RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 42, NUMBER 17 15 DECEMBER 1990-I

Ground-state structures and the random-state energy of the Madelung lattice

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(Received 22 August 1990)

We consider the classic Madelung problem of a lattice with N sites labeled i, each occupied by either an A or a B atom, and bearing a point charge Q_i that depends on the environment of i. We find that out of the 2^N possible lattice configurations of this binary $A_{1-x}B_x$ fcc alloy, the lowest-energy "ground-state structures" are the A_3B, A_2B_2, and AB_3 ordered superlattices with ordering vector $(1,0,\frac{1}{2})$. On the other hand, for the pseudobinary $A_{1-x}B_xC$ zinc-blende alloy, the ground state corresponds to phase separation into $AC+BC$. Contrary to the accepted view, the Madelung energy of the random binary alloy is found to be nonvanishing.

Calculations of the electrostatic Madelung energies E_M have long played a significant role in assessing qualitative trends of structural preference between various crystal types. The dependence of E_M on the ion configuration in a lattice has been used in the past to discuss the relative stabilities of a broad range of ionic or partially ionic crystals, including not only the classic[1,2] system of alkali-metal halides, but also high-T_c superconductors,[3] organic charge-transfer salts,[4] intercalated graphite,[5] semiconductor alloys,[6] metallic clusters,[7] intermetallic compounds,[8] and various crystal surfaces and interfaces.[9]

Consider the classic Madelung problem[1,2] of a simple lattice (e.g., fcc) with $N\rightarrow\infty$ sites $i=1,2,\ldots,N$, each bearing a net charge Q_i and occupied either by an A atom (labeled with a spin variable $\hat{S}_i=-1$) or by a B atom (labeled as $\hat{S}_i=+1$). Each of the 2^N possible lattice configurations σ has a Madelung energy $E_M(\sigma)$ per atom. It can be expressed as an infinite-range Ising-type Hamiltonian

$$E_M(\sigma)=\frac{1}{2N}\sum_{i,j}{}'\frac{Q_iQ_j}{|\mathbf{R}_i-\mathbf{R}_j|}=\frac{1}{2N}\sum_{i,j}{}'\hat{S}_i\hat{S}_jJ_{ij}\,, \quad (1)$$

where the prime excludes the $i=j$ term, and J_{ij} denotes the bare Coulomb interaction energy

$$J_{ij}=\frac{Q_iQ_j}{|\mathbf{R}_i-\mathbf{R}_j|}\hat{S}_i\hat{S}_j\,, \quad (2)$$

between charge Q_i on lattice site $\mathbf{R}_i$ and Q_j on $\mathbf{R}_j$. Traditional approaches to the electrostatic lattice-stability problem[1-9] have often contrasted $E_M(\sigma)$ of a small number of "competing" configurations σ, deciding thereby between alternative crystal structures. However, (i) the configuration corresponding to the global minimum of $E_M(\sigma)$ (out of 2^N possible configurations) on a given Bravais lattice has not been identified, nor has (ii) the configurationally averaged Madelung energy $E_M(R)$ of the *random* (R) binary $A_{1-x}B_x$ alloy been calculated. As recognized early on by Mott,[10] both questions are central to theories of phase stability of systems exhibiting charge transfer, where the Madelung "ordering energy" $\Delta E_M(O)=E_M(O)-E_M(R)$ (of some ordered arrangement O, relative to the random alloy at the same composition) can provide a significant driving force either to phase separation or to selective long-range ordering.

