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Electronic structure of random Ago 5pdo 5 and Ago 5Auo 5 alloys

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The electronic density of states and mixing enthalpies of random substitutional A& B„alloys have often been described within the single-site

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treated exactly while

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exact random values, so the predictions improve succes-
sively.
For the fcc Ao 5Bo ~ alloy, for example, the SQS-8,
consists of an eight-atom supercell best defined as an
A&82 A3B2 superlattice along the [113] direction (i.e.,
one monolayer of A, followed by two monolayers of B, followed by three monolayers of A, and finally by two monolayers of B, all perpendicular to the [113]direction). Figure 1 depicts this

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5 AND.

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. 10 473

D), and total DOS (E). Section

V summarizes the main

conclusion: we find that the present approach gives

a

realistic alloy DOS, exhibits environmental effects lacking in the SCPA, and is easier to apply.

II. CHOICES OF ALLOY SYSTEMS

We have selected for this first application of the SQS concept to metal alloys two fcc systems: AgPd and AgAu. The AgPd system was chosen primarily because it appears to be very popular among practitioners of the SCPA: it has been previously treated by the Korringa-Kohn-Rostoker (KKR)-CPA [Refs. 1, 10, 21(c), and
37

—45] method (both self-consistently and non-self-consistently), tight-binding CPA, model Hamiltonian CPA, and linear-muffin-tin-orbitals CPA.

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For

AgAu, there was

a previous non-self-consistent relativis-
tic KKR-CPA calculation. To develop an intuition on the anticipated properties of this alloy system and those for AgAu, we have collected in Table

I (Refs. 47

—51)
some data on the relevant Pd, Ag, and Au free atoms [LDA (Refs. 50,51) calculated atomic

s and

d orbital en-

ergies and the phenomenological Pauling's electronega-
tivities] and the elemental solid metals (LAPW-
calculated positions and widths of d bands, measured photoelectric

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The calculated equilibrium lattice parameters of the pure solids are

a(Ag) =4.008 A, a(Au) =4.056 A, a(Pd) =3.848 A
(5)
compared with the room-temperature

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loy and possible long-range order at low temperature.
This result convicts with the simple expectation based on
the tight-binding model that binary alloys of all late
transition metals should phase separate rather than or-
der. To examine this issue more closely, we have calcu-
lated the formation enthalpies of ordered Agpd in the L le (CuAu-I), L li (CuPt), and B2 (CsC1) structures (Fig.
5), finding that bH(L1,)=—60.4 meV/atom; that is,
this structure is stable both with respect to phase separa-tion (hH &0, as also noticed by Takizawa and Terakura) and disordering at T=0 [i.e., AH(L 1 i) & EH(SQS)]. The B2 structure is unstable with
respect to phase separation [it has b,H(B2)=+19.7
meV/atom and, therefore, is outside the range in Fig. 5]. Low-temperature studies of possible L1, ordered phases in the Ag-Pd system are lacking (the existing phase dia-
gram is limited to rather high temperatures, T~ 1200 K, exhibiting continuous fcc solid solutions). Diffused scattering experiments on the disordered alloy could po-tentially indicate such ordering tendencies.
For the AgAu random alloy, we find the mixing enthal-py and lattice constant

EH (x = —,

'

)=—44. 7 me V/atom,

a,q

=0.998a,

(10)

p — (a)

~

I

I
I

I

Eo -40- 8CO)-60— I

E
~

-80
cn Q

C~ -20-
CO

40

Ol " -40-
LU

L1, [Ag Pd (
I i I I I a I s
I

'

I

'

I

'

I

'

I

Random

14g 4U I

8Q I I I I I I I ~
0.98 0.99 1.00 1.01 1.02

Reduced Lattice Constant a/a, q

FIG. 5. Calculated excess energy EE(a) vs lattice constant a for the random alloys (modeled by the energy of SQS-8 and shown as solid circles and solid lines) and some ordered phases

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the unit cell]. The differences

bp, (r)=p„„„(r)—p,„(r) (14)
for AgPd and AgAu are depicted as contour plots in Fig.
6. We see that relative to this atomic reference system, charge is transferred oQthe

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TABLE III. Angular and atomic site decomposed charge (in unit of e) inside the muffin-tin (MT) sphere of radii of 2.55 a.u. for the Ago, Pdo ~ alloy in the SQS-8 structure and for its pure metal constituents at the alloy's volume. The alloy vs metal differences are also given. Charges outside the MT spheres are not included in this table. The column headed "first neighbor" gives the
configurations of atoms in the first-neighbor shell (a total of 12 atoms), and "Degen. "is the number of times that this type of atomic
arrangement appears in the SQS-8 unit cell.

Atom

Ag(2)
Ag(s)
Ag(7a)
A (7b)
Ag(8)

Average
Diff.
Metal

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0.10-

0.05:—(')
0---

-0.05;

A

Au

0.15.

0.10.'-()
0.05—
CD 0---

C3 -0.05;

015 () 0.10—
0.05.

—

0
-0.05 —.
-0.10.

