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First-principles calculation of Diffuse Intensity Spectrum of Binary Alloys

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Abstract

The Short Range Order Diffuse Intensity Spectrum is obtained for Cu-Au and Cu-Pt systems from the first-principles which consists of electronic structure calculation and the Cluster Variation Method. The result clearly reprodues the observed intensity maxima for both the systems.

1. Introduction

In spite of the fact that extensive amounts of studies on alloy phases depend on scattering experiments, theoretical investigation on Short Range Order Diffuse Intensity (hereafter SROI) has not been carried out except for analysis based on the Krivoglaz-Clapp-Moss (KCM) formula [1] which is derived within the Bragg-Williams (hereafter BW) approximation. [2] The BW approximation, however, has been criticized for the lack of reliability of calculated results. As was pointed out in the global phase diagram investigation [3], correct topology of a phase boundary obtained by the Monte Carlo calculation (hereafter MC) [4] can hardly be reproduced by the BW approximation. More critical breakdown in the BW approximation is the fact that the instability temperature, at which disordered phase becomes inherently unstable and spontaneous decomposition sets in, is incorrectly predicted even for a relatively simple $L1_0$-disorder-$L1_2$ equilibria which are stabilized with first nearest neighbor pair interaction energy only. The predicted instability locus lies above the stable $L1_0$ ordered phase field, which is by no means acceptable. These facts imply intrinsic insufficiencies of the BW model in the description of thermodynamics of an alloy system.

The Cluster Variation Method (hereafter CVM) [5] has been widely employed for the studies of alloy thermodynamics. The advantage of the CVM originates from the fact that the wide range of atomic correlations are explicitly incorporated in the Free energy functional. Hence, a transition temperature at which cooperative behavior of atoms is taken place is determined with high accuracy. Moreover, relevant thermodynamic quantities associated with an equilibrium phase such as short range and long range order parameters can be obtained systematically from a single free energy formula. By combining with electronic structure calculations, various thermodynamic quantities including a phase dia-

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gram have been derived even from the first-principles. [6, 7, 8]

Recently, the **k**-space formulation of the CVM is performed by Sanchez [9] and the SROI calculations are successfuly carried out for the Ising system. In order to avoid the numerical difficulties, however, the calculations are limited to the one dimensional chain and two dimensional square lattice within the pair and square approximaitons. Later, the calculation is extended to fcc lattices with first and second nearest neighbor pair interaction energies by Mohri et al. [10] based on the Tetrahedron-Octahedron approximation. [3, 11] Mohri et al. [12] also attempted the first-principles calculation of the SROI for Cu-Au system and the main feature of the spectrum which is characterized by the intensity maxima at (1, 0, 0) position and its equivalents in the **k**-space is correctly reproduced.

It has been well known that Cu-Pt system forms quite unique $L1_1$ ordered structure in the vicinity of the equi-atomic composition which has not been observed in any other alloy systems. As will be described later, according to the symmetry consideration [13,14] based on the concept of the Special Point family [14] , the intensity maxima of the SROI for the disordered phase above $L1_1$ ordered phase field are expected to appear at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ position and its equivalents. Although this is confirmed by various diffraction studies first-principles calculation of SROI has not been attempted yet. The main objective of the present study is to extend the first-principles calculation of the SROI performed for the Cu-Au system to Cu-Pt system. The derived **k**-space spectrum is expected to provide a unique measure for the reliability of the employed first-principles model.

Since the formal aspect of the calculation procedure have been amply demonstrated in the previous publications [6-10] , only essential results are shown in this breif report. The organization of the present report is as follows. In the next section the theoretical back ground is briefly reviewed, and the calculated results are demonstrated and discussed in the final section. For the sake of completeness, part of the previous results for Cu-Au system are reproduced.

2. Theory of Short Range Order Diffuse Intensity Spectrum

A thermodynamic system incessantly undergoes microscopic fluctuation which, in fact, triggers phase transition. SROI is caused by the modulation of atomic scattering factor through the configurational fluctuation of constituent atoms. The structure factor S_p at lattice point p is, in general, written as

$$S_p = \langle S_p \rangle + \Delta S_p \qquad , (1)$$

where $\langle S_p \rangle$ is the average value of the structure factor over an entire crystal and ΔS_p is due to the fluctuation. Then the scattering amplitude of incident beam is given by

$$\langle S_p \cdot S_{p'}^* \rangle = |\langle S_p \rangle|^2 + \langle \Delta S_p \cdot \Delta S_{p'}^* \rangle \qquad , (2)$$

where the first term on the right hand side corresponds to the ordinary Bragg diffraction while the second term, which indicates the correlation of scattering amplitude resulting from two lattice points, is responsible for the diffuse scattering amplitude.

