8814 C. WOLVERTON AND ALEX ZUNGER

tentimes (but not always)

the minimum of J2(k) also
corresponds to the peak wave vector of the LRO state,
ki,RQ (e.g., as observed in Bragg difFraction). Thus, in
many cases, the mean-field expectation based on Eq.
(3) is that the peak wave vectors of SRO and LRO co-
incide: ksRO ——kqR~. This equivalence between ksR~
and kI,Ro actually occurs in an overwhelming number
of alloys. In particular, a peak at ksRQ = (000) in-
dicates association of like atoins ("clustering")

and is

accompanied via Eq. (3) with phase-separating LRO,
while an "off-I" (ksRQ g (000)) peak in asRQ indi-
cates association of unlike atoms ("anticlustering") and
is accompanied by compound-forming LRO. Cases (i)
(ksitQ ——kLitQ = (000)) and (iii) (ksitQ = ki,RQ W (000)) in Table I refer to these classic cases of clustering/phase-separating and anticlustering/compound-forming alloys,
respectively. Sometimes it is assumed that this is ahoays
the case. For example, recent calculations of SRO in ¹i

Pt by Pinski et al. have been interpreted to imply LRO with the same underlying wave vectors. Direct calcula-tions of the LRO with the same nonrelativistic Hamilto-

nian showed, however, that ksRQ $ ki,RQ.
Calculations that go beyond the mean-Geld approx-
imation (such as those in this paper) use J2(k) in a
Monte Carlo algorithm. The resulting ksRO need not
be related to kz,R~. A number of possible relations be-
tween SRO and LRO wave vectors are enumerated in

Table I. Cases involving "non-special-points, "

(ii)5 and
(iii)b, are exemplified by Ni-Au (Refs. 13 and 14) and
Cu-Pd (Refs. 15—17) alloys, respectively. In the Ni-Au
system, the assessed composition-temperature phase di-

8816 C. WOLVERTON AND ALEX ZUNGER 52

SRO of Ni V with T-independent J's 1-x x

x = 0.25 x = 0.33 x = 0.40 x=050

0)

(200)

(0
(200)

(0
(200) (200)

FIG. 2. Monte Carlo simulated annealing calculated values of nsRo (k) for Niiq V alloys in the (hi'cO) plane. The calculations
endent J tota ener ies. The black shading in the contour plots 's derived from first-principles tota energies. e
00 2250 1700,

were performed using T-indepen en f

s

0 attern. The calculations for x = 0.25 0.33, 0.40, and 0.50 were performed at 230,
f =025 ' h' and 1400 K, respectively. Contours are all sps aced by 0.5, except or x =.,

in h 10

SRO of Ni V with T-dependent J's 1-x x

x=025 x = 0.33 x = 0.40 x = 0.50

0)

(200)

(0
(200) (200) (200)

FIG. 3. Same as Fig. 2, except with T-dependentnt Jf

's.s. The calculations for x = 0 25 0.33 0.40 and 0.50 were performed at 1700 1875, 1900, and 1600 K, respectively. Contours are all spaced by 0.5.)

52 FIRST-PRINCIPLES THEORY OF SHORT-RANGE ORDER,... 8817

SRO of Pd &

„V„with T-independent J's

x = 0.25 x = 0.30 x=Q33 x = 0.40 x = 0.50

0) 5

(200)

(0
(200) (200) (200) (200)
FIG. 4. Monte

50

8818 C. WOLVERTON AND ALEX ZUNGER 52

TABLE II. Dominant wave vectors of long- and short-range order in fcc-based Ni-V and Pd-V alloys. "Case/type" refers to the classification of Table I. Jt(T)

52 FIRST-PRINCIPLES THEORY OF SHORT-RANGE ORDER,... 8819

BL 0 '% F
0
0 2

o 0

L12

0

0 0

~ —g&
0
Pl

D022

1st A: 8A+48 1st A: 8A+4B, 8A+48
1st 8: 12A+OB 1st 8: 12A+OB
2nd A: 6A+OB 2nd A: 6A+OB,

