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Systematization of the stable crystal structure of all AB-type binary compounds:
A pseudopotential orbital-radii approach

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We discuss the role of the classical crossing paints of the nonlocal density-functional atomic pseudopotentials in systematizing the crystal structures of all binary Aft compounds {with A +8}.We show how these pseudopotential radii (r, }

can be used to "predict" the stable crystal structure of ail known {565}binary compounds. We discuss the correlation between [

r,)

and semiclassical scales for bonding in solids.

I. INTRODUCTION

Our experience in understanding the occurrence of a large variety of crystal structures in nature has been traditionally expressed

A j.KX ZIIXGER 22

calculated

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tronic and crystal structure.
The success of this approach in correctly "pre-
dicting" the structural regularities of as many as 565 binary compounds using elemental coordinates that pertain directly only to the s and P electrons (and only indirectly to the d electrons through the screening potential, produced by them) presents
a striking result: It suggests that the structural pprt AE, of the cohesive energy may be do-minated by the s-p electrons.
This points to the possibility that, while the relatively localized d electrons determine both central cell effects (such as octahedral ligand fiel'd and Jahn-Teller stabilizations) and the reg-ularities in the structure-insensitive cohesive energy &E, of crystalline and liquid alloys, the longer range s-P wave functions are responsible for stabilizing one complex space-group arrange-ment rather than another. There is a striking resemblance between this result and the semiclas-sica,l ideas indicating a correlation between the stable crystal structure of transition-metal sys-tems and the number of s and P electrons, put forward by Engel'4

"

in 1939 and subsequently
greatly refined by Brewer.

"

In the Engel-Brewer
approach, the d electrons play an important but indirect role in determining the energy required for exciting the ground atomic configuration to one that has available for

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of

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p(r) =+Jg ~

|l'y(r) ~
In the pseudopotential representation, one seeks
to replace the external potential V„,(r) by a pseu-
dopotential V„(r,r') such that the lowest eigen-
states y&(r) have properties of valence, rather than core wave functions. The pseudopotential single-particle equation is hence:

-',v' + V (r,r') + Vt'

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Z& PZ,
v,'."(r) = l(rr(r) —)I+]-—'+v..[p,1+v,lp. l+v Ip,])r(v, lp. +p„]-v,lp, l —v, fp„])

+Iv tp, +p„l-v Ip. l —v Ip.1]+Iv.,fp.l —v.,]v]I+ v. lp.] —v„]v] + v Ip„]-v fv]),

where the "Pauli potentiairr U, (x) is given by

p„,c'„'„',0„,(~)

and the core, valence, and pseudocharge densi-
ties are given as

P.(&) = g ~ g (~) ~

'.

p.(r) =g-I p.",(r) I',

The atomic pseudopotential in Eq. (10) has a simple physical interpretation. The "Pauli po-tential" U, (r) is the only term in n

'

(r) that de-
pends on the wave function it operates on (i.e., "nonlocal"), whereas all other terms in Eq. (10) are common to all angular momenta (i.e.,

"local").
For atomic valence orbitals that lack a matching
l component in the core, the all-electron valence orbitals g"„,(x) are nodeless, hence X„,=g"„, and, from Eq. (11), U, (x) =0 for such states. In these eases, the pseudopotential is local and purely attractive due to the dominance of the all-electron

term, -(Z, +Z„)/x. In all other cases, U,(x) is positive and strongly repulsive, but confined to the atomic-core region. U, (x) replaces the core-valence orthogonality constraint and is a realiza-tion in coordinate space of Pauli's exclusion prin-ciple.

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to normalized and nodeless g„,(r). This is

a

manifestation

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10

~ e

Q

g

4

2

0
C
O
2

O

0'0
O -4

I I I I I

0 0.

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TABLE I. Classical crossing points of the self-consistently screened nonlocal atomic pseudopotentials (including the centrifugal term), in a.u. The core shell is defined in each case as the rare-gas configuration of the preceding rovy.
The Kohn and Sham

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3.0
~ Cs

1.0

0)
~

'e2 2.0—
l4K
o 15—
0
V
I

~ 1.0—
CL

E

LLI 0.5—

0.0

I I I I I

0.0 0.5 1.0 1.5 2.0 2.5 3.0

rp (a. u.]

