Time-Evolution of $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle^*$ Special Point Ordering in *fcc*-Based Binary Alloys Studied by Monte Carlo Simulation

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The Monte Carlo method of simulation was employed in the study of time-evolution of atomic long-range ordering with $k^* = \frac{1}{2} \frac{1}{2} \frac{1}{2}$ in an *fcc* Ising-model system with first- and second-neighbor pairwise interactions $V(1)$ and $V(2)$. The results should refer to the ordering behavior of carbon atoms and vacancies in metalloid-deficient transition-metal monocarbides, such as TiC_{1-x} and NbC_{1-x} . Fourier power spectra of the obtained atom-configuration involve diffuse streaks in the early stage of the ordering process, and then exhibit sharp spots at $k^* = \frac{1}{2} \frac{1}{2} \frac{1}{2}$ and its equivalent positions in the late stage. When $V(1)$ has a tendency to create unlike-atom pairs in a similar way to $V(2)$, the spectra in the early stage resemble diffraction patterns of TiC_{1-x} and NbC_{1-x} with short-range order. Warren-Cowley parameters α 's for atomic pair-correlations increase monotonically with time in even-order coordination shells, suggesting continuous evolution of the $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ -type ordering. In contrast, the values of α for odd-order coordination shells first get enhanced with time and then decrease after reaching a peak. The behavior of odd-order α 's is explained in terms of the destructive interference (or frustration) between interactions $V(1)$ and $V(2)$. Two different ordered structures of CuPt ($R\bar{3}m$) and cubic ($Fd\bar{3}m$) types, which are degenerate in the internal energy, simultaneously appear and their ordered domains grow with time.

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I. Introduction

Transition-metal monocarbides MC_{1-x} with the NaCl-type cubic structure have been drawing much interest for their potentials in high-temperature structural materials, because of their favorable mechanical properties at elevated temperatures and light specific gravity. The compounds MC_{1-x} are obtained in a wide range of carbon composition; *e.g.*, TiC_{1-x} extends from $x=0.03$ to 0.5. The deviation of composition from stoichiometry MC when $x>0$ introduces vacancies into the octahedral sites for carbon atoms⁽¹⁾. It is well known that the carbon atoms and the structural vacancies on the octahedral sites undergo short-range or long-range ordering in a wide variety of MC_{1-x} compounds⁽²⁾⁻⁽⁴⁾. For example, TiC_{1-x} with $x>0.3$ gives rise to superlattice reflections due to long-range ordering (LRO) at $k^* = \frac{1}{2} \frac{1}{2} \frac{1}{2}$ and its equivalent positions in diffraction patterns of X-rays⁽⁵⁾, electrons⁽⁶⁾⁻⁽⁹⁾ or neutrons⁽¹⁰⁾⁻⁽¹³⁾, when annealed at a temperature below about 1100 K. At higher temperatures or higher carbon contents, diffuse streaks due to short-range ordering (SRO) appear in the diffraction patterns. Figure 1 shows an example of the change of electron diffraction pattern with evolution of ordering in $\text{TiC}_{0.59}$ ⁽⁹⁾. Besides TiC_{1-x} , VC_{1-x} and NbC_{1-x} also exhibit similar diffuse streaks or

superlattice reflections⁽⁷⁾⁽¹¹⁾⁽¹⁴⁾. It has been revealed that the mechanical properties of MC_{1-x} depend on the state of order⁽⁸⁾⁽⁹⁾.

Since the octahedral sites in the NaCl-type structure form an *fcc* sublattice, as shown in Fig. 2(a), the rearrangement of carbon atoms and vacancies on the sublattice in MC_{1-x} can be regarded as an analogy with the ordering phenomena encountered in *fcc*-based substitutional solid solutions A_{1-x}B_x ⁽¹⁵⁾. Namely, A and B correspond to the carbon atoms and vacancies, respectively. There exist two candidates for the *fcc*-base ordered structure causing $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ superlattice reflections⁽¹⁶⁾: trigonal $R\bar{3}m$ (CuPt)-type and cubic $Fd\bar{3}m$ -type, which are illustrated in Fig. 2(b) and (c), respectively. Their stoichiometric composition is $\text{A}_{0.5}\text{B}_{0.5}$ (or $\text{MC}_{0.5}$). The former type has a layered structure with alternate stacking of A and B planes along one of the four $\langle 111 \rangle$ directions, while the latter has alternate A_3B and AB_3 planes along the four $\langle 111 \rangle$ directions. The two forms of ordered structure are identical to each other in pair correlations of A and B elements up to infinity. It follows that they are degenerate in the internal energy if it is given as a function of atomic pairwise interactions of A and B within a rigid *fcc* lattice⁽¹⁶⁾. In the framework of pairwise interactions of atoms with their first and second nearest neighbors, these two structures appear in an equiatomic alloy $\text{A}_{0.5}\text{B}_{0.5}$ as the ground state when