8820 C. WOLVERTON AND ALEX ZUNGER 52

Ni3V - L12 Ni3V - DQ22

200

100
0
LL

0

& -100
f/)
O
-200

150

100

E 50
0
LL

0

-50

Vl

O -100
C5

FIG. 7. LAP W calculated
DOS for Ni3V in the DO22
and L12 structures. Shown

are both nonmagnetic (NM)
and ferromagnetic (FM) calcu-
lations. (Note that the FM cal-
culation for the DOq2 structure
converged to the NM solution.)
The vertical dotted lines indi-
cate the calculated Fermi level.
The calculations shown are for
knT = 2

FIRST-PRINCIPLES THEORY OF SHORT-RANGE ORDER,... 8821

where Nq q

is the total number of valence electrons. Once

n(e, T) and p(T) are determined for a given temperature, the entropy due to electronic excitations may be com-puted &om the integral

9 ~ (T): f

B(E T)(f(E T)hfdf(E T)

+[1—f(e, T)]in[1 —f(e, T)]) de. {7)

where the third term is the T-independent ion-ion

8822 C. WOLVERTON AND ALEX ZUNGER 52

the L12 and D02z structures [Eq. (4)] with

a quadratic
temperature dependence

AF(T)

= AE(T

= 0)

—AT

where

A is

a constant. In

a previous paper, we used
Eq. (16) in our calculations of SRO in NisV and PdsV by mapping

a quadratic

T dependence onto

a three- and
four-body interaction, J3 and K4, respectively. In the spirit of

a model calculation, we adjusted the constant

A

in Eq. (16) so as to bring the calculated SRO of NisV and Pd3V in agreement with neutron diffuse scattering mea-surements. The values of A (= Ast) that reproduce the observed SRO patterns in NisV and PdsV [Ast

———54.

4
and

—50.
1 (Ry atom), respectively] are used here in
Figs.

3 and

52 FIRST p 8823 - RINCIPLES THE&Ry 0FSH&RT-RANG

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F. Effects of spin'

polarizat' ion

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100

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50-

Ni3V - L1 2

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Energy

/
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/

1

Level 1 — - NM
Level 2 - NM
——

8824 C. WOLVERTON AND ALEX ZUNGER

PdsV, respectively). For the L12 structures, however,
spin polarization splits the large peak in the DOS near
eJ;, so that n(e~) i8 signifi'cantly reduced as compared with
NM calculations. This leads to larger magnetic moments
on the V atoms in the L12 structures (p~ = 0.8 and
1.2 for NisV and PdsV, respectively) than in the D022
structures. This reduction of n(e~) due to spin polar-
ization has recently been shown to affect the D02q/Llz structural stability in a large variety of PdsA (A = Sd)
compounds ~ ~ and has also been shown to qualitatively
change the ordering tendency of Fe-Co alloys. ~ ~ Also, in contrast to all the NM calculations, the T dependence of the I12 DOS is not negligible for the spin-polarized
calculations: At low T, the FM DOS is significantly dis-
tinct from the NM DOS; however, as T is increased, the FM calculations converge towards the NM solution (with no magnetic moments) and thus, the FM DOS evolves towards the NM DOS.

The effect of spin polarization on E,~, S I, and E ~

is

illustrated in Figs. 9 and 10. Contrasting

evolves

52 FIRST-PRINCIPLES THEORY OF SHORT-RANGE ORDER,... 8825

count for only ~30 and 50% of the discrepancy between
AF(T) of experiment and that of LDA at T=O in NiqV
and Pd3V, respectively.
Our results for the effects of electronic excitations

(level 1) and spin polarization on b F(T) are summarized
in Fig. 12. We see that the two nonconfigurational exci-
tations are not ad.ditive: In Ni3V, electronic excitations

and spin polarization each independently reduce b,F(T) by 27 and 8%, respectively. These percentages are 26 and 44% in PdsV. However, the combination of the two
effects leads to reductions of 28 and 51%%uo in NisV and

PdsV, significantly less than the sum of the two e6'ects
independently. Hence these efFects do not fully account
for the T dependence of the interactions used here (Afit)
to calculate SRO.

