Two-dimensional discrete Coulomb alloy

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We study an $A_{1-x}B_x$ alloy on a two-dimensional triangular lattice. The ions $A$ and $B$ have different charges, with a background charge to ensure neutrality, and are constrained to lie at the discrete sites defined by a fixed triangular lattice. We study the various structures formed at different compositions $x$ by doing computer simulations to find the lowest energy, using an energy minimization scheme, together with simulated annealing. Like ions try to avoid each other because of charge repulsion, which leads to structures, which are very different from those in a random alloy. At low concentrations, a triangular Wigner lattice is formed, which evolves continuously up to a concentration of $x = 1/3$. For higher concentrations, $1/3 \leq x \leq 1/2$ there are long polymer chains, with occasional branches. We show that there is a symmetry about $x = 1/2$, which is the percolation point for nearest neighbors on the triangular lattice. At certain special stoichiometries, regular superlattices are formed, which usually have a slightly lower energy than a disordered configuration. The powder-diffraction patterns are calculated. The magnetic properties of this structure are also studied, and it is shown that the high-temperature susceptibility could be a useful diagnostic tool, in that it is very sensitive to the number of nearest-neighbor magnetic pairs. This work contributes to a better understanding of layered double hydroxides like Ni$_{1-x}$Al$_x$(OH)$_2$(CO$_3$)$_{y/2}$·yH$_2$O. [S0163-1829(99)12001-0]

I. INTRODUCTION

We introduce and study the properties of a model alloy system, which consists of two different types of charged ions with concentration $x$ and $1-x$, that are free to move on the sites of a triangular lattice in order to achieve the lowest energy configuration. We were directed to this study by experiments on the layer double hydroxides, where the metal ions in the galleries can form an alloy. A typical example of such a layered double hydroxide (LDH) is Ni$_{1-x}$Al$_x$(OH)$_2$(CO$_3$)$_{y/2}$·yH$_2$O. A detailed description of the structure of this compound is given by Solin et al. In this structure, the Ni$^{2+}$ ions and the Al$^{3+}$ ions occupy discrete positions, within the layers, on two-dimensional (2D) triangular lattice sites. This is a very unusual alloy, as although it is substitutional, the two types of ions, Ni$^{2+}$ and Al$^{3+}$, have different charge states. This is a system which can only occur in two dimensions because another layer, assumed to be shielded from the layer of interest, is needed to ensure charge neutrality.

Starting from pure Ni(OH)$_2$, and as Al$^{3+}$ ions are substituted for Ni$^{2+}$ ions, carbonate ions (CO$_3$)$^{2-}$ must also be added between the metal layers, for charge compensation, with two Al$^{3+}$ ions being associated with each (CO$_3$)$_{y/2}$. In addition, water is introduced into the gallery with approximately 5–6 water molecules being packed around each carbonate ion, so that $y \approx 2.5x$, for all concentrations $x$. This two-dimensional alloy provides a very unusual and interesting situation, where we expect the actual configuration of the Ni$^{2+}$ and Al$^{3+}$ ions to be correlated and therefore quite nonrandom. The Coulomb interactions between the metal ions are of the usual Coulomb kind, and the compensating charges above and below the layers provide for overall charge neutrality. We assume that these compensating charges are shielded from the layer of interest and will not consider them further in this paper.

Based on the structure of the LDH compound, it is reasonable for us to assume that the structure of the Ni-Al layer is determined by the Coulomb interactions of the ions within each layer, and that the screening between layers is sufficiently large that a single layer model will suffice. The magnetic properties of the Ni$^{2+}$ ions are of particular interest (the Al$^{3+}$ ions are nonmagnetic) and the magnetic properties of this system are sensitive to the actual arrangement of the Ni$^{2+}$ ions within the layers. The magnetic exchange interactions themselves are smaller by about $10^{-3}$ compared to the Coulomb interactions, and play no role in determining the structure.

