Calculation of Short-Range-Order Diffuse Intensity for a Two Dimensional Square Lattice within Cluster Variation Method

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The Cluster Variation Method (CVM) within the square approximation is employed to calculate Short-Range-Order diffuse intensity spectrum for a binary alloy in a two dimensional square lattice. The peak intensity at 1:1 stoichiometric composition is attained at \((k_x, k_y) = (0.5, 0.5)\) in the \(k\)-space. The instability temperature determined by the calculation of the Short-Range-Order diffuse intensity coincides with the phase boundary, indicating that the transition is of second-order. The integrated intensity in a Brillouin zone is also calculated to examine the level of the approximation.

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1. Introduction

Once the analytical expression of the free energy functional is obtained, one can derive various thermodynamic quantities from a single formula. First order derivative of the free energy gives information of phase equilibrium, while the second order derivative provides that of the stability of a given system. In fact, various theoretical calculations of a phase diagram have been advanced, and some of them refer to the stability of the system against concentration fluctuations, i.e. spinodal decomposition for a phase separating system. For an ordering system, on the other hand, the stability is posed as an excitation and an amplification of a particular concentration wave. Such an information of the concentration wave is conveyed by the Short Range Order Diffuse Intensity spectrum (hereafter abbreviated as SROI) in the \(k\)-space which is obtained by the Fourier transform of the second order derivative of the free energy functional. Contrary to the remarkable advancement of theoretical calculations of a phase diagram, however, not much studies have been attempted for the stability analysis based on SROI calculations. In fact, to the best of authors’ knowledge, theoretical investigations of SROI have been centered around either three-dimensional realistic lattices by laborious numerical calculation or lower dimensional lattices at 1:1 stoichiometric composition with purely analytical calculation.

The purpose of the present study is to calculate both the concentration and temperature dependences of SROI for a two dimensional square lattice for which the Cluster Variation Method (CVM) is employed to describe the free energy functional. The organization of the present report is as follows. In the next section, the calculation procedure is briefly summarized, and the calculated results are demonstrated and discussed in the third section followed by conclusions in the last section.

2. Theoretical Calculation

2.1 Free energy

The free energy is formally obtained by minimizing the following functional

\[
F = \sum_{\sigma} E(\sigma)X(\sigma) + k_B T \sum_{\sigma} X(\sigma) \ln X(\sigma) \tag{1}
\]

where \(E(\sigma)\) and \(X(\sigma)\) are, respectively, the energy and the probability for a configuration \(\sigma\) which takes \(2^N\) values for a binary system with \(N\) lattice sites, \(k_B\) the Boltzmann constant and \(T\) is the absolute temperature. For a large value of \(N\), it is a formidable task to carry out the minimization over all \(2^N\) configurations under the normalization condition, \(\sum \sigma X(\sigma) = 1\). Therefore, in the present study, both internal energy and entropy are approximated in the following way.

The internal energy \(E\), which is the first term of eq. (1), is written as a sum of the nearest neighbor pair interaction energies,

\[
E = \sum_{\sigma} E(\sigma)X(\sigma) \approx \frac{z}{2} N \sum_{ij} e_{ij} y_{ij} \tag{2}
\]

where \(z\) is a coordination number (in the present case, \(z = 4\)), \(e_{ij}\) and \(y_{ij}\) are, respectively, the interaction energy and the probability of finding \(i\)-\(j\) pair in the nearest neighbor. The entropy \(S\), the second term of eq. (1), is most conveniently described based on the recipe provided by the CVM which is capable of introducing the wide range of atomic correlations. Within the square approximation of the CVM, the entropy \(S\) is written as

\[
S = k_B \sum_{\sigma} X(\sigma) \ln X(\sigma) \approx k_B \ln \left( \frac{\prod_{ij} y_{ij} N!}{\prod_i x_i N! \prod_{ijkl} w_{ijkl} N!} \right) \tag{3}
\]

where \(x_i\) and \(w_{ijkl}\) are, respectively, the point and square
The ordered phase at the ground state at $1:1$ stoichiometric composition with a two-dimensional square lattice investigated in the present study. An open circle (solid circle) indicates $A$ ($B$) atom which preferentially occupies $\alpha$ ($\beta$) sublattice.

where $\langle \sigma(k) \rangle$ and $\langle |\sigma(k)|^2 \rangle$ are, respectively, the Fourier transforms of point ($\langle \sigma(p) \rangle$) and pair ($\langle \sigma(p)\sigma(p') \rangle$) correlation functions. Note that $\sigma(p)$ and $\sigma(p')$ is a spin variable at a lattice point $p(p')$ and takes $+1$ and $-1$ depending upon $A$ and $B$ atoms, respectively.

