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Short- and long-range order of the binary Madelung lattice

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We discuss the infiuence of point-ion electrostatics on the long- (LRO) and short-range order (SRO) in binary fcc-, bcc-, and simple-cubic- (sc) based alloys. The electrostatic problem is studied by a combination of (a) a model for the distribution of point charges on lattice sites, motivated by
recent first-principles calculations, (b) a mapping of the infinite-ranged Coulomb interaction onto a
rapidly convergent series of effective interactions, and (c) Monte Carlo simulated annealing of the ensuing Ising-like expansion. This provides a means to identify the lowest energy structures ("ground states") at zero temperature and the dominant wave vectors of the SRO at high temperatures, which
are stabilized by ionic interactions. (i) We confirm previous results that the three ground states of
the fcc Madelung lattice are the D022 (AsB and ABs) and "40" (AB) structures, which can all be described as (210) superlattices. We further find that the ground states of the bcc and sc Madelung lattices are CsCl and NaCl, respectively. (ii) Despite the fact that the structure "40" has the lowest
electrostatic energy of any fcc-type compound, this structure is very rare in nature. We find that
this rarity could imply that a highly ionic fcc AB compound will transform to the bcc structure CsCl that is electrostatically more stable for the same charge distribution. The exception is when the energy required to promote the e)cmental solids A+ B from fcc to bcc is larger than the gain in electrostatic energy. (iii) Monte Carlo and mean-field calculations both demonstrate that the
dominant wave vectors of LRO and SRO coincide for the bcc and sc Madelung lattices. However,
for compositions x & 0.33 and x & 0.67 on the fcc lattice, mean-field calculations incorrectly predict
SRO peaks at the (1—0) points, whereas Monte Carlo calculations show SRO peaks at the (100) points. Thus, in describing fcc electrostatics, the mean-field theory of SRO is seen to qualitatively
fail. (iv) Electrostatic point-ion interactions lead to significant SRO correlations. Near the transition
temperature, these correlations account for a & 60% change in the energy of the random alloy.

I. INTRODUCTION:
THE MADELUNG LATTICE PROBLEM

When different atoms are brought together to form an
alloy or compound, the redistribution of charge densities
as compared to their atomic densities may lead to what is
commonly referred to as "charge transfer. " The electro-
static contributions to the total energy of an alloy or com-
pound due to charge transfer have been widely used to
discuss the structural stability of not only alkali halides,
but also coordination compounds ' and semiconductor
and intermetallic alloys. Whereas in Ob initio total energy calculations '

the electrostatic contribution is

calculated from the continuous electronic charge density p(r), in simpler approaches one discretizes the (electronic plus nuclear) charge density into a set of point charges. The ensuing electrostatic Madelung (M) energy EM has been widely used as one of the energy terms deciding structural stability of compounds and alloys. ' We discuss in this paper the manner in which the point-ion electrostatics decides the long- and short-range order in
binary fcc-, bcc-, and simple-cubic- (sc) based alloys.
While the electrostatic contribution is clearly not the
only term entering the total energy, it is interesting to see that it leads to clear structural preferences for both short- and long-range order.
In the point-ion Madelung model of a given lat-tice (e.g., fcc, bcc, and sc), each of the N —+ oo sites

i = 1, 2,..., K is assigned a net charge Q; and is occupied

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First, evaluating EM(cr) from Ewald's method for all
possible 2 configurations of N lattice sites occupied
by A and B atoms can be laborious. This problem
can be addressed by using lattice-gas techniques which
efIiciently search the 2 space for the lowest energy
configurations. ' However, in the formulation of Eqs.
(1) and (2), the bare interactions J,i

are infinite in range
and are dependent upon the configuration through the
configuration dependence of the charges Q;. Both these
facts make the Ising series written in terms of the bare in-
teractions cumbersome, as much of the literature to date
on Ising models concerns interactions which are rela-
tively short ranged and configuration independent. How-
ever, as shown recently, it is possible to exactly renor-
malize the infinite ranged series of Eq. (1) expressed in
terms of bare Coulomb interactions into a short-ranged,
highly convergent series expressed in terms of effective in-teractions which are configuration independent. This will
be illustrated in Sec. II. Hence the standard techniques
used to deal with Ising models may be applied to this series of efI'ective interactions.