Thus the problem is quite general, simple, and well posed. Given two kinds of ions, $A^{m+}$ and $B^{n+}$ (with $m \neq n$), interacting via Coulomb interactions within the plane, how are the ions arranged on a 2D triangular lattice at different concentrations? This is the model system we study in this paper. Because the Coulomb interaction couples all pairs of ions, and is long range, it is not possible to make an analytic calculation, and so we set up a computer simulation. The model and the simulations are described in the next section. We find two general classes of nonrandom structures. The problem is symmetric about the concentration $x = 1/2$. For $x \leq 1/3$, we find that like ions stay apart maximally and hence form a dilute triangular lattice at low $x$. This is effectively a Wigner lattice and we show that the energetics of the 2D Wigner lattice with a continuum background for charge neutrality agree very well with our results at small $x$. This
Wigner-like lattice evolves continuously up to a concentration of \( x = 1/3 \). For higher concentrations \( 1/3 < x \leq 1/2 \), the lowest energy configurations consist of long separated polymer chains. Percolation between nearest-neighbor sites occurs at \( x = 1/2 \), and the structures are repeated for \( x \geq 1/2 \) with the two ions interchanged so that the configurations at polymer chain structures formed when \( 1/3 \) lattice limit at a small concentration lattices at special concentrations. We also study series of ordered lowest energy structures. We also discuss the Wigner lattice limit at a small concentration \( x \) and also the various polymer chain structures formed when \( 1/3 < x \leq 1/2 \). In Sec. III, we describe how the powder-diffraction patterns are fully randomly oriented layered double hydroxides, and end with a brief conclusion.

The layout of this paper is as follows. In the next section, we define the problem mathematically, and set up a computer simulation, involving the Coulomb sums, to find the lowest energy structures. We also study series of ordered lattices at special concentrations \( x \). We discuss the Wigner lattice limit at a small concentration \( x \) and also the various polymer chain structures formed when \( 1/3 < x \leq 1/2 \). In Sec. III, we describe how the powder-diffraction patterns are computed for samples which are randomly oriented within the plane (2D powder average) and also for samples that are fully randomly oriented (3D powder averages). In Sec. IV, we study the magnetic properties of this system, with emphasis on the behavior of the susceptibility. In Sec. V, we discuss the present experimental situation with reference to the layered double hydroxides, and end with a brief conclusion.

II. THE MODEL AND COMPUTER SIMULATIONS

We define a two-dimensional lattice of sites that form a perfect triangular network, where the nearest-neighbor distance is \( a \). Ions of two kinds \( A^+ \) and \( B^+ \) are placed on the sites of the triangular network and form a 2D Coulomb alloy \( A_{1-x}B_x \). The total Coulomb energy

\[
E_T = \sum_{(ij)} \frac{q_i q_j}{r_{ij}}
\]

is a minimum at equilibrium. We imagine a compensating uniform background, within the layer to ensure overall charge neutrality. This then defines the model system. Note that the charges interact with a \( r^{-1} \) potential and so there are no long-range effects as would be expected in 2D from a ln \( r \) interaction, in a system with overall charge neutrality. Thus there are no effects of the kind that lead to shape dependence in 3D, with a \( r^{-1} \) potential. To incorporate the charge neutrality, we define a mean charge \( \bar{q} \) and fluctuations \( \Delta_m \) and \( \Delta_m \) from the mean at the \( A \) and \( B \) sites, respectively, where

\[
\bar{q} = (1-x)m + xn,
\]

\[
\Delta_m = m - \bar{q},
\]

\[
\Delta_m = n - \bar{q}.
\]

Note that while the charge deviations \( \Delta_m \) and \( \Delta_m \) depend on the composition \( x \), the charges are the same at all \( A \) and at all \( B \) sites for a given composition. Equation (1) is now rewritten as

\[
E_T = \sum_{(ij)} \frac{(\bar{q} + \Delta_i)(\bar{q} + \Delta_j)}{r_{ij}} = \sum_{(ij)} \frac{\bar{q}^2}{r_{ij}} + 2\bar{q} \sum_{(ij)} \frac{\Delta_i}{r_{ij}} + \sum_{(ij)} \frac{\Delta_i \Delta_j}{r_{ij}}.
\]

The first term in Eq. (5) is configuration independent, and cancelled by the compensating uniform background charge that we have already discussed. The second term can be easily shown to vanish by using Eqs. (2)–(4). Therefore instead of minimizing the total energy \( E_T \), we only have to minimize the last term in Eq. (5), which we will refer to as the energy \( E(x) \) from now on

\[
E(x) = \sum_{(ij)} \frac{\Delta_i \Delta_j}{r_{ij}},
\]

where we have emphasized explicitly the composition dependence. The angular brackets in the summations above denote that each pair is only counted once. An aim of this paper is to find the minimum energy configurations associated with Eq. (6), and to study the associated structures in real space. We note that because of the way the energy is defined in Eq. (6) via the \( \Delta \), the energy and structures and all related quantities are symmetric about \( x = 1/2 \), and hence we have

\[
E(1-x) = E(x).
\]

The symmetry (7) is associated with interchanging the \( A \) and \( B \) sites. It is also noticed that since this is a charge-neutral system, we may apply Ewald’s method\(^5,6\) to calculate the total Coulomb sum as discussed in the Appendix.