FIG. 4. Correlation between Ashcroft's empty-core
pseudopotential radius and the p-orbital radius of the
present density-functional screened pseudopotential (Table I).

empty-core radii used to fit resistivity data may be identified, within a linear scale factor, with the y screened pseudopotential coordinate (Fig. 4). Whereas the alkaii elements are characterized
predominantly by a single coordinate (Fig. 3), in
line with their free-electron properties associated
with a shallow pseudopotential, the elements to
their right are characterized by a dual-coordinate system. The regularities in these dual coordinates also reQect well-known chemical trends: For ex-ample, the tendency towards metalization in the
C —Si-Ge- Sn —and Pb series is represented by the increased delocalization and reduced depth in their pseudopotentials, etc.
Having discussed the periodic trends

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0.5
I)

I
I

0.4 +

I
I

O.3 +

I
I

ot2 A

~ 0
V

5 I
u.

o o.o

I
I
I

~ -0.1
I

tgK

I
I

-0.3 —y

I I I I I I I I I I

——Nb

d, lvl

r, IVI

r, INbl
maxlvl

"maxlNbl

-04—

-0.5
0.0

I I I I I I I I I I I I I

0.2 0.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 2.6 2.8 Distance(a. u.)

FIG. 7. Radial z-type all-electron wave functions for V and Nb. x ~ denotes the position of the outer orbital maxima, is the screened pseudopotential radius, and d~ is the average node position. Note that y~ is pinned inwards of the
last node and outwards of d~.

finite overlap occurs. Since the present x,' coor-
dinate scales approximately with the orbital energy

& „

the former coordinate is a realization of

Slater's electronegativity in a pseudopotential re-presentation.
The orbital radii r, also form an interesting distance scale.

"

Consider an all-electron valence
atomic wave function such as the 4s and 5s orbitals

of V and Nb, respectively, depicted in Fig. 7. These wave functions have their outer maxima at

the points denoted by z and have a number of nodes inwards to y. An algebraic average taken

for all node positions in each wave function shows

that these average positions (denoted by d,) are pinned at a certain distance from the pseudopoten-tial orbital radius x,. Figure 8 shows the average node position d, of the outer all-electron s-type valence orbital plotted against x„and Fig. 9 shows similar results for d orbitals (only the first and last element of each row are denoted by the chemi-cal symbol). We find that the orbital radius r, scales linearly with the average node position, where the row-dependent scale factor increases monotonically with the position of the period in the table of elements (e.g.,

the scale equals 1.0, 1.5,
2.0, 2.3, and 2.7 for periods 1-5, respectively).

1.0

CO ~ ~

lo 1.0—
IX
o

0

cOe~ I&
0)

Z -o.s
I

Ul
tO

Rb

tg

s

I 'rn D
g g0.5—
SZ

PeO- P D % e

K

0.00 0 0.5 1.0
r,)a.u.)

2.0

FIG. 8. Correlation between the average node position in the valence all-electron g wave function and the screened pseudopotential radius y, (Table I). The first and last atom of each row are denoted by

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3.0

2.5—

3.0

lO

0)
.2

~ 2.0— tO
'oI
l9

1.5—

2.0
ld

ts

'

1.0

0.0

'

Li

I I I I I I

Ne Na Ar K Cu Kr

1.0
0.0

I

0.5

I I

1.0 0.5

r,ra.u.]

I

1.0

FIG. 10. Relation between Pauling's tetrahedral radius

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B. Screening length and orbital radii

One can view the quantity x,' as being an orbital-
dependent screening constant pertinent to the
scattering of valence electrons from an effective
core. For the nontransition elements, one finds

(cf. Fig. 13), as expected, that r,'

falls off mono-

tonically with decreasing valence charge Z„, re-flecting a more effective screening. However, for the 3d, 4d, and 5d transition series (Fig. 14), one finds two distinct behaviors: Although x~' is

a

simple, monotonic function, both z,'

and r&' show
a

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I I I I I I i I I I I I I I I I I

0.25

g

0.20

ro

th

~D

Cl

CC 0.15

0.10

Ca Ti Cr Fe Ni Zn Ge
I I I I I I I I I I I I I I I I

K Sc V iiln Co Cu Ga As SeBr

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elements. Other plots (e.g., correlation of
r-~ ~

or ~r,"+x~ ~

between the various schemes)
lead to similar conclusions.

V. APPLICATIONS TO PREDICTION OF CRYSTAL STRUCTURE OF 565 BINARY COMPOUNDS

A. Structural plots

The orbital radii (y,) derived here can be applied to systematize the stable crystal structure of corn-

pounds in the same way as discussed by St. John
and Bloch, ' Machlin et al.,

~ and Zunger and
Cohen.