The second difficulty with a direct search of E~(0) is that this requires a model associating sites i with charges Q;. The association of sites and charges is not trivial ex-cept for the cases of ordered arrangements of atoms for which all chemically identical atoms are also symmetry
equivalent and hence have identical local environments.
For instance, in the perfectly ordered NaCl structure, all Na sites i have only Cl atoms as nearest neighbors and thus can be assigned the charges Q, = +1 for all i. Simi-
larly, all Cl sites j are surrounded exclusively by Na and have Q~ = —1 for all j. However, in a random Nao sClo 5
alloy, some Na atoms are coordinated locally only by Na
atoms and hence have Q; 0, like in metallic Na, while
other Na atoms could be surrounded locally by all Cl
atoms and consequently could have Q, +1, like in the
ionic Na~l crystal. Thus, in order to use Eq. (1) to re-alistically model the electrostatics in alloys, one must
first determine a physically reasonable description for
the distribution of charges on lattice sites. Recent first-
principles charge density calculations for both ordered
and disordered transition metal ' and semiconductor

alloys have shown that the efI'ective charge on each site primarily depends on the identity of atoms in the nearest-neighbor coordination shell around it, e.g.,

the number of

unlike nearest neighbors. This suggests that a realistic
model in screened solids is one with a linear dependence
of the charge on the number of unlike nearest neighbors:

where S; is —1 (+1) if an A (B) atom is located at site i.
S;+I, indicates the occupation of the Z lattice sites which
are nearest neighbors to i and hence the summation in
Eq. (3) indicates the number of unlike nearest neighbors
surrounding the site i. A is a constant that indicates
the magnitude of the charge transfer. The maximum
possible amount of charge transfer Q „=2ZA is then given by Eq. (3) for an atom coordinated completely by

unlike nearest neighbors. For example, in the fcc lattice the coordination number is Z=12, so the charge on an A atom surrounded by n B atoms and 12 —n A atoms
isQ; =2An. AsO) n&12, wehaveO&Q,) 24A

depending on the value of n. Using the charge model of Eq. (3), deduced from first-principles calculations2e and more recently derived from the coherent-potential approximation, the lattice Madelung energy may be
written as

where nM(0) is the Madelung constant for the config-
uration o, d is the nearest-neighbor distance, and Q ~ is the optimum amount of charge transfer possible for simple, ordered arrangements of atoms with only two symmetry-distinct types of atoms. The Madelung en-ergy [Eq. (4)] is purely attractive and thus EM ~ —oo as d ~ 0. Therefore, we optimize the Madelung constant n~ rather than the Madelung energy of Eq. (4). This is equivalent to finding the states of minimum Madelung energy for a fixed value of d and Q ~. Considering the CuAu, CsC1, and NaC1 structures (based on the fcc, bcc, and sc lattices, respectively), we have Q &

——16A, 16A,

and 12A. For the bcc and sc lattices, Q ~

= Q „=16A
and 12A, respectively, since for these lattice types it is possible to completely satisfy the ordering tendencies

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6878 C. WOLVERTON AND ALEX ZUNGER

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FIG. 1. Conventional unit cells for the ground state struc-tures of the fcc, bcc, and sc Madelung lattice. In addition to the lowest energy states of each lattice, the energetically competitive Llo and L12 fcc-based structures are shown.

In this paper, we focus on several problems regarding the Madelung lattice.

(i) Although the equimolar (120) structure ("40")is a ground state of the fcc Madelung lattice, surprisingly
it is rarely if ever observed experimentally in fcc-based
alloys. Given that Eq. (3) was demonstrated2 '

to

be an excellent approximation to direct local-density ap-proximation (LDA) calculations, one must conclude that either charge transfer is never the dominant effect at equiatomic composition or when it is dominant, geomet-rical factors such as lattice topology serve to make other non-fcc structures more stable. We find that the CsC1

structure has the highest Madelung constant (and conse-
quently, the lowest energy) of any fcc-, bcc-, or sc-based structure. Hence, even in alloy systems where charge transfer is a dominant- effect, an fcc alloy would prefer to
transform to the bcc CsCl structure, which, for the same
ionic charges, produces the maximal electrostatic stabi-
lization. An exception would occur for an ionic alloy sys-
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6880 C. WOLVERTON AND ALEX ZUNGER

tion in Eq. (9) contains only a small number of nonzero
terms. Also, a nonzero value of Kq implies that there
are triangles of nearest-neighbor bonds in the lattice or
that the lattice is frustrated. It is then readily apparent
from Table I that the fcc lattice is frustrated (Ki g 0),
but bcc and sc are not (Ki ——0). Other values of K simply indicate the extent to which more distant pairs in the lattice are linked by common nearest neighbors. Thus K gives some qualitative indication of the extent
to which the lattice is "open" or "close packed. " It is
apparent that the fcc lattice has many more nonzero val-ues for K than do bcc and sc and hence is more close packed. Similarly, the sc lattice has very few pairs of atoms which share common nearest neighbors and thus may be described as an open lattice structure. By using Eq. (9)