Since diffuse scattering intensity is the Fourier transformation of the amplitude, the scattering intensity is written as

$$I(\mathbf{k}) = I_e \sum_{p} \sum_{p'} \langle \Delta S_p \cdot \Delta S_{p'}^{*} \rangle e^{i2\pi \mathbf{k}(\mathbf{r}_p - \mathbf{r}_{p'})} \quad , \quad (3)$$

where I_e is the scattering intensity due to a single electron. The Fourier transformation of above equation can be performed by noting the following relations.

$$\begin{aligned} \langle \Delta S_p \cdot \Delta S_{p'}^{*} \rangle &= \langle S_p \cdot S_{p'}^{*} \rangle - |\langle S_p \rangle|^2 \\ &\propto \langle \sigma_p \sigma_{p'} \rangle - \langle \sigma_p \rangle \cdot \langle \sigma_{p'} \rangle \end{aligned} \quad , \quad (4)$$

where $\langle \sigma_p \rangle$ and $\langle \sigma_p \sigma_{p'} \rangle$ are the point and pair correlation functions, respectively. The substitution of the eq. (4) into the eq. (3) yields the kinematic short range order intensity as

$$I(\mathbf{k}) = \langle |\sigma(\mathbf{k})|^2 \rangle - |\langle \sigma(\mathbf{k}) \rangle|^2 \quad , \quad (5)$$

where the Fourier transformation of is defined by

$$\sigma(\mathbf{k}) = \sum_{p} \sigma_p e^{i2\Pi \mathbf{k} \cdot \mathbf{r}_p} \quad . \quad (6)$$

By noting the formal definition of multisite correlation functions

$$\langle \sigma_{p_1} \sigma_{p_2} \cdots\cdots \sigma_{p_n} \rangle = (-k_B T)^n \frac{1}{z} \frac{\partial^n Z}{\partial \mu_{p_1} \cdot \partial \mu_{p_2} \cdots\cdots \partial \mu_{p_n}} \quad (7)$$

with the staggered chemical potential and the partition function Z given by the following sum over all possible atomic configurations J

$$Z = \sum_{J} e^{-E_J / k_B T} \quad , \quad (8)$$

where E_J is the internal energy for configuration J, one could rewrite eq.(4) by the general expression ;

$$\langle \sigma_p \sigma_{p'} \rangle - \langle \sigma_p \rangle \langle \sigma_{p'} \rangle = -k_B T \frac{\partial^2 F}{\partial \mu_p \cdot \partial \mu_{p'}} \quad . \quad (9)$$

The Fourier transformation of the right hand side of eq. (9) can be performed by utilizing the translational symmetry of the disordered phase, and one can finally reach the following concice expression.

$$\begin{aligned} I(\mathbf{k}) &= \langle |\sigma(\mathbf{k})|^2 \rangle - |\langle \sigma(\mathbf{k}) \rangle|^2 \\ &= N k_B T \{ F''^{-1}(\mathbf{k}) \}_{11} \end{aligned} \quad . \quad (10)$$

Hence, once the free enrgy functional F is described in a real space, the (1,1) element of the inverse matrix of the Fourier transformed second order derivative matrix uniquely provides the SROI.

3. Results and Discussions

By employing the ASW [15] on the basis of the local-density approximation to the density functional theory, we first calculated the total energies of selected ordered compounds. Then, by operating the Cluster Expansion Method [16] , the effective interaction energies are extracted as a function of lattice parameter.

For Cu-Au system, a tetrahedron cluster is taken as the basic cluster of the cluster expansion, hence the effective interaction energies up to tetrahedron many body interaction energy are extracted and are demonstrated in Fig.1. [17] It should be noted that the first nearest neighbor pair interaction energy is sufficient to stabililze the $L1_0$ or $L1_1$ phases appeared in the Cu-Au system. While for Cu-Pt system, the second nearest neighbour pair interaction is neccesary to stabilize the $L1_1$ phase which is a peculiar phase observed only in the Cu-Pt ystem. Therefore, the basic cluster employed for the expansion is the combination of the tetrahedron and octahedron clusters, which provides the multisite interaction energies up to the octahedron cluster energy in addition to the first and second nearest neighbor pair interactions. The results are shown in Fig. 2. Note that the effective interac-

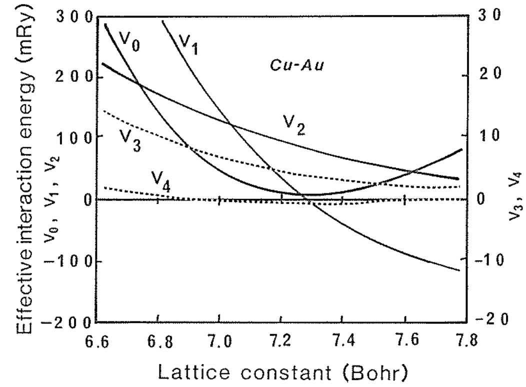

Fig. 1 Effective interaction energies v_i for i-point cluster for Cu-Au system as a function of lattice parameter. [17] v_0 is equivalent to the heats of formation of a complete random solid solution at 50at%.