A. Simulation method

To find out the minimum energy configuration at a given concentration \( x \), we use a Monte Carlo method\(^7\) together with simulated annealing. We choose 2D samples with a convenient size of \( 18 \times 20 \), and with periodic boundary conditions in both directions. The sample contains 360 sites, on a triangular lattice and the supercell is a parallelogram with a base of \( 18a \) and a height of \( 10\sqrt{3}a \). We start from a random configuration, at a high initial temperature. Pairs of sites are selected at random. If the two sites have like ions on them, no further action is taken. If the two sites have different ions on them, then the ions are interchanged and the charge in the Coulomb energy \( \Delta E \) is computed using Eq. (6). A Boltzmann factor \( \exp(-\Delta E/k_B T) \) is calculated where \( T \) is the temperature of the simulated annealing and \( k_B \) is Boltzman’s constant. A Metropolis criterion\(^7\) is used to decide whether a move is accepted or rejected. At each temperature, this procedure is continued until the system has reached equilibrium, and the temperature is reduced gradually to zero. We find that the Coulomb sums are rapidly converging and we did not find it necessary to sum out further than 40 sites from each site. For a given configuration, we used Ewald’s method to calculate the exact total energy. We emphasize that the temperatures used in this simulated annealing have nothing to do with the actual temperatures at which the samples are made. The annealing procedure used here is merely a convenient artifact to assist in reaching the lowest energy configuration at zero temperature. A typical configuration is shown in Fig. 1.
In most cases this Monte Carlo annealing procedure works well, when compared to the exact known energies of some regular arrangements that are discussed in the next section. Although we were able to obtain reasonable energies at these special concentrations \( x \), we had some difficulty in getting crystalline structures from Monte Carlo rearrangements. In order to obtain a better result, we introduced a temperature profile in the 18\( \times \)20 sample so that at the center, the temperature is the lowest and becomes higher away from the center. This idea comes from the process of crystallization, with nucleation centers. We will refer to this as thermal profile simulated annealing. It was successful in many cases, as for example in the crystalline structure shown in Fig. 2. However at compositions where there are competing crystalline structures, it is very difficult to avoid domain formation as shown in Fig. 3.

B. Regular superstructures

1. Triangular superlattices

At certain values of the composition \( x \), it is possible to form regular superstructures. The most important class of these are when one set of ions, say \( B \), lies on a triangular network, where the separation between nearest-neighbor \( B \) ions is \( \sqrt{3}a \). This leads to a set of compositions \( x = \frac{l}{n} \), where \( l = 3, 4, 7, 9, 12, \) etc. are positive integers. The general expression for \( l \) on the triangular lattice is given by \( l = n^2 + m^2 + nm \), where \( n, m \) are non-negative integers. An example of such a triangular superlattice is shown in Fig. 2 where \( l = 3 \) and hence the concentration \( x = 1/3 \).

Using the symmetry property (7), we can generate another series of related structures with \( x \). Of course many other sets of regular superlattice structures can be formed, but most are not interesting as they are not close to minimum energy states. However, we mention that there are some other superstructures that have an energy very close to the minimum energy of the triangular lattice superstructures. For example, the rectangular superstructure at \( x = 1/4 \) is one such example and is shown in Fig. 3, which has an energy only slightly higher than the \( l = 4 \) triangular superlattice.

Note that the energies of these structures can be found by the exact enumeration of Eq. (6). Some care must be taken as many of these periodic structures are not commensurate with the 18\( \times \)20 sample size used, and so cannot be formed in the simulations. In such cases we adjusted the size of the supercell to be slightly larger or smaller, so that the structure of interest was commensurate, and had the chance to form.

2. Polymer chains

Although for concentrations \( 0 < x < 1/3 \), the \( B \) atoms form a triangular superlattice at the commensurate points, and otherwise a pseudotriangular lattice, there is no evidence for this type of structure for \( 1/3 < x < 1/2 \). At \( x = 1/2 \) the simulated annealing computations (see next subsection) suggest that the lowest energy state consists of long parallel chains, as shown in Fig. 4, while for \( 1/3 < x < 1/2 \) chains of finite length...
occur. From the computations it is not clear what is the true lowest energy state in this region. We have examined a number of possible configurations and of these the one with lowest energy is a state with short chains, all of the same length, arranged in a rectangular array. An example is shown in Fig. 5 for \( x = 3/7 \). Commensurate configurations of this type are only possible for concentrations \( x = l/2(l+1) \) where \( l \) is any integer. These states all have slightly lower energies than the nonregular structures found in simulated annealing.

