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First-principles statistical mechanics of structural stability of intermetallic compounds

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metrics: CuAu orders in the fcc L 10 structure,

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O(10)—O(10),

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ing Hamiltonian' which includes "interactions" pz=pk between k pseudospins separated by up to the mth neighbor distance (the choice k=2, m =1 corre-
sponds to the classic, ' '

nearest-neighbor pair interac-
tion case). Since the configurational property P(cr) can depend in general on the external volume V (or pressure)

of the lattice, so will the cluster contributions Ipf].
It is useful to expand the configurational property P(o) with respect to some reference configuration On. e possibility is to expand it relative to the property P of equivalent amounts of pure A and pure B lattices. The cluster expansions for o = 3 and o.=Bare

and

P(A, V)= g g (—1)"Di, pi, (V)

m k

P(B, V)= g g (+1)"Di, pi, (V),

m k

(2.13)

(2.14)

The cluster expansion for AP is then

(2. 16)

where i)=1 for k=even and

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are extracted, for example, through fits of the observed
dissociation energies, molecular conformations, and
vibrations, ' ' "

or fits of calculated ' '

(e.g., by
the Hartree-Fock or density functional ' ' Born-
Oppenheimer energyOppenheiTj ET BT /Xi4 8.46 Tf 176.78 783.44 Tdurf8 8.pseudopote BT /Xi4 9.01 Tf 563.78 76.56 T648the surf8 8.76 Tf fs)BT /Xi4 8.47 Tf 152.44 684.5surof

byfu44 684556 T648the I,

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single-particle

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N,

pF y[ll (s)] 'P(s), ~D F
or (if X~ (N,) by minimizing the weighted variance'
2 NF

g co, P(s) —g?IF(s)D~pF =minimum,

F

with the weights
co, =48Xc(s)/Xo(s).

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cluster expansion permits (but does not require) that pF depend on composition: the situation here is analogous

to the ex ansion of a wave function P (o)b.y a finite set of (obviously nonunique) basis orbitals pF that cou, u

o e expa

need not depend on an energy parameter. We have previ-ously shown how an optimal set of structures can be selected so as to avoid any near-linear dependence (i.e., obtain a numerically stable inverse matrix iiF '). In the

SB Name:
(other)
Formula:

A1,(fcc) L12

A3B; AB3 A38; AB3

(P1 P2)

A28; AB

Crystal
Structure

A
~ B

Example
Bravais
Lattice
Unit
Cell
Vectors

Soace Group:
Int. Tables:
Shoenf lies:
Number:

Pearson Symbol:
Equivalent
Superlattice

Cu

Face-centered Cubic

(0,1/2, 1/2)
(1/2, 0, 1/2)
(1/2, 1/2, 0)

Fm3m
5

225
cF4

None

Cu3 Au

Simple Cubic

(1, 0, 0)
(0, 1, 0)
(P, P, 1)

Pm3m
1

221

None

TiAI3

Body-centered
Tetragonal
(1, 0, 0)
(0, 1, 0)
(1/2, 1/2, 1)

l4/mmm
17
o4h
139

A38 along [201]

Body-centered
Tetragonal
(1/2, 1/2, p)
(1/2, -1/2, 0)
(1/2, P, 3/2)

l4/mmm
17
04h

t16

A2B1 along [001]

SB Name:
(other)
Formula:

L10

AB

L11

AB

(CH, "40")

A282

(Z2)

A2B2

Crystal
Structure

A
~ B

Example
Bravais
Lattice
Unit
Cell
Vectors

Space Group:
Int. Tables:
Shoenf lies:
Number:

Pearson Symbol:
Equivalent
Superlattice

CuAu-I

Simple Tetragonal

(1/2, 1/2, 0)
(-1/2, 0,1/2)
(0, 0,, 1)

P4/mmm
1

o4h
123
tp4

A&B& along [001]

CuPt
Rhombohedral

(Triagonal)
(1/2, 1/2, 1)
(1,1/2, 1/2)
(1/2, 1, 1/2)

R3m
5
03d
166
hR32

A&8& along [111]

Nbp

Body-centered
Tetragonal

(1, 00)
(0, 1, 0)
(1/2, 1/2, 1)

l4&/amd
19
o4h
141
ti8

A2B2 along [201]

Simple Tetragonal

(1/2, 1/2, 0)
(-1/2, 1/2, 0)
(0, 0, 2)

P4/nmm
7

129

tps

A282 along [001]

FIG. 3. Crystal structure information for the fcc cornmpoun oundss used in thee cluster c expansion.. Table III gives the lattice-averaged a ice avera e spin products Vik Vi for th ese structures. In cases where a structurbereicht (SB) symbol is unavai a e, we ave
top).

