

544.225.22

... , ... , 88000, ... , 54
 e-mail: crystal_lab457@yahoo.com

α- β- SiS₂. -
 ,
 α- SiS₂ -
 $E_{gd} = 2.95$ $E_{gi} = 2.44$ (T₁→X₈), β- -
 α- SiS₂ -
 : , , ().

1.

(DFT) -
 Si-S [1], -
 : -
 (SiS₂), -
 1366 - SiS₂. ,
 (SiS), -
 1475 .

β- : α- [2-4].

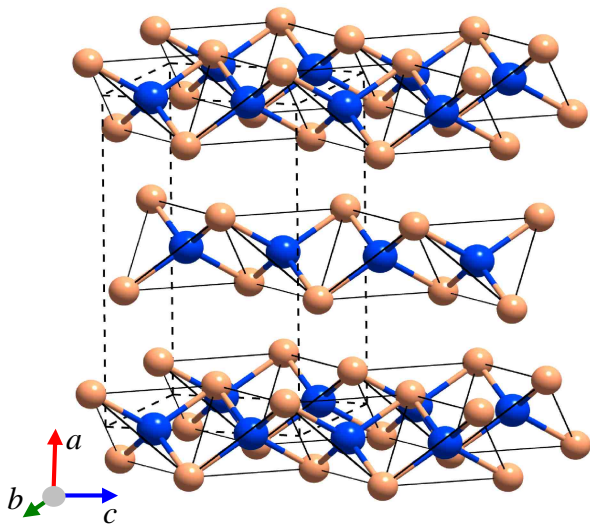
2.

α- -
 , -
 [SiS₄] [2-4]. $Ibam-D_{2h}^{26}$, -
 - (. 1) [2]. -
 , -
 α- , [SiS₄], -
 - (. 1, -
 SiS₂ [5-7],). α-SiS₂ -

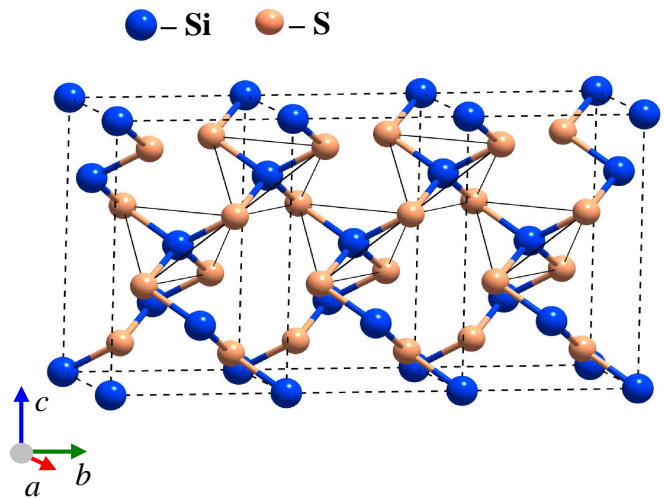
5,55 Å,
 Si-S = 2,133 Å.

()

		Å						
				x	y	z		
α -SiS ₂	$D_{2h}^{26}, Ibam,$ Z = 4	a = 9.583 b = 5.614 c = 5.547	Si	0.0	0.0	0.25	4a	[2]
			S	0.1182	0.2088	0.0	8j	
		a = 8.43745 b = 5.79983 c = 5.66081	Si	0.0	0.0	0.25	4a	GGA
			S	0.13134	0.21461	0.0	8j	
β -SiS ₂	$D_{2d}^{12}, I\bar{4}2d,$ Z = 4	a = 5.420 c = 8.718	Si	0	0	0	4a	[3,4]
			S	0.2272	0.250	0.125	8d	
		a = 5.35237 c = 8.92605	Si	0	0	0	4a	GGA
			S	0.24535	0.25000	0.12500	8d	



.1. α -



() β - () SiS₂.

S-Si-S = 81, 99, 114 116°

[SiS₄].

β - SiS₂

[3, 4].

$I\bar{4}2d,$

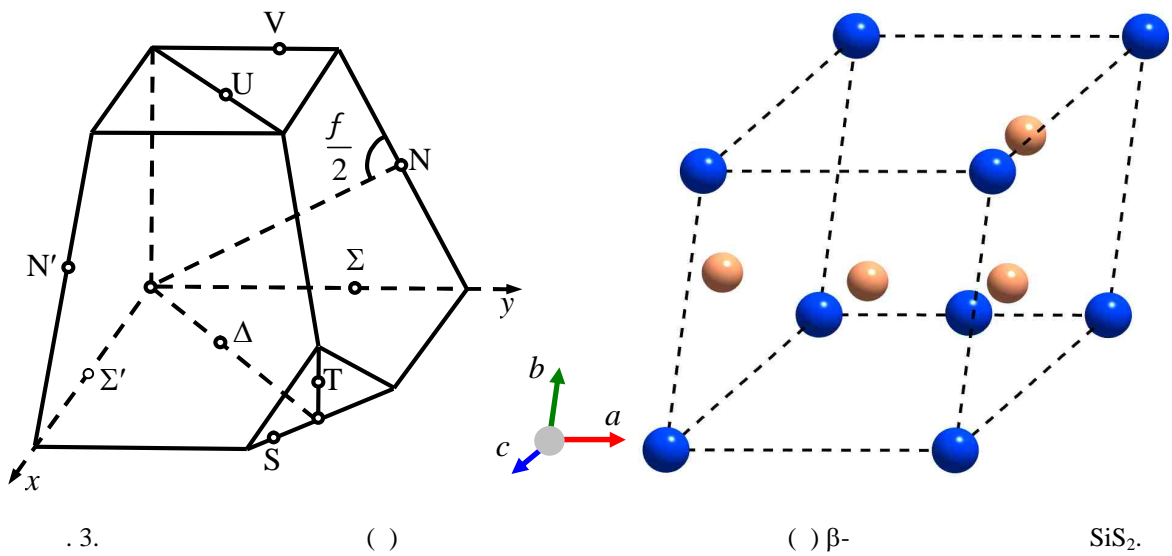
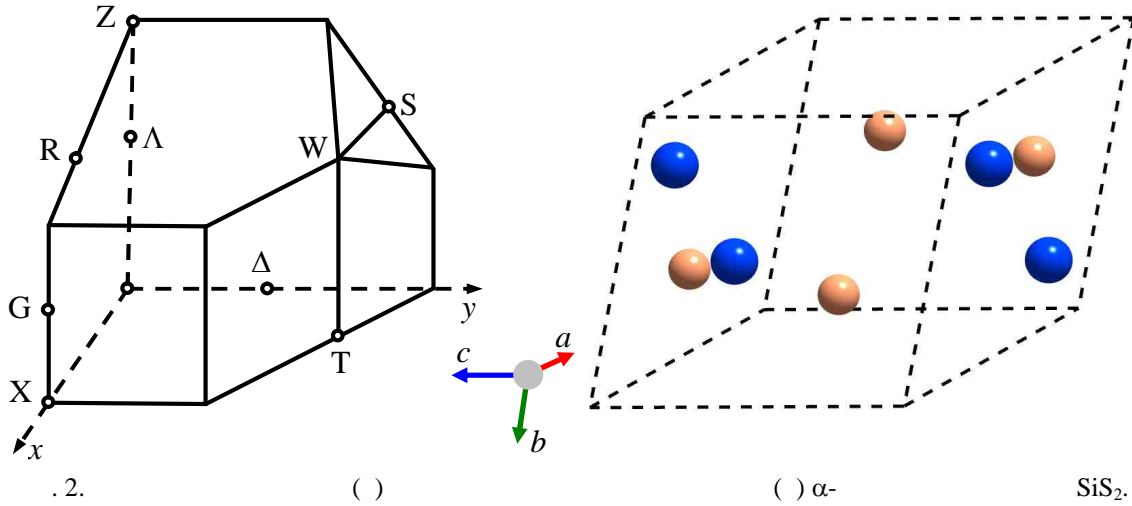
17 %

