Two-Dimensional Ordering of Solute Nanoclusters at a Close-Packed Stacking Fault: Modeling and Experimental Analysis

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Predicting the equilibrium ordered structures at internal interfaces, especially in the case of nanometer-scale chemical heterogeneities, is an ongoing challenge in materials science. In this study, we established an ab-initio coarse-grained modeling technique for describing the phase-like behavior of a close-packed stacking-fault-type interface containing solute nanoclusters, which undergo a two-dimensional disorder-order transition, depending on the temperature and composition. Notably, this approach can predict the two-dimensional medium-range ordering in the nanocluster arrays realized in Mg-based alloys, in a manner consistent with scanning tunneling microscopy-based measurements. We predicted that the repulsively interacting solute-cluster system undergoes a continuous evolution into a highly ordered densely packed morphology while maintaining a high degree of six-fold orientational order, which is attributable mainly to an entropic effect. The uncovered interaction-dependent ordering properties may be useful for the design of nanostructured materials utilizing the self-organization of two-dimensional nanocluster arrays in the close-packed interfaces.

Structural transformations at interfaces are of fundamental interest as complex examples of phase transitions in low-dimensional systems (see, for example, Refs. 1–3). Recent works have shown that a variety of interfaces such as grain boundaries, heterophase boundaries, and surfaces can be considered as separate, quasi-two-dimensional “phases” that may undergo phase-like transitions in which their structural and chemical properties change abruptly at critical values of the thermodynamic parameters4–7. Such interfacial phases (termed “complexions”) are not intrinsically stable as stand-alone phases but are thermodynamically stabilized by the boundaries provided by the adjoining bulk regions. If a significant fraction of the interfaces in a material undergoes a transition, the cumulative effect can cause a dramatic change in the macroscopic properties of the material. However, the nature of the interfaces is highly complex, and it has been an ongoing challenge to link material performance to the internal interface structure and the related atomic migration mechanism.

Recently, two-dimensional crystalline materials have gained great significance in the design and study of structural and functional materials with novel properties that are absent in three-dimensional materials8. In particular, the self-assembly and organization of two-dimensional crystals from micro- and nanosized particles is being used to fabricate tailored materials with specific functionalities9–12. In multicomponent solids, various internal interfaces (e.g., grain boundaries, stacking faults, and twin boundaries) can serve as two-dimensional platforms for the segregation and self-assembly of solute clusters owing to the interaction, disposition, and ordering of the dissolved solute atoms. As a result, the structures of the solute-enriched interfaces go through two-dimensional transitions between thermodynamic states such that the interfacial energy is lowered. Such a nanometer-scale modulated template—atoms and/or nanoparticles of different elements confined in a two-dimensional geometry—promises a great diversity of anisotropic superlattices and phase behaviors. If the phase-like behaviors of interfaces with vastly different properties were to be clarified with respect to the chemical and heat-treatment conditions, it would allow for the control of material properties on a level not previously realizable8. A long-range goal in materials science is to develop quantitative and predictive “interface diagrams” as a new tool that aids the fabrication of materials by design14.
In this paper, we propose and demonstrate a coarse-grained (CG) modeling approach based on ab initio calculations for predicting the equilibrium superlattice structures of solute nanoclusters confined in an atomically close-packed stacking-fault (SF)-type interface. The approach exploits the intriguing solute-enriched layers observed in Mg–M–Y (M = Al or Zn) nanolamellar phases with a long-period stacking order (LPSO)\(^{15,16}\) as examples of multicomponent SF complexes. We investigate the energetic stability and two-dimensional ordering with varying packing density of \(L1_2\)-type core-shell-like \(M_6Y_8\) clusters (with diameters of 0.7–0.8 nm) in the SF, depending on the temperature and composition, by considering effective intercluster interactions derived from first-principles calculations based on the density functional theory (DFT). Further, we report nanometer-scale direct observations of solute nanoclusters of a Mg–Zn–Y LPSO phase using scanning tunneling microscopy (STM) to confirm the self-assembly and two-dimensional morphology of Zn–Y clusters along the SF interface in real space. Using the results of quantitative analyses of the STM images in combination with the ab initio CG Monte Carlo (CGMC) calculations, we characterize the positional and orientational orders of the solute clusters in two dimensions, in particular the transformation of the possible local ordering patterns of clusters, considering them analogous to two-dimensional colloidal hard-sphere systems\(^{17–19}\).