$$V(2) < 0, \quad \text{and} \quad -1 < \rho < 2, \quad (1)$$

as shown in the Clapp-Moss diagram⁽¹⁷⁾ given in Fig. 3.

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Fig. 1 Electron diffraction patterns of $\text{TiC}_{0.59}$ in various states of order at 1320 K (a), 1270 K (b) and room temperature (c). The degree of order is evolved from (a) to (c). The left column gives $(1\bar{1}0)^*$ patterns, and the right is of $(001)^*$. Please note that $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ superlattice reflections are slightly elongated almost perpendicular to the scattering vector in the $(1\bar{1}0)^*$ pattern of (b). Double reflections of $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ causes additional spots at 001 and its equivalent positions in the $(1\bar{1}0)^*$ pattern of (c). (Courtesy of Dr. S. Tsurekawa and Prof. H. Yoshinaga).

Here, the parameters $V(n)$ s for the n -th coordination shells are defined in the usual way as

$$V(n) = E_{AB}(n) - \frac{E_{AA}(n) + E_{BB}(n)}{2}, \quad (2)$$

with the interaction energy between i and j atoms of $E_{ij}(n)$, and ρ is the ratio of $V(1)/V(2)$. The system prefers unlike A-B atom pairs of n -th nearest neighbors (n NN) if $V(n)$ is negative, and like-atom pairs of A-A and B-B if it is positive.

It has been unclear as yet which of the $R\bar{3}m$ and the $Fd\bar{3}m$ types is the stable ordered structure in TiC_{1-x} and related compounds, even though the controversy has

been going on for many years⁽³⁾⁽⁴⁾⁽¹²⁾. Tsurekawa *et al.*⁽⁸⁾⁽¹⁸⁾ have recently identified $R\bar{3}m$ -type ordered domains in $\text{TiC}_{0.59}$ by high resolution transmission electron microscopy (HRTEM) and micro-beam electron diffraction. Lorenzelli *et al.*⁽⁵⁾ reported that X-ray diffraction of ordered $\text{TiC}_{0.625}$ involves $\{420\}$ fundamental peaks split by a trigonal lattice distortion as small as 0.26° . The above two experimental results clearly support development of the $R\bar{3}m$ -type structure in TiC_{1-x} , but they cannot rule out the possibility of the alternative structure of $Fd\bar{3}m$. A subsidiary peak is faintly noticed between the pair of split $\{420\}$ reflections for the trigonal phase in Fig. 1(c) of Ref. (5). This suggests that a cubic phase

Fig. 2 Fundamental rock-salt structure (a) and two possible ordered structures of CuPt (b) and cubic types (c). In (a) open circles indicate transition-metal atoms, and shaded ones octahedral sites for carbon atoms. In (b) and (c) only an *fcc* sublattice of the octahedral sites is drawn, where closed and open circles refer to carbon atoms (A) and vacancies (B).

Fig. 3 Clapp-Moss diagram for the ground states in an *fcc* base $A_{0.5}B_{0.5}$ equiatomic alloy as a function of the ratio of $V(1)/V(2) [= \rho]$. The indices indicate the special points k^* , at which the internal energy takes minima when it is given as a function of wave number of concentration modulation. The shaded area is of interest in the present study. The ratios for the five cases considered here are shown by arrows.

should coexist with the $R\bar{3}m$ -type structure. Landesman *et al.*⁽¹⁹⁾ calculated electronic structures in various carbides. According to their theoretical calculations, $V(2)$ is the predominant interaction in the ordering, and many-body interactions⁽²⁰⁾ are too weak to resolve the degeneracy of $R\bar{3}m$ and $Fd3m$ structures. The difference in the internal energy between the two structures has been estimated to be less than 5 meV⁽⁴⁾.

