PHYSICAL REVIE% B VOLUME 32, NUMBER 4 15 AUGUST 1985

Structural and chemical changes in binary versus ternary tetrahedral semiconductors

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The properties of a prototype ternary semiconductor with the chalcopyrite structure —MgSiP2 —are studied
as a function of lattice constant, tetragonal distortion, and anion displacement with the use of the ab initio
density-functional method. This system is then used as a general model for understanding the chemical
and structural differences between a binary tetrahedral semiconductor (e.g., zinc blende) and its isoelec-
tronic ternary analog (e.g., MgSiP2).

Fourfold-coordinated tetrahedrally bonded ternary

A "B' Cq semiconductors (e.g., MgSiP2, space group D2d, Fig. I) are related generically to their binary zinc-blende A'"Cv analogs (e.g., A1P, space group Td2) in the same way
as the latter are related to the diamondlike 8' 8' homopo-
lar semiconductors (e.g., Si, space group 0»). Much as a
(hypothetical) nuclear disproportionation converts the dia-
mond structure of '"Si' Si into the zinc-blende structure
' Al' P, so does an analogous cation disproportionation con-vert the (doubled unit cell) zinc-blende structure of
' Al' AlP2 into the chalcopyrite structure ' Mg' SiP2. All
three structure types show a fourfold tetrahedral coordina-
tion with an average of four electrons per atom (Grimm-Sommerfeld compounds) and exhibit covalent semiconduct-

ing properties. ' Ho~ever, whereas the diamond-to-zinc-
blende sequence offers but a single added (chemical)
feature (the distinction between a cation and an anion), the
zinc-blende-to-chalcopyrite sequence offers, in addition to a
new chemicaf degree of freedom (the distinction between
one and two cations), two new structural degrees of free-
dom. These are2 (i) the ability of the crystallographic c axis
to deviate from twice the a axis (denoted here as the tetrag-
onal distortion q = c/2a), and (ii) the ability of the anion to
be displaced from its ideal tetrahedral site, creating two dis-
similar anion-cation bond lengths Rqc and Rttc [a distortion
denoted here by the bond-alternation parameter u =—~

1

Mg 8i P
FIG. 1. Crystal structure of MgSiP2. The coordinates of the P atom on the lower left corner are (u, /a4a, c/8).

+ (RA2c —Rt2tc)/a2]. In the diamond and zinc-blende struc-tures q

=—1, u =—~. The structural and chemical changes at-
tendant upon the formation of a ternary sp-bonded
tetrahedral structure from two binary systems are pertinent
to the understanding of locally or coherently ordered solid
solutions formed from binary semiconductors (e.g.,
GaAs+ AlAs GaA1As2). The simplistic but com.44Td (chemij ET BT /X2e

/8).

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BULK PROPERTIES

The calculated structural constants of MgSiP2 (Table I)
agree to within 1%—3% with the experimental values, "
showing that the pseudopotential local-density theory is able
to predict not only the volume of the unit cell (as has been
done before for binary semiconductors'2), but also more
subtle properties such as the tetragonal distortion and inter-
nal displacements. We have also included in Table I the
predictions of the "conservation of tetrahedral bonds"
(CTB) model, shown previously to reproduce the trends in
the structural parameters of chalcopyrite semiconductors.
The present ab initio model is seen to be more accurate.
The analysis of the total-energy surface shows that
MgSiP2 is very soft with respect to volume conserving (i.e., a2c = const) distortions which alter the value of the tetrago-nal parameter q = c/2a. The calculated values of the elastic
moduli (X +A.~), A.„„,and X „(in the notation of

Landau and Lifshitz') are 219, 69, and 73 x 109 N/m2,
respectively. These have not yet been measured (compare,
however, with the similar values' of 230, 166, and 64&109
N/m2, respectively, measured for Si). The calculated pho-
non frequency cu„of the chalcopyrite I ~ optical phonon
(derived from a zinc-blende W~ phonon) is 320 cm
Although it has not been measured for MgSiP2, it has been
measured for several similar diphosphide compounds,

"

giv-

ing values in the range of 310—330 cm '. Since the I ~ pho-
non involves only displacements of P atoms (associated with
changes in u), we expect the actual I ~ phonon frequency of
MgSiP2 to be in the same range, as pre67 5c2dT BT /Xi8.49 Tf 218 400.11 Td (I)Tj ET 263.56 502.33 Tde 256.8L4U6 399.67 33 399 Td Td (~)Tj.3311

1+2~ 5
5~
3~t4

a

5.7A

c/a = 1.7

0 = 0.29 JL5~=:=~

BAND STRUCTURE

TABLE I. Comparison of calculated (calc) and experimental

Ref.

11) (expt) structural of MgSiP2 with those of its
analogs A1P and Si. The predictions of the empirical CTB model

Ref.

2) are also shown.

a

A)

MgSiP2

calc)

MgSiP2

expt)

MgSiP2 (CTB)
AlP (calc)
AlP (expt)
Si (calc)
Si (expt)

718a
63
41
5.467"
40
5.431'

1.
1.87

0.288
0.
0.284

'Reference 25. 26.

The calculated band structure (Fig. 2) similar

the

one previously calculated for the experimental geometry
mixed-basis with the all-electron, potential-variation
(PVMB)

but deviates in some details

the

results of previous empirical pseudopotential calculations.
There are three valence bands: (i)

I

some silicon s contribution,

a Si-P and (iii) a
predominantly phosphorus p total
compares width of 12.4 eV well with the experimental
9 12.8+0. eV, and its main features with
the observed x-ra3.56 502.33 Tde 2561 Tf 151.44 237.89 Td (photoemission)Tj ET BT /Xi1 2579 Tf 212.67 237.89 Td (spectra.)Tj ET BT /Xi1 8.68 Tf 243
4„symmetry with I 5 en-

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model24whichassumesthatAcFisproportionalto(q—1).
TheI3,stateatthebottomoftheconductionbandof
MgSiP2isantibondingbetweenthephosphorussandtheca-tionp,functions.Itismostlylocalizedinthecationicinter-stitialsite.Ithasantibondingcharacteralongtheatomic
chainsinthe(110)planebutisbondingalongthechainsin
the(011)and(101)planes;itisthusstabilizedbyatetrago-naldistortionwhichlowersthevalueofq.
Theliftingofthedegeneracyofthevalence-bandmax-imumandthestabilizationoftheconduction-band
minimumwithdecreasingqdominatether'eductionofthe
bandgap.Ifinourrelaxationprocesswefirstrelaxuand
thenq(thechangeinvolumeissosmallthatitgivesa
negligiblecontribution),wefindEEg=0.19eVand
AEg"=—0.68eV.Ifwerelaxintheoppositeorder,wefind
AEg=—0.84eVandAEg=0.35eV.Inbothcases,theto-talstructuralcontributionAEg=AEg+AEg~=—0.49eV
reducesthebandgapbecausethetetragonaldistortion
lowersthebandgapmorethantheanionicdisplacementin-creasesit.
Thesensitivityofthebandgaptotetragonaldistortionsis
reflectedinthedeformationpotentials,i.e.,
theenergy
derivativesofthebandgapwithrespecttothestructural
parameters.Attheequilibriumgeometrywefind
BEgBEgBEg
a=0.5eV,c=5.8eV,u=2.4eV.(3)
Qa
'
Qc

36stilizatiohow/Xi3 8.54 Tf
105.56684.11 T
ET364
36strs4
364
364