**SF interfaces in Mg-based nanolamellar LPSO phases**

Understanding the behavior of multicomponent SF complexes is of importance for designing metal-based nanolamellar phases, especially those of the \(h_{m}c_{n}h_{k}\) type (here, \(h\) and \(c\) represent hexagonal and cubic close-packed motifs, respectively; \(m\), \(n\), and \(k\) are integers), which are emerging as a new category of nanostructured materials with unique structural and mechanical properties (see, for example, Refs. 20–22). In particular, it is worth emphasizing that Mg-based nanolamellar phases with a LPSO structure (hereafter simply called “LPSO phases”) formed in ternary Mg–M–RE (rare earth) alloys have recently attracted significant attention owing to their use in the strengthening of Mg alloys and as promising components for designing advanced lightweight structural materials\(^{15,16,23}\). In such phases, the two-dimensional SF-type interfaces containing solute atoms can play a significant role in the formation of a nanostructured state with low-energy boundaries. As a result, the phases are allowed to contain a high density of SFs and exhibit continuously regular nanolamellar structures formed by SF boundaries, which are an inherent part of their crystal lattice.

Recent advances in the analytical techniques such as diffraction, scattering, spectroscopy, microscopy, and imaging have improved our fundamental understanding of the characteristics of ordered arrangements of solute atoms at the internal SF interfaces in ternary Mg–M–RE LPSO alloys\(^{24–27}\). Yokobayashi et al.\(^{24}\) found that an annealed Mg–Al–Gd ternary alloy exhibited a characteristic solute ordering in the \(18R\)-type (i.e., \(h_{hc}ch\); rhombohedral stacking, where the vertical bar indicates the position of the SF boundary) LPSO phases. In these phases, there exists a six-fold in-plane ordering of the local \(L1_2\)-type \(Al_6Gd_8\) clusters at an intercluster distance of \(2\sqrt{3}a_{Mg} (=1.1 \text{ nm})\) in the \(hcch\)-type close-packed atomic layers containing \(I_2\)-type SF (as shown in Fig. 1), where \(a_{Mg}\) is the unit-cell length along the \(a\) axis of hexagonal close-packed (hcp) Mg (\(\approx 0.32\) nm). It was suggested that a local \(L1_2\)-type short-range order, expressed in terms of similar \(Zn_6Y_8\) clusters, is also formed in the Mg–Zn–Y system\(^{24,25}\). Indeed, it was recently reported that a highly ordered Mg–Zn–Y LPSO structure of the \(10H\)-type (i.e., \(h_{hc}ch\); hexagonal stacking) is formed in well-annealed Mg\(_{75}Zn_{10}Y_{15}\) (at.%.) alloys, with an analogous six-fold alignment of the \(Zn_6Y_8\) clusters noticed along the SF in a periodic manner\(^{27}\). However, many of the Mg–Zn–Y LPSO alloys with a lower Zn/Y concentration found so far do not necessarily exhibit such a clear in-plane ordering in electron micrographs\(^{24,25}\), and their detailed structures at equilibrium remain to be identified. Not only for scientific interests but also for materials...
design, the inherent natures of heterogeneities and medium-range orders in two-dimensional solute-cluster packing should be elucidated, as this will allow the effective synthesis of versatile Mg–M–RE LPSO structures. This is because solute nanoclusters concurrently having good “stability” and “dispersibility” along the SF will effectively decrease the SF energy with small amounts of M/RE elements and robustly stabilize the nanomellar structure with a high density of SFs. This, in turn, will affect the overall mechanical properties, thermostability, and chemical resistance of the materials.

Results

Coarse-grained Monte Carlo modeling. The strong binding of M/RE atoms to SFs and of M–RE and RE–RE pairs is the major driving force for the formation of the MgRE₆₈-type nanoclusters in the SF interface in Mg–M–RE LPSO structures. The binding of solute atoms to SFs, which arises from the difference between the dissolution energies of the solute atom in the hcp layer and in the faulted layer, contributes to the segregation of the solute atoms from the surrounding matrix to the SF interfaces. Further, the attractive interaction of the first nearest-neighbor M–RE and the second nearest-neighbor RE–RE pairs in the close-packed SF interface enhances the formation of the nanosized clusters with an L1₂-type short-range order.

