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Comparison of two cluster-expansion methods for the energetics of Pd-V alloys

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The formation energies of substitutional transition-metal alloys are examined by several means.
First, two types of direct total-energy calculations are considered, namely, (i) the local-density ap-
proximation (LDA), aud (ii) a tight-binding (TB) approximation thereof. Second, these directly calculated total energies are used to construct two Ising-like cluster expansions that, if sufBciently accurate, could be used to construct the full statistical mechanics of transition-metal alloys. These are (a) the Connolly-Williams (CW) method, and (b) direct configurational averaging (DCA). Fi-nally, the ability of these two cluster expansions [(a) and (b)] to fit and predict a large number of the underlying directly calculated [(i) aud (ii)] total energies is tested, by the average prediction error y. These tests are performed for a large number of Pd-V alloys, and also to a more limited extent, for the Pd-Rh, Pd-Ti, and Pt-V systems. We find for Pd-V that (i) direct TB

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N

llf(~) =

N):IIBf(~)

L
R

(4)

where the sumxnation is over the Nl, space group opera-
tions (R) of the lattice. The completeness and orthonor-mality of the set (Ilf(o)) of spin productsm in the space of all configurations assures that expansions (2) and (3) are exact if all 2~ figures are used to describe all 2N con-
figurational energies. The exact, rigorous nature of the
expansions is true whether or not atoms relax off their nominal lattice sites, since the relaxed energy is a xxnique function of the xxrtrelaxed configuration.
While mathematical completeness requires that all 2+
terms be included in Eqs. (2) and (3), physical intuition suggests that

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dom alloys, impurities, and antiphase boundaries. When
using a CE, it is, therefore, imperative to examine its
ability to produce reasonable predictive errors [Eq. (12)].

LDA Tight-Binding

II. ACCURACY ISSUES IN THE DCA AND CW
METHODS

Direct LDA

direct

(b)

', (d)

The efficacy ofthe aforementioned approaches depends on several factors, which may be grouped into two broad categories:

(1) The accuracy with ivhich the input E«„,q(o') is
computed. In the DCA method, the configurations used

to determine Jt [Eq. (7)] have random occupations of the N sites and as many as 1500 sites per configuration. This large number of atoms currently precludes the use of ac-curate first-principles techniques to calculate E«,«&(o). On the other hand, in the CW method one assumes at the outset that only Nz figures are retained, so practically
any

4 N & Nz configurations will do for the purpose
of calculating Jt [Eq. (6)]. One thus selects the most
convenient ones: configurations that correspond to var-
ious periodic, ordered

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must contain significant multibody terms (terms corre-
sponding to figures with three or more points). Thus,
the Pd-V system provides a stringent test of the conver-
gence of the cluster expansions.
The LMTO-AHA calculations were performed semirel-
ativistically (including scalar relativistic corrections and excluding spin-orbit terms) with equal sphere radii for Pd and V. All structures were allowed to deform hydro-statically to their equilibrium volume, but cell-internal and cell-external relaxations were not considered. Two sets of LMTO-ASA calculations are discussed here. The structural energies of twenty compounds were com-puted by the present authors, for which the exchange-
correlation potential of von Barth and

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TABLE II. Pd-V structural energies for fcc superstructures. Direct LDA energies are from LMTO-ASA calculations described in the text. All energies in meV/atom. Designations in quotation marks indicate an alternate labeling scheme for structures
for which no standard Strukturbericht exists.

Superlattice
A (Pd)
B (V)

(001) Struct:
AgBg
A2Bg
A3Bg
Ag B3
AgBg
Ag B2

Structure
Designation
fcc
fcc

Llp
CC Z2))
ccz]"
C4Z3)l
44@1

))
c4p 2)'l

LDA
direct
0.0
0.0

-366.6(-353.8)
-314.8(-292.4)
-225.9
-229.5

Direct
TB
direct
0.0
0.0

- 539
-355

-2ss(-2vs)
-310(-371)
-354
"437

TB
CE-DCA

0.0
0.0

- 517
-276
-274
-260
-366
-346

Cluster expansion
TB
CE-CWM

0.0~
0.0

-521
-362
-284
-339
-378
-453

LDA
CE-CWM

0.0
0.0

-358.1
-307.1
-235.1
-238.7
-317.6
-322.4

(111)Struct:
AgBg
Ag Bg
A3Bg
Ag Bs
AgBg
AgBg

Lli
«V2
ccV 1)l
44V3)l
cc 1)l
cc 2)l

-241.3 -394
-287

-213(-209)
-260(-262)
-265
-336

-289
- 185
- 168
- 162
-224
-216

-404
- 263
-204
-262
-271
-350

-246.0
- 184.8
- 154.6
- 144.0
-209.1
- 195.1

(011) Struct:
AgBg
ASBg
Ag B3
AgBg
AgBg
ASBg
Ag B5
A4Bg
AgB4
A3B3

Al BgAgB3
AgBg A3Bg
Ag Bg Ag Bg

cc

44Y]))
ccY3))