So far, the theoretical arguments on the stability of $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle^*$ special point ordering in MC_{1-x} compounds have been mostly limited to their ground states at abso-

lute zero temperature and have not been extended to kinetics of time-evolution of the ordering at a finite temperature. The calculation by Landesman *et al.* mentioned above suggests that the pair-approximation would be valid for the atomic interactions in TiC_{1-x} and its relatives, and the ordering phenomena may be described well by an *fcc* Ising model with pairwise interactions. These features of MC_{1-x} compounds strongly motivate us to carry out a simulation of $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle^*$ special point ordering due to pairwise interactions in an *fcc* Ising model. The nature of an Ising system with multiple-degenerate ground states is also full of interest from the point of view of statistical mechanics.

The aim of the present study is to understand kinetic behavior of $\langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle^*$ special point ordering in a simple Ising model for an *fcc*-based alloy of $A_{0.5}B_{0.5}$ with pairwise interactions $V(1)$ and $V(2)$ by the Monte-Carlo method. Our interest is focused mainly on how long-range order develops from a disordered state in a system with multiple-degenerate ground states, and whether or not the configurational entropy at a finite temperature may dissolve the degeneracy between the $R\bar{3}m$ and the $Fd3m$ structures. The Monte-Carlo method of simulation is well fit to this purpose, because of no need to assume the final stable structure.

II. Model and Simulation

We consider a system of $32 \times 32 \times 32$ *fcc* unit cells (131,072 lattice sites) with periodic boundary conditions. Half of the sites are occupied by A atoms, and the rest by B atoms. The configurational energy of the $A_{0.5}B_{0.5}$ system is given by

$$E = -V(1) \sum_{\langle 1NN \rangle} \sigma_i \sigma_j - V(2) \sum_{\langle 2NN \rangle} \sigma_i \sigma_j, \quad (3)$$

with the site-occupation operator defined by $\sigma_A = +1$ and $\sigma_B = -1$, and $\langle 1NN \rangle$ and $\langle 2NN \rangle$ denoting summation over nearest and next-nearest neighbor pairs of i - j , respectively. Nearest-neighboring atoms are directly exchanged with each other in the scheme of Kawasaki spin-flip dynamics⁽²¹⁾. The exchanging probability for a pair of 1NN is assumed to be

$$W(\Delta E, T) = \frac{1}{2} \left[1 - \tanh \left(\frac{\Delta E}{2k_B T} \right) \right], \quad (4)$$

where ΔE is the energy gain caused by the exchange, and k_B and T have their usual meanings. In the present study, we assumed five cases of $V(1)$ and $V(2)$, as listed in Table 1 (see also Fig. 3). Here, T_c stands for the critical temperature of order-disorder transition, which was estimated from the equilibrium states obtained by Phani *et al.*⁽²²⁾ The temperature T was set to $T_c/3$ in every case.

The Monte Carlo simulation and the following data processing were done in FACOM VP-2600 and M-1800 installed at the computer center of Kyushu University. In the simulation, equal numbers of A and B atoms were at first distributed randomly on the lattice sites, and then the atoms were exchanged with each other, according to

Table 1 Pairwise interactions used in the simulation (in unit of $[k_B T_C]$).

	(i)	(ii)	(iii)	(iv)	(v)
$V(1)/k_B T_C$	-0.270	-0.117	0	0.033	0.184
$V(2)/k_B T_C$	-0.270	-0.234	-0.222	-0.203	-0.335
$V(1)/V(2) [= \rho]$	1.0	0.5	0	-0.163	-0.55