We had previously pointed out that, on the basis of DFT analyses, the in-plane interaction between L1₂-type solute clusters in Mg–M–RE LPSO structures could be considered “repulsive”, depending on the element present within the clusters. The DFT results indicated that the significant displacements of RE atoms were induced by the off-lattice relaxation of the L1₂-type MgRE₆₈ clusters, especially in the Zn–Y cluster systems, and could be attributed to the transition from a cross-linked (attractive) to unlinked (repulsive) nature of the clusters owing to the change in the electronic structure. Here, we evaluated the pair-wise intercluster interaction energies, which effectively include both chemical and strain-induced contributions, for the Al₆Y₈ and Zn₆Y₈ clusters in the SF interface on the basis of DFT calculations (details in the Methods section); these are listed in Table 1. Table 1 shows clearly that the intercluster interaction was purely repulsive between the Zn₆Y₈ clusters over the range of distances studied (from 0.942 nm to 0.314 nm) but distinctly attractive between the Al₆Y₈ ones at d = 2.029 nm, which corresponds to the intercluster separation in the ideal model with a complete solute ordering. The sign of the interaction energy at d = 2.029 nm was opposite with respect to the ideal model with a complete solute ordering. This indicates that the Al₆Y₈ clusters tend to gather near each other even at low cluster densities, owing to the binding between the clusters at d = 2.029 nm, which corresponds to the preferred intercluster distance of 2.65 nm, and decreases dramatically as the density increases for the Zn₆Y₈ clusters.

In the Al–Y cluster system, peak 1 is completely dominant and little affected by the change in the cluster density, whereas peak 2 is observed only at 700 K and low ρclst. This indicates that the Al₆Y₈ clusters tend to gather near each other even at low cluster densities, owing to the binding between the clusters at d = 2.029 nm, which corresponds to the preferred intercluster distance of 2.65 nm, and decreases dramatically as the density increases for the Zn₆Y₈ clusters.

Conversely, in the case of the Zn–Y cluster system, a clear trade-off relationship exists between the relative heights of the two peaks in the RDFs; peak 2 steadily emerges at low ρclst, along with peak 1. This indicates that the Al₆Y₈ clusters tend to gather near each other even at low cluster densities, owing to the binding between the clusters at d = 2.029 nm, which corresponds to the preferred intercluster distance of 2.65 nm, and decreases dramatically as the density increases for the Zn₆Y₈ clusters.

Table 1 | Pair-wise intercluster interaction energy for the Al₆Y₈ and Zn₆Y₈ clusters in the stacking-fault interface. A positive energy corresponds to a repulsive interaction. The intercluster distance d is defined as the distance between the clusters that occupy the 4th nearest neighbor (NN) sites on the triangular lattice with a spacing of aMg

| Site (NN) | d [aMg] | E[d=2.029 nm] [eV] | Intercluster geometry |
|----------|---------|---------------------|----------------------|
| 0        | 0       | 10.255              | Overlapped            |
| 1        | 1       | 10.255              | Overlapped            |
| 2        | 1.73    | 10.255              | Overlapped            |
| 3        | 2       | 10.255              | Overlapped            |
| 4        | 2.65    | 10.255              | Overlapped            |
| 5        | 3       | 10.255              | Overlapped            |
| 6        | 3.46    | 10.255              | Overlapped            |
| 7        | 3.61    | 10.255              | Overlapped            |
| 8        | 4       | 10.255              | Overlapped            |
it is interesting to see that the Zn₆Y₈ clusters are positionally less ordered and rather homogeneously dispersed at low ρ_{clus}, owing to their repulsive interactions; instead, they maintain a high degree of six-fold orientational order (a so-called “hexatic” order⁷⁻¹⁹) over a wide density range. These indicate that the Zn₆Y₈ clusters are arranged in mainly two kinds of six-fold domain structures with

Figure 2 | In-plane radial distribution functions (RDFs) of the intercluster distance for (a) Al₆Y₈ and (b) Zn₆Y₈ cluster systems with various cluster densities, as determined from CGMC simulations. The open bars and dashed lines represent the original RDFs and those smoothened by Bézier curves as visual guides, respectively.
we had previously reported that two-dimensional spatially inhomogeneous electronic systems as well as images spatially
on the triangular lattice were imaged and identified using STM. In addition, the structures at the domain boundaries of the clusters typically range from several nanometers to a few tens of nanometers.