α -

β -
[SiS₄]

SiS₂

$X \ Y \ (\ . \ 1, \)$.
 $1/4$
 - ABINIT SIESTA.
 $XY \ YZ$
 $Z \ .$
 $2.13 \ \text{\AA}$,
 $S-Si-S = 105.2 \ 118.5^\circ$,
 $Si-S-Si = 109.4^\circ$,
 $Si-S$
 $(2.13 \ \text{\AA})$
 $(1.17 \ \text{\AA}) \ (1.04 \ \text{\AA})$.
 SiS_2
 $[SiS_4]$, $\beta-SiS_2$
 $[SiS_4]$, $\alpha-SiS_2$
 $[SiS_4]$.
 $\alpha- \beta- SiS_2$. 1.
4.
4.1.
3.
 $(\ . \ 2, \)$ $(\ . \ 3, \)$
 $[8,9]$
 (LDA)
 (GGA)
 $[10,11]$,
 ABINIT SIESTA [12–
 15].
 S
 Si



α - SiS_2 , $j(x,y,0)$, $[20]$, $a(0,0,1/4)$

- : 1, 7, 6, 4, 2, 1, 7, 5, 3, 4, 6, 1, 8, 6, 4, 7 \downarrow 4, 2, 1, 6 ...
- X: $X_7, X_1, X_6, X_4, X_8, X_7, X_1, X_3, X_5, X_6, X_4, X_6, X_7, X_2, X_4, X_1 \downarrow X_8, X_4, X_1, X_6 \dots$
- T: $T_1, T_1, T_4, T_4, T_2, T_1, T_1, T_3, T_3, T_4, T_4, T_4, T_2, T_1, T_4, T_1 \downarrow T_2, T_4, T_1, T_4 \dots$
- W: $\{W_1 \oplus W_2\}, \{W_3 \oplus W_4\}, \{W_1 \oplus W_2\}, \{W_3 \oplus W_4\}, \{W_1 \oplus W_2\}, \{W_3 \oplus W_4\}, \{W_3 \oplus W_4\},$
 $\{W_1 \oplus W_2\} \downarrow \{W_1 \oplus W_2\}, \{W_3 \oplus W_4\} \dots$
- S: $S_1, S_1, S_1, S_1, S_1, S_1, S_1, S_1 \downarrow S_1, S_1 \dots$
- R: $R_1, R_1, R_1, R_1, R_1, R_1, R_1, R_1 \downarrow R_1, R_1 \dots$

- SiS_2 :

$$2(X_7 \oplus X_1 \oplus X_4 \oplus X_6) - 2(1 \oplus 7 \oplus 6 \oplus 4) - 2(2T_1 \oplus 2T_4) - 2(\{W_1 \oplus W_2\} + \{W_3 \oplus W_4\}) - 2(2S_1) - 2(2R_1)$$

$$\begin{aligned}
 & X_1+X_2 - 2+ 1 - T_1+T_2 - \{W_1\oplus W_2\} - S_1 - R_1 \\
 & X_5+ X_6 - 6+ 5 - T_3+T_4 - \{W_3\oplus W_4\} - S_1 - R_1 \\
 & X_3+ X_4 - 4+ 3 - T_3+T_4 - \{W_3\oplus W_4\} - S_1 - R_1 \\
 & X_7+ X_8 - 8+ 7 - T_1+T_2 - \{W_1\oplus W_2\} - S_1 - R_1.
 \end{aligned}$$

1/2.

(. 2),

$a(0,0,1/4)$ $j(x,y,0)$,
Si S,

()

-SiS₂.

« ».

. 3–6

2

$a(0,0,1/4)$	$f(x,0,1/4)$
$b(1/2,0,1/4)$	$g(0,y,1/4)$
$c(0,0,0)$	$h(0,0,z)$
$d(1/2,0,0)$	$i(0,1/2,z)$
$e(1/4,1/4,1/4)$	$j(x,y,0); k(x,y,z)$

$D_{2h}^{26}(\alpha\text{-SiS}_2)$,

Q,

$(h_s^* = Qh_s)$.