We note that the rectangular symmetry of these states is quite different from the triangular symmetry. It appears that the point \( x = 1/3 \) marks the transition between the two types of symmetry and may be regarded as a phase transition at zero temperature as a function of \( x \). The order parameter of this transition however is not known at present.

One piece of evidence which is consistent with these states being the true lowest state comes from a count of the number of nearest-neighbor pairs of \( B \) atoms, i.e., the number of bonds. For commensurate lattices we find that the number of bonds per \( B \) atom is given by

\[
N_b = \begin{cases} 
0, & 0 < x < \frac{1}{3}, \\
3 - \frac{1}{x}, & \frac{1}{3} \leq x < \frac{2}{3}, \\
3 \left( 2 - \frac{1}{x} \right), & \frac{2}{3} \leq x < 1.
\end{cases}
\]

These results assume the regular triangular arrangement for \( x < 1/3 \) and \( x > 2/3 \) and the regular rectangular arrangement for \( 1/3 < x < 2/3 \). As can be seen from Fig. 14 the numerical values obtained from simulated annealing are in quite excellent agreement with these formulas.

C. Noncrystalline structures

The energies for the computer simulated minimum-energy structures at different concentrations \( x \) are shown in Fig. 6. We were able to obtain these minimum energy structures in some runs for \( 0 < x < 1 \) using thermal profile simulated annealing which we discussed earlier. The energies for some exact periodic structures, which were discussed in the previous section, are also shown. As can be just be seen, at those special concentrations \( x \) where a superlattice structure exists, the energy of the computed structure tends to be lower to approach the energy of the superlattice structure, but does not always quite reach it. At \( x = 1/3 \), computer simulation does give the exact honeycomb supercell structure (Fig. 2). At some concentrations there can be more than one periodic structure which are almost but not quite degenerate. In this case we find, even using thermal profile simulated annealing, that domains of each type of structure are formed.

For example, we know that at \( x = 1/4 \) the \( kagomé \) structure is the lowest energy configuration. However, there is another superlattice structure with energy very close to that of the \( kagomé \), shown in Fig. 3, which forms a rectangular superlattice. The computer simulation result shown in Fig. 3 indicates that the ions get trapped locally and domains of both kinds of structures are formed.

D. Percolation

In addition to the superlattice structures discussed above, there are other interesting structural features. We observe that even though this is a 2D system with Coulomb repulsions, percolation still occurs at \( x = 0.5 \), as is the case for a random alloy. At \( x = 0.5 \), the computer simulation shows each of the two kinds of ions form infinite nearest-neighbor chains, as shown in Fig. 7. We also notice that like ions try to stay as far away as possible from each other to minimize the Coulomb energy. Therefore, at \( x = 0.5 \), loops are energetically very unfavorable and long chains are preferred.
Branches are less energetically unfavorable than loops and occur more often in the simulations.

Nevertheless we believe that at $x = 0.5$, the true lowest energy structure has infinite straight chains. Chains of the two types of ion alternate as shown in Fig. 7. Even states with chains which are not straight such as the infinite zigzag state with zigzag length 3, shown in Fig. 8, have slightly higher energy. This can be partially understood by noting that in the former there are no second-neighbor like-ion pairs, while in the latter, there are second-neighbor like-ion pairs which raise the energy. In Fig. 9, energies for both straight chains and zigzag chains are shown as open squares. The lowest data point at $x = 0.5$ is for straight chains and the points above are for zigzag chains with different zigzag lengths. The lowest (irregular) energy configuration for $x = 1/2$ obtained from the simulation is shown in Fig. 4.