The experimental values obtained from the individual STM images (18R1, 18R2, and 18R3) and an ideal model (from Ref. 27) for the 

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Figure 4 | Ensemble-averaged global orientational order parameter of the Al$_x$Y$_8$ and Zn$_x$Y$_8$ cluster systems (squares) as a function of the cluster density. The experimental values obtained from the individual STM images (18R1, 18R2, and 18R3) and an ideal model (from Ref. 27) for the Mg–Zn–Y LPSO phase are also plotted for comparison (solid circles).
Figure 5 | STM results of the cluster arrangements in the 18R-type LPSO phase inside a Mg_{85}Zn_{6}Y_{9} (at.%) alloy. (a–c) STM images of the cleaved surface of the LPSO phase obtained by applying a positive bias voltage on the sample. Three kinds of cluster arrangements were noticed in the STM images (18R1, 18R2, and 18R3), and their cluster densities were measured to be (a) 0.69–0.72 nm$^{-2}$, (b) 0.62–0.65 nm$^{-2}$, and (c) 0.57–0.60 nm$^{-2}$, respectively. The tunneling parameters are: (a) $V_{t} = 0.7$ V, $I_{t} = 1.5$ nA; (b, c) $V_{t} = 0.8$ V, $I_{t} = 1.0$ nA. (d–f) cluster arrangements extracted from the STM images (color-coded by the $\psi_j$ value) and their local orientational order parameter fields represented by the vectors (Re($\psi_j$), Im($\psi_j$)). The clusters in the edge region (dark-blue circles) are treated as boundaries and excluded from the calculation of the averages.
that each cluster maintained a high $|\psi_j|$ value and that the OOP vectors ($\text{Re}(\psi_j), \text{Im}(\psi_j)$) were loosely aligned with those of the neighbors in nearly the same direction; consequently, the OOPs appear to be correlated in almost all the fields comprising several hundreds of clusters. It is interesting to note that the orientational orders in the cluster arrangements are quasi-long range whereas their positional orders remain short range, as in the intermediate hexatic phase of colloidal hard-sphere systems\textsuperscript{17–19}.

Discussion

It is notable that the employed CG model, which was based on DFT calculations, for the Zn–Y cluster system provided results that were in good agreement with the results of the STM analyses. This implies that the intercluster interaction evaluated here could correctly extract the essential features of the in-plane ordering of the solute nanoclusters with a “hard-sphere-like” character in the Mg matrix. In particular, the CGMC simulations at 700 K were able to reproduce not only the overall variation in the relative heights of the two characteristic peaks in the RDFs (Fig. 6) but also the global six-fold OOPs (Fig. 4) seen in the STM results at the experimental cluster densitites. This fact suggests the possibility that, owing to the rapid quenching of the specimen in air from the solidification temperature, the cluster morphology formed at a high temperature was kinetically frozen and its original shape was retained throughout the experiment. Our findings indicate that the increase in the volume fraction of the solute clusters results in a continuous transformation with an increase in the haxatic order in a push-and-shove manner, which can explain the steady reduction of the radial correlation length between the clusters with maintaining a six-fold pattern that was observed in synchrotron radiation small-angle X-ray scattering measurements for Mg\textsubscript{85}Zn\textsubscript{6}Y\textsubscript{9} (at.%) LPSO alloys during the annealing at high temperatures\textsuperscript{20,21}.