D_{2h}^{26}

S (1/2,0,0)

R (0,1/2,0)

	h_1	\tilde{h}_2	h_{25}	\tilde{h}_{26}	
S ₁	2	0	0	0	
S ₂	2	0	0	0	
D _{1/2}	2	0	0	0	
S ₁ ×D _{1/2}	4	0	0	0	2S ₂
	h_1	\tilde{h}_3	h_{25}	\tilde{h}_{27}	
R ₁	2	0	0	0	
R ₂	2	0	0	0	
D _{1/2}	2	0	0	0	
R ₁ ×D _{1/2}	4	0	0	0	2R ₂

D_{2h}^{26}

T (0,0,1/2)

g T		h_1	h_4	h_{25}	h_{28}	
		T_1^+	T_1	1	1	1
T_1^-	T_2	1	1	-1	-1	
T_2^+	T_3	1	-1	1	-1	
T_2^-	T_4	1	-1	-1	1	
T_5		1	i	1	i	
T_6		1	i	-1	-i	
T_7		1	-i	1	-i	
T_8		1	-i	-1	i	
$\{T_5 \oplus T_7\}$		2	0	2	0	
$\{T_6 \oplus T_8\}$		2	0	-2	0	
$D_{1/2}$		2	0	-2	0	-
$T_1 \times D_{1/2}$		2	0	-2	0	$\{T_6 \oplus T_8\}$
$T_2 \times D_{1/2}$		2	0	2	0	$\{T_5 \oplus T_7\}$
$T_3 \times D_{1/2}$		2	0	-2	0	$\{T_6 \oplus T_8\}$
$T_4 \times D_{1/2}$		2	0	2	0	$\{T_5 \oplus T_7\}$

D_{2h}^{26}

W (1/4,1/4,1/4)

g W		h_1	h_4	\tilde{h}_3	\tilde{h}_2	
		W_1	1	1	i	i
W_2	1	1	-i	-i		
W_3	1	-1	i	-i		
W_4	1	-1	-i	i		
$\{W_1 \oplus W_2\}$		2	2	0	0	
$\{W_3 \oplus W_4\}$		2	-2	0	0	
W_5		2	0	0	0	
$D_{1/2}$		2	0	0	0	-
$\{W_1 \oplus W_2\} \times D_{1/2}$		4	0	0	0	$2W_5$
$\{W_3 \oplus W_4\} \times D_{1/2}$		4	0	0	0	

D_{2h}^{26}

(0,0,0) X (1/2,1/2,1/2)

g		g X		h_1	h_4	\tilde{h}_3	\tilde{h}_2	h_{25}	h_{28}	\tilde{h}_{27}	\tilde{h}_{26}		
				1^+	1	X_2^+	X_7	1	1	1	1	1	1
1^-	2	X_2^-	X_8	1	1	1	1	-1	-1	-1	-1		
3^+	3	X_4^+	X_5	1	-1	-1	1	1	-1	-1	1		
3^-	4	X_4^-	X_6	1	-1	-1	1	-1	1	1	-1		
4^+	5	X_3^+	X_3	1	-1	1	-1	1	-1	1	-1		
4^-	6	X_3^-	X_4	1	-1	1	-1	-1	1	-1	1		
2^+	7	X_1^+	X_1	1	1	-1	-1	1	1	-1	-1		
2^-	8	X_1^-	X_2	1	1	-1	-1	-1	-1	1	1		
	9		X_9	2	0	0	0	2	0	0	0		
	10		X_{10}	2	0	0	0	-2	0	0	0		
$D_{1/2}$				2	0	0	0	-2	0	0	0	-	
$1 \times D_{1/2}$		$X_7 \times D_{1/2}$		2	0	0	0	-2	0	0	0	10	X_{10}
$2 \times D_{1/2}$		$X_8 \times D_{1/2}$		2	0	0	0	2	0	0	0	9	X_9
$3 \times D_{1/2}$		$X_5 \times D_{1/2}$		2	0	0	0	-2	0	0	0	10	X_{10}
$4 \times D_{1/2}$		$X_6 \times D_{1/2}$		2	0	0	0	2	0	0	0	9	X_9
$5 \times D_{1/2}$		$X_3 \times D_{1/2}$		2	0	0	0	-2	0	0	0	10	X_{10}
$6 \times D_{1/2}$		$X_4 \times D_{1/2}$		2	0	0	0	2	0	0	0	9	X_9
$7 \times D_{1/2}$		$X_1 \times D_{1/2}$		2	0	0	0	-2	0	0	0	10	X_{10}
$8 \times D_{1/2}$		$X_2 \times D_{1/2}$		2	0	0	0	2	0	0	0	9	X_9

D_{2h}^{26} ,

$a(0,0,1/4)$

		X	T	W
I_1	$1 \oplus 2$	$X_1 \oplus X_2$	$T_1 \oplus T_2$	$\{W_1 \oplus W_2\}$
I_2	$7 \oplus 8$	$X_7 \oplus X_8$	$T_1 \oplus T_2$	$\{W_1 \oplus W_2\}$
I_3	$5 \oplus 6$	$X_5 \oplus X_6$	$T_3 \oplus T_4$	$\{W_3 \oplus W_4\}$
I_4	$3 \oplus 4$	$X_3 \oplus X_4$	$T_3 \oplus T_4$	$\{W_3 \oplus W_4\}$

$j(x,y,0)$

		X	T	W
A'	$1 \oplus 7 \oplus 6 \oplus 4$	$X_7 \oplus X_1 \oplus X_4 \oplus X_6$	$2T_1 \oplus 2T_4$	$\{W_1 \oplus W_2\} \oplus \{W_3 \oplus W_4\}$
A''	$2 \oplus 8 \oplus 5 \oplus 3$	$X_8 \oplus X_2 \oplus X_3 \oplus X_5$	$2T_2 \oplus 2T_3$	$\{W_1 \oplus W_2\} \oplus \{W_3 \oplus W_4\}$

