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Zinc-blende —wurtzite polytypism in semiconductors

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The zinc-blende (ZB) and wurtzite (W) structures are the most common crystal forms of binary octet semiconductors. In this work we have developed a simple scaling that systematizes the T=O energy difference bE~ za between W and ZB for all simple binary semiconductors. We have first calculated the energy difference hE

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bly into the

W structure above

a critical temperature T,

.

For ZnS, CdSe, CuCl, CuBr, and CuI, T, =1020+5'C,

"

95+5 C,'

and 407, 386, and 396'C, respectively. The
determination of the intrinsically stabler crystal modification is difficult, however, when (i) neither

W nor

ZB is the stable low-temperature phase (e.g.

,

in MgO,
MgS, MgSe, MnO, and CdO the low-temperatures ground state is the NaC1 structure), or when (ii) only epit axial growth parameters are known. We are nevertheless interested in examining the intrinsic

W vs Zb structural

stability in as many cases as possible (even if neither is the ground state).
Epitaxially induced distortions of the bulk stability are manifested in two ways. First, even if the equilibrium molar volumes of the bulk

W and ZB modifications of

a

given compound are similar, on

a (001) ZB substrate it is
geometrically possible to grow only the ZB form as

a

defect-free film; the

W form growing on such

a substrate

will necessarily have fivefold- and sixfold-coordinated atoms whose large defect formation energies will suppress growth of the

W form. Hence, growth of CdSe, ' ZnTe, '
ZnSe, and ZnS (Ref. 14) on

a (001) GaAs substrate results

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3.0

2.5

(a) Pseudopotential Radii

NaCI

(b) Wave-function Radii

CI

NaCI

16

(c) Dielectric Model

o 1.5
c5

~.0—

0.5

0.0

a

+

W
Ja + A
o
E3 Q

o~ ZB
o &e ~o

X

o o }K
o

0

o
o
o

o
o

o

o

oox
o
o

o

o

o o
0 o
o
oo

ZB o
o o

ZB

0.1 0.2 0.3 0.4 0.5 -0.5 0 0.5 1 1.5 2

R,ia, R„la,

4 8 12

E ~(R)t)

ZB o W

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carbon, whose ground state (graphite} is neither

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TABLE I. (Continued).

(A)

%urtzite

C

ZB

(A)

~+W —78

(me V/atom) (meV/atom)

GaAs present
Expt. '

3.912 6.441 1.647 0.374 5.654 5.65325

12.02 —0.35

present
Expt.

Expt. "
Theo r.'

2.490
2.51

2.50

4.144
4.12

4.14

1.665
1.6414

1.656

0.374 3.539

3.5670

25.3

30

—0.76

Si

present
Expt. ~
Theor. q

3.800 6.269 1.650 0.374 5.392 5.43075

11.72

10

—0.76

Cds present 4.121
Expt. ' 4.1367

6.682
6.7161

1.621
1.6235

0.377 5.811
5.818

—0.4

ZnS

present

Expt. '
Expt.'
Theor. "

3.777
3.8230

6.188
6.2605

1.638
1.6378

0.375 5.345

5.4102

3.1

1.865

—0.1

ZnSe

present

Expt. "
Expt."

3.974
4.003

6.506
6.540

1.637
1.6338

0.375 5.618

5.6676

5.3 —0.5

ZnTe present
Expt. "

4.273 6.989 1.636 0.375 6.045 6.009

6.4 —01

'Reference 34, at T=298 K.
Reference 35, using plane-wave pseudopotentials with the Wigner exchange correlation, a cutoff basis
set of 34 Ry, and 6 and 10 special k points for W and ZB.
'Reference 36.
Reference 37.

'Reference 20, at room temperature.
Reference 38, using plane-wave pseudopotentials with the Wigner exchange correlation, a cutoff basis
set of 34 Ry, and 6 and 10 special k points for W and ZB.
~Reference 39, at c/a= 1.624 and ideal u.
"Reference 40, using the plane-wave pseudopotentials method, and 30 and 60 special k points for %' and
ZB.
'Reference 41.

"Reference 42, at T=291.15 K.
"Reference 43, at room temperature.
'Reference 44, at T=300 K.
Reference 45.
"Reference 46.

Reference 47, using plane-wave pseudopotentials with Hedin-Lundquist exchange correlation, a cutoff

basis set of 64 Ry, and 21 and 10 special k points for %' and ZB, respectively.
Reference 48, at T=287. 15 K.
qReference 49, using plane-wave pseudopotentials with %'igner exchange correlation, a cutoff basis set
of 11.5 Ry, and 27 and 28 special k points for W and ZB, respectively.
'Reference 50, at room temperature.
'Reference 51, at room temperature.
'Reference 52, at T=298 K.
"Reference 53, using plane-wave pseudopotentials with Ceperley-Alder exchange-correlation, a cutoff
basis set of 25 Ry, and 16 sampling k points per plane, in ideal W.
"Reference 14.

"Reference 54, at room temperature.
"Reference SS.

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0

TABLE II. r, and r~ orbital radii (in A) from

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30
20
10
0

E 10- O
(g -20

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Wave-function Orbital Radii

O

O
Q)

20

10

0

10 Ga
Al

Ga
AI
In

B

Be

~cd

&Mg

20

10'

SiGe
Si

Agl
sic

GeC 0

- 10

-20

30 I I I I I I I I I I I

(c) I-VI I c

-30

(a) III-V

N P As Sb

Cdi
Mg
Ca
ZA

Hg

I I I

0 S Se Te

-40

(d) IV-IV

I I I I I I

FIG. 7. Predicted W—ZB energy differences EEw zB(AB) from the wave-function M v -function orbital radii [Eq. (8)] for (a) the III-V series, (b) the II-VI series, and (c) the I-VII and IV-IV anion series.

of the ZB—+W phase transition in CdSe (Ref. 10) estab-
lished conclusively, however, that ZB is the stable low-
temperature phase, in

conclusively,

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Pseudopotential Orbital Radii Wave-function Orbital Radii

E
O

)Q)

E

16

As

Sb Se

As
P

Se E
D

Q)

E

16
As
Sb
8

Sb

Te

Se =Se
S

- 16—

LLI

-24

t
N

-32

(a)
I I I I

B AIGaln

I I I I I I I

Be Mg Ca Mn 2n Cd Hg

(a)
-32
B AIGaln

(b)
I I I

Be Mg Ca Mn Zn Cd Hg

FIG. 8. Anion trends from the pseudopotential orbital radii (Refs. 23 and 24).

selenides, and tellurides. Like oxides, nitrides also strongly stabilize the W structure over ZB.
It is interesting to note the trend for the III-V corn-pounds. We find

~EW—ZB(l~) + ~Ew —ZB(A~) +~Ew —ZB(G~)

for X=P,As, Sb using either choice of orbital radii [Figs. 8(a) and 9(a)]. This trend, unlike the anion trends of Figs. 6 and 7, is nonmonotonic with respect to the position of the column III cation in a Periodic Table row. Insofar as

b,E (A,B}~R (A,B) constitutes an orbital ionicity scale, this suggests All to be more ionic than GaX, in agreement with the calculation of Christensen, Satpathy, and Pawlowska, but in conflict with Phillips' scale. '

K. hE~ z for compounds

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