Note that such predicted ordering patterns of the Zn–Y clusters in Figs. 2(b) and 3(b) have a mainly entropic origin; there are no significant attractive interactions among the clusters. Generally, haxatic ordering occurs in a two-dimensional hard-sphere system because the loss of the configurational (orientational) entropy of the particles in a dense packing is overcompensated by the high translational (positional) entropy of the particles\textsuperscript{17}. In this sense, the ordering behavior of the attractive Al–Y clusters is dominated by the chemical trapping of clusters by the neighboring bonds, whereas that of the repulsive Zn–Y clusters is dominated by the topological trapping of clusters by each other in cages. Such an ordering mechanism of the cluster arrangements resulting from the entropic effect can be expected to be robust and flexible enough to allow fluctuations in the composition and stoichiometry for the multicomponent interfaces formed in Mg–M–RE nanolamellar phases.

In this study, the experimental analysis on the spatially ordered patterns of the clusters was based on the premise that the dark contrast spots observed in the STM images corresponded to the Zn–Y nanoclusters of the L\textsubscript{12}-type and its derivatives. It was most probable that an accumulation of electrons around the clusters, which was caused by the strong chemical bonds formed inside the cluster by the Zn–Y atoms with relatively large atomic number, contributed to the origin of the contrast in the STM images. Also, the size, density, and geometric patterns of dark contrast spots were consistent with those in the solute-cluster superlattices observed in other experimental studies\textsuperscript{24–27,31}. Nevertheless, the careful investigation of the electronic structure, in particular the local density of states close to the Fermi level, is preferably required to clarify the contrast mechanism and to identify chemical species in the STM images of the specimen. Such an analysis will be the subject of the future work.

In summary, the computational approach employed in this study could successfully predict the nature of two-dimensionally ordered arrangements of Zn–Y nanoclusters in a Mg-based nanolamellar phase, in a manner consistent with STM observations performed in real space. This combined computational-experimental analysis provides clear insights into the phase-like behavior of a close-packed SF interface showing a disorder-order transition in a solute-cluster superlattice. In addition, the controversial issue of the composition dependence of in-plane orderings in the Mg–M–Y LPSO phases was resolved by examining the characteristics of the ordering behavior of attractively or repulsively interacting nanoclusters in the SF interface. We predicted that, as the number of clusters per SF interface is increased (owing to solute segregation and clustering at high temperatures), the system undergoes a continuous evolution into a highly ordered densely packed one while maintaining a high degree of six-fold orientational order, which is attributable mainly to an entropic effect. This approach should help engineer nanometer-scale chemical modulation and ordering in metal-based nanolamellar systems\textsuperscript{20–22}.

Methods

**Ab initio intercluster interaction.** The energetics and equilibrium structure of the Mg-based LPSO phases containing L\textsubscript{12}-type M\textsubscript{1}M\textsubscript{3}Y\textsubscript{2} (M = Al or Zn) clusters were obtained from DFT calculations with the projector-augmented-wave method\textsuperscript{28,29} using the Vienna Ab initio Simulation Package (VASP)\textsuperscript{30}. We applied the generalized gradient approximation of the Perdew–Wang\textsuperscript{31} form for the exchange-correlation functional in DFT. The 18R-type LPSO structures with various intercluster distances (d) were modeled using 84- to 192-atom triclinic (or monoclinic) cells with lattice constants of a = d and b = c = \sqrt{3}d (or vice versa) containing an 18-layer intrinsic SF and Mg\textsubscript{16}Y\textsubscript{8} cluster(s) at the middle of their unit cells (see Supplementary Fig. S1 online), which are formed with only a single six-layer structural block—i.e., through hhcchh stacking—by choosing its stacking vector to be the c axis of the triclinic (or monoclinic) cell. Note that the 144-atom cell (i.e., Mg\textsubscript{16}M\textsubscript{1}M\textsubscript{3}Y\textsubscript{16} crystal) corresponds to an ideal model with a complete solute ordering at d = \sqrt{3}a\textsubscript{ab}, that stems from the 1M polytype (space group of C\textsubscript{2/m}m\textsubscript{1}) for the 18R-type Mg–M–Y order-disorder structures. Calculations to determine the formation energies and the intercluster interaction were performed using these unit cells of the Mg–M–Y system, with a plane-wave energy cutoff of 345.3 eV using a Monkhorst-Pack\textsuperscript{32} k-point mesh for integration over the Brillouin zone and a Methfessel–Paxton smearing method\textsuperscript{33} with a width of 0.2 eV, while using the tetrahedron method with a Blochl correction\textsuperscript{34} to determine the total energies. Structural relaxations were performed until the forces on each atom were less than 3 meV/Å.