Regarding question (i), we note that classic lattice models of statistical mechanics[11] are able to search effectively for the ground-state configuration of *finite-range* Ising Hamiltonians. However, the slow decay with distance of J_{ij} of Eq. (2) and the *conditional*[2] (rather than absolute) convergence of the Ising series of Eq. (1), have not been conducive to a similar analysis for electrostatic Ising Hamiltonians. Regarding question (ii), we note that modern theories of alloy phase stability[12-14] based on the "site-coherent potential approximations" (SCPA) (Ref. 13) have tacitly assumed $E_M(R)\equiv 0$ for binary $A_{1-x}B_x$ systems at all compositions x. This conclusion reflects the simplistic assumption that at a given composition the net charge Q_i on a site i does not depend on the environment of this site; all A atoms are assumed to have the same net charge (and so do all B atoms). It then follows that the configuration average $\langle Q_iQ_j\rangle_R$ in Eq. (1) factors into the product $\langle Q_i\rangle_R\langle Q_j\rangle_R$ which is zero (on account of global charge neutrality $\langle Q_i\rangle_R=0$), hence,[14] $E_M(R)=0$. However, as suspected by Mott,[10] the assumption that in arbitrary atomic configurations the net atomic charges do not depend on the environment is not supported by self-consistent determinations of the charge density.[15]

We have addressed questions (i) and (ii) by replacing $\{J_{ij}\}$ of Eqs. (1) and (2) by a set of *renormalized* interactions $\{\tilde{J}\}$ that transforms Eq. (1) to a rapidly convergent Ising series. Analysis of this renormalized Ising Hamiltonian is then used to obtain the ground-state structures and the energy of random alloy; we find that it is finite. We illustrate this general method for binary fcc $A_{1-x}B_x$ and pseudobinary zinc-blende $A_{1-x}B_xC$ alloys.

We start by selecting a physically motivated model for the distribution $\{Q_i\}$ of point charges on the various lattice sites i. A random distribution of many A and B atoms on a fixed lattice generally creates various crystallographically inequivalent A sites (and separately, B sites) that are distinguished by different local atomic arrangements around them. It then seems reasonable to assume[10,15] that an atom surrounded locally by atoms of the same chemical type would have a smaller net charge than an atom surrounded, e.g., by atoms of the opposite type. We hence model the net charge Q_i to be proportional to the number of atoms of *opposite* type in the first coordination shell (containing Z atoms):

$$Q_i = \lambda \sum_{k=1}^{Z} (\hat{S}_i - \hat{S}_k^{(i+1)}) , \tag{3}$$

where $\hat{S}_i$ is the spin on site i, $\hat{S}_k^{(i+1)}$ is the spin on one of the Z atoms that are nearest neighbors to site i, and λ is a scaling constant determining the maximum charge transfer ($2Z\lambda$). The charge distribution of Eq. (3) has the following properties: (i) the charges on A's and B's have opposite signs; different A sites (and different B sites) can have different charges reflecting variations in the local atomic arrangements; (ii) electroneutrality $\sum_i Q_i = 0$ is naturally satisfied; (iii) E_M of Eq. (1) is symmetrical with respect to the $A \leftrightarrow B$ replacement; and (iv) it reduces to standard definitions[1,2] for prototype AB ordered lattices.

We next cast Eq. (1) into a renormalized series by using the cluster expansion method[16] as follows: We define a set of "figures" $\{f\}$ which are clusters of atoms with k_f vertices (e.g., $k_f = 2$ are pairs) separated by up to the mth neighbor distance. For each figure we define its spin products $\Pi_f(\sigma) = \hat{S}_{1_f} \hat{S}_{2_f} \ldots \hat{S}_{k_f}$. Using the symmetry of the (empty) lattice and the orthogonality relations[16(a)] between $\Pi_f(\sigma)$'s we can rigorously expand the Madelung energy in a series of orthonormal functions as

$$E_M(\sigma) = \sum_F D_F \bar{\Pi}_F(\sigma) \tilde{J}_F , \tag{4}$$

where F is a prototype figure (there are ND_F symmetry-related figures in the lattice),

$$\bar{\Pi}_F(\sigma) = \frac{1}{ND_F} \sum_{f \in F} \Pi_f(\sigma) \tag{5}$$

is the "lattice-averaged spin product," and $\tilde{J}_F$ is the *effective* interaction energy of the figure of type F. It can be calculated by specializing Eq. (4) to a set of N_s ordered structures $\{s\}$ and inverting[16(b)] it. This yields a set of N_s effective interaction energies $\tilde{J}_F$,

$$\tilde{J}_F = \sum_s^{N_s} [\bar{\Pi}_F(s) D_F]^{-1} E_M(s) . \tag{6}$$

Equations (1) and (6) show that these effective ("renormalized") interactions

$$\tilde{J}_F = \sum_s^{N_s} [\bar{\Pi}_F(s) D_F]^{-1} \sum_{i,j}{}' \frac{1}{2N} \Pi_{i,j}(s) J_{ij} \tag{7}$$

represent a sum over all *bare* Coulomb interactions J_{ij} of Eq. (2). We next demonstrate that this renormalized Ising series represents also a rapidly convergent expansion. Note that to the extent that the terms of Eq. (4) are negligible past a maximum figure $F_{\max}$, we can determine from Eq. (6) N_s values of $\tilde{J}_F$, given the *exact* Madelung energy $E_M(s)$ of N_s linearly-independent structures $\{s\}$. The problem is to find $F_{\max}$ that produces a sufficiently small truncation error. To do this, we first truncate Eq. (4) at a trial $F_{\max}$ value, evaluate N_s values of $\tilde{J}_F$ using Eq. (6) [where $E_M(s)$ is calculated exactly by Ewald's method[2]], and then use these $\tilde{J}_F$'s in Eq. (4) to *predict*[17] $E_M(s')$ for *another* set of structures $\{s'\} \neq \{s\}$. In the second step we contrast these predictions with the exact (Ewald) values of $\{E_M(s')\}$; the difference ("prediction error") is minimized iteratively by increasing $F_{\max}$. Because of the pairwise nature of the Coulomb interaction [Eq. (2)], only pair interactions are nonzero in Eq. (4). Table I shows that truncating $F_{\max}$ at the sixth fcc neighbor (i.e., using seven $\tilde{J}_F$'s and seven basis structures given at the top section of Table I) already gives a satisfactorily small prediction error (standard deviation $\chi = 0.00068$) for the Madelung constants α_M. We use the definition $\alpha_M(s) = -2rE_M(s)/(16\lambda)^2$, where $r = \sqrt{2}a/2$ is the nearest-neighbor distance of the fcc lattice, and the scaling factor is chosen as 16λ so that $\alpha_M(L1_0) = 1.59436$ is the conventional result for the CuAu-I($L1_0$) structure (see Table I). The resulting renormalized pair interactions $\tilde{J}_m$ for the binary fcc system (where m is the order of neighbor distance) are

$$\begin{aligned} &\tilde{J}_1 = -0.32393, \quad \tilde{J}_2 = 0.08281, \quad \tilde{J}_3 = 0.06093 , \\ &\tilde{J}_4 = 0.03446, \quad \tilde{J}_5 = 0.00139, \quad \tilde{J}_6 = 0.00048 . \end{aligned} \tag{8}$$

TABLE I. Calculated Madelung constants of fcc crystal structures with point-charge distribution given by Eq. (3). The first three columns give, respectively, the structure symbol, its chemical formula (written as a superlattice A_pB_q, where p and q are the repeat periods), and the superlattice orientation. The $L1_2$ structure (Ref. 11) is not a superlattice. The fourth column gives the exact Madelung constants calculated by Ewald's method (denoted as α_M^{exact}), while the last column gives the predicted Madelung constants α_M^{pred} using the cluster expansion of Eq. (4) with interaction parameters $\tilde{J}_F$ given by Eq. (8). These were obtained by invertion [Eq. (6)], using the top seven ("basis set") structures in this table. The structures in the second part of the table are linearly-dependent to those in the first part, so their Madelung constants are predicted exactly. The third part of the table gives the Madelung constants of the structures that are independent; the standard deviation for these predictions is as small as 0.00068.

Structure type	Formula	Orientation	α_M^{exact}	α_M^{pred}
		Structures in basis set		
$A1$	A/B		0.0	0.0
$L1_0$	AB	[001]	1.59436	1.59436
$L1_1$	AB	[111]	0.69509	0.69509
"40"	A_2B_2	[201]	1.63664	1.63664
$Z2$	A_2B_2	[001]	−0.13537	−0.13537
$Y2$	A_2B_2	[110]	0.58882	0.58882
$\beta1/\beta2$	A_2B/AB_2	[001]	0.44863	0.44863
		Linearly-dependent structures (examples)		
$L1_2$	A_3B/AB_3		1.19577	1.19577
DO_{22}	A_3B/AB_3	[201]	1.21691	1.21691
$Y1/Y3$	A_3B/AB_3	[110]	0.69300	0.69300
$Z1/Z3$	A_3B/AB_3	[001]	0.33090	0.33090
		Linearly-independent structures (examples)		
$\alpha1/\alpha2$	A_2B/AB_2	[111]	0.07207	0.07133
$\gamma1/\gamma2$	A_2B/AB_2	[110]	1.20458	1.20544
$V1/V3$	A_3B/AB_3	[111]	0.05351	0.05302
$W1/W3$	A_3B/AB_3	[113]	0.70740	0.70646
$V2$	A_2B_2	[111]	−0.24053	−0.24150
$W2$	A_2B_2	[113]	1.06725	1.06537
$SQS8$	$A_2B_3A_2B_1$	[113]	0.75445	0.75328
Random	$A_{0.5}B_{0.5}$	· · ·	0.73952	0.73865

These exhibit a rapid decay with m, in sharp contrast with the slowly decaying bare Coulomb interactions J_{ij} of Eq. (2). Comparing Eqs. (2) and (7) we note that whereas $\{J_{ij}\}$ are positive-definite, $\tilde{J}_F$ could be either positive or negative; we find [Eq. (8)] that the dominant effective first-neighbor term $\tilde{J}_1$ is antiferromagnetic ($\tilde{J}_1 < 0$), whereas the remaining interactions are ferromagnetic ($\tilde{J}_{m>1} > 0$). The fcc Coulomb lattice is hence frustrated.

The rapid convergence and practical completeness of this set $\{\tilde{J}_F\}$ allows us to calculate the configuration average $\langle E_M \rangle_R \equiv E_M(R)$ for the random alloy. Using in Eq. (4) the configurationally averaged pair correlation functions $\langle \bar{\Pi}_F \rangle_R = (2x-1)^2$ appropriate to the random alloy, we find $\alpha_M(R,x) = 0.738\,65\ [4x(1-x)]$, in excellent agreement with the analytic result $\alpha_M(R,x) = 0.739\,52\ [4x(1-x)]$, which can be obtained by substituting Eq. (3) into Eq. (1) and evaluating explicitly its configurational average. The excellent agreement between the analytic result and that of the truncated cluster expansion lends credence to the latter approach which was previously used[17] in cases where an exact result was unavailable [i.e., where the expansion Eq. (4) was applied to the *total* electron plus ion energy of a lattice]. The dashed line in Fig. 1 shows our calculated composition dependence of $E_M(R,x)$; the horizontal solid line shows the conventional SCPA result[12–14,18] obtained with uncorrelated charges. Contrary to the latter, our result indicates that the random alloy does influence the ordering energy $\Delta E_M(O)$; assuming that[12–14,18] $E_M(R,x) = 0$, then greatly exaggerates the stability of ordered charge-transfer structures relative to the random alloy.

The rapid convergence of the renormalized Ising series facilitates the search among 2^N configurations for the ground-state structures[11,17] of the binary Madelung lattice. The results (diamond-shaped symbols in Fig. 1) obtained with the interactions of Eq. (8) and the method of Ref. 17 show that the ground state consists of the pure end-point solids $A(x=0)$ and $B(x=1)$, as well as the three superlattices with the $(1,0,\frac{1}{2})$ ordering vector: the A_3B DO_{22} structure (space group D_{4h}^{17}, the TiAl$_3$-type), A_2B_2 (space group D_{4h}^{19}, the NbP-type structure), and AB_3 in the DO_{22} structure. Figure 1 also shows as open circles excited configurations whose energies are just above the ground-state lines. We see that the A_3B, AB, and AB_3 structures ($L1_2$, $L1_0$, and $L1_2$ crystal types, respectively) with the (0,0,1) ordering vector are less stable than the corresponding structures with the $(1,0,\frac{1}{2})$ ordering vectors and that the random alloy has yet a higher energy.