, . 3–6,

h_s (

$D_{1/2}(h_s)$,

), . 3–6,

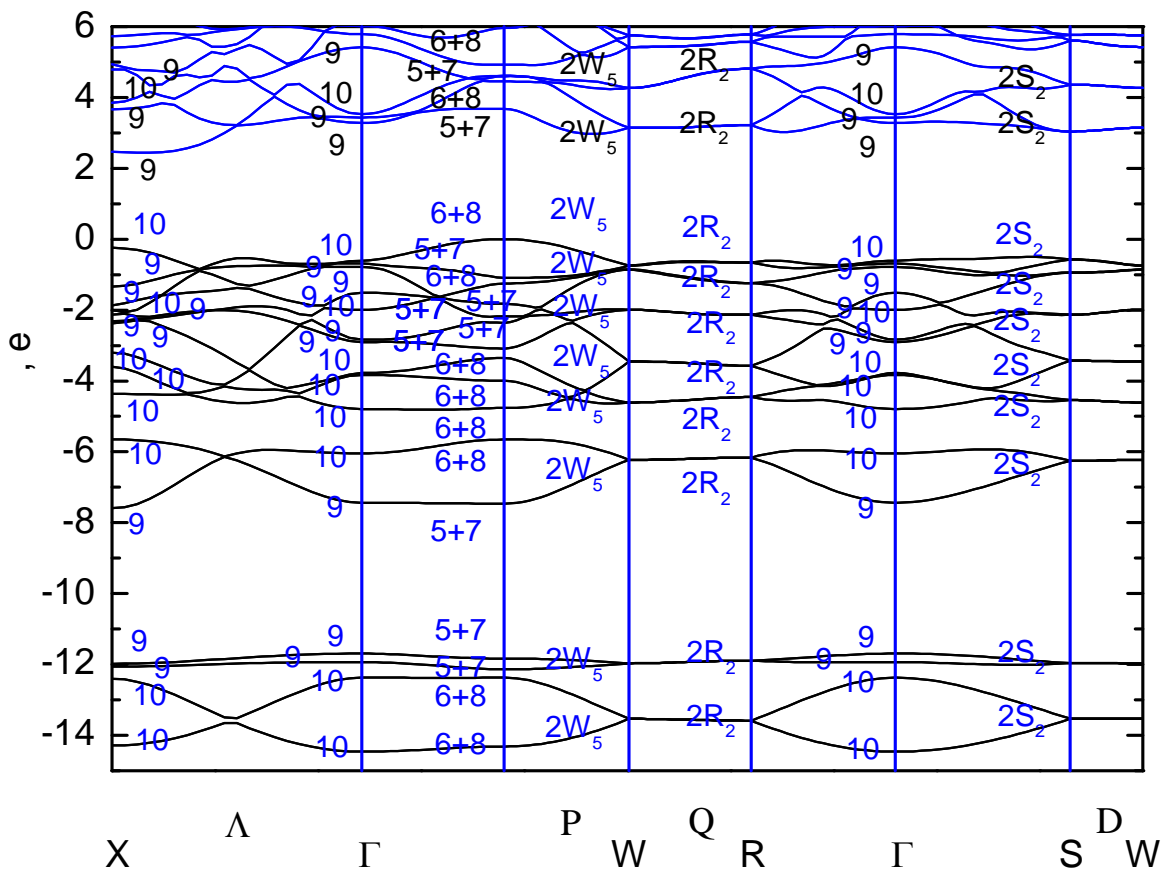
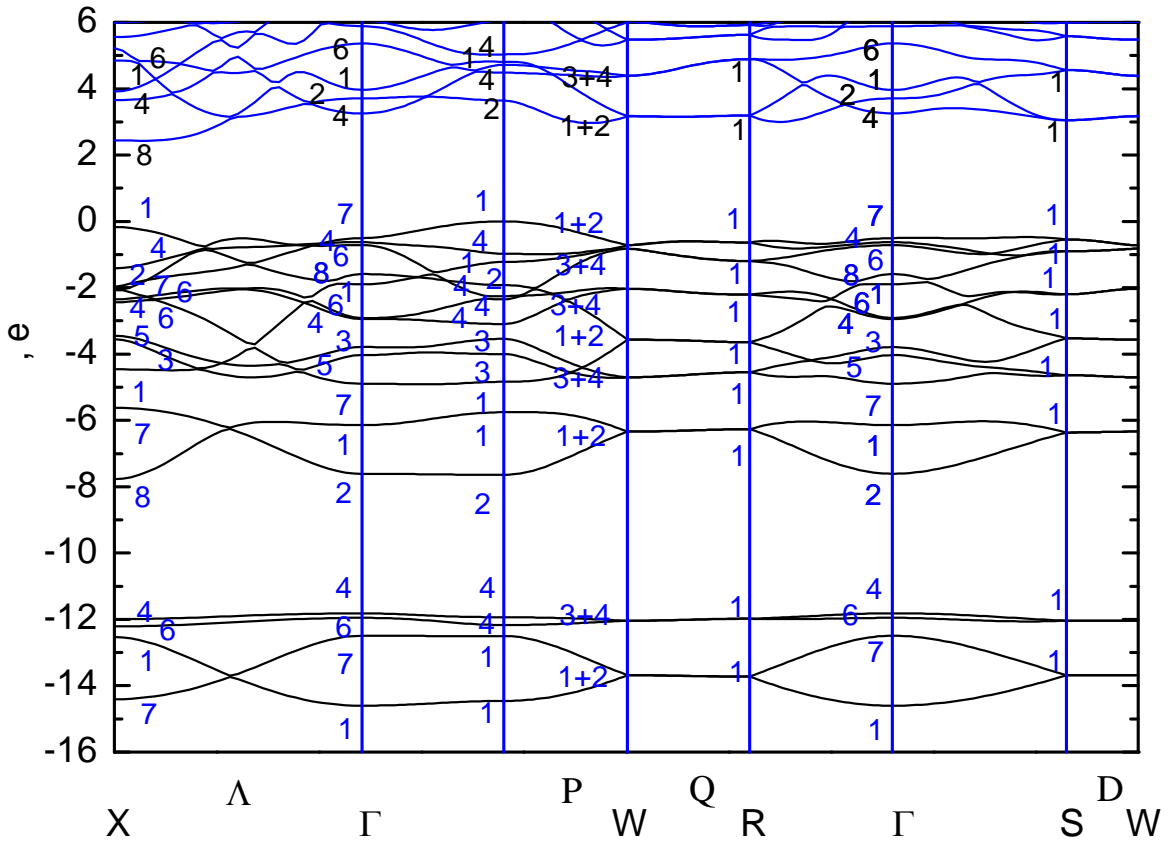
$\dagger^{(r)}$ $D_{1/2}$ -
 $\dagger^{(r)} \times D_{1/2}$ - α -
 $f^{(s)}$,
 $\dagger^{(r)} \times D_{1/2} = \sum_s p_s f^{(s)}$. VBIII), (VBI, VBII, N(E)
4.2. (. 2, 3,) [SiS₄]
 . 4 5 SiS₂
 . 4 5 ,
 , VBII VBI
 $E_{VB} = 14.6$. α -SiS₂ SiS₂ (. 4.),
 $E_{VB} = 14.37$, 0.23 β -
 α - Λ , X, T, W
 SiS₂ . 8. α -) α -
 » α - SiS₂ (. 4). « 1, X
 X₈.