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present study we h ave usesed 12 fcc and 12 bcc structures that satisfy the above conditions. They are shown in Fi s. 3 and 4 that also give the unit cell vectors, Bravais lattices, space groups, and structu -

yp y

Figs. 3 an a as
re-t e s mbols. In

cases where ere a structure-type s symbol is unavai a le in the

the lattice-averaged spin products IIHk s) and degenera-cies Dk, m [E. (2.12)] (D is set, for convenience, to uni- 0, 1

SB Name:
(other)
Formula:

A2, (bcc)

A;B

003

A3B; AB3

L6p

A3B; AB3

C11b

A2B; AB2

Crystal
Structure

QA
B

0

Example W Bi F3, Cs3Sb Cu Ti3 MoSi2

Bravais
Lattice
Unit
Cell
Vectors

Space Group:

{-1/2, 1/2, 1/2)
(1/2, -1/2, 1/2)
(1/2, 1/2, -1/2)

(0, 1, 1)
(1, 0, 1)
{1, 1, 0)

(1, 0, 0)
(0, 1, 1)
(0, -1, 1)

Body Centered Cubic Face Centered Cubic Simple Tetragonal Body - Centered

Tetragonal

(1, 0, 0)
(0, 1, 0)

(1/2, 1/2,) 3/2)

Int. Tables
Shoe nf lies:
Number:

Pearson Symbol:
Equivalent
Superi attice

Im3m

o'

h

229
cI2
None

Fm3m

p5
225
cF16

A3B1 along [11 1]

P4/mmm

tP4
None

l4/mmm
17
04h
139
tI6

A2B1 along [001]

SB Name:
(other)
Formula:

B2

AB AB

B32

A282

B11

A282

Crystal
Structure

Qa

Example
Bravais
Lattice
Unit
Cell
Vectors

Space Group:
Int. Tables:
Shoenf lies:
Number:

Pearson Symbol:

CsCl

Simple Cubic
(1,

Simple Simple

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TABLE II. Definition of the basic figures in the fcc and the bcc lattices and their degeneracies DF. We use the lattice

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ev

a5

bQ

6

o
O

bQ

E

o
V

O l~ ~ O ~ O
I

-l~ O ~ -I -I -I

I I

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TABLE VII. The interactions DFU+ for the volume cluster

expansion (in cm /g-at.) of Eq. (4.9) for Al& Ni compounds.
V' '(s) of Tas(s)

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Eqs. (4.13). The upper part of Table VIII (denoted "structures belonging to basis") gives the point charges obtained by this model and the "exact" Madelung con-stant aM(s) obtained by applying Ewald's method to these structures. We then cluster-expand these aM(s) us-

ing a set of pair-interactions Ipz) with I =1, 2, 3, 4,

and

5 (Since the Madelung energy represents pair interac-tions, all k&2 interaction energies pk vanish. This in-creases the linear dependence of structures. In this case, out of the 12 canonical structures, only six of them are linearly independent.

) Minimizing the variance of Eq.
(4.3) yields

pz~& =0.73675 p2

]

= 0.32393,

p2

2 =0.08345, p2

3

0 06093

p24 =0.03478, pq

5 =0.001 39

. (4.15)

Note that this cluster expansion converges rapidly with the interatomic separation m, unlike the interaction po-tentials p2 of Eq. (3.2). These elfective cluster energies of Eq. (4.15) can then be used to calculate the Madelung constants using the cluster expansion (CE) of

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basis" (calculated directly by Ewald's methods) with
those predicted by the cluster expansion, using the
coefficients of Eq. (4.15). The agreement is seen to be
very good. We hence judge this expansion to be con-
verged to within the error limit reAected in Table VIII.
Having established the convergence and transferability of the cluster expansion coefficients for Madelung con-stants, we can use Eq. (2.18) and predict the Madelung energy for the perfectly random (R) alloy. This gives, within the charge model of Eq. (4.13)

aM(R, x)=4x(1—x) X0.7368 (for X, =12) (4.17a)

using the 12 canonical structures and Ave effective pair interactions, or

aM(R, x) =4x (1—x) X0.7392 (for X, =27) (4.17b)

using in the basis all structures of Table VIII and six effective pair interactions.

