PHYSICAL REVIEW B VOLUME 45, NUMBER 20 15 MAY 1992-II

Rapid Communications

Rapid Communications are intended for the accelerated publication ofimportant new results and are therefore given priority
treatment

PREDICTIONS AND SYSTEMATIZATIONS OF THE ZINC-... 12 131

gions occupied predominantly by compounds belonging to a single structure. The orbital radii determined from ab initio local-density formalism'

' were first applied to 565

12132 CHIN-YU YEH, Z. W. LU, S. FROYEN, AND ALEX ZUNGER

N

(a)

P As Sb

Ga
Al
In

0 S Se Te

Zn
Mg
Cd
)

E 0
O

E

I 4-
lQ
N
UJ

Al

- 16

-20 -14—
I I I

Al Ga

I I

As Sb

Zn Cd Hg

0 S Se Te

FIG. 3. Predicted W-ZB energy differences DEIL zs(AB)-
[Eq. (3)] for (a) the III-V series and (b) the II-VI series. The
insets depict the trends with the cations.

anion chemical series of the III-V and II-VI compounds. Excluding for the moment those compounds for which
I&Ew za I

is compa-rable to the standard deviation cr of the
fit, we find that our model correctly describes, with only a few exceptions, the overall W vs ZB structural preferences
established experimentally: ' Column III nitrides and
column IIB oxides tend to adopt the W structure, whereas heavier anions stabilize the ZB structure. The exceptions relative to the previously accepted structural designations are CdSe, HgSe,

PREDICTIONS AND SYSTEMATIZATIONS OF THE ZINC-... 12133

&En za(BeS) & &Etr za(BeSe), in agreement with the
model [Fig. 3(b)]. This reflects the fact that while atomic
sizes r =r, +rz generally increase as one moves down a
column in the Periodic Table, first-row cations are partic-
ularly small. Hence, when the cation is a first-row ele-
ment the global anion-cation size difference (rq —rtt(in-
creases when the anion gets heavier (except for BeO), but
for second-row cations and beyond this difference de-
creases. The anion dependence of hE is generally mono-
tonic with respect to the anion position in a column.
(iv) Cation rules. As seen in the insets to Fig. 3, AE can be nonmonotonie with respect to the cation position in
a column: For III-V's the hE~ zq energy sequence is
InX(AIX (GaX. Insofar as /JE (A,B) a:R(A, B)

constitutes an orbital ionicity scale, this suggests A1L to

be more ionic than GaL, in agreement with the calcula-
tion of Christensen, Satpathy, and Pawlowska, but in
conflict with Phillips scale. '
In summary, we found that the 8'-ZB energy difference
exhibits a remarkable linear scaling with the renormalized
orbital radii [Eq. (4)]. This is used to unravel simple
chemical trends within homological series. Apparent conflicts between this model and experiment lead to a sug-
gested reassignment of the true ground state of MgTe
(NiAs-type) and CdSe (ZB).

This work was supported by the Office of Energy
Research (OER) [Division of Materials Science of the
Office of Basic Energy Science (BES)],U.S. Department of Energy, under Contract No. DE-AC02-77-CH00178.

'P. Villars and L. Calvert, Pearson sMa'ndbook of Crystallo-graphic Data for Intermetallic Phases (American Society for Metals, Metals Park, OH, 1985).
2R. W. G. Wyckoff, Crystal Structure, 2nd ed. (Interscience, New York, 1963), Vol. I.
K. Schubert, Kristallstruktren Z~ei komponenti ger Phasen (Springer-Verlag, Berlin, 1964}.
4P. Eckerlin and H. Kandler, in Structural Data of the Ele
ments and Intermetallic Phases, edited by K. H. Hellwege
and A. M. Hellwege, Landolt-Bornstein, New Series, Group
III, Vol. 6 (Springer-Verlag, Berlin, 1971); IVumerical Data
and Functional Relationship in Science and Technology,
edited by O. Madelung, Landolt-Bornstein, New Series,
Group III, Vol. 17, Pts. a and b (Springer-Verlag, Berlin, 1982);ibid., edited by M. Schulz and H. Weiss, Vol. 17, Pts.
c and d (Springer-Verlag, Berlin, 1984).
sE. Parthe, Crystal Chemistry of Tetrahedral Structures (Gor-don and Breach, New York, 1964).
V. A. Fedorov, V. A. Ganshin, and Yu. N. Korkishko, Phys. Status. Solidi (a) 126, K5 (1991).
7R. Rapoport and C. W. F. T. Pistorius, Phys. Rev. 172, 838 (1968).
L. Patrick, D. R. Hamilton, and W. J Choyke, Phys. Rev. 143, 526 (1966).
9Diamond, Silicon Carbide and Related 8'ide Bandgap Semi-conductors, edited by J. T. Glass, R. Messier, and N.
Fujimori, MRS Symposia Proceedings No. 162 (Materials
Research Society, Pittsburgh, 1990).
'nJ. C. Phillips, Bonds and Bands in Semiconductors (Academ-ic, New York, 1973).
' 'J. St. John and A. N. Bloch, Phys. Rev. Lett. 33, 1095 (1974). '2A. Zunger and M. L. Cohen, Phys. Rev. Lett. 41, 53 (1978). '3A. Zunger, Phys. Rev. B 22, 5839 (1980); Phys.

Villars

Bonling

CrystaO.

M.

'

J.

Phys. Phillips,

17,

(J. VillarA,

ess-Commion

(1930);
1984);

M. Villars andF. ibi.

C. Phillips, 0 Lett. VillarA, and H. Rev.

M.

and

Phillips, Phys.

B

(1884);

K. ortaen, J. C. M.

Phillips,

(1991). ibid. a

(a)

D.

M.

J.

Phys.
Zunger,

the ostal

energy

of the

r.and

the energy

for

u for ls

to

the

for

the

inAs o e

hEcalculition
except

the

1276). CheD.

S.

Zunger, and Phys. ~ei

Rev.

S. Pawlowska, N.
B