6882 C. WOLVERTON AND ALEX ZUNGER

IV. RESULTS

A. T = 0 K long-range order ("ground states")

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D

-0.4

-0.6—
O
-0.8
- 1.0
- 1.2
CD

Q) -1.6
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- 1.8

Ground-state Energies of the Madelung Lattice

CsCI
0

I 10 ~ 1.5944
"40" ~ 1.6366
NaCI + 1.7476
CsCI o 1.7627

0.0 0.2 0.4 0.6
Concentration x

0.8 1.0

FIG. 3. Ground state structures and random energies of
the fcc, bcc, and sc Madelung lattices. The fcc-, bcc-, and
sc-based structures are shown as 611ed circles, empty circles,
and crosses. In addition to the lowest energy structures on
each lattice, several structures are also shown which have en-ergies close to the ground state line. The inset shows the equiatomic structures and also gives the numerical values of the Madelung constants, as calculated from a cluster expan-sion with the first 20 pair interactions Jo qo (see Table II). The cluster expansion values for the Madelung constants all agree with the exact (as per the Ewaid method) values to five significant digits.

The LRO ground states and random energies for the fcc, bcc, and sc Madelung lattices are shown in Fig. 3. From the ground state searches, we find the following features.

(i) As in the work of Magri et at., we find (in addition to the pure constituents A and B) the three lowest en-ergy fcc-based configurations to be the D022 (AsB and ABs) and "40" (AB) structures, all of which are com-posed out of composition waves along the (120) direction in reciprocal space. (The D022 structure is composed out
of a combination of (120), (100), and (000) composition
waves; however, the (120) wave has the largest ampli-
tude.) The (100)-based structures Llo (AB) and L12 (AsB and ABs) are, however, energetically in close com-
petition. Conventional unit cells for all of these struc-
tures are shown in Fig. 1.
(ii) For each of the bcc and sc lattices, only one inter-mediate compound appears in the ground state analysis at equiatomic composition. These are the CsCl bcc-based and NaCl sc-based structures, which may be described by (100) and 2

(111) composition waves, respectively.
Thus, at equiatomic composition, there is an interesting competition between the (12 0)-, (100)-, and 2

(111)-type
waves for the fcc, bcc, and sc lattices. This competi-

tion is illustrated in greater detail in the inset of Fig.
3. Of the ordered equiatomic compounds, both the bcc-based CsCl and sc-based NaCl have a higher Madelung constant (lower electrostatic energy) than the fcc-based structures. The CsCl has the lowest Madelung energy
(highest Madelung constant). The relative orders of
electrostatic stability of the four equiatomic compounds (CsC1, NaC1, Llo, and "40") are not directly amenable
to a simple nearest-neighbor-only description: Ifthe clus-
ter expansion of Eq. (5) is prematurely truncated at the first-, second-, third-, or fourth-neighbor effective inter-actions (Table II), the lowest energy structure at x = 1/2 is incorrectly predicted to be Llo (degenerate with "40"), Llo, "40", or NaCl, respectively. Only when the first five shells of effective interactions are retained (Ta-ble II) does the cluster expansion give the correct order of stability (as confirmed by Ewald-method calculations) as shown in Fig. 3. Subsequently adding more shells of effective interactions (f'rom the 6th to the 20th neighbor shell) does not change the qualitative order of stability
between the x = 1/2 structures and also makes a negli-
gible quantitative change to the Madelung constants of
these structures. These facts again imply the conver-
gence of the cluster expansion of the Madelung lattice with only the first five shells of efrective interactions. (iii) Although the ordered bcc (CsCl) and sc (NaCl)
structures are electrostatically more stable than those
of fcc, the random fcc solid solutions are much lower in energy than the bcc or sc solid solutions (Fig. 3). In-deed, it is observed in the ionic Cu-Pd system that, although the LRO at equiatomic composition is the bcc-based CsC1 structure, the alloy disorders into an fcc solid solution. The relative energies of random alloys on dif-ferent lattices are described in

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SHORT- AND LONG-R-RANGE ORDER OF THE BINARY... 6883

nfi uration o base d on thee fcc, bcc, or sc lattices
as depicted in Fig.. 3 refers f to an energy
a concentration-weig -wei htede average of puree constituent con en-ergies in the same lattice structure as o. In general, g the lattice on whichich o is based may not bee thee equilibrium e both the constituents of thee alloy. Hence