E. Relation to Wigner lattices

A Wigner lattice is one in which charges on lattice sites interact via a Coulomb interaction in a uniform background of opposite charge, such that there is overall charge neutrality. In 2D these were studied by Meissner et al. and Bonsall and Maradudin. For a triangular lattice of charges $e$ with nearest-neighbor spacing $a_W$, the energy per lattice site is

$$ E = -2.1067 \frac{e^2}{a_W}. $$

(9)

In addition the number of $B$ sites is $x$ times the total number of sites on the original triangular lattice leading to an energy per lattice site of

$$ E = -2.1067(1-x)^2x^{1/2} \frac{e^2}{a}. $$

(10)

In the correlated lattice at very low $x$, the commensurate superlattices of $B$ atoms are triangular, as shown in Fig. 10, with a lattice spacing $a_W = \sqrt{3}a = a/\sqrt{x}$ (see subsection B). Taking the charge difference between the two types of charge to be $e$, then the overall charge neutrality of the layer means that the $B$ atoms have an effective charge $(1-x)e$ and the (more numerous) $A$ atoms an effective charge $-xe$. For very low $x$, the $A$ atoms can be regarded as forming a uniform background and hence we have an effective Wigner lattice. Clearly the energy of this superlattice per $B$ site is

$$ E = -2.1067(1-x)^2x^{3/2} \frac{e^2}{a}. $$

(11)

This formula is shown as the smooth curve in Fig. 11. It is asymptotically exact as $x \to 0$. However, it is remarkable that it gives a very reasonable fit to the numerical data over the whole range $0 < x \leq 1/3$.

III. POWDER-DIFFRACTION PATTERNS

We compute the powder-diffraction patterns as would be seen in x-ray-diffraction experiments. By applying periodic
boundary conditions, a piece of the 18×20 sample is treated like a primitive cell with the N ions inside being its basis. Then for a reciprocal-lattice vector \( \mathbf{K} \) of the supercell, we have

\[
|S(\mathbf{K})|^2 \propto \sum_{i}^{N} f_i e^{i \mathbf{K} \cdot \mathbf{r}_i}^2,
\]

where \( |S(\mathbf{K})|^2 \) is the scattered intensity. Here \( f_i \) is the atomic form factor, which can take on the values \( f_A \) and \( f_B \) for the two kinds of ions, respectively. Defining the average form factor

\[
\langle f \rangle = (1-x)f_A + xf_B,
\]

then, for an ensemble average we have

\[
|S(\mathbf{K})|^2 \propto \sum_{ij} \left( f_i - \langle f \rangle \right) \left( f_j - \langle f \rangle \right) e^{i \mathbf{K} \cdot \left( \mathbf{r}_i - \mathbf{r}_j \right)}
\]

\[
+ \langle f \rangle^2 \sum_{ij} e^{i \mathbf{K} \cdot \left( \mathbf{r}_i - \mathbf{r}_j \right)}.
\]

The second term in this equation is just the scattering from the underlying triangular network and is not of much interest here. The first term involving a summation in Eq. (14) contains the interesting information about the structure. Since

\[
f_A - \langle f \rangle = x(f_A - f_B),
\]

\[
f_B - \langle f \rangle = (x-1)(f_A - f_B)
\]

the first term is reduced to

\[
(f_A - f_B)^2 \sum_{ij} f_i f_j e^{i \mathbf{K} \cdot \left( \mathbf{r}_i - \mathbf{r}_j \right)},
\]

where \( f_i \) and \( f_j \) take the value \( x \) for \( A^+ \) ions and \( x-1 \) for \( B^+ \) ions. Now the term \( (f_A - f_B)^2 \) in Eq. (16) is factored out so that we monitor only the last part of Eq. (16), and define a reduced scattered intensity \( I(\mathbf{K}) \) by

\[
I(\mathbf{K}) = \sum_{ij} f_i f_j e^{i \mathbf{K} \cdot \left( \mathbf{r}_i - \mathbf{r}_j \right)}.
\]

**A. Powder-diffraction pattern in 3D**

If the layers within the crystallites are oriented in all possible directions with equal probability, we need to average over these orientations. To calculate the 3D powder-diffraction pattern, let us assume the 2D layer is in the X-Y plane, then the contribution from a particular \( \mathbf{K} \) is

\[
\frac{1}{4\pi} \int d\Omega I(\mathbf{K}) \delta(q \sin \theta - K_x) \delta(q \cos \theta - K_y)
\]

\[
= \frac{1}{2\pi} \frac{I(\mathbf{K})}{\sqrt{q^2 - (K_x^2 + K_y^2)}},
\]

and the intensity (17) becomes

\[
I(q) = \sum_{K_x^2 + K_y^2 < q^2} \frac{1}{2\pi} \frac{I(\mathbf{K})}{\sqrt{q_x^2 + q_y^2}}.
\]

**FIG. 12.** The 3D powder-diffraction pattern for a honeycomb superlattice structure with \( x=0.33 \) and the computer simulated structure at \( x=0.35 \). The vertical lines indicate the positions of the diffraction peaks of the underlying triangular lattice.