a vectorizable Monte Carlo algorithm for the model mentioned above. This algorithm is based on a generalized checkerboard principle⁽²³⁾, in which the lattice of $32 \times 32 \times 32 \times 4$ sites is divided into $256(4 \times 4 \times 4 \times 4)$ interpenetrating simple-cubic sublattices, whose lattice dimension is 4 times that of the *fcc* unit cell. A pair of nearest-neighbor sublattices are chosen at random, and then 512($8 \times 8 \times 8$) pairs of 1NN atoms on the sublattices attempt to exchange through comparison of the values of eq. (4) with 512 shuffled random numbers $R \in [0, 1]$, in one cycle of a vectorized “DO” loop. Here, the atom pairs with $W > R$ are permitted to exchange. The atom configurations after appropriate times of the vectorized attempts to exchange are stored. Each 1536(256×6) cycles of the attempts corresponds to one Monte Carlo step (MCS), which is equivalent to one attempt per 1NN pair. We have confirmed that no considerable discrepancies arise between the results obtained by the vectorized algorithm and by a conventional scalar-type one, in which one atom pair of 1NN attempts to exchange at a time.

III. Results and Discussion

1. Fourier power spectra

First, we present the Fourier power spectra of atomic configuration obtained by the simulation, in order to compare the results with the electron diffraction patterns of TiC_{1-x} . One can see in Fig. 4 the change in $(110)^*$, $(1\bar{1}0)^*$ and $(001)^*$ Fourier power spectra during the ordering process when $\rho = 1.0 [= V(1)/V(2)]$. With progress of the ordering, diffuse contour comes out of mist of spectrum, and merges into sharp superspots around $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ positions which characterize the development of LRO of the $R\bar{3}m$ and/or the $Fd\bar{3}m$ types. The spectrum contour obtained at 2.0 MCS resembles diffuse streaks appearing in Fig. 1(a) as well as in electron diffraction patterns of several MC_{1-x} compounds with SRO⁽⁷⁾. The shape of the diffuse streaks is known to be strikingly similar to that of the Fermi surface for a simple cubic metal having one free electron per atom⁽²⁴⁾, as illustrated in Fig. 5(a-2). De Ridder *et al.*⁽²⁵⁾ have shown that the trajectory of diffuse streaks in Fig. 5(a-2) corresponds to the reciprocal shape function of an octahedron cluster of atoms given in Fig. 5(a-1). The diffuse intensity seen in Fig. 4(c, d) is therefore interpreted in terms of randomly dispersed octahedron-clusters with 1NN and 2NN atomic correlation of SRO. With further aging, the diffuse intensity is concentrated at $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ positions for the stable LRO state, fading out from the $(001)^*$ spectrum. It should be noted in Fig.

4 that the evolution of ordering slightly releases the curvature of diffuse streaks in the $\{110\}^*$ spectra and changes the contour appearing in $(001)^*$ from circular to rectangular. The intensity maps at 10 and 100 MCS look consistent with the reciprocal shape function in Fig. 5(b-2) for a cube cluster of 2NN atoms, rather than that for an octahedron in Fig. 5(a-2). The variation of Fourier spectra shown in Fig. 4 indicates that the atomic correlation between 2NN atoms gets enhanced with aging after 2 MCS, leading to the LRO state. One can notice that the Fourier spectra lose the cubic symmetry, the $(110)^*$ and the $(1\bar{1}0)^*$ spectra not being equivalent to each other. It suggests the formation of non-cubic ordered phases, or the $R\bar{3}m$ -type.

The Fourier power spectra at 2 and 100 MCS for various ρ values $[= V(1)/V(2)]$ are compared with each other in Fig. 6. One can recognize in (a) that the intensity distribution in the spectra varies depending on the value of ρ . The diffuse streaks are extended from $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ positions, moving away from the fundamental reciprocal lattice points, when the value of ρ is positive (or when both $V(1)$ and $V(2)$ are negative). In contrast, the extension of diffuse streaks occurs toward the fundamental points for negative ρ 's. Almost isotropic diffuse spots are obtained at $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ positions when ρ or $V(1)$ is zero. Similar dependence of diffuse intensity distribution on the sign of ρ or $V(1)$ has been found in our previous simulation of ordering in epitaxial growth of III-V semiconductor alloys⁽²⁶⁾⁽²⁷⁾. Comparing Fig. 6(a) with Fig. 1, one can conclude that the real systems, such as TiC_{1-x} and NbC_{1-x} , have a positive value of ρ . Landesman *et al.*⁽¹⁹⁾ theoretically evaluated a very small but positive value of ρ for $\text{TiC}_{0.5}$. The spectra for these ρ -values become almost identical to each other after prolonged aging for 100 MCS [Fig. 6(b)]. No significant difference is recognized among the five spectra in Fig. 6(b). Figure 6 clearly shows that the variation of the ratio ρ within the range of interest causes little difference in the final equilibrium state of LRO, but influences the early-to-intermediate stage in the ordering process.