Based on the fluctuation theory, a pair correlation function can be expressed as the second order derivatives of the free energy with respect to correlation functions which is written as

$$F_{ss'}(r) = \frac{\delta^2 F}{\delta \xi_s(p) \delta \xi_{s'}(p')}$$

where $r$ is the vector between the two lattice points $p$ and $p'$, $\xi(p)$ and $\xi(p')$ is the correlation function equivalent to $\langle \sigma(p) \rangle$ and $\langle \sigma(p') \rangle$, and $s(s')$ indicates a type of the cluster associated with a lattice point $p(p')$. It should be noted that, since the direction of the atomic correlation must be taken into consideration for the Fourier transformation, the number of the correlation functions for the SROI calculation is larger than that needed for an ordinary phase diagram calculation.

The Fourier transform, $F_{ss'}(k)$, of the second order derivatives matrix, $F_{ss'}(r)$, are performed by utilizing the translational symmetry of the disordered phase. Then, the SROI is obtained as

$$I_{SRO}(k) = k_B T N F_{1i}^{-1}(k)$$

where $F_{1i}^{-1}(k)$ is the first entry of the inverse matrix of $F_{ss'}(k)$.

3. Results and Discussion

3.1 Intensity distribution

Figure 3 shows the variation of the SROI with the composition at a fixed normalized temperature $k_B T/\varepsilon = 2.5$. One sees that the wave vector corresponding to the peak SROI is independent of the composition and is located at $(0.5, 0.5)$. This particular wave vector $(0.5, 0.5)$ indicates an ordering wave propagating along the [11] direction with a wave length of $\sqrt{2}/a$ where $a$ is a lattice constant. An amplification and an excitation of this concentration wave yields the ordered phase shown in Fig. 1.

A peak intensity decreases and an entire shape becomes diffuse with deviating from $1:1$ stoichiometric composition. These changes are caused by the following two factors, (1) the loss of the short-range-order and (2) the decrease of an integrated intensity, which are both enhanced with deviating from $1:1$ stoichiometric composition.

3.2 Instability temperature ($T_0$)

The instability temperature, $T_0$, is defined as the temperature at which the determinant of the matrix $F_{ss'}(k)$ vanishes. Hence, at $T_0$, SROI at the peak wave vector blows up. One can, therefore, determine the instability temperature by the condition of $T/I = 0$. The temperature dependences of $T/I$ at the peak wave vector $(0.5, 0.5)$ for the four compositions in Fig. 3 are shown in Fig. 4. The obtained instability temperatures at these compositions are plotted in the phase diagram in Fig. 2. The instability temperatures exactly coincide with transition temperatures, confirming the second order nature of the transition. In fact, such a criterion of the second
order transition agrees with more general Landau-Lifshitz’s criteria.7)

3.3 Integrated intensity

It is readily shown that the integration of eq. (8) yields

\[ \sum_k \mathcal{I}_{\text{SRO}}(k) = 4NC(1 - c), \] (9)

which suggests that the integrated intensity depends only on the composition \( c \). The calculated integrated intensities over the first Brillouin zone are shown in Fig. 5. The solid and dotted lines are calculated within the square approximation of the CVM at the composition \( c = 0.5 \) and \( 0.4 \), respectively. Both the curves show the same tendency that the integrated intensity stays at a constant level in high temperatures and diverges sharply in the low temperature range. It should be noted that the constant value in the high temperature for each composition is exactly the one obtained from eq. (9).

The conservation of the integrated intensity is a measure of the level of the approximation in the free energy functional. It is interesting to compare the present results with the one obtained by conventional point approximation (Bragg-Williams approximation)8) which is indicated by a broken line. One confirms that the diverging behavior is well suppressed in the present square approximation, which suggests that the present square approximation is far better approximation than the B-W approximation.

4. Conclusion

The SROI for a binary alloy with a two dimensional square lattice is investigated theoretically with the CVM in the square approximation. The peak intensity at 1 : 1 stoichiometric composition is realized at \((k_x, k_y) = (0.5, 0.5)\) in the \( k \)-space, representing an ordering wave which yields an underlying ordered phase. The instability temperature obtained from the SROI coincides with the transition temperature, confirming the second order nature of the order-disorder transition in the two dimensional square lattice. The diverging behavior of the integrated intensity in the low temperature range is remarkably suppressed as compared with the one calculated by a conventional Bragg-Williams approximation.

REFERENCES