The individual superlattice reflections have a Warren line shape which has the characteristic square-root behavior. The summation in Eq. (19) results in a smoothly varying intensity \( I(q) \) if enough superlattice points are summed over. This occurs if the sample size is large enough. In order to help with this smoothing process in our model, we broaden the square-root function in Eq. (19) by introducing a small imaginary part in \( q \). That is, instead of calculating \( I(q) \), we calculate \( R(I(q + i\varepsilon)) \). We choose \( \varepsilon \) to be 0.001 in our calculations so that the line shapes are pretty smooth while the peak information is still well represented.

In Fig. 12, we show the powder-diffraction patterns for the honeycomb superlattice structure at \( x=1/3 \) and for the structure we obtained from computer simulation at \( x=0.35 \) (the curves have already been normalized and smoothed). The vertical lines indicate the positions of the diffraction peaks of the underlying triangular lattice. Therefore, we conclude at \( x=0.35 \), the honeycomb structure still dominates.

**B. Powder diffraction in 2D**

In the previous section, we have calculated the 3D powder diffraction, which is the usual case encountered experimentally. However, if we do a 2D average, as shown in the following:

\[
\frac{1}{2\pi} \int_{0}^{2\pi} d\theta I(\mathbf{K}) \delta(\cos \theta - K_x) \delta(\sin \theta - K_y)
\]

\[
= \frac{1}{2\pi} \frac{R(I(\mathbf{K}))}{\sqrt{q_x^2 + q_y^2}},
\]

and sum it up to get the total diffraction intensity

\[
I(q) = \sum_{K_x^2 + K_y^2 < q^2} \frac{1}{2\pi} \frac{R(I(\mathbf{K}))}{\sqrt{q_x^2 + q_y^2}}.
\]
then we will have sharper peaks as shown in Fig. 13. Therefore, we would suggest that if this kind of experiment would be realized, it would be easier to study the structures from these 2D diffraction patterns. Note that in the 2D case, we also have to smooth the curves, which is done by approximating the $\delta$ function by a Gaussian. The point is that the 2D powder-diffraction pattern is clearly much sharper than the 3D powder-diffraction pattern in Fig. 13.

IV. MAGNETIC PROPERTIES

Since the structures of these materials change so very much as a function of concentration the magnetic properties will also change drastically. We shall concentrate in this section on a few magnetic features which differentiate clearly between the correlated structures we predict and a random arrangement of magnetic and nonmagnetic ions on a triangular lattice. We consider only the zero-field susceptibility per magnetic atom $\chi$, since this should be straightforward to measure, although we can also calculate the magnetic contribution to the specific heat.

We assume that the magnetic interaction is isotropic Heisenberg exchange between nearest neighbors only and is antiferromagnetic in sign. The strength of the interaction is unknown but is probably of order of magnitude $10^{-3}$ of the Coulomb interaction.

The susceptibility per magnetic atom, $\chi$, is given at high $T$ for all concentrations by

$$
\chi = \frac{S(S+1)}{3T}. 
$$

For finite clusters the susceptibility at low $T$ will diverge if the ground state has a net magnetic moment or tends to zero otherwise. Hence the total susceptibility will be reduced in the random structures.

For $S=1$ we have calculated the exact susceptibility of all clusters up to size 4 at all $T$. We have also calculated the fractions of atoms which belong to each of these clusters assuming a random arrangement. If $x=0.1$ only 4.1% of atoms are in clusters with size greater than 4 but at $x=0.35$ there are just over 70%. Clearly we can only obtain good results for $x<0.1$.

Our comparison of the two cases for $x=0.1$ is shown in Fig. 15. The features to note are as follows:

FIG. 15. Plot of the inverse susceptibility $1/\chi$ vs $T$ for the correlated and random lattices at $x=0.1$. 

FIG. 14. Number of magnetic nearest-neighbor pairs per magnetic ion at different concentrations. The open squares are for regular lattices or linear chain structures. The solid triangles are for simulated lattices. The trisection curve is an analytic form based on the exact lattice structures in the first and third sections and on the linear chain structure in the second section, as given in Eq. (8).
(a) At low \( T \) the slope is greater than \( \frac{4}{3} \) because many atoms are in clusters with size greater than 1 and these have a reduced susceptibility per atom.