"

Having, however, the orbital radii of
all atoms belonging to the first five rows in the Periodic Table, the present theory can be applied to a far larger data base of crystals (565) than has been attempted previously (50-80 compounds).
Our first step was to compile a list of binary A.B compounds whose atoms belong to the first five rows of the Periodic Table. We were interested

TABLE II. AB crystal structures used in the structural plots. When two entries appear for the number of compounds, the first indicates the number of suboctet compounds and the second denotes the number of nontransition element superoctet compounds.

Stncktu rb eri chte
or Pear son symbols

Space
group Unit cell Prototype

Number of
compounds

B1
B2
. B3

a4

Em3m
Pm3m
E43m
P63mc
Ed3m

Octet

cubic
cubic
cubic
hexagonal
cubic

NaC1
CsCl
ZnS
ZnO
diamond

65

29
11
4

Total

B1
B2
B8g
B10
B11
B16
B19
B20
B27
B31
B32
B33
B35
B37
Ba

cp64
j'zP24
L10
m C24
mC32
mP16
mP32
oC16
oC16
oC48
oI8
oP16
tI8
tI32
tI32
tI64

Fm3m
Pm3m

P63/mme I 4/nmm
P4/nmm
Pnma
Pmma

P2(3
Pnma
Pnma
Fd3m
Cmcm
P6/mmm
I4/mcm
P6m2
P43n
P63/mme
P4/mmm
C2/m
C2/c

P3(/c
P2(/n
Cmcm
Cmca
Cmc2g
Immm
P2&2&2&

r4/mmm

I4) /a
I4/mcm
I4&/acd

Nonoctet

cubic
cubic
hexagonal
tetragonal
tetragonal
orthorhombic
orthorhombic
cubic
orthorhombic
orthorhombic
cubic
orthorhombic
hexagonal
tetragonal
hexagonal
cubic
hexagonal
tetragonal
mono clinic
mono clinic
mono clinic
mono clinic
orthorhombic
orthorhombic
orthorhombic
orthorhombic
orthorhombic

tetragonal
tetragonal
tetragonal
tetragonal

NaC1
CsCl
NiAs
PbO
CuTi
GeS
CuCd
FeSi
FeB
MnP
NaTl
CrB
CoSn
SeTl
MoP
KGe
LiO
GuAu
AsGe
NaSi
AsLi
NS

Nang
KO
SiP
HbO
NaP
HgC1
LiGe
TlTe
NaPb

33+8
122+2
62+ 3
0+2
7

0+7
11
17
16
30
7
41
3
0+3

6
3
27
0+4
1

0+5
1
1

0+1
4
6
0+3
1

0+1
7

453

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R"s- ~(

"rr"+) —(re+re) ~,
R '= (r,"-r" ~

+ ~r'- r'~.

(21)

Here, R" is a measure of the difference between
the total effective core radii of atoms 4 and B

(i.e., size mismatch), whereas R,"s measures the
sum of the orbital nonlocality of the s and p4 T Td (e+re))9.04 ~r'-

s

R, the

A LK X ZUNGER

3.0- Legend
0 BS(N.Ctj
O B2i~ti
V Ba,fNiA I
Q B16[GeSI
D BRtMnPI

V B32[NaTI) 0 B33:-Bt(CrB
8 oP64(KG)
& g 8 L1o{CuAu)
~ mC24[AaGe
e mC32[NaSi
8 mP16{AaLt)
— OC16[NaHg)

1.S -0 tl64(NaPb) ~O

1.0—

0.0—

V' Vivat,&& 0@ 0

tt)t V ~ 0 0 0
o o oooo

V V ~ Q
V ~O
V
V V

mc 24
oC 16

I

0.0 0.5

R (a.u.)

I

1.0

FIG. 20. Structural separation plot for the 356 binary nonoctet coxnpounds, obtained with the density-functional orbital radii, witli R, = ((r&+ re)-(t&+ r,)[, R, =

I tq —rs I+ I+t —+ I

'

of assessing the true success of the method.
The remarkable

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3$- p
0
8

84-

e

e
2.5-

8

Legend
Bb (Qo
B19(A
811 (C
820 (Fe
B27 (Fe
B3? (Se
B35 (C
hp24 (L
oC16 (K
o18 (Rb
mP32 (
tI32 (LI
oP16 (N

pounds. All the superoctet compounds (a total of
34) could be separated clearly as well (Fig. 22 and discussion below). This illustrates the predictive ability of the present approach.