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to another. For examp lee, thee prromotion energy om cc to bcc may be written

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&E"—&Ebcc"= fcc Ebcc [E~+a —E~+aj
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based on the bcc lattice as t e sum o

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6884 C. WOLVERTON AND ALEX ZUNGER

E&+& —E&+& (0 and the orders of stability could be

reversed, provided that E&+&—E&+& is sufficiently neg-
ative so as to overcome the difI'erence between the CsCl
and "40" electrostatic

SHORT- AND LONG-RANGE ORDER OF THE BINARY... 6885

&om the high-temperature disordered phase to the low-temperature CsCl or NaC1 structure are both second or-der (or weakly first order) and therefore without further
refinements to the Monte Carlo (such as finite size scal-
ing), we cannot give accurate values of the transition tem-peratures. The Monte Carlo calculations show that the

SRO peaks at the (1QQ) points for bcc and the —(ill) points for sc lattices for all compositions. These k vec-tors are identical to those for the long-range ordered CsCl and NaCl states, the T=O K ground states for bcc and sc. Consequently, the mean-field calculations show remark-ably good agreement with Monte Carlo.

D. T g 0 K SRO in the fcc Madelung lattice:
A failure of mean-field theory

The SRO(k) for the fcc Madelung lattice from Monte Carlo and mean-field (with and without Onsager correc-

tions) calculations are contrasted in Fig. 6 as contour plots in the (hkQ) plane. Black shading inside the high-est contour locates the peaks in the SRO patterns. The Monte Carlo calculations show the transitions on the fcc

lattice to be first order (marked by a strong

6886 C. WOLVERTON AND ALEX ZUNGER

TABLE III. Properties of the fcc Madelung lattice as a function of composition x. The long-range ordered ground states are given, as are the reciprocal-space peak positions of the SRO, as determined by Monte Carlo (MC) and mean-field (MF) statistics. AE/Ji is the normalized T=o Madelung
energy difference between the (100)- and (1—0)-type structures normalized by the effective near-
est-neighbor pair interaction Ji. For x = 1/4 it is AE/Ji ——[E(Llz) —E(D022)]/Ji and for x = 1/2 it is AE/Ji ——[E(Llo) —E("40")]/Ji. Transition temperatures T, as determined by Monte Carlo are given in units of (16A) /2dke, where ke is the Boltzmann constant.

Stoichiometry
Ground state

SRO (MC)
SRO (MF)
AE/ Ji
T, (MC)

x = 1

5

A4B

A+ Dpgg
(100)
(1-'0)

x = 1

4

A3B

Do„
(loo)
(110)
+0.065
0.95

x=3—1
A2B

D022 + "40"
(100), (1—0)
(1-'0)

x=12
AB
cc40))

(1 —, 'o)
(1-', 0)
+0.130
0.91

rection does not change the dominant wave vectors of the SRO (this correction serves, however, to renormalize
the temperature scale). In contrast to mean-field cal-
culations, which show SRO peaks at the (120) points,
the Monte Carlo calculations clearly show that the SBO
peaks actually exist at the (100) points for x = — and —,
tvhereas for x = s, there are peaks at both the (120) and
(100) points of nearly equal intensity. Of the composi-
tions considered, only x = 2

shows peaks at the (120)
points, as computed by Monte Carlo. Thus, for several compositions, the dominant wave vectors of the SRO are not equivalent to those of the LRO, in qualitative con-trast with mean-field theory.
The crossover between the (1&0)- and (100)-point SRO
intensities is shown in Fig. 7. In this figure, the normal-
ized SRO of type k, i.e., B(k) = SRO(k)/[SRO(100) + SRO(120)] is plotted (for k=(1&0) and k=(100)) as a
function of alloy composition. The crossover occurs for
compositions x 0.33 and x 0.67. The mean-field

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c o 0.5
CD 0
e ~ 0.4
E
0
0.3
(6

0.2

(100)

Mean-field result

0.2 0.4

(1 1/2 0)

R(1 1/2 0)

R(100)

0.6

(100)

0.8

Concentration (x)

FIG. 7. (100) versus (1—0) SRO intensity for the fcc
Madelung lattice as a function of alloy composition. The
crossover between (100)- and (1—0)-point SRO occurs at
x 0.33 and x 0.67 for the Monte Carlo calculations,
whereas mean-field calculations of the SRO show no such

crossover and indicate (1—0)-point SRO throughout the en-
tire concentration range. (The symbols represent the actual
calculated points; curves are drawn merely to guide the eye.) The Monte Carlo (mean-field) results are shown by the solid (dashed) curves.