2. Warren-Cowley parameters

To illustrate the ordering process in more detail, we see changes in Warren-Cowley short-range order parameters $\alpha(n)$, which are defined⁽²⁸⁾ as

$$\alpha(n) = 1 - \frac{P_{BA}(n)}{x} \quad (5)$$

Here, $P_{BA}(n)$ is the probability of finding a B atom at a lattice point in the n -th coordinate shell centered on an A atom, and $x (= 0.5$ in the present case) is the atomic fraction of B. The parameter $\alpha(n)$ takes a positive value if the number of like-atom pairs of n NN is larger than that in the completely disordered state, while it turns negative if unlike-atom pairs of A-B are predominant in n NN.

Figure 7 gives time-evolution of $\alpha(n)$ s in the process with $\rho = 1.0$. In the initial disordered state, the values of $\alpha(n)$ s are dispersed within a limited range between -10^{-3} and 10^{-3} , which is regarded as the extent of statistical ran-

Fig. 4 Snapshots of Fourier power spectra of atom configurations in the ordering process for $\rho=1.0$. Left: $(110)^*$, center: $(1\bar{1}0)^*$, and right: $(001)^*$. (a) 0.0625; (b) 0.125, (c) 0.5, (d) 2, (e) 10 and (f) 100 MCS. The fundamental lattice points are encircled in (a).

domness in our system. With the progress of atom exchange, $\alpha(4)$ and $\alpha(8)$ monotonically increase to unity, while $\alpha(2)$ and $\alpha(6)$ approach -1 , as shown in (a). The absolute values of α parameters are compared with each other in (b). The magnitude of α with even n 's decays with the interatomic distance n in the early-to-intermediate stage, but they are almost equalized in the late stage after 500 MCS. It suggests that the atomic correlation

gets continuously enhanced and extended with time. The α parameters for odd-numbered n 's, on the other hand, should vanish in the perfect LRO state as well as in the completely disordered state. Nevertheless, the parameters with odd n 's are first enhanced in the early stage in a similar way as those with even n 's, and then they are attenuated in the later stage after reaching a peak. Interestingly, the peaks appear in sequence of n , as

Fig. 5 Octahedron (a-1) and cubic (b-1) SRO clusters and their reciprocal shape functions (a, b-2)⁽²⁵⁾.

Fig. 6 (110) Fourier power spectra of atom configuration at 2 (a) and 100 (b) MCS as a function of ρ . From top to bottom: $\rho=1.0, 0.5, 0, -0.163$ and -0.55 .

Fig. 7 Time-evolution of Warren-Cowley parameters $\alpha(n)$ in the ordering process for $\rho=1.0$ (a). Their absolute values are compared with each other in (b). Peaks of $\alpha(n)$ with odd n 's are indicated by arrows in (b).

indicated by arrows in Fig. 7(b).

Figure 8 gives temporal changes of $\alpha(n)$ s in the processes with $\rho=-0.55$ and 0. In both processes, $\alpha(n)$ s for even shell-orders n are continuously amplified with time in the same way as in the previous case with $\rho=1.0$. In (a) for $\rho=-0.55$, the α -parameters with odd n 's again draw concave or convex curves, but the signs of them, $\alpha(1$ or $7)>0$ and $\alpha(3$ or $5)<0$, are completely reversed against the case of $\rho=1.0$, in which $\alpha(1$ or $7)<0$ and $\alpha(3$ or $5)>0$. We have confirmed the similar reversals of the sign between $\rho=-0.163$ and $\rho=0.5$ also. The change in sign of $\alpha(n)$ s is associated with the variation of diffuse contour depending on ρ seen in Fig. 6(a). It is indicated that $V(1)$ determines the behavior of α 's with odd n 's and the shape of diffuse scattering contour in the early stage. When $V(1)=0$, α 's for $n=1, 3$ and 5 are weakly biased toward the positive side in the early-to-intermediate