8

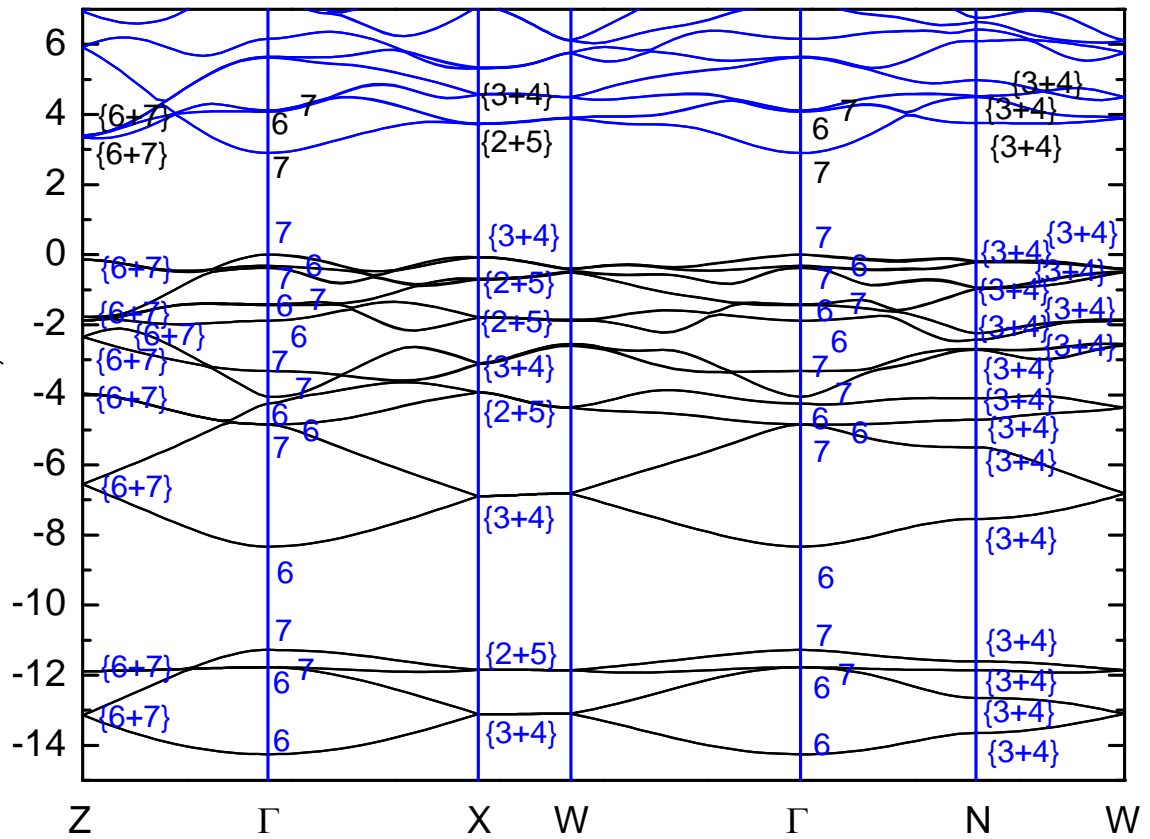
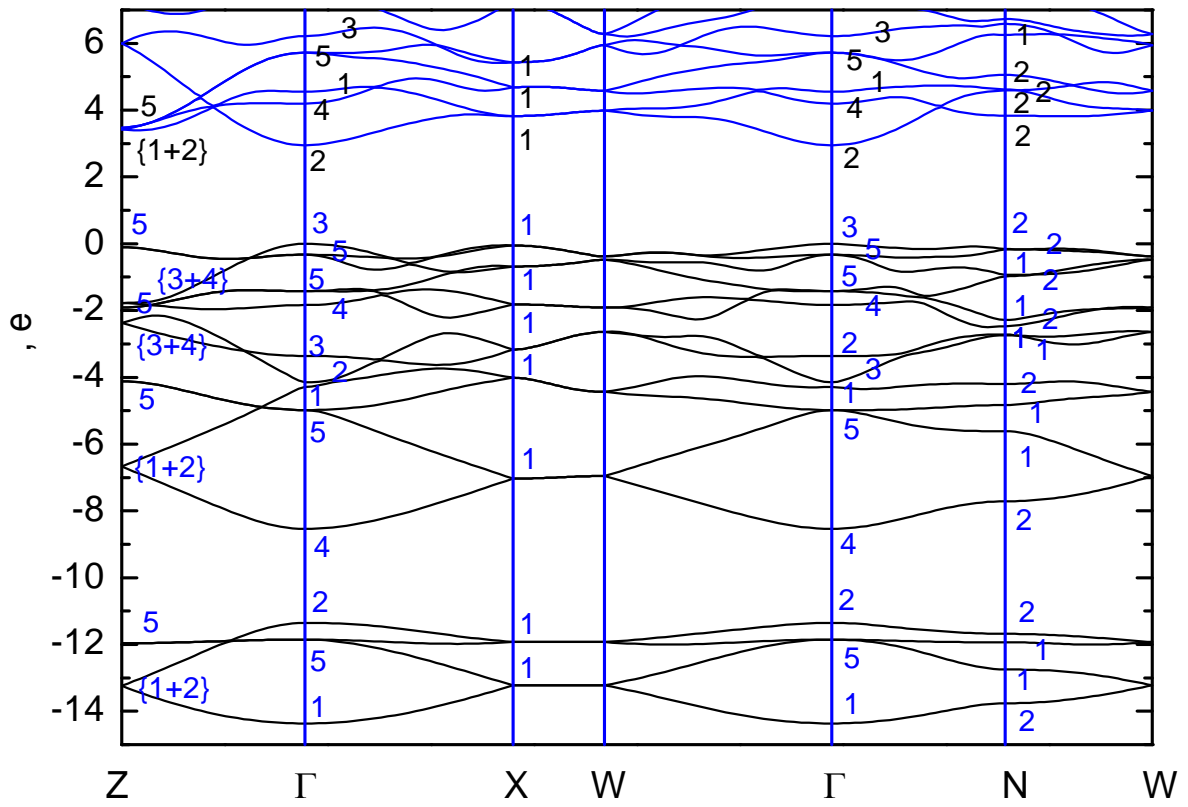
SiS₂