MoPtq type
MoPtq type
ccY5))
ccY5 l)
d

ccY4)')
"Y4d"
ccY6))
4cY7)')
ccY7)l
d

ccY8)')

-393.5(-368.0)
- 181.1(-182.8)
- 191.5
- 123.1
- 185.6
- 174.4
-218.3
-240.8
-293.0
-270.4

-430

-393(-322')
-356(-349')
-471
-377

-338
-343
-253
-469
-287
-234
- 167
-235
-244
-251
-399
-346
-389

-414
-335
-340
-466
-373
-225
-229
-272
-324
-316
-400
-402
-437

-265.9
-253.9
- 178.8
-359.5
- 174.9
- 177.0
- 116.6
- 189.9
-201.2
-208.8
-286.0
-246.3
-284.5

(201) Struct:
Ag B2
A3Bj

ARABS

A4Bg
Ag B4

(401) Struct:
ASBgAgBj.
Ag B5Ag Bg

CH, or "40"
D02g
Doing

D1 (Ni4Mo)
Dl (Ni4Mo)

D02s
Dog3

-243.V(-24S.Vb)
-348.4(-340.3)
-2o2.v(-2os. 3b)
-269.6
- 160.0

- 524

-3ss(-3vv)
- 311(-312)
309
-237

-357
-345

-473
-439
-273

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C. Cluster expansion —AEcE &~ and ALECK z~

The methodology of the CW method relies on (a) the
choice of figures and (b) the choice of configurations.
(a) Figures: We will use the same extended set of fig-
ures in the CW and DCA approaches. These are the
"empty" figure [corresponding to a constant term in the cluster expansion of Eq. (3)j, the "point" figure, the first-through fourth-nearest-neighbor pairs, four triplet fig-ures, and four quadruplet figures. The vertices of these 14 figures are given in Table III as well as the degenera-cies Dy. For the TB fit, is was found that including all

TABLE III. Vertices and degeneracies of fcc 6gures used in the CW and DCA-based cluster expansions.

Figure

Empty
Jp

Degeneracy
Dy

Site positions
(in units of a=2)

Point

(0,0,0)

Pairs
J2
K2
I2
M2

6
3
12
6

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

Triplets
J3
Kp
1.3

8
12
24
6

(0 0 0) (111 0)i(1 0 1)
(0,0,0),(1,1,0),(2,0,0)
(0,0,0),(1,1,0),(2,1,1)
(0,0,0),(1,1,0),(2,2,0)

Quadruplets
J4
K4
M4

SQ

2
12
6
3

(0,0,0),(1,1,0),(1,0,1),(0,1,1)
(0,0,0),(1,1,0),(1,0,1),(2,0,0)
(0,0,0),(1,1,0),(2,2,0),(3,3,0)
(0,0,0),(1,1,0),(-1,1,0),(0,2,0)

should keep in mind that the TB values are overbound by roughly 20 meV/atom due to volume deformation ef-fects.

The direct TB results, Ed;„,i(0'), for o = ordered, peri-odic configurations are shown in the fourth column of Ta-ble II. The two charge

J2in

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that the sensitivity of the fits of Mikapolas et nl. were
due to (1) the small number of long-ranged figures used
in the expansion and (2) the use of a direct inversion of
Eq. (6), rather than the singular value decomposition of
Eq. (5).

D. Cluster expansion —LLE&E D&A

- 100

-200

O 300 + UJ

~ O
-400

- 500

(a)
X= 18.8

oo

The DCA calculations for Pd-V have been described

in depth previously. 4 Here, we merely give the salient de-tails. The interaction energies are obtained via Eq. (7), using the recursion method, along with the formalism of "orbital peeling" to avoid numerical instabilities asso-ciated with taking

taking

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ergy difFerences between two competing configurations at
the same composition (e.g., L12 —D022 or Llo —"40")
are adequately represented by the fit. The predictive er-
rors of the fits should be considered in light of the errors
inherent in the direct LDA calculations, which are 10
meV/atom or less.

/g vs /g

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&Ed',
,t(~)

= E."(~)

—[(1

—~)E,"(&)
+xE. (B)],
b,ELDA,

(

)

= ELDA(
)

—[(1

—)ELDA(A)
ELDA (B)]

(18a)

Eq. (21),

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- 100

-300

-400

-600

- 100

-200

-300

-400

-600
0

(001) Structures

Z3
P---
Z1

L10

(111)Structures

L11P--------

~ OCA

P CWM

~ OCA

P CWM

in columns

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F. Ducastelle, Order and Phase Stability in Alloys (Else-vier, New York, 1991).
J. Kanamori and Y. Kakehashi, J. Phys. (Paris) Colloq. 38, C7-274 (1977).
Z.-W. Lu, S.-H. Wei, and A. Zunger, Phys. Rev. Lett. 66, 1753 (1991).
C. Wolverton, G. Ceder, D. de Fontaine,

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