Fig. 8 Time-evolution of Warren-Cowley parameters $\alpha(n)$ in the ordering processes when $\rho = -0.55$ (a) and 0 (b).

stage, as shown in Fig. 8(b). This bias is probably due to the following conservation law:

$$\sum_{n \neq 0} Z(n)\alpha(n) = 0, \quad (6)$$

where negative $\alpha(2)$ is dominant. Here, $Z(n)$ refers to the number of lattice points in the n -th coordination shell.

The $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ -type LRO is formed exclusively through the ordering interactions of negative $V(2)$. The pairwise interactions of $V(1)$ play no contribution to the formation of LRO, as evident from the fact that this type of LRO appears even when $V(1)=0$ (or $\rho=0$). In the very early stage of the ordering, however, the interactions of $V(1)$ tend to form like- or unlike-atom pairs in the first coordination shells, depending on its sign. The sign of $\alpha(1)$ therefore corresponds to that of $V(1)$. At the same time, negative $V(2)$ forms A-B pairs of 2NN and makes $\alpha(2)$ negative. The coupling of 1NN and 2NN pairs causes additional atomic correlations for outer coordination shells in a limited range, resulting in an SRO state where the

magnitude of α rapidly decays with shell-number n . The sign of $\alpha(n)$ s with $n > 2$ is explained in terms of the propagation of 1NN and 2NN correlations on *fcc* lattice sites; e.g., $\text{sign}[\alpha(3)] = \text{sign}[\alpha(5)] = \text{sign}[\alpha(1) \times \alpha(2)] = \text{sign}[-\alpha(1)]$, since $\langle 1 \frac{1}{2} \frac{1}{2} \rangle_{n=3} = \langle 0 \frac{1}{2} \frac{1}{2} \rangle_{n=1} + \langle 100 \rangle_{n=2}$, and $\langle \frac{3}{2} \frac{1}{2} 0 \rangle_{n=5} = \langle \frac{1}{2} \frac{1}{2} 0 \rangle_{n=1} + \langle 100 \rangle_{n=2}$. Thus, both $V(1)$ and $V(2)$ enhance short-range atomic correlations and amplify $\alpha(n)$ s with time in the early stage of the ordering.

Whether $V(1)$ is positive or negative, the multiple interactions of $V(1)$ give rise to like-atom pairs of 2NN atoms, in contrast to unlike-atom pairs by negative $V(2)$. The destructive interference between atomic interactions $V(1)$ and $V(2)$ intensifies with development of the ordering, and therefore becomes significant in the following stage. The atomic correlations in odd-order coordination shells attributed to $V(1)$ are therefore frustrated by the development of even-order correlations due to $V(2)$, since the latter interaction predominates the later stage of ordering. Thus, the α parameters for odd n 's draw a peak and attenuate with time in the intermediate-to-late stage, while α 's for even n 's are enhanced monotonically over the whole process, as shown in Figs. 7 and 8. Similar overshooting behaviors of structural parameters have been found in ordering processes of $L1_0$ and DO_3 types simulated by the Path-Probability-Method⁽²⁹⁾ and the master equation approach⁽³⁰⁾, respectively. The peaks of α 's appearing in sequence of n are suggestive of the extension of correlation length, or growth of ordered domains with time. The temporal change in Warren-Cowley parameters indicates that the ordering is initiated with the short-range pairing of atoms, and evolves continuously by the enhancement and the extension of atomic correlation to a macroscopic range.

3. Degeneracy of $R\bar{3}m$ and $Fd\bar{3}m$ structures

As mentioned in Section I, the present model system has the two types of ordered structures, which are illustrated in Fig. 2(b, c), in the ground state. This section addresses whether or not the degeneracy is resolved at a finite temperature.