calculations show no such crossover and thus fail quali-

tatively for x + 0.33 and x & 0.67. Also, it should be noted that there exists no composition for which there is quantitative agreement between mean-field and Monte Carlo calculations.
The non-mean-Beld behavior of the SRO of the fcc Madelung lattice may be understood in terms of the model calculations of Fig. 8. In this figure, the normal-ized SRO of type k at x = 2

is plotted as a function of

the energy difference AE = E(Llo) —E("40") normal-ized by Ji. For x = 4, we use AE = E(L12) —E(D02z). These calculations are performed for a variety of diferent sets and ranges of model efFective interactions Jt (i.e., not those of the Madelung lattice). The solid vertical
lines delineate (100) from (120) LRO and the dashed
vertical lines separate (100) from (120) SRO, as com-puted by Monte Carlo. Thus the region between the ver-tical solid and dashed lines indicates

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SHORT- AND LONG-RANGE ORDER OF THE BINARY... 6887

0.8—

x=1/2

(100) Ground State (1—0) Ground State 1

2

(a) 1st and 2nd NN

Pairs

x = 1/4

(100) Ground State (1—0) Ground State 1

2

I

(c) I 1st and 2nd NN
Pairs 0.8—

06 R(1
C)

II '4 R(1
0 0.2—

(f)

M

Q) ~ 0

c (b)
0.8— CO
E

R{100)
I

1st - 4th NN
Pairs

R(1

'4 R(1

0.8—
R(100)

L

0.2—

"".-. Mean-Field Result

1st - 4th NN
Pairs

0.6—

0
R(1 1//2 0)

0.6—

0.4—

0.2—

0
-0.3

I
I
II I

-0.2 -0.1 0.0 0.1 0.2

[E(L10) E(40)] /J1

0.2— R(11/20) -' I

I
I
I

I

0.1 0.2

[E(L12) - E(D022)]

/ J)

0

I

0.3 -0.3 -0.2 -0.1 0.0 0.3

FIG. 8. Model calculations of the normalized SRO intensity R(k) as a function of AE/Ji with (a) and (c) first- and
second-neighbor pair interactions and (b) and (d) first- through fourth-neighbor pair interactions. Parts (a) and (b) indicate
calculations performed for composition x = 1/2 and (c) and (d) indicate analogous calculations for x = 1/4. TBT /Xi11 6.48 Tf 35911 8.3 438

an12 /Xi1i2 /Xi11 8.MonET BT /Xi11 8.8 Tf 47(8—)Tj 6439.89 TXi11 8.Carlo8.32 Tf 207.11 459 Td (no80/Xi1i2 /Xi11 8.r43 Tf70.44 438.33 T

(a)
2Xi11 8.78Carlo8.32 Tf 207.11 459 (I)Tj426439.89 TBT /Xi133 Tut Tf 470.44 438.33 Td (1/ ET BT48.56 442Xi11 8.78werT BT /Xi11 8.8 Tf 40d (seco3T /Xi2 /.4826 Tfl 8

an16 BT /E86bor

(2i11 8.46211 3347 Tf 448.44.67 459.11 Td (wit6))T73T /X BT Tj Ef,.11 595.22 Td ("Tj ET BT Td (oXi11T BT /XXi11 9.98 Tf 317.119dj ET B101)ulaE4/Xi11 6.5

6888 C. %'OLVERTON AND ALEX ZUNGER

CC-CPA. Many current SRO calculations based on the S-
CPA (Refs. 26 and 32—35) employ the mean-field approx-

32

SHORT- AND LONG-RANGE ORDER OF THE BINARY... 6889

0.0

-0.2

TABLE IV. Dominant wave vectors of the long- and
short-range order for the fcc, bcc, and sc Madelung lattices.
U
CU

~o
U

-0.4

-0.6

-0.8

- 1.0

- 1.2

Random (T=oo)----
fcc
bcc

sc

Do», "40"
CsCl (B2)
NaC1 (Bl)

(1-'0)
(100)
—(111)

LRO
Lattice Ground states Wave vector

SRO
Wave vectors
4 2

1

(100) (1—0)
(100) (100)
~

(111) —(111)

- 1.4

- 1.6
- 1.8

C. WOLVERTON AND ALEX ZUNGER

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In characterizing the charge density in terms of charge transfer, one is faced with the fact that there is no unique way to apportion a three-dimensional

Ozaced