	E_{VB} ,	k_V	k_C	E_{gi} ,	E_{gd} ,	E_{VB1} ,	E_{VB2} ,	E_{VB3} ,	ΔE_1 ,	ΔE_2 ,
α -SiS ₂	14.6	T ₁	X ₈	2.44	2.62	4.91	2.15	2.78	0.71	4.05
β -SiS ₂	14.37	₃	₂	3.39	2.95	2.5	6.38	3.02	0.35	2.81

. 8 : E_{VB} - , k_V -
 , k_C - ; E_{VB1} , E_{VB2} , E_{VB3} -
 ; ΔE_1 , ΔE_2 - ; E_{gi} -
 ; E_{gd} -
 : (0,0,0), T (0,0,1/2), X (1/2,1/2,1/2).



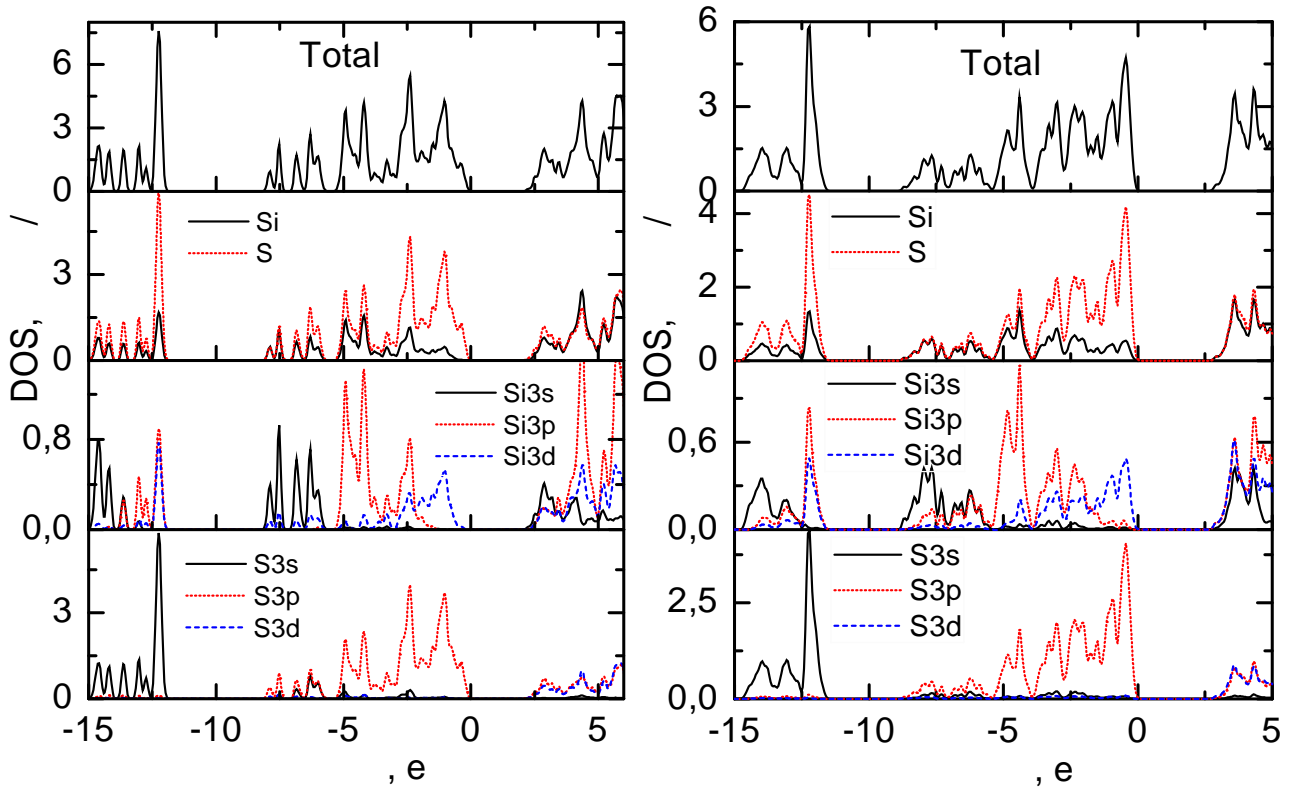
4. () - α - SiS_2 .



.5.

β -

SiS₂.



. 6.

α - () β -SiS₂ ().

X X₁ X₈.
SiS₂

$E_{gi} = 2.44$
 β -SiS₂

S 3p- S 3p-
p-p , S-S [SiS₄],

(3 2)
 β - SiS₂

$E_{gd} = 2.95$

S 3p- , S-S

4.3.

$p_{x,y}$

SiS₂.

3d- Si.
 β - SiS₂

α - β - SiS₂ . 6.
s-, p-, d-

3 -
3d- (. 6,).