At present, we do not have a satisfactory explanation for the physical mechanism behind the fitted value of A. It is interesting to consider physical mechanisms other
than electronic excitations or spin polarization, which
could be responsible for the discrepancy between Ast and ALD", i.e.,

for further lowering BF(T) at finite temper-
atures. One such excitation is that of lattice vibrations:

If the vibrational &ee energy of the L12 and D022 struc-tures are sufBciently different, they may also contribute

120

100

Elec. Excit
T=1500K

Non-Mag.
T=OK

Spin-Pol ~
TWK

Spin-Pol. +
Elec. Excit
T=1500K
L12

/
/

-49 /
/
/
/

ik

,

-41

to a T dependence of AF(T). Also, electron-phonon or spin-orbit coupling could distinguish L12 from DOq2. Johnson et al. performed a non-spin-polarized level
2 LDA calculation for the energy differences between
L12 and D022 for Ni3V and Pd3V at 6nite T. These
authors' calculations involved a concentration wave ex-

tension of the coherent potential approximation, im-
plemented within the Korringa-Kohn-Rostoker multiple-
scattering &amework, as well as the following speci6cs: The atomic sphere approximation (ASA) was used with equal sphere sizes, the calculations were performed scalar relativistically, no charge correlations were included, and
relaxation of the DO~2 structure was neglected. Johnson

et al. found AF(T) values of —0.4 and —1.5 meV/atom for Ni3V and Pd3V at T = 700 and 850 K, respectively.
These values are to be contrasted with our non-spin-
polarized level 2 values at these temperatures: +94 and

20—

0

-20—

-40—

80
E
60
O
40—

I-
LL
CI

~ Level 1

- NM

Level 2- NM
——-Level 3- NM
0 Level 1

- FM

Expt.
T (Expt.)

+77

+105

D022 O
~-21

PcIBV

+76

Expt.
21

80

Elec. Except.
T=1200K

Non-Mag. Spin-Pol ~

T~K T-QK T=1200K

60

40

C5

20—

I-

U 0 CI

-20— T (Expt.)

+52

/
/

34/
/
/
/
+70

DO22
~-16

L12

sk

31

ik

& -21

+39

+34 Expt.
- 16~ P

-40
0

I

400

I, ~ I ',, I

800 1200 1600

Temperature [K]

li

2000 2400

FIG. 11. LAPW calculated free energy difrerences due to electronic excitations between the Llq and D022 structures for Ni3V and Pd3V.

FIG. 12. Ni3V and Pd3V free energy differences
(meV/atom) between the L12 and DOqq structures due to
electronic excitations, spin polarization, and a combination
of the two eKects. The dotted lines indicate the "experimen-

tally inferred" values (Refs. 20 and 22) of+12 + 5 and +2.4 + 0.3 meV/atom for NisV and PdsV, measured at T = 1373 K and 1128 K, respectively.

8826 C. WOLVERTON AND ALEX ZUNGER

+58 meV/atoin. Our calculations include charge corre-
lations and are full potential, thus avoiding the ASA. An
LDA-based theory, which includes E,~

in a level 2 fash-

ion should, at best, obtain a value of AF(T) at finite T,
which is only slightly reduced compared to that of LDA at T=O, i.e., AE(T = 0) of +105 and +70 meV/atom [see Eq. (4)]. We therefore find the strong reduction of AE(T = 0) —AF(T) that Johnson et al. found to be inexplicable.

V. CONCLUSIONS

We have studied the effects of composition and tem-perature on the SRO, electronic excitations, and spin po-larization in Niq V and Pdq V alloys. We find sev-eral compositions for which the dominant wave vectors of LRO and SRO do not coincide, and several shifts of the SRO peaks as a function of composition and tem-Perature: (i) In Niq 7sVo 2s, the SRO shows

52 FIRST-PRINCIPLES THEORY OF

8828 C. %OLVERTON AND ALEX ZUNGER 52

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e n(e) f(e

—p) de

+kT

n