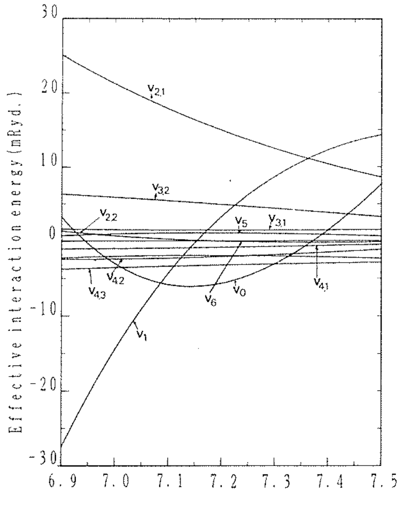

Fig. 2 Effective interaction energies $v_{m,n}$ for Cu-Pt system as a function of lattice parameter. m and n represent the number of lattice point in the cluster and the type of the cluster, respectively.

tion energies shown in Figs. 1 and 2 are for the ground state of electronic system. In order to incorporate the temperature dependency into the effective interaction energies, the Debye-Gruneisen model is employed to calculate the vibrational free energy of the selected ordered compounds. Our preliminary investigation indicates that the modification of the lattice vibration effects quite significantly affects the transition temperature for the Cu-Pt system, while not appreciable for the Cu-Au system. In both cases, however, the main topology of the SROI spectrum is unaltered. Since the details of the theoretical procedure based on the

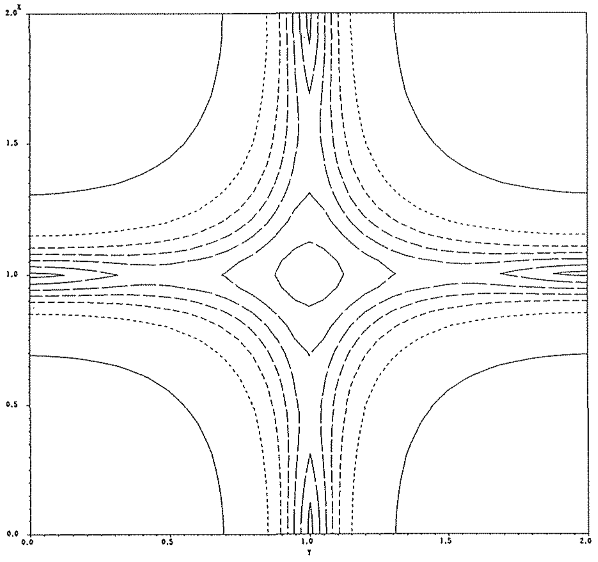

Fig. 3 Short range order diffuse intensity spectrum for Cu-Au system on (100) in the k-space at 1053K obtained by the first-principles calculation for 1 : 1 stoichiometry. [12] The level of the approximation employed for the CVM is the tetrahedron-octahedron approximation.

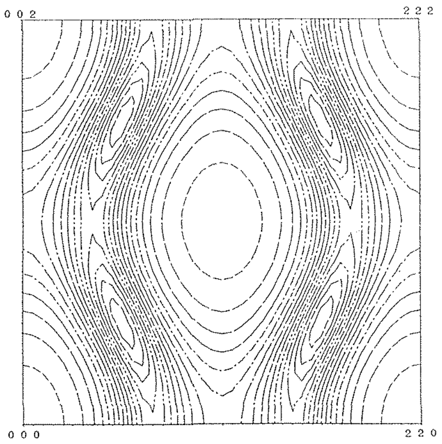

Fig. 4 Short Range order diffuse intensity spectrum for Cu-Pt system on $(1\bar{1}0)$ in the k-space at 1984K obtained by the first-principles calculation for 1 : 1 stoichiometry.

Debye-Gruneisen model is not described in this report, the reader interested in the details should refer to the previous reports [18-21]. For both the systems, Tetrahedron-Octahedron approximation of the CVM is employed to evaluate the configurational entropy term.

The SROI spectrum calculated at 1053K for Cu-Au system on (001) plane and at 1984K for Cu-Pt system on $(1\bar{1}0)$ plane in the k-space are demonstrated in Figs 3. [12] and 4, respectively. Both spectrum are at 1 : 1 stoichiometry. One can confirm that the intensity maxima appear at (1, 0, 0) and its equivalents for Cu-Au and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ and its equivalents for Cu-Pt, respectively, which agree with experimental results. As was described in the introduction section, these intensity maxima are predicted based on the following symmetry analysis.