&noiyric results for & &M &R

3. Discussion ofthe Madelung energies

In the remainder of this paper we will apply the same cluster expansion procedure used above for the Madelung energies (Sec. IV E 1) to calculate the total electron plus
ion energies. In the latter case, analytic results are not
available for comparison. However, the agreement found here between the truncated cluster expansion and the an-alytic results for the Madelung lattice, lend credence to
this general procedure. Observe, in particular, that
despite the long range of the bare Coulomb interactions p;i of Eq. (3.2), the renormalized interactions used throughout this paper [e.g., Eq. (3.3) and (4.15)] are of
considerably shorter range, leading to a rapid conver-
gence of the cluster expansion.
Our results E~(R)%0 [Eqs. (4.14) and (4.22)] should be contrasted with EM(R):—0 assumed by all models that are based on the homogeneous SCPA. The contribution of the Madelung energy to the "ordering energies"

(4.23)

where

F,(x)=—4x(1—x)(2Z, ICi), —

(4.20) I' »()=x4x(1—x)K
and K is the number of

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V(s) =(1—x,) V(A)+x,(B), (5.3)

suggested that little precision is lost for the Cu com-
pounds if we linearize the equilibrium volumes and bulk
moduli with respect to composition, i.e.,

V(CuPd) =88. 168 a. u.

B(CuPd)=1. 935 Mbar,

B '(CuPd) =5.60,

(5.5)

V(Cu) =76.882 a. u.

B(Cu)=1.798 Mbar B'(Cu)=5. 86,

V(Pd) =99.454 a.u.

B(Pd)=2.072 Mbar, B'(Pd)=5. 33.

The 50%-50% linear averages of the above are

(5.4)

and similarly for B(s). For example, the LAPW calculat-
ed volumes, bulk moduli B, and their pressure derivatives

B' for the bcc elemental solids are V (CuPd)=87.744 a. u.
B (CuPd)=1. 952 Mbar,

B' (CuPd) =5.62,

(5.6)

i.e.,

the averages are within better than 1% from the
directly calculated values. Results in the same range are
obtained for Cu3Pt and CuPt3 in the I.lz structure. We
hence use the linearized volumes and bulk moduli for the

whereas the directly calculated values for the CsC1 struc-
ture of (CuPd) are

TABLE X. Formation enthalpies hH (in meV/atom) of the unrelaxed (ur) and relaxed (r) fcc compounds considered here, and the unit cell volumes (in cm /mole) at which the calculations were performed. The first line gives the unit cell volume, the second line gives the unrelaxed KH„„and the third line gives the relaxed hH,. All Cu-based compounds are calculated using the LAPW method with the Wigner exchange correlation, whereas the Al-Ni compounds were calculated using the LMTO method with the von Barth-Hedin

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Cu compounds [this constitutes a significant computa-tional economy as we only need

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TABLE XII. Comparison of the directly calculated (LAPW or LMTQ) and the cluster-expanded

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viate from what simple rules might suggest (e.g., Zen's rule for molar volumes or ideal fcc positions for atomic coordinates); we refer collectively to these deviations as
"relaxation. " We will distinguish "volume relaxation"
(when molar

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1000

500

xAux,'

fCC

J4 1)x10

4QQI

200

200

100

Rh

(8J3 1)x10

:(SJ3 1)x10
-500—

- 1000 i
LO CU

1000—
(b)

(12J2 3)x10

0— (6J24)x10
(3J2 2)x10~

- 500—

-200

*

-400
Au Cu
400

200 =

12J2 3 ~3J
0-—

-200-

6J

6J2 4

- 100—

-200
Pt Cu
200
(f)

100-
3J2 2

0

- 100—

6J2 4

2,3

- 1000
0.2
Cu

-400 -200

0.2 0.4 Q.6 Q.8 0.2 0 4 Q 6 0 8 Au Cu Pt Cu ' '

Rh

Composition x

FIG. 5. Fcc interaction energies Jq [V(x)] obtained from the cluster expansion for (a) and (b) Cu, „Au„, (c) and (d) Cu, „Pt„,
(e) and (f) Cu& Rh.