If one is to consider the pairs of related crystal structures mentioned above as belonging to single

generalized structural groups, the total number of misplaced compounds (5 octet and 32 nonoctet) forms only 7% of the total data base of binary compounds. The present theory is hence more than 90/o successful.

2.0—

B. Discussion of "misplaced" compounds

1.5-
0
K

1.0-

as-

OA)-

mP32

Qo

B20
B3?
B35

A

e

6

0

~h
O

0

e% p
OO

O oO

qO

819+811

I

0.5

R (a.u)

I

1.0

FIG. 21. Structural separation plot for the 81 binary nonoctet compounds, obtained with the density-functional orbital radii, with

son. '

In fact, examination of the thermochemical

data (Refs. 12 and 13 and references therein) in-dicates that if a certain compound exists in two of
these related structures at somewhat different

temperatures, the difference in their standard
heats of formation is often as small as 0.3 kcal/

mole. (For example, AgCd in the B19 structure
has AH=0. 094+0.004 eV, whereas the B2 struc-
ture has a heat formation of 0.080 + 0.Td (whereas)Tj ET BT T BT /Xi20 9.2 Tf 121.94 28.38 4

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TABLE III. Compounds which are misplaced in the
present theory (out of a total of 565).

Expected
Compound structure

Structural
domain(s) in
which it is
found

gAB

(a.u.)

gAB

(a.u.)

1. CuF
2. MgS
3. BeO
4. Mg Te
5. MgSe

B3
Bl
84
84
Bl

Octet

Bl
B3
Bl-B3
Bl-B3
Bl-B3-B4

1.635
0.93
0.615
0.36
0.745

0.375
0.25
0.305
0.32
0.285

1. CoAl
. 2. FeAl
3. NiAl
4. CoGa
5. FeGa
6. NiGa
7. NiIn
8. MnIn
9. CoPt
10. TiAl
11. OsSi
12. CoBe
13. MBe
14. NaPb
15. AuBe
16. FeC
17. TiB
18. PtB
19. IrPb
20. AgCa
21. Hfpt
22. ¹iHf
23. NiLa
24. NiZr
25. PtLa
26. RhLa
27. Zr Pt
28. PdLa
29. AuLa
30. NiY
31. PtY
32. LaCu

82
B2
B2
B2
B2
B2
B2
82
Ll

p

Ll

p

82
82
82
@64
820
81
Bl

BS)
88(
B33
B33
B33
833
B33
B33
833
B33
833
B27-B33
B27
B27
827

Nonoctet

BSg-B31-B20

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of 0.049 and 0.03 eV (i.e.,

-2 —lkT) for

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hence different tetragonalities.
It is interesting to note that the present scheme
also predicts unusual electronic ProPerties of
compounds belonging to the same structural
group. For instance, the B2 compounds CsAu and
RbAu that appear in Fig. 20 as isolated from the other 147 B2+I-10 suboctet compounds have semi-conducting properties while all other suboctet compounds belonging to these structures seem to be metals. A recent calculation of the electronic

band structure of CsAu (Ref. 119) has indicated that if relativistic corrections are neglected, Cshu appears to be a metal, which disagrees with experiment, whereas the inclusion of relativistic effects lowers the Au s valence band to form a semiconductor. It is remarkable indeed that such

complicated electronic-structure factors are re-
quired in quantum-mechanical band-structure cal-culations to reveal the

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SIP SUPER OCTET
16 AB Compounds (8)
(VKC = 9)

SUPEROCTKT

18 AS Compounds (b)
(VEC = 10)

aSIAS 7- p 0
GeS Sns

ctl
5

gg 4

„GeP
oP8
olnS

GaS hP8, hR2
~GaSe ~ InSe oTIS

oInTe oTISe
GaTe a
HgCI
a

kgBr
tI8

mC24
TITe

tI32 kgI

GeSe
oSnSe
PbSo

GeTe SnAs

SnTe
oBiTe
PbTe

oBISe TICim
o

PbSe
TIBr

PbPo B2

B10
a SnO

aPbO

TIF

0
0.0

I

0,5

I

0.5 1.0 0.0 1.0

~r,

'- r,"~ (a.u)