The formation energies (E\textsubscript{f}) of the Mg–M–Y LPSO structures are defined as follows:

$$E_{\text{f}}(\text{Mg}_n\text{M}_m\text{Y}_n) = E_{\text{tot}}(\text{Mg}_n\text{M}_m\text{Y}_n) - n\Delta E_{\text{f}}(\text{Mg})$$

where $E_{\text{tot}}$ represents the DFT-calculated total energies of the cells, $\Delta E_{\text{f}}(\text{Mg})$ and $\Delta E_{\text{f}}(\text{M})$ refer to the numbers of Mg, M, and Y atoms in each unit cell, and $N$ is the total number of atoms in the cell so that $N = n\text{Mg} + m\text{M} + n\text{Y}$. Note that $E_{\text{tot}}$ is with respect to the reference energy $E_{\text{ref}}$ of pure Mg, Mg, and Y in its equilibrium structure (hcp for Mg, Zn, and Y and face-centered cubic for Al). Supplementary Table S1 lists the $E_{\text{f}}$ values and lattice parameters of 18R-type Mg–M–Y LPSO structures with various intercluster distances obtained from the DFT calculations.
We defined the pair-interaction energies between the MgY clusters of L2₁ type as follows:

\[ E^{\text{pair}}(d) = \frac{1}{n^{\text{pair}}(\text{NB})} \sum_{\text{NB}} \delta^{\text{pair}}(d) \times \left( E^{\text{HB}} + E^{\text{IC}1} - 2E^{\text{IC}2} \right), \]  

where \( d \) is the intercluster distance ranging from \( \sqrt{3}a_{\text{Mg}} \) to \( 4a_{\text{Mg}} \) in the I_{3} SF lattice. \( E^{\text{HB}} \) represents the total energy for the 18R-type lattice structure, with the letters A, B, and C representing the composition of the unit cell containing the same number of atoms, i.e., A = Mg_{18}N_{60}, B = Mg_{18}N_{60}, and C = Mg_{18}N_{60}, respectively. These correspond to the 13824-atom system of the 18R-type lattice structure. The value of \( |\psi| = |\psi_1| = \text{constant} \) and \( |\psi_2| = \text{constant} \) is the angle between the shortest periodic vector equivalent to \( x_1 - x_2 \) and an arbitrary but fixed reference vector. The value of \( \langle \psi | \hat{\sigma}_z | \psi \rangle \) is equal to one if all the clusters sit on a perfect crystalline lattice, whereas it becomes nearly zero if the structure is disordered. \( \phi_j \) can be represented as a vector (\( \text{Re}(\psi_j), \text{Im}(\psi_j) \)) and rotates by \( 2\pi \) as the lattice is rotated by an angle of \( \pi/3 \) without changing the reference vector.

Coarse-grained Monte Carlo modeling. In this study, the MgY clusters were modeled as single CG particles with a chosen core radius to prevent them from coalescing with the other clusters. The CG particles interact with each other through the pair potential, which consists of a short-range soft-core repulsion—modeled as an artificial energy barrier up to a few \( \text{eV} \) within a core radius of \( 2a_{\text{Mg}} \), corresponding to the third nearest-neighbor distance in the triangular lattice with a spacing of \( 3a_{\text{Mg}} \)—and a longer-range intercluster energy evaluated from the DFT calculations, as listed in Table 1. Consequently, the CG particles can be prevented from overlapping and coalescing with each other, while being kept at an excluded distance of \( 2a_{\text{Mg}} \) in the configurations equilibrated at the target temperatures.