verge with respect to the figure sizes in the sense that
among pair interactions the nearest-neighbor terms
D2 ~ J2 &

are considerably larger than the longer-range
pair interactions, and the three- and four-body terms are
rather small. This is illustrated in Fig. g for x= —,. (ii)

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300 -
)
250 - {2,1)

200—

fcc CuAu
x=1/2

200.
(d)
(2,1)
150—

2(2,)Tj ET BT /Xi22 5.91 Tf 123422 T65 Td (.4) 1) C ETj ET BT /Xi22 3.92 Td 15974 691778 Td (1OlTj ET BT /Xi22 5.432Tf 37037 691333 Td (—)Tj ET BT /Xi22 42895Tf 31 T61144 Td (.IITj ET BT /Xi22 4286 Tf 26014 T59733 Td (I)Tj ET BT /Xi22 96.26Tf 37289 T59.89 Td (250)Tj ET BT /Xi22 53896Tf 26014 T59333 Td (

xjTj ET BT /Xi22 8.9X Tf 215434 T49918 Td (x)(4)Tj ET BT /Xi22 4.91 Tf 916257 T49914 Td (.)

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demonstrated that a converged Ising representation of the quantum-mechanically calculated excess total energy can indeed be obtained from

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B. Predicted ground-state structures

Figure 9 depicts the ground-state lines for the alloy
systems studied here. The symmetries established clearly
from experiment are also found theoretically, even
though we have purposely omitted from the basis set used
to extract Jz some of the structures which are known to be ground states. Note that while high-temperature-

ordered phases are relatively easy to detect experimental-ly, some of the potentially low temperature "ground-state structures" discussed in this section might be more difficult to observe (due to the slow atomic diff'usion rates at low temperatures). In what follows we summarize the pertinent low temperature experimental

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SB Name: (Nb Nis) (D1,D7)

Formula: ASB* ABS A7B;AB7

Crystal
Structure

OA
~ B

0 0 0 0 0

0 0 0

e 0

0

~

0 e

,~a ~a
0

0

0 0 0

0

0 ~ D C
C) O

o 0

0

Example:
Bravais Lattice:
Unit
Cell
Vectors

Space group:
Pearson Symbol:
Super lattice:

bNiS

Simple Tetragonal

(0, 1/2, 3/2)
(3/2, 0, 3/2)
(3/2, 1/2, 0)
P4/mmm (04~h)

None

Ca7oe
Face - centered Cubic

(0, 1, 1)
(1, 0, 1)
(1, 1, 0)
Fm3m (Oh)
cF32
None

'

rin intermetallic transitionn metala alloys that are genera 11y not ob-
eed unstable

'

formation for commonly occurring '
rif that these structures are in ee

FIG~ 10.~ Crystal structure information
serve d in thee CuAu and CuRh treated here. ere. We use our c1uster-e-expansion method to veri y t a (Sec. VIC). See caption to Fig. 3 for further details.

below the line connecting B2 (x =——, ') with Pd (x = 1),
hence, could form at low temperatures.

3. CQ1—x AQx

Experimentally, a 1 Cu, „Auu [Fig. 1(a)] shows at low
temperatures the fcc-based Cu3Au — 2
cture at x =—'2t Cu Au forms the

2d ('2t)88(Crystal)2.11 562.78 Td (bNiS)Tj0.42 Tf 132.56 289 T0.11 Td (could)Tj c-based —

3. Cu, that

occurring

1(a)]

c)(Cu,)Tj ET BT /Xi2553.5.89 Tfi25135.11 427 Td (commonly)Tj ET BTXi25 /97fi2513517 TduCu,

See

(x1(a)]

1(a)]

(Sec. th

ou tra lin C

Au

Fig. axC (

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SB Name:
Formula:

(03,05)
A583, ASB5

(04)

A4B4

Crystal
Structure

QA
B

0

0

3
~ 0

~ =

(

Example:
Bravais Lattice:
Unit
Cell
Vectors

Space group:
Pearson Symbol:
Super lattice:

"GasPt5"
Body-centered Cubic
(-1, 1, 1)

(1, -1, 1)
(1, 1, -1)
lm3m, (Oh)

Q

None

Face - centered Cubic

(0, 1, 1)
(1, 0, 1)
(1, 1, 0)
7

Fd3m (Oh)

None

FIG. 11. Crystal structures, see captionion to Fi'g.. 10.