FIG. 22. Structural separation plot for the 34 super-
octet compounds A B + with valence electron concen-
trations (VEC) equal to 9 [Fig. 22(a)] and 10 fFig. 22(b)]. The structural groups are defined in Table III and in

AppendixA. The symbolR[Fig. 22(b)] denoted arhombo-
hedral structure. In the 91 domain of Fig. 22(b) we have also included the compounds with VEC= 9, 11 (see text).

of the P-orbital electronegativity difference be-tween atoms & and B, while 8, measures the s-p nonlocality on the two sites. The reason that ~r~s r-~~ forms a better structural

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GaSe, GeTe, SnTe, InSe), and the orthorhombic-
ally distorted B1 compound TlF. It is seen that
the seven different structures of the VEC=9 com-
pounds, as well as the six different VEC=10
structures, are very clearly resolved, the only
exception out of these 34 compounds being the B37 compound TlS which is marginally displaced into the neighboring hP8 hR2-domain [Fig. 22(a)].
It is important to emphasize that the ability to separate structures shown by the present orbital radii (Figs.

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Shaw Parameters

0 0
0

0
0

C)0 o
3 Igl 0 cP P

oI-j

+

oR

I

'INI

"

'LOI o & 'o

& 5 8 o%g

LEBEND

Q- 81 T- 881
831 +- CP64

H- TI60 +- 832 0- 82 0- 833 X- 816

- L1O
IH- NC20

Q- NC32
g- OC16
+- NP16

-0. 1 0.5 0.8

R2

I

1.7 2. 0 2. 3 2. 6

FIG. 25. Structural separation plot for the nouoctet compounds using

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scale of structural energy hE,. A similar result was recently reported'-3' for NiAl.
One would therefore

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22) with a remarkable success, exceeding 95 lo.
The compounds for which the present theory does
not predict the correct crystal structure are

exce149ETj E49E439 8.5bT BT /Xi29 9.67 Tf 3(succes2.0 BT49E0i29 8.largelTf 262.38 671.17 Td (crystR,)6B

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InLa, IrA1, IrQa, IrSc, LaT1, LiAg**, LiAu*,
LiHg, LiPb*, LiTl, MgHg, MgLa, MgSc, MgSr*,
MgT1, MgY*, MnAu*, MnHg, MnIn, MnIr* MnPd,
MnPt**, MnRh*, MnZn*, NiAl, NiBe, NiQa,
NiIn**, NiSc, NiZn**, OsA1, OsSi**, PdAl*,
PdBe, PdCu, PdIn, PdLi, PdSc, PtSc, RbAu, ReAl, RhAl, RhQa, RhHf**, RhIn, RhMg, RhSc, RhY, RuAl, RuQa, RuHf, RuSc, RuTa*, SrCd, SrHg, SrTl', TcHf, TcTa, TiCo, TiFe**, TiIr, TiNi, TiOs, TiRe, TiRu, TiTc, TiZn, VMn, VOs, VHu*, VTc, YIn, YTl, ZnLa, ZnSc, ZnY, ZrOs, ZrPt**, ZrRu*, ZrZn.

TlBr, T1Cl

82, Pm3m, CsCI type, superoctet

810(tP4)/nmm, PbO ty pe, superoctet

PbO**, SnO**

Bl1, P4/nmm, CuTi type

HfAu, PdTa, TiAu, TiCd, TiCu, ZrAg, ZrCd.

816,

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mP16, P2&/c, LiAs type
KSb, LiAs, NaQe, NaSb.

(oP16, Pbca, CdSb, superoctetg
CdAs, CdSb, ZnAs, ZnSb.

mP32, PZ&/n, NS type, superoctet

AsS**, AsSe**, NS, NSe, PS**.

tI8, l4/mmm, HgC1 type, superoctet
HgBr, HgC1, HgI.

NaHg.

oC16, Cmcm, NaHg type
LiQe.

tI32„ I4&/a, LiGe type

KO.

oC16, Cmca, KO type
KC, NaC.

(tl32, I4&/acd, NaC type

SiP.

oC48, Cmc2&, SiP type, superoctet
T1Te.

tl32, I4/mcm, TlTe type, superoctet

ol8, Itnmm, RbO type
CsO, CsS, RbO, BbS.

oP16, P2&2&2&, NaP type
KAs, KP, NaAs, NaP, RbAs, RbP.

tl46, l4&/acd, NaPb type
CsPb, CsSn, KPb, KSn, NaPb, BbPb, HbSn.

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J.

'THE

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