(b) At high \( T \) the slope becomes close to \( \frac{7}{4} \) since the high-\( T \) \( \chi \) of a cluster of size \( N \) is the same as for \( N \) isolated atoms. Note that on the figure the slope is slightly greater than \( \frac{7}{4} \) at high \( T \) because of the \( 4\% \) of magnetic atoms in clusters of size greater than 4 which have not been included.

(c) At high \( T \) there is a shift in the straight line so that it lies above the correlated line. This is due to the fact that for interacting clusters there are terms of order \( JT^2 \) reducing \( \chi \).

(d) The change from the low-\( T \) to high-\( T \) is the curved section. This occurs in the region \( T = J \). If \( J \) is not known it may be difficult to identify this region. However, a clear signature of the random lattice will be a nonzero intercept of the high-\( T \) straight line at \( T = 0 \). An intercept of 0 within experimental error indicates either a correlated lattice or a vanishingly small \( J \).

For \( 0.1 < x < 0.3 \), we expect exactly the same features. We cannot calculate the detailed shape of the curve but the effects noted above will all be present and furthermore considerably enhanced.

The behavior for \( x > 0.3 \) is more complicated. In the correlated lattice nearest-neighbor pairs rapidly become more important and then higher clusters. At \( x = 0.3 \) the correlated lattice percolates and the magnetic properties will be those of infinite 1D chains. For \( x > 0.3 \) the various 2D structures observed will all have particular magnetic properties which can probably only be calculated approximately numerically at general \( T \). These properties may be related to those of spin glasses. We hope to study some of these properties and also the magnetic specific heat in a later paper. However, although the detailed behavior is complex, the high-\( T \) result for all \( x \) is straightforward, as noted above.

V. LAYER DOUBLE HYDROXIDES

The purpose of this paper is to find out how the two kinds of ions are arranged within the triangular lattice layers for any concentration \( x \). Early in 1969, Taylor cited evidence for \( \sqrt{3} \times \sqrt{3} \) and \( \sqrt{13} \times \sqrt{13} \) superlattice structures in the compound Mg\(_{1-x}\)Fe\(_x\)(OH)\(_2\)(CO\(_3\))\(_{x/2}\) \( \cdot \) yH\(_2\)O at \( x \approx 0.33 \). Brindly and Kikkawa tried to ascribe this to the supercell structure of the Mg\(_{1-x}\)Fe\(_x\) layers, but could not explain the \( \sqrt{13} \times \sqrt{13} \) structure. Recently Solin and his co-workers found that there is a \( \sqrt{13} \times \sqrt{13} \) ordering of the carbonate ions in the Ni-Al LDH at \( x \approx 0.33 \). Accordingly the Mg\(_{1-x}\)Fe\(_x\) layers in Brindly’s work probably have nothing to do with the \( \sqrt{13} \times \sqrt{13} \) structure. Apart from that, their x-ray-diffraction measurements also indicate a \( \sqrt{3} \times \sqrt{3} \) honeycomb superlattice ordering of the Ni\(_{1-x}\)Al\(_x\) layers at \( x \approx 0.33 \). At some other concentrations they have been studying, no supercell structures have been detected yet.

VI. CONCLUSIONS

We have studied the various structures that can occur on the 2D discrete Coulomb alloy. This system is very unusual as the two ions have different charge states, which are compensated by other ions above and below the metal layers of interest. We have shown that at low concentrations, a Wigner lattice is formed which has triangular symmetry. This evolves continuously up to a concentration \( x \approx 0/3 \), when there is a phase transition to a structure with rectangular symmetry.

We have computed the diffraction patterns from these structures, and we show that the high-temperature magnetic susceptibility would be a good probe to discriminate these highly correlated structures from those found in random solid solutions, where the ions randomly occupy the sites of the underlying triangular lattice. This study originated from questions posed by the layered double hydroxides, but the questions that arise are general.

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APPENDIX: 2D EWALD’S METHOD

In our calculation of the Coulomb interaction energy for the 2D charge-neutralized alloy, we have used Evjen’s method with a finite-size cutoff.