For the equilibrium simulations of the CG cluster model, \( 48a_{\text{Mg}} \times 24a_{\text{Mg}} \) (i.e., \( 15.34 \text{ nm} \times 13.29 \text{ nm} \)) two-dimensional triangular lattices containing 2304 lattice sites were used. These correspond to the 13824-atom system of the 18R-type LPSO structure (here assumed to comprise a single six-layer structural block) based on the all-atom representation. As an initial configuration, CG particles expressing Mg, Y, or MgY clusters were randomly distributed on the sites of a triangular lattice \( \sqrt{3}a_{\text{Mg}} \times a_{\text{Mg}} \), with a composition of Mg–2.8 at.\%M–3.7 at.\%Y (i.e., 64 clusters) to Mg–8.3 at.\%M–11.1 at.\%Y (i.e., 192 clusters) with a M/Y ratio of 3/2, where \( 1 \) is the number of intercluster pairs (per cluster) in the unit cell and \( n^{\text{NB}} \) is the number of clusters in the unit cell, so that \( n^{\text{NB}} = 8, n^{\text{NB}} = 2, n^{\text{NB}} = 1, \) and \( n^{\text{NB}} = 1 \). Here, we suppose that the contribution of each intercluster pair (at the same \( d \)) to the interaction energy is equivalent to that of the others. The bracket in equation (2) represents a part of the interaction energy between clusters, which is extracted in a pair-wise fashion from the cluster arrangements with different coordination numbers (see Supplementary Fig. S2 online). This value is divided by the net number of intercluster pairs to obtain the contribution of a single pair interaction \( E^{\text{pair}} \). Table 1 lists the \( E^{\text{pair}} \) values obtained from the DFT calculations. Note that a negative value of \( E^{\text{pair}} \) corresponds to an attractive interaction under this definition.

Orientational order parameter. As in a two-dimensional hard-sphere system, the global orientational order parameter \( \psi \) of the CG cluster system is given by

\[ \psi = \frac{1}{N} \sum_{j=1}^{N} \psi_j, \]  

which is the spatial average of the local orientational order parameter \( \psi_j \). where \( i = \sqrt{-1} \). The sum is over the six closest neighbors \( k \) of the cluster \( j \) and \( \phi_j \) is the angle between the shortest periodic vector equivalent to \( x_1 - x_2 \) and an arbitrary but fixed reference vector. The value of \( |\psi| = |\psi_1| = \text{constant} \) and \( |\psi_2| = \text{constant} \) is the angle between the shortest periodic vector equivalent to \( x_1 - x_2 \) and an arbitrary but fixed reference vector. The value of \( \langle \psi | \hat{\sigma}_z | \psi \rangle \) is equal to one if all the clusters sit on a perfect crystalline lattice, whereas it becomes nearly zero if the structure is disordered. \( \phi_j \) can be represented as a vector (\( \text{Re}(\psi_j), \text{Im}(\psi_j) \)) and rotates by \( 2\pi \) as the lattice is rotated by an angle of \( \pi/3 \) without changing the reference vector.
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Author contributions

H.K. and S.K. designed the study and drafted the manuscript. H.K. carried out the numerical simulations and analyzed the data. S.K. and A.Y. carried out the experiments and analyzed the data. A.S. and S.O. supervised the work and provided critical feedback on the manuscript. All authors contributed to discussion of the results.

Additional information

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Corrigendum: Two-Dimensional Ordering of Solute Nanoclusters at a Close-Packed Stacking Fault: Modeling and Experimental Analysis

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This Article contains an error in the calculation of the orientational order parameters (OOPs). The OOPs were overestimated, particularly at low cluster densities, due to an erroneous procedure for the summation of components with different signs. The correct Figures 3–5 appear below as Figure 1, Figure 2 and Figure 3 respectively.

There is also a typographical error in the Results section under subheading ‘Coarse-grained Monte Carlo modeling’.

“This fact is also confirmed by the behavior of the |Ψ₆| value for the Zn–Y clusters equilibrated at 300 K, which shows a clear two-step increase with an increase in the cluster density and remains constant at approximately 0.87–0.90 in the intermediate range of ρclst from 0.628 to 0.863 nm⁻², as shown in Fig. 4.”

should read:

“This fact is also confirmed by the behavior of the |Ψ₆| value for the Zn–Y clusters equilibrated at 300 K, which shows a clear two-step increase with an increase in the cluster density and remains constant at approximately 0.73–0.89 in the intermediate range of ρclst from 0.628 to 0.863 nm⁻², as shown in Fig. 4.”
Figure 1.

Figure 2.
Figure 3.