The second order derivative matrix of the Free enregy functional $F_{nn'}$ (p, p′) possesses the point group symmetry, hence the Fourier transform $F_{11'}$ $(\mathbf{k})$, the eq. (10), has the same point group symmetry with the translational symmetry of the reciprocal lattice. It can be shown that the gradient of any scalar function with the space group symmetry of the crystal lattice must vanish at points where two or more symmetry elements interesect, otherwise the invariance of the gradient would be violated. [13, 14] Any scalar function, therefore, takes its extremum values at those points which are called Special Points (SP) and are also known as Wyckoff positions in the International X-ray Tables. For the fcc lattice, there are four SP's, (0, 0, 0), (1, 0, 0), $(1, \frac{1}{2}, 0)$ and $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. [13, 14]

It should be noted that the ordereing wave vector $\mathbf{k}_0$ which minimizes $|F_{11'}(\mathbf{k})|$ depends on details of a free energy functional. For the constant first and second nearest neighobr pair interaction model, the mathematical analysis has been performed based on the eigen value expansion around an equilibrium state, and it has been demonstrated that the ordereing wave vectors are classified, as a function of α value which is the ratio of the second to the first nearest neighbor pair interaction energies, into the four groups which coincide with the SP families described above.

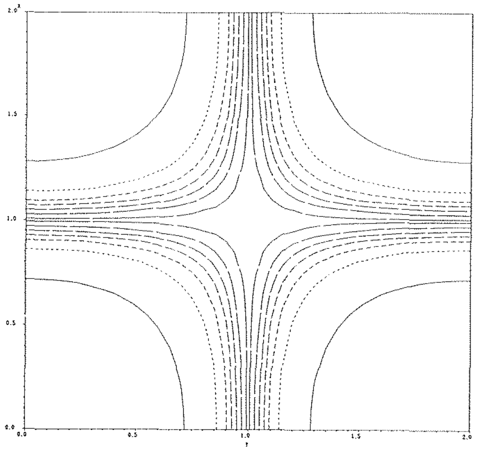

Fig. 5 Short range order diffuse intensity spectrum for Cu-Au system on (100) in the k-space at 1025K obtained by the first-principles calculation for 1 : 1 stoichiometry. The level of the approximation employed for the CVM is the tetrahedron approximation.

Among these, the Cu-Au system is characteirzed as the one belonging to the (1,0,0) SP family. As is shown in the Fig. 1, however, the second nearest neighbor pair interaction energy is not taken into account in this study, and for such a system with vanishing α value, gorund state is degenerated between (1, 0, 0) and (1, $\frac{1}{2}$, 0) families. [22] It should be emphasized that the lifting of the degeneracy in the finite temperature is purely an entropy effect and is not an energy effect. This can be clearly understood by comparing the Fig. 3 with Fig. 5 which is obtained based on the same set of the effective interaction energies with tetrahedron approximation of the CVM. One can confirm that the degeneracy along ⟨1k0⟩ type direction in the Fig. 5 is lifted in the Fig. 3 by explicitly incorporating the second nearest neighbor pair correlation in the entropy formula through the tetrahedron-octahedron approximation.

On the otherhand, in the Ising model, the $L1_1$ ordered phase of Cu-Pt system is stabilized with $\alpha > 0.5$ [22] and belongs to ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$) SP family [13, 14] . The Fig. 2, however, indicates the α's for the entire range of lattice parameter are less than 0.5 which falls into the (1, $\frac{1}{2}$, 0) SP family. Despite this, the resultant SROI predicts the correct spectrum. We believe that the manybody interaction energies play crucial role for this non-Ising behavior.

Finally, an alternative approach of the first-principles SROI calculation is suggested. The present calculation is based on the Cluster Expansion Method for which a set of selected ordered phases are assigned. Then the information of the SP family to which the system belongs is implied in advance through the choice of ordered cmompounds. Perhaps, more consistent way is to start with the total energy of a disordered phase. In this connection, the Coherent Potential Approximation (CPA) [23] followed by the Generalized Perturbation Method (GPM) [24] is thought to be quite useful. The SROI study based on the CPA-GPM remained as the future work, which is expected to provide complimentary results.

In the present investigation, we successfully obtained the SROI spectrum for the two alloy systems belonging to different symmetry groups based on the first-principles calculation. Since, as was mentioned in the introduction section, body of experimental works on alloy phases are carried out by scattering techniques, we believe that the **k**-space information derived by the first-principles calcualtion which is directly comparable with experimental results is quite informative.

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