We know for a 3D lattice, in Ewald’s method, the potential at a particular site is

\[
\varphi(i) = \frac{4\pi}{\Delta} \sum_G S(G) G^{-2} \exp(-G^2/4\eta) - 2\sum_l q_l (\eta/\pi)^{1/2} + \sum_G \frac{q_l}{r_l} F((\eta/2 \cdot r_l)) \tag{A1}
\]

The 2D Ewald’s potential is obtained by taking the limit in one direction of the 3D case. Assume the primitive vectors for a 3D lattice are

\[
\mathbf{a}_1 = a_1 \hat{x}, \quad \mathbf{a}_2 = a_2 \hat{y}, \quad \mathbf{a}_3 = a_3 \hat{z} \tag{A2}
\]

with \( \mathbf{a}_1 \) and \( \mathbf{a}_2 \) describing our 2D lattice. The reciprocal-lattice vectors are

\[
\mathbf{b}_1 = \frac{2\pi}{a_1} \hat{x}, \quad \mathbf{b}_2 = \frac{2\pi}{a_2} \hat{y}, \quad \mathbf{b}_3 = \frac{2\pi}{a_3} \hat{z} \tag{A3}
\]

Taking the limit \( a_3 \to \infty \), we conveniently retrieve the 2D lattice.

For the first part of Eq. (A1),

\[
G = n_1 \mathbf{b}_1 + n_2 \mathbf{b}_2 + n_3 \mathbf{b}_3 \tag{A4}
\]
\[ G^2 = n_1^2 b_1^2 + n_2^2 b_2^2 + n_3^2 b_3^2 = G_{xy}^2 + G_{z}^2, \] (A5)

\[ \Delta = a_1 a_2 a_3, \] (A6)

\[ S(G) = \sum_{i} q_i \exp(iG \cdot r_i), \] (A7)

and

\[ G_{xy} = n_1 b_1 + n_2 b_2. \] (A8)

Since all \( r_i \) in Eq. (A7) are in the \( x \)-\( y \) plane, we have

\[ S(G) = \sum_{i} q_i \exp(iG_{xy} \cdot r_i) = \sum_{i} q_i \cos(G_{xy} \cdot r_i) = S(G_{xy}). \] (A9)

In the limit of \( a_3 \to \infty \), i.e., \( b_3 \to 0 \), the summation over \( n_3 \) is reduced to an integral, i.e.,

\[ \sum_{G_{z}} - \sum_{G_{x}} \sum_{G_{y}} \sum_{G_{z}} = \sum_{G_{x}} \sum_{G_{y}} \sum_{G_{z}} \frac{a_3}{2\pi} \int_{-\infty}^{+\infty} dG_{z}. \] (A10)

After some elementary manipulations, we have

\[ \frac{4\pi}{\Delta} \sum_{G} S(G) G^{-2} \exp(-G^2/4\eta) = \frac{2\pi}{a_1 a_2 a_{xy}} \sum_{G_{xy}} S(G_{xy}) \frac{1}{G_{xy}} F \left( \frac{G_{xy}}{2\sqrt{\eta}} \right). \] (A11)

The definition of \( F(x) \) is given below.

In the second summation in Eq. (A1),

\[ F(x) = \frac{2}{\sqrt{\pi}} \int_{-\infty}^{\infty} e^{-x^2} ds, \] (A12)

\[ r_l = r_{n_1 n_2} + n_3 a_3, \] (A13)

where

\[ r_{n_1 n_2} = n_1 a_1 + n_2 a_2. \] (A15)

Because \( F(x) \) goes to zero very fast with the increase of \( x \), only the terms with small \( r_l \)'s will be important. Therefore, when \( a_3 \to \infty \), we may consider only the terms with \( n_3 = 0 \). So

\[ r_l = r_{n_1 n_2}. \] (A16)

Thus we are summing over only a 2D lattice.

The total Coulomb potential at a particular site for our 2D system is given by

\[ \varphi(i) = \frac{2\pi}{a_1 a_2 a_{xy}} \sum_{G_{xy}} S(G_{xy}) \frac{1}{G_{xy}} F \left( \frac{G_{xy}}{2\sqrt{\eta}} \right) - 2q_i (\eta/\pi)^{1/2} \]

\[ + \sum_{l} \frac{q_l}{r_l} F(\eta^{1/2} r_l). \] (A17)

Just as in the 3D case, both summations will converge. The value of the total potential \( \varphi \) is independent of the parameter \( \eta \), but the rapidity of convergence depends on the value chosen for this parameter. In practice, we choose the parameter \( \eta \) so that the computer time will be a minimum. It happens that for this particular system we are discussing in this paper, the choice of \( \eta \) which will minimize the computer time will make the contribution of the first summation so small that it can be simply neglected. Therefore in our calculation, we actually use the formula

\[ \varphi(i) = -2q_i (\eta/\pi)^{1/2} + \sum_{l} \frac{q_l}{r_l} F(\eta^{1/2} r_l), \] (A18)

with some appropriate choice of \( \eta \). This summation is a variant of Evjen’s method.

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