(VBIII)

3s-, 3p-, 3d-

s-
(VBII),

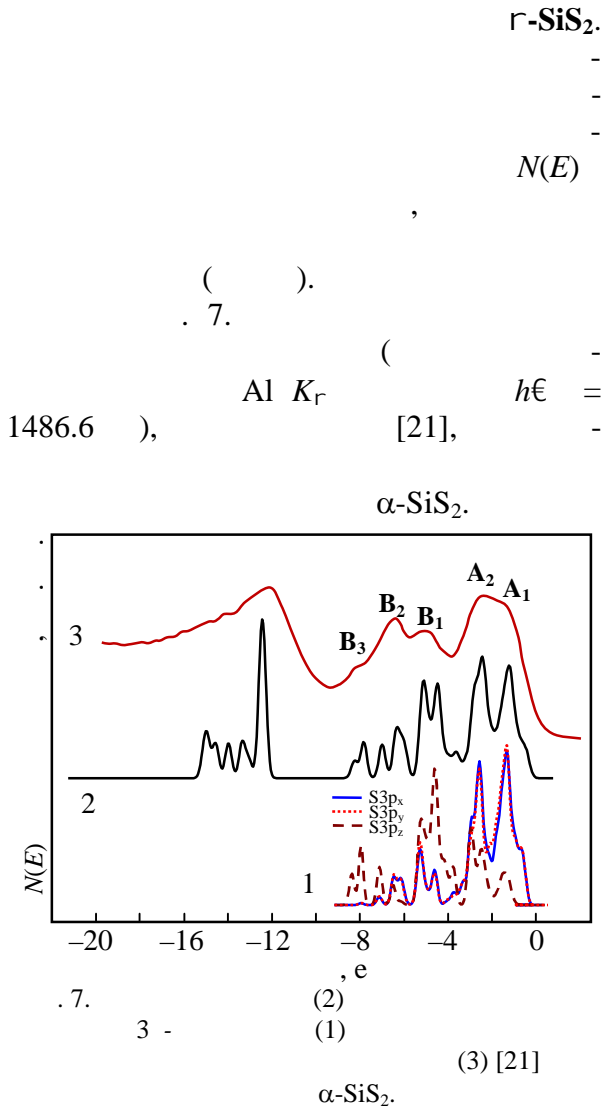
Si i S

3s-

3p-

(VBI)

4.4.

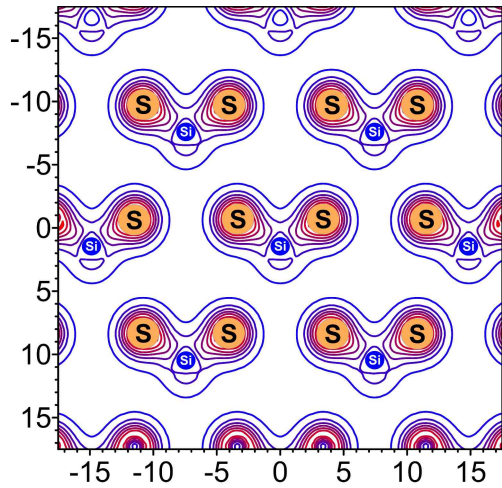


$N(E)$
 $(.6,)$
 $\alpha\text{-SiS}_2$
 $3s-$
 1 2 3
 $3-$

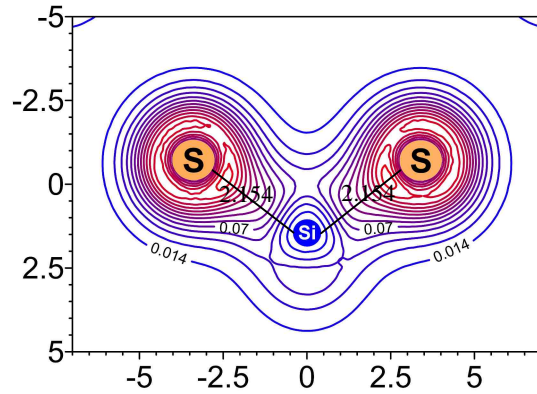
$3s-$ i $3p-$ 2 $3s-$ $3-$ $3-$
 $\sim 1:1.$
 $(2, .7)$
 $3p_{x,y}$ $(.7, 1)$
 $\alpha\text{-SiS}_2$ 2
 $3_{x,y}$ $3d-$ $3p-$

-SiS_2
 $DFT-$
4.5.
 SiS_2 $\alpha-$ $\beta-$
 $2D$
 $[\text{SiS}_4]$
 S-Si-S.

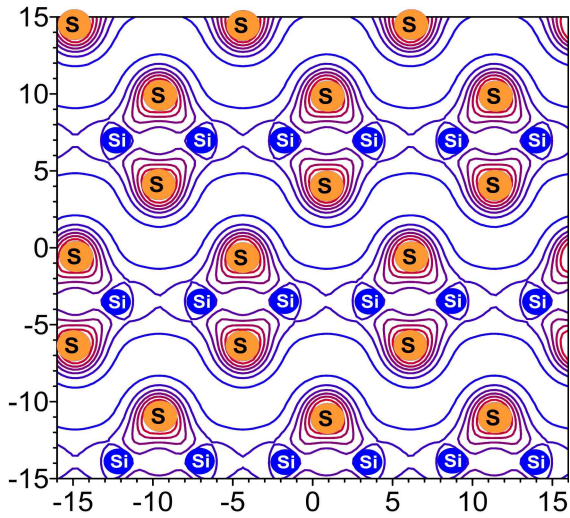
$\beta-$ $\text{SiS}_2,$ $[\text{SiS}_4]$ $\alpha-$
 $.8 - 11.$
 $\alpha-$
 $.9$
 $(001),$ S-Si-S-Si.
 Si S. $.8 - 11,$
 $[\text{SiS}_4]$
 $\rho(\mathbf{r}),$



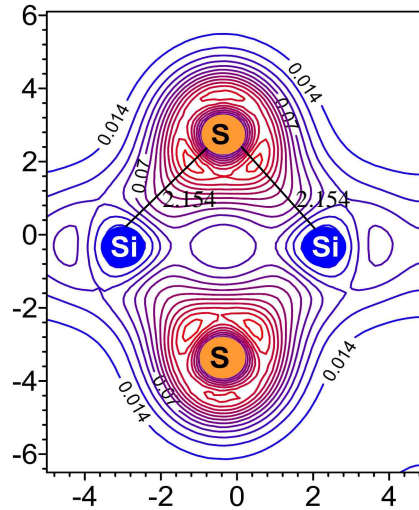
. 8.
S-Si-S: - (100), 1/2



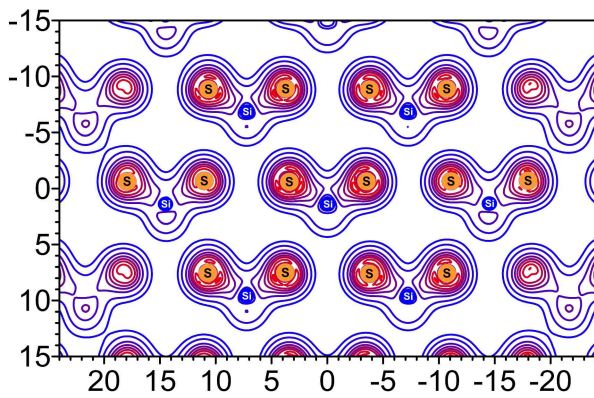
α -Si₂



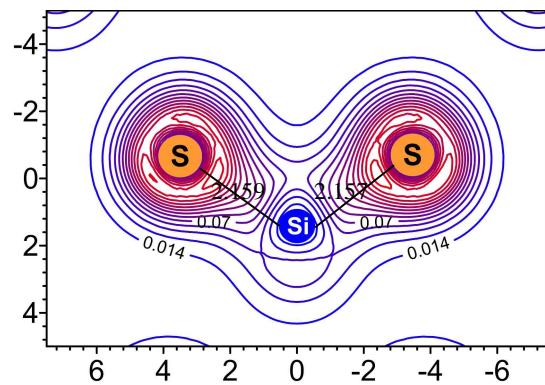
. 9.
[SiS₄]



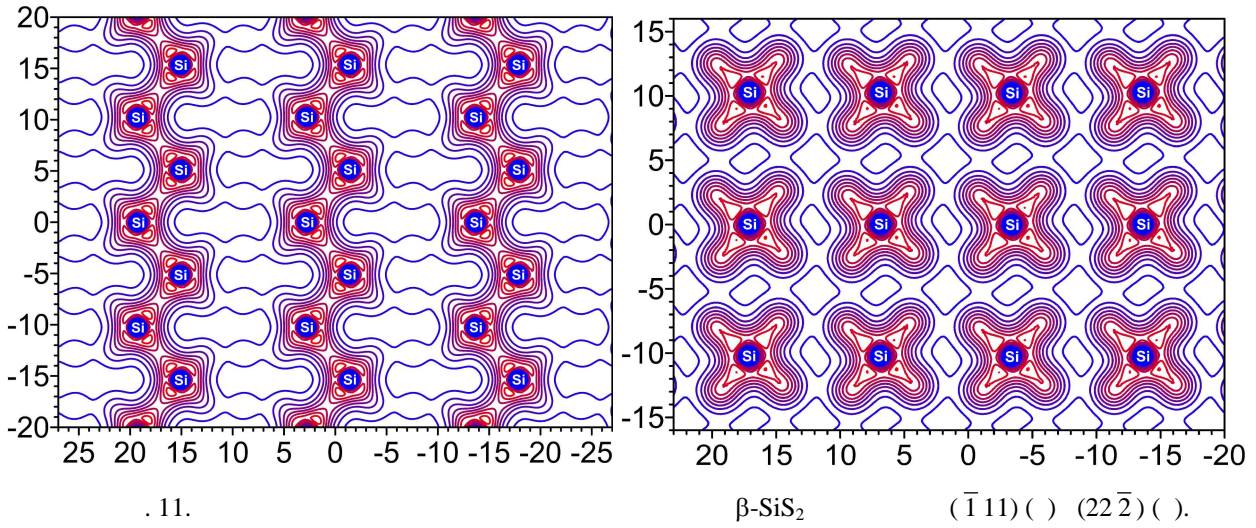
α -Si₂: - (001),
; -



. 10.
- (001); -



β -Si₂ S-Si-S:
[SiS₄].



SiS₂, [SiS₄], S-Si-S, α - β -SiS₂, $\rho(\mathbf{r})$, (001), α -SiS₂ (001), (1D), α -SiS₂, 3D, (11), Si-S, [SiS₄], Si 3, S 3s-, [SiS₄], SiS₂, S,

SiS₂

α- β-

SiS₂,

α-SiS₂

[SiS₄],

1. ... Si-S // ... – 2000. – . 45, 3. – . 545–547.
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ELECTRONIC STRUCTURE OF THE LOW AND HIGH PRESSURE PHASES OF SILICON DISULFIDE

The energy band structure, total and partial densities of states and spatial distribution of electron density in the α -low and β -high pressure phases of SiS_2 has been calculated by the density functional method. The symmetry analysis was carried out for both phases, which has allowed to establish the wave functions symmetries in the set of Brillouin zone high-symmetry points and to find of the band representation structures for valence bands. From the results of the band structure calculations follow that α -orthorhombic phase of SiS_2 is an indirect-band-gap semiconductor with the calculated band gap $E_{\text{gi}} = 2.44$ eV (transition $\text{T}_1 \rightarrow \text{X}_8$), and β -phase – the direct-band-gap semiconductor with $E_{\text{gd}} = 2.95$ eV. The theoretically calculated energy distribution of the total valence band density of states of α -phase SiS_2 qualitatively and quantitatively transmits the main features of the experimental X-ray photoelectron spectrum (XPS).

Keywords: silicon disulphide, polymorphism, electronic structure, density of states.

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β - SiS_2 α - SiS_2

$E_{\text{gd}} = 2.95$ $E_{\text{gi}} = 2.44$ ($\text{T}_1 \rightarrow \text{X}_8$), β - α - SiS_2