h At x=—'

energy still further. x = —, we predict the fcc-based configuration denotet d D7 (see Fig. 10), whose stability is not an experimental fact.
In addition d to these ground-state structures we have ave

identified other metastable structures whose energies are
not far from th e GSL. For example, our calculations
place the DO 22 configuration just 2.2 meV above thee

groun a statet at xx=——„

' while the DO3 energy is ur e

SB Name:
Formula:

(Mn2Au5)
A, o84., A4B, o

(9 0)
A28;AB2

Crystal
Structure

OA
~ B

4 0 0 0 0 0

0 0

~

0 ~

Example:
Bravais Lattice:
Unit
Cell
Vectors

Space group:
Pearson Symbol:

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D. The I. 1& and "D4"structures: an interesting observation

Figure 11 depicts the "D4" structure with composition
A4B4..

it has the fcc Bravais lattice and the I'd3m space group. Inspection of its "lattice averaged spin products" IIk (s) show that they are identical to those of the L 1, structure of composition AB (having a trigonal Bravais lattice and space group 83m; see Fig. 3) except for J4 i for which D4 i

II4 i(L 1 i

)=—2 (Table III), while

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ed in this

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tures out of a limited set of only O(10) possibilities. The
most stable experimentally observed ground-state struc-
tures of Cu& „Au~, Cu& „Pdx, Cu& „Pt~, Cu& xRhx,
and Al, Ni„are correctly identified and a few addition-
al low-temperature candidate structures are offered as predictions. The same method for extracting renormal-
ized interactions works for simpler lattice properties,
such as molar volumes and electrostatic energies. A
unified description of general atomic relaxations is, how-ever, lacking. In addition to this shortcoming, the main
approximations in our treatment are the following.
(i) Use of Vegard's rule for determining the equilibrium
volumes. Section VB examined this approximation and
found it to introduce negligible errors in all cases but
Al& Ni for which this approximation was not used.
(ii) Neglect of vibrational entropies. This can contrib-ute significantly when one contrasts different Bravais 1at-tices (e.g., fcc versus bcc) at finite temperatures, a com-parison avoided here.

(iii) Renormalization of the contribution of large figures to the entropy. This approximation was tested quantitatively against Monte Carlo simulations [Ref. 27(b) Fig. 15] and was found to introduce negligible er-rors in the enthalpy and phase diagrams.
(iv) Truncation of the cluster expansion and use of a
finite number of structures to extract interaction energies. This is a rather controllable approximation whose conse-quences are checked quantitatively in our transferability tests (Tables XII—XVI).

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and

67

Physical

V.

L.

F.

and R.

2 T(.rted)Tj ET BT /Xi30 6 Td 78 216.449539.33 Td (elit-)Tj ET BT /Xi30 7.97 Tf 747.8f 386.67 Td ctnllic

Properties

of

W.(New)Tj ET BT /Xi30 8.94 Tf8637.638.94.78 Td (York,)Tj ET BT /Xi30 8.88 T58.13 688.89 Td(1978).

Phaan in

traddition

and

ij Ej/t- enomenaca, edited

197446,

Vol.

M.

ntainuce,

in State Solid

Phamics,

edited

by

H.

and
M. c NY 19

and J.

Phhsai,

J.

Phys.

par(a))Tj ET BT /Xi30 9.12 T5 313.43 358.44 TdC(folqid.)Tj ET BT /Xi30

{1987).

M.

and Kelrk,

in

trafenor (tion)Tj ET BT /Xi30 8.76 Tf 521.129668.44 Td (M.)Tj ET BT /Xi30 8.12 Tf 531.129668.33 Td (Solams,)Tj ET BT /Xi30 0156 Tf 740.78 367.33 Td (edited)Tj ET BT /Xi Phase

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No.

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FIRST-PRINCIPLES STATISTICAL

LU, WEI, ZUNGER, FROTA-PESSOA, AND FERREIRA

but included the fifth pair (2,5). This is so since passing from the origin to (3,1,1), following a path through nearest neigh-bors, one passes through the intermediate sites (1,1,1) and (2,0,0), while in going from the origin to the fifth neighbor at (2,2,2) only the intermediate site (1,1,1) is passed. This cri-terion is being used to establish an hierarchy of interactions permitting to select the most important figure prototypes. It must be checked in specific cases, if this hierarchy bears a re-lation to the way the series