Figure 9 shows (001) cross-sectional views of the $R\bar{3}m$ and the $Fd\bar{3}m$ structures. These two candidates involve different types of the tetrahedron units of 1NN atoms, as shown in this figure. The $R\bar{3}m$ type consists of A_3B_1 and A_1B_3 tetrahedra, while the $Fd\bar{3}m$ type contains A_2B_2 , A_4B_0 and A_0B_4 units. The fractions of the tetrahedra and their self-energies are given in Table 2. Figure 10 shows the change in fractions of tetrahedra during the ordering processes when $\rho=1.0$ (a) and $\rho=-0.55$ (b). The A_2B_2 tetrahedra rapidly increase in the early stage in the case of $\rho=1.0$. This behavior gives us an impression as if the $Fd\bar{3}m$ structure could be formed predominantly. But, note that the A_4B_0 and A_0B_4 clusters, which also are members of $Fd\bar{3}m$, decrease at the same time. The fraction of A_2B_2 is lowered down in the following stage after reaching a maximum around 0.3 MCS. It should be noted that the change of A_2B_2 fraction is consistent with that of $\alpha(1)$ shown in Fig. 7. Both reach a maximum at almost

Fig. 9 (001) sectional views of the ordered structures of CuPt ($R\bar{3}m$) (a) and cubic ($Fd\bar{3}m$) types (b). Larger and smaller circles refer to the top surface and the underlying planes, respectively. A and B atoms are given by closed and open circles. Tetrahedron- and double-tetrahedron-units of the structures are delineated by solid- and dotted-lines, respectively.

Table 2 Self energies and fractions of tetrahedron clusters in LRO states.

Types	A_4B_0	A_3B_1	A_2B_2	A_1B_3	A_0B_4
E_{Self}	$-3V(1)$	0	$V(1)$	0	$-3V(1)$
$R\bar{3}m$	0	0.5	0	0.5	0
$Fd\bar{3}m$	0.125	0	0.75	0	0.125

Fig. 10 Change in the fractions of tetrahedron clusters during the processes for $\rho=1.0$ (a) and -0.55 (b).

the same time. The populations of A_3B_1 and A_1B_3 , on the other hand, keep constant over the whole process. Contrary to the case of $\rho=1.0$, the fraction of A_2B_2 first

decreases and then increases in the case of $\rho=-0.55$, as shown in Fig. 10(b), but those of A_3B_1 and A_1B_3 almost remain fixed in the same manner as in the former case. The behavior of the tetrahedra in the early stage is explainable in terms of their self-energies E_{self} , which are given as a function of $V(1)$ in Table 2. The tetrahedra with lowest E_{self} increase in the early stage. Hence, the short-range ordering between 1NN atoms due to $V(1)$ is responsible for the change in the fractions of A_2B_2 , A_4B_0 and A_0B_4 in the early stage. In the later stage, the tetrahedra with lowest E_{self} decrease with the enhancement of longer-range correlations, in a similar way to odd-order $\alpha(n)$ s.

Next, our interest is focused on the behavior of the double-tetrahedra depicted by dotted lines in Fig. 9. The two structures of LRO consist of the double-tetrahedron components in fractions given in Table 3. Figure 11 presents the change of the fractions in the process for $\rho=1.0$. Weak oscillation is seen in the fraction of $A_3B_3(F)$ type in the early stage. This oscillation is probably associated with the short-range ordering of 1NN atoms, since the $A_3B_3(F)$ type is made of a couple of A_2B_2 tetrahedra. In general, every double-tetrahedron component of interest increases with the progress of ordering. In the late stage after 100 MCS, the fractions of $A_3B_3(F)$ and $A_3B_3(R)$ are about twice those of $A_4B_2(F)$ (or $A_2B_4(F)$) and $A_4B_2(R)$ (or $A_2B_4(R)$), respectively. The ratios of the fractions in the late stage indicate the formation of LRO, being consistent with the values in LRO structures listed in Table 3. It seems that both of the LRO phases exist and continue to grow in the late stage.

Table 3 Fractions of double-tetrahedrons in LRO states.

Types	$A_4B_2(R)$	$A_3B_3(R)$	$A_2B_4(R)$	$A_4B_2(F)$	$A_3B_3(F)$	$A_2B_4(F)$
$R\bar{3}m$	0.25	0.5	0.25	—	—	—
$Fd\bar{3}m$	—	—	—	0.25	0.5	0.25

Fig. 11 Temporal change in populations of various double-tetrahedron clusters in the process with $\rho=1.0$. The types of the clusters are seen in Table 3.

