., Kohn W. Inhomogeneous Electron Gas // Phys. Rev. – 1964. – V. 136, 3. – P. B864–B871.
17. Kohn W., Sham L.J. Self-Consistent Equations Including Exchange and Correlation Effects // Phys. Rev. – 1965. – V.140, 4. – P. A1133–A1138.
18. Hartwigsen C., Goedecker S., Hutter J. Relativistic separable dual-space Gaussian pseudopotentials from H to Rn // Phys. Rev. B. – 1998. – V. 58, 7. – P. 3641–3662.
19. Ceperley D.M., Alder B.J. Ground State of the Electron Gas by a Stochastic Method // Phys. Rev. Lett. – 1980. – V.45, 7. – P. 566–569.
20. ... ..  
... .., 1981. –  
420 .

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## ELECTRONIC STRUCTURE OF $\text{Sn}_2\text{S}_3$

The energy band structure, the spectra of total and local partial densities of states for  $\text{Sn}_2\text{S}_3$  crystal are calculated within the density functional theory. On the base of these results a detailed analysis of the valence states is performed. It is established that  $\text{Sn}_2\text{S}_3$  is an indirect-band semiconductor with the theoretically evaluated band gap of  $E_{\text{gi}} = 0.53$  eV. The calculated energy distributions of total and S3p partial densities of states are compared with known experimental X-ray photoelectron (XPS) and emission (XES) spectra. The electronic density maps in different planes are obtained, and the crystal can be characterized as an ion-covalent compound with the prevailing concentration of a charge on the S–Sn bonds in coordination  $\psi$ -tetrahedra and octahedra. It is revealed an important role of lone electronic pair in the formation of the  $\text{Sn}_2\text{S}_3$  atomic and electronic structures.

**Keywords:** tin sesquisulfide, electronic structure, density of states, lone pair.

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### $\text{Sn}_2\text{S}_3$

$\text{Sn}_2\text{S}_3$ ;

$\text{Sn}_2\text{S}_3$

$E_{\text{gi}} = 0.53$   
S3p-

( )

( )

S–Sn

$\psi$ -

$\text{Sn}_2\text{S}_3$ .

: