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Electronic structure of the ternary pnictide semiconductors ZnSiP2, ZnoePq, ZnSnP2, ZnsiAs2, and MgSiP2

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Self-consistent all-electron density-functional electronic-structure calculations are reported for five II-IV-V2 chalcopyrite-structure semiconductors. Chemical trends in the band structure, bonding, and charge distribution are identified. The

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good agreement with the available experimental data, the
present calculations are intended to answer some ques-
tions about these compounds, such as covalency versus
ionicity and the role of Zn

d orbitals, that the EPM does
not treat well.

The II-IV-Vz ternary pnictides (A'"'8" 'Cz ') can be
thought of as ternary analogs of the binary III-V zinc-
blende semiconductors. ' There are three notable

differences: (i) replacement of half of the atoms of the
column-III element by those of column-IIA (Mg) or -IIB
(Zn, Cd) element, and the other half by those of column-IV (Si, Ge, or Sn) element in an ordered fashion, leading
to the double crystallographic unit cell shown in Fig. 1,
(the primitiue unit cell being now

4 times larger); (ii)

a

slight tetragonal compression (except in ZnSnCz '

com-

pounds) along the c axis, leading to nonideal tetragonal distortion parameters rI

—=c/2a& 1; and (iii)

a distortion of
the anion sublattice involving

a shift by each anion away
from its nearest neighbors of one cation and towards those of the other kind of cation. This leads to

a nonideal anion

displacement parameter u& —,

. The present authors have
shown that the anion shift is primarily

a consequence

of atomic sizes (tetrahedral covalent radii) in that if the
column-II atom is larger than the column-IV atom, then
each 3'"'

—C' ' bond is lengthened and each 8" '—C'
bond is shortened relative to an ideal zinc-blende structure

with the ternary compound's lattice constant. This is the case in all known II-IV-V2 materials

—except the
ZnSnC2 systems, where the situation is

—

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T), + T2, '
i N)c(&)

T3„+T4„'

(5)
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-2 I

Ql 4

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LLI -6

T4. + Tsv' "'

Zn d-band

-8

- 10

- 12

- 14—

Tqv + Tzv' '
C" s ba

(~)

,, N(2)

1v
1v

N

MgsiP2 FIG. 5. Generic band-structure diagram of a II-IV-V2 ter-nary pnictide.

FIG. 4. Self-consistent band structure of MgSip2 using the Ceperley-Alder exchange-correlation. Crystal-structure parame-ters are given in Table I.

mixed-basis (PVMB) approach, which has been described in detail elsewhere. ' %e have employed the Ceperley-Alder form of the exchange-correlation function. The

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TABLE II. Calculated valence-band energies (in eV) at high-symmetry points, given relative to I 4„' [the valence-band (VB) maximum, except in ZnSnP2]. For notation, refer to Fig. 5. The Ceperley correlation was used, together with the crystal-structure parameters of Table I {but u =0.3134 for MgSiP2).

on1pound ZnSiP2 ZnGeP2 ZnSnP2 ZnSiAs2 MgSiP2

Upper VB:
Maxima

(2) r,„
I 5v ~cF (2)

3u+ 4u
N(5)

1u

0.00
—0.30
—1.25
—0.67

0.00
—0.33
—1.50
—0.86

0.00
+0.012
—1.52
—1.00

0.00
—0.32
—1.26
—0.69

0.00
—0.22
—0.38
—0.31

Minima

(1) I 4u
T4v+ T5u

~(4)

lu

—4.84
—3.94
—5.28

—5.10
—4.09
—5.51

—5.18
—3.77
—5.24

—4.81
—3.97
—5.25

—4.53
—3.69
—4.19

a(")-C(' band:
(2) I 4u
I

(2)
2v

T(2)

Sv

N(3)

1u

—6.37
—8.79
—7.00
—7.25

—7.02
—8.89
—7.73
—7.87

—6.32
—7.74
—6.70
—6.93

—6.48
—8.75
—7.17
—7.35

—4.67
—8.76
—6.36
—6.55

Zn 3d bands
Maximum at I
Minimum at I
Maximum at T
Minimum at T
Maximum at N
Minimum at N

—8.61 —9.20 —8.78 —9.24 —8.90 —9.15

—8.86 —9.52 —9.08
9.35 —9.10 —9.34

—9.01 —9.47 —9.06 —9.44 —9.24 —9.46

—8.92 —9.29 —9.01 —9.30 —9.07 —9.26

C('

s bands:

(1) I 5u
I 3u

(1) r, „
T1v+ T2v
T5N(1)
N(2)

1v

N(1)

1v

—10.81 —10.96 —10.87
—11.84 —12.18 —11.49

—10.53 —10.62 —10.64
—10.53 —10.64 —10.58
—13.15 —13.46 —12.67
—10.54 —10.65 —10.61
—12.18 —12.50 —11.58

—1i.03
—11.01

—9.66
—9.59
—13.26 —12.78
—11.04 —9.75

—11.30
—12.11

—9.94
—11.64

—12.40 —11.80

the P or As orbitals. The third band is the Zn 3d state
which is relatively narrow, and either intersects the
8' '—C' '

band (in ZnGeP2, ZnSiAs2, and ZnSiP2), or

Feature

ZnCxeP2

Expt. Calc.
Position of maximum in upper VB
Bottom of upper VB
Ge—P bond
Center of Zn 3d
P 3s band center

2.3
5.5
7.0
9.7
12.5

2.1
5.5
7.8
9.2
11.5

TABLE III. Comparison of observed (Ref. 16) x-ray pho-toelectron spectroscopy (XPS) and calculated positions of struc-tures in the density of states of ZnGeP2 compounds. Results are given relative to the I 4„' state; Al Ka x rays were used in the XPS measurements (Ref. 16). All energies are given in eV.

appears just below it (in ZnSnP2). The closeness of the Zn d band to the 8' '—C' '

bonding valence band.63Tj ET BT

r6Xi3 7.05 Tf3455.79.6687 Tf 160.82 3Tj 3 158ffilcuity

the

given Zn

in

pho-

—.67 Tf /X19y

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TABLE IV. Calculated and measured lowest direct and pseudodirect band gaps and

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1oo =

10-& =

10-& =

Zn

Zn

I

ZnSiP2
CBM

ZnSiP2
VBM

Si

Si

tg
QP lo&—

N $0'~

C 10t =
Cl

0 io0-

V
OP

LLi 10' =

MgSiP2
CBM

MgSiP2
VBM

Si

Si

Mg

iog R 6
0.0 2.0 4.0 6.0 8.0 10.0 0,0 2.0 4.0

(

6.0 8.0 10.0

10&:-

ZnGeP2
CBM

10 & —,

C$
10 2-.

10&
1oi =

Cl

Q soa—
V

I 10'=

Zn

ZnGeP2
VBM

Ge

Ge

100:-

Zn ZnSnPg
CBM

Sn

10'--

10

100:—

M/1 A

ZnSnP2
VBM

R

lO-31
0.0

t 1 I T

2.0 40 6.0 8.0 1000.0 20 4.0 6.0 8.0 10.0

Distance (a.u.)

FIG. 6. Electronic charge density along the A' "—C' '

and 8" '—C' '

bonds at the top of the valence

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Distance (a.u.}
0.0 1.0 2.0 3.Q 4.0 5.0 6.0 7.0 8.0 9.010.011.0 00 I I I I I I I I
1.0-
2.0-
3.0-
4.0-
5.0-

Q.Q 1.0 2.0 3.0 4.0 5.0 6.0 7.0 8.0 9.010.011.012.0

I I I I I I I I I I I

7.0-

9.0-
gj

10.0- I

V
0.0
5$

1.0-

Q 2.0-
3.0-
4.0-
5.0-
6.0—
7.0-
8.0-
9.0—
10.0—

FIG. 8. Calculated electronic charge density in the upper valence band {cf.Fig. 5) of ternary pnictides. The contours are logarith-mically spaced. Solid circles

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Distance {a.u.}
0.0 1.0 2.0 3.0 4.0 5 0 6.0 7.0 8 0 9.010.0 11.0 0.0
1.0-
2.0-
3.0-
4.0-
5.0-
6.0-
7.0-
8.0-
9.0-
10.0-

Distance (a.U)
0.0 1.0 2.0 3.D 4-0 5.0 6.0 7.0 8.D 9.0 10.0 11.0 12.0 13.0
O.D

3.0-

4.D- lgI 5.0-
6.0-
lh

7.0-
8.0-
9.0-
10.0-
0.0
1.0-
2.0-
3.0-
4.0—
5.0-
V

05 6.0-
7.0—
l3
8.0-
9.0—
10.0—

0.0-
1.0—
2.0—
3.0—
4.0—
5.0—
6.0-
7.0—
8.0—
9.0—
10.0—

FIG. 10. Calculated electronic charge density corresponding
to the 8" '-C' ' band and the Zn 3d band near it. The contours are logarithmically spaced. The solid circles indicate the core regions. The 10 -e/a. u. contours around the C' '

and 8" '
atoms are shaded to hed

C'

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Distance (a.u.)
0.0 1.0 2.Q 3.0 4.0 5.Q 6.0 7.0 8.0 9.010.011.012.0 0.0

Distance (a.u.)
~... 4 0 5.0 6.0 7.0 8.0 9.0 10.0 11.0 12.0 13.0 0.0 1.0 2.0 3.0 4.0 ~ ~ ~.. ~ ~ ~ 13.0
0.0

2.0—
3.0—
4.0—

6.0—
7.0-
8.0-
9.0—
10.0-

2.0—

3.0-

4.0- 05I 5.0-

C
6.0—
lh

7.0-

8.0—

9.0—

1.0-

..0-~g
4.0—

gp 5.0-
V

~ 60- tg
70- Vl
O
8.0—
9.0—
10.0—

----::~ P s ban

10.0

FIG. 13. Calculated electronic charge density of thee Si-P
bando The f MgSiP. The contours are logarithmically space. e
solid circles indicate the core regions. The 10 -e/a. u. con-
d P d Si are shaded to highlight the strong —i
bond. Notice that unlike the Zn-based pnictides (Fig. 12), th is and in M SiP2 shows a strong interaction wit t e i S s'site and extends well into the domain of the A'"' site (as no d states are available on this site to repel the density away

a3289eromite 10.

0

0-

13.

0-

4.

0—

6.

0-

0-

8.

0-

10.

0—

and

FIG.

12.

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Distance (a.u.)
Oeo 1e0 2 0 3 0 4so 5 0 SIO?eo 8eo 9 0 10 0 11 so OeO 1 0 2 0 3eo 4 0 5eo 6 0?eo 8 0 9 0 1Geo 1 1e012so

t

'

r

1.0-

3.0-

6.0-

?.0-

8.0-

9.0-
lg
10.0-
U
C O.O
lg
ro 1.0-

~ ~

2.O-

4.0-

5.0-

?.0-

8.0-

9.0-

10.0-

FIG. 14. Total valence charge density of (a) ZnSiP2, (b) ZnSnP2, (c) ZnGeP2, and (d) ZnSiAs&. The contours are logarithmically
spaced the solid circles denote the core regions. The 10 '-e/a. u.'

) contours on the bonds are shaded to highlight the maxima in the bond charges.

the majority of the charge lies

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C9

I qQO =

gsiP2
OtaP
Ch&&98

qp-1 =

q 0-2

I

2.0 S.Q

S~:.-

-

4Q 8.0 qo.p

Mg
qp. p oo

The shaded

g 0-3 —
4.Q

pjStgACe (a' '

p bond»n Mg

QJ Q 0

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PM calculations, inv
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ZnSiP2

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2.2—
2.0

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0.4
0.2
0.0
-0.2
-0.4

- 1.4
0.25

I

0.26 0.27

T3v+ T4v

I I

0.28 0.2 0.30

Anion D~sp lacement

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FIG. 18. Variati
Z SiF2 wi

0=4 co
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states in n

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V. CALCUI. ATED X-RAY-S AY-SCATTERING FACTORS

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)/2 0

(MgSiPz in Fig.. 17), the A
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v . e of d electrons '

the presence o
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values). H owever,

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TABLE VII. Calculated x-ray-scattering factors of ZnSiPq, ZnSnP2, and MgSiP2 for the indicated values of thc anion displacement paraIIlctcrs Q. Thc scattcrlng factors RI'c 1n units of clcctrons pcI' PIImltlVC lllllt CC1?. T?iC iCC1PI'OCR?-1RttlCC VCCt01'S RI'C dlVldCd llltO thrCC gl'011PS (RCf. 23) [(1)—(111)]. Group (i) contains zinc-blende-like factors, group

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Reciprocal-
lattice
vectors

(1,2, 2

)

(1,0, 2

)

(1,0, 2

)

ZnSiP2

u =0.2691

16.50
13.96
11.33

TABLE VII.

ZnSiP2

u =0.2500

14.33
15.81
13.03

(Continued).

ZnSnP2

Q =0.2390

19.71
18.31
16.67

MgSiP~
9 =0.3134

11.41
7.37

MgSiP2
u =0.2848

6.44
4.73

TABLE VIII. Calculated x-ray-scattering factors for ZnGeP2 and ZnSiAs2, compared with the ex-perimental data of Lind and Grant (Ref. 31) (divided by 2 to normalize the same unit-cell volume).
[The notation (n, l,I) of Ref. 31 corresponds to our notation (n, I,rn /2).]
ZnGeP~ (u =0.25816)
p.g,(G) pexpt(G)

ZnSiAs2 (u =0.26575)
p..i.(G) pexpt(G)
Group (i)
(0,0,0)
(2,0,0)
(0,0,2)
(2,0,2)
(1,1,3)
(3,1,1)
(2,2,2)
(2,0,4)
(2,4,

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Vyssh.