Fig. 12 (001) sectional views of atom configuration at 100 (a), 500 (b) and 1000 MCS (c) in the process with $\rho=1.0$. Here, A and B atoms are given by closed circles and cross symbols, respectively. LRO domains of the $Fd\bar{3}m$ - and $R\bar{3}m$ -structures are identified by their characteristic patterns of atomic arrangement (see Fig. 9). Please note that domains are growing along antiphase boundaries of the other phase, as indicated by arrows.

Figure 12 demonstrates an example of (001) sectional views of time-evolution of LRO in the late stage after 100 MCS. One can confirm directly that the two types of ordered phases coexist and prevail in the system at 100 MCS, and the domains of the two phases coarsen with further annealing. It should be noticed that the $R\bar{3}m$ phase tends to penetrate $Fd\bar{3}m$ domains along the antiphase boundaries, and vice versa, as indicated by arrows in Fig. 12. This tendency results from the fact that the interphase boundary between $Fd\bar{3}m$ and $R\bar{3}m$ causes excess energy of $-V(2)$ per a^2 less than $-4V(2)/a^2$ or $-2V(2)/a^2$ involved in the antiphase or the twin boundaries. Here, a is the lattice constant of the fundamental fcc lattice. The interconnecting mixture of the two phases is therefore regarded as a metastable state in the present model system. Figure 11 suggests that the $R\bar{3}m$ and the $Fd\bar{3}m$ phases share the system almost evenly in the late stage, and the system shows little preference between the two. It is therefore concluded that the degeneracy between the $R\bar{3}m$ and the $Fd\bar{3}m$ phases remains in the ordering process at a finite temperature. The reason why the system keeps the degeneracy at a finite temperature may be that the ordering evolves from SRO to LRO in a continuous manner as discussed in the preceding section, and both of the LRO phases have the same number (eight) of variants.

An X-ray diffraction pattern of $\text{TiC}_{0.625}$ annealed for 4 days at 1020 K, which has been reported in Refs. (3)–(5), looks indicative of coexistence of trigonal and cubic phases, as mentioned in Section I. If the degenerate state appearing in Fig. 12 would be the case in TiC_{1-x} , it could explain the X-ray diffraction pattern. However, the model used in this study possesses some unrealistic assumptions, such as a rigid lattice of atomic sites and direct exchange of atoms, and so on. It is difficult to conclude straightforwardly from the result thus obtained that both structures of $R\bar{3}m$ and $Fd\bar{3}m$ would be stable in the real TiC_{1-x} system at a finite temperature. We may at least draw a conclusion that the configurational part of

entropy has little effect on removal of the degeneracy between the $R\bar{3}m$ and the $Fd\bar{3}m$ structures.

IV. Conclusions

In the present study, we have carried out the Monte Carlo simulation of long-range ordering with $k^* = \frac{1}{2} \frac{1}{2} \frac{1}{2}$ in an fcc Ising-model system with pairwise interactions between the first and second nearest neighbors $V(1)$ and $V(2)$. The main conclusions are drawn as follows:

(1) The Fourier power spectra of atom-configuration involve characteristic diffuse streaks in the early stage of the process. They explain well diffraction patterns of TiC_{1-x} and NbC_{1-x} with short-range order, when both $V(1)$ and $V(2)$ are negative.

(2) The second nearest neighbor interactions $V(2)$ enhance the Warren-Cowley parameters $\alpha(n)$ for even-order coordination shells monotonically with time, leading to continuous evolution of the $\frac{1}{2} \frac{1}{2} \frac{1}{2}$ -type ordering.

(3) The values of $\alpha(n)$ for odd n 's first increase in the early stage with the first nearest neighbor interactions $V(1)$, but then decrease after reaching a peak owing to the destructive interference between $V(1)$ and $V(2)$.

(4) The long-range ordering forms two different structures of CuPt ($R\bar{3}m$) and cubic ($Fd\bar{3}m$) types at the same time. The degeneracy between the two types of LRO remains in the ordering process due to pairwise interactions in a rigid fcc lattice at a finite temperature.

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