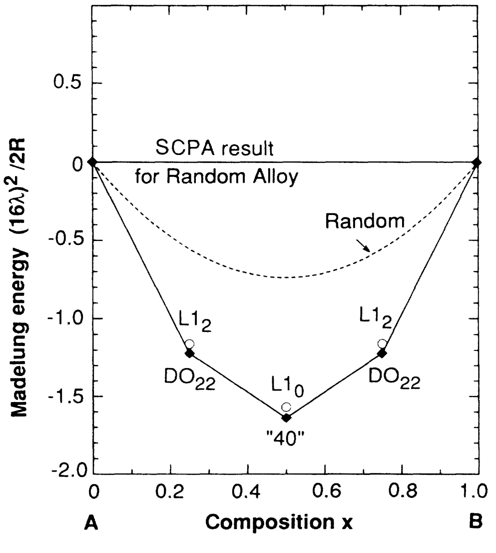

FIG. 1. Calculated ground-state structures (solid lines connecting diamond-shaped symbols) of the binary fcc Madelung lattice $A_{1-x}B_x$ with charge distribution given by Eq. (3). Open circles denote E_M of the three unstable (001) ordered structures. The dashed line gives the energy of the random alloy in this model, while the horizontal solid line gives the (rather poor) SCPA (Refs. 12–14, 18) approximation to the random alloy.

The concept that the net charge is decided primarily by the local environment can be extended to *pseudobinary* $A_{1-x}B_xC$ alloys whose constituents (AC and BC) have, e.g., the zinc-blende structure. Since the A and B atoms are always coordinated there by four C atoms (much like in pure AC and BC), this model gives $Q_i(A) = Q_A$ and $Q_i(B) = Q_B$ for all A and B sites, respectively, where Q_A and Q_B are the charges on A and B in the constituents.

TABLE II. Calculated Madelung constants α_M [Eq. (10)] for pseudobinary tetrahedral alloys with point-charge distribution given by Eq. (9). The structure types are defined in the caption of Table I. α_M^{exact} are the exact geometrical constants [Eq. (10)] calculated by Ewald's method, α_M^{pred} are the predicted constants using the cluster expansion of Eq. (4) with seven basis set structures. This gives the interaction parameters $\tilde{J}_0 = 2.516\,43$, $\tilde{J}_1 = 0.459\,61$, $\tilde{J}_2 = 0.013\,95$, $\tilde{J}_3 = 0.004\,98$, $\tilde{J}_4 = -0.004\,94$, $\tilde{J}_5 = -0.000\,07$, and $\tilde{J}_6 = 0.001\,14$. See caption of Table I for the explanation of the three sections of this Table. The standard deviation for the predictions if 0.001 93.

Structure type	α_M^{exact}	α_M^{pred}
	Structures in basis set	
A/B	5.349 87	5.349 87
$L1_0$	1.594 36	1.594 36
$L1_1$	2.440 39	2.440 39
"40"	1.636 64	1.636 64
$Z2$	3.434 73	3.434 73
$Y2$	2.516 91	2.516 91
$\beta1/\beta2$	2.820 92	2.820 92
	Linearly-dependent structures (examples)	
$L1_2$	2.533 24	2.533 24
DO_{22}	2.554 38	2.554 38
$Y1/Y3$	2.994 51	2.994 51
$Z1/Z3$	3.453 42	3.453 42
	Linearly-independent structures (examples)	
$\alpha1/\alpha2$	3.407 56	3.412 09
$\gamma1/\gamma2$	2.238 27	2.239 31
$V1/V3$	3.893 13	3.895 40
$W1/W3$	2.975 80	2.975 91
$V2$	3.891 12	3.895 66
$W2$	2.056 46	2.056 68
$SQS8$	2.520 89	2.521 32
Random ($x=0.5$)	2.515 99	2.516 43