—

-0.15—
0 2 4 6 8 10 12
Number of like atoms in first shell

FICz. 8. Plot of the total charge transfer inside the muffin-tin spheres of Ag-Au, Ag-Pd, and Cu-Pd with respect to the pure solid (from Table IV) as a function

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tential can couple VCA states either in a first-order
manner (appropriate to degenerate VCA states) or in the
second-order manner (non-degenerate VCA states). The
coupling is inversely proportional to the initial energy
difference between the states and leads to repulsion of the
deep (shallow) state into yet deeper (shallower) binding
energies. Furthermore, alloy band hybridization can in-
duce LDOS, which does not exist in pure metal.
(iv) Charge trans-fer effects. Band repulsion and hy-
bridization effects can intermix states, resulting in charge
transfer. Transfer of electronic charge onto (off) an atom
raises (lowers) the Coulomb repulsion on that site, hence reducing (increasing) the binding energy of the level. The
shift due to this effect can be modeled through

d

=Udd bN d +Uds AN (17)

where Udd and Ud, are the (positive) d-d and d-
conduction Coulomb repulsion energies on site n, while
ENd and 6, are the excess d and conduction charges on site u, respectively, relative to the corresponding elemen-
tal solids. Note that the direction of d and conduction
charge transfer need not be equal and hence, ANd and could have opposite signs. The intraatomic
Coulomb eff'ect of Eq (17) might be partially ofFset by the
interatomic Madelung effect: transfer of charge off

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(i) Volume deformation effects (i.e., compression of Ag
and dilation of Pd) shift the Ag state to deeper binding
energies (and broaden their LDOS), while they shift the Pd states to shallower binding energies and narrow their LDOS (Fig. 3). These changes can be largely understood in terms of compression and dilation of the elemental
solids. Indeed, compression of pure Ag from its equilibri-
um volume to that of the alloy [Eq. (8)] increases the d
band width from 3.59 to 4.36 eV close to the partial
width in the alloy (4.41 eV). Conversely, dilation of pure Pd to the alloy's volume reduces its bandwidth from 5.68 to 5.23 eV, again close to the alloy value (5.28 eV). Hence, alloy bandwidths remain virtually the same as in their elemental solids at the same volume. The fact that the Pd d band width in the alloy is slightly larger than in the (dilated) fcc metal is highlighted in Fig. 9(g) by the shaded area. This leads to a larger Pd d occupancy in the alloy, hence to additional Pd charge denoted in Fig. 9(g)

as b,g =+0.086e. Conversely, the narrowing of the Ag
d band at deep energy in the alloy [Fig. 9(c)] leads to a (slight) loss of d charge (EQ =—0.007e).
(ii) Alloy fluctuation effects smear the sharp features of the Ag and Pd DOS [Fig. 11(a) and 11(c)]into a series of narrowly spaced structures [Fig. 11(b)], reAecting the ex-
istence in the alloy of a distribution of local environ-
ments. To clarify environmental effects on the DOS, we
show in Figs. 12(a) and 12(b) the Ag-centered [part (a)] and Pd-centered [part (b)] LDOS of Ago 5Pdo 5. In the SCPA approach, there is but a single LDOS for each type, i.e., one for 2 and one for B. Figure 12 shows our

2.0-

1.0-

I

a=3.93A i

I I

Ag

:(d)

I

'

(

'

I

a=4.o8A

0.5.

-

0.0
~ C~

rn 20.
1.5-

Q 1.0—

CO& o.5- O
o o
I-
2.0.

—

I ~ I
I

'

I ' I f

'

I

'

I

14&o. 'do.sI
(b)

I
I
I
I
I
I
I
I
I
1

: Ag05Au a=a a=a

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

a=a
Au a=a

1.5.

-

(c)
1.0—

0.5.

-

0.0

I

- 10 -8 -6 -4 -2 0 2 -10 -8
Energy (eV)

-6 -4 -2 0 2

FIG. 11. Total DOS of (a) elemental solid Ag at a =3.928 A, (b) the AgPd SQS at the same a, and (c) elemental so1id Pd at the same a. The Fermi energies were aligned. Note that while Figs. 9(d) and 9(h) give the Ag and Pd DOS inside the MT spheres, the plots in parts (a) and (c) here give the full DOS in the whole lattice space. Part (d) gives the total DOS of elernen-tal solid Ag at a=4.080 A. Part (e) gives the results for the AgAu SQS at the same a, while part (Q gives elemental solid Au at the same a. Note that while Figs. 10(d) and 10(h) give the Ag and Pd DOS inside the MT spheres, the plots in parts (d) and (f) here give the full DOS in the whole lattice space.

0.00:

-0.10:—

Atom-centered DOS
Ago. 5 Pdo.5
- -. (c)

Atom-centered DOS
Ago 5 Au05

I

0.10:-

Ag) 0.00
(0 -0.10:—

2:(c)

1 —. Ag
E

~ ~

0

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results for

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theories describe, on the other hand, all local environ-ments as being identical, so each is characterized by the macroscopic composition. They are indeed intended to
determine only the statistically average LDOS of the
component species, producing a single function that does
not resolve environmental effects. While there certainly exist alloy properties that depend only on the global com-position (e.g.,

the molecular weight of A, B„), many
properties reAect local coupling and hence depend specifically on the atomic arrangements and composition about sites. In applications where a single averaged DOS suffices, the SCPA is adequate. If, on the other hand, one
is interested in local environmental efFects, one needs to
go beyond the SCPA. We know, for example, that one
component of the total energy of an alloy —the electro-
static point charge energy —is incorrectly described by
such effective medium single site approaches that neglect
fluctuations. Since there are no paralle/Xi13 8.82 Tf 215.8 Tf 265.11 621 Td (pPA)Tj ET BT /Xi13 8.79 Tf 215978 521.Td (and)Tj ET BT /Xi13 9

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