The charges on the different C atoms are then decided by the electroneutrality condition for each C-centered A_nB_{4-n} $(0 \leq n \leq 4)$ tetrahedron. This gives the charge distribution for $A_{1-x}B_xC$ alloy as[6]

$$Q_i = \bar{Q} + \Delta Q\, \hat{S}_i \quad (i \text{ in the } A,B \text{ sublattice})$$

$$Q_j = -\left[\bar{Q} + \frac{\Delta Q}{4} \sum_i \hat{S}_i^{(j)}\right] \quad (j \text{ in the } C \text{ sublattice}) , \tag{9}$$

where $\bar{Q} = (Q_A + Q_B)/2$, $\Delta Q = (Q_B - Q_A)/2$, and $\hat{S}_i^{(j)}$ is the spin variable for the occupation of the four tetrahedral vertices i centered at j. Using Eq. (9), the Madelung energy of the $A_{1-x}B_xC$ semiconductor lattices can be expressed as

$$E_M(\sigma) = -\frac{\alpha_{\mathrm{ZB}} \bar{Q}^2}{d} - \frac{\alpha_M(\sigma) \Delta Q^2}{2r} - \frac{\beta_M(\sigma) \Delta Q \bar{Q}}{d} , \tag{10}$$

where $\alpha_{\mathrm{ZB}} = 1.638055$ is the Madelung constant of the zinc-blende (ZB) lattice, $\beta_M(\sigma) = 4\alpha_{\mathrm{ZB}}[x(\sigma) - 0.5]$, $d = \sqrt{3}/4a$ is the nearest-neighbor anion-cation distance, and $\alpha_M(\sigma)$ is a geometrical constant to be calculated below.

We have repeated for $A_{1-x}B_xC$ (Table II) the same procedure used above for $A_{1-x}B_x$. The results are given in Table II. We see that the predicted values for ordered structures agree very well with those calculated directly by Ewald's method, and that the result $\alpha_M(R, x = 0.5) = 2.51643$ for the random pseudobinary alloy also agrees well with the exact value[6] $\alpha_M(R, x = 0.5) = 2.51599$.

Unlike the case in *binary* $A_{1-x}B_x$ alloys, the dominant effective interactions in pseudobinary $A_{1-x}B_xC$ systems (given in the caption to Table II) are found to be ferromagnetic, hence, the ground state corresponds to phase separation. This reflects the fact that the (negative) Madelung energy of $A_{1-x}B_xC$ is minimal for the AC and BC *constituents,* since, relative to the average charge value $(\Delta Q = 0)$ the constituents exhibit the largest charge fluctuation $(\pm \Delta Q)$ on the common sublattice C. Note that the trend of stability of $(AC)_n(BC)_n$ superlattices predicted by this model (i.e., [111] structures have the next lowest energy after the phase-separated system) is consistent with first-principles total-energy calculations for lattice matched semiconductor superlattices.[19]

In summary, we have shown that cluster expansion used previously in numerous calculations of phase diagrams[17] is capable of describing electrostatic point-ion energies of systems with correlated charge transfer. We have demonstrated that although the bare Coulomb interactions between point charges is long ranged, the renormalized interactions are short ranged and rapidly convergent, reflecting local charge neutrality. We find that the Madelung energy of the random alloy with correlated point charges is nonvanishing, hence, unlike the assumptions underlying the popular SCPA,[12–14,18] Coulomb energies of random alloys can contribute significantly to ordering energies.

This work was supported by the Department of Energy under Contract No. DE-AC02-77-CH00178. We thank D. D. Johnson and F. Ducastelle for helpful discussions on the Madelung energy in the SCPA.

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