Analytic Solutions of Quadratic Lattice Bethe Model of Binary Alloys

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1. Introduction

Alloy consists of several kinds of atoms which make superlattice order, and this superlattice order breaks down in consequence of thermal agitation, as the temperature increases. This characteristic makes difficult to study alloy systems, due to its complexity of considering randomness of their configurations. One of the simplest one is the Bragg-Williams approximation [1] which models alloy system similar to the Ising model, within the mean-field theory. It calculates the energy of the system from the interchange energy between different atoms proportional to the order parameter of the system. Another one is the Bethe approximation [2], which utilizes the partition function of the short-range interactions between atoms, and also considers the long-range interactions. In the previous study, the analytic and numerical results of Bragg-Williams approximation were given [3]. In this present work, analytic results of Bethe approximation are given, and also the two different models of alloy are to be compared. Their interaction parameters of the ordered state were obtained from the density functional calculations. Moreover, the results are also to be compared with experimental values, in order to verify the relevances of the alloy models we considered.

2. Calculation models

For the case of binary alloys which consist of two atoms A and B, the equilibrium condition of Bragg-Williams approximation is obtained by equating two functions f_1 and f_2 such that

$$f_1(\phi) \equiv \ln\left\{\frac{p(1-r-a+rp)}{(1-p)(a-rp)}\right\} = \frac{\Delta}{kT} \equiv f_2(\phi) \tag{1}$$

where p is the probability for an A atom to occupy at one of the A-sublattice, and a, and r are parameters which represent the value of p for complete disorder, and the fraction of the number of A-sites, respectively. Also, ϕ is the order parameter of the alloy, which is defined by $\phi = (p-a)/(q-a)$, with q as the maximum value of p, and Δ is the value of increased internal energy by interchanging an A atom in the A-sublattice with a B atom in the B-sublattice.

Meanwhile, the Bethe approximation, which considers local flluctuations of the order parameter, utilizes the partition function,

$$Z_{nm} = g_{nm}\left(\frac{\epsilon+x}{1+\epsilon x}\right)^n\left(\frac{\epsilon+x^2}{1+\epsilon x^2}\right)^{\left(\frac{1}{2}z-1\right)n-\frac{1}{2}m}\left(\frac{x(1+\epsilon)}{1+\epsilon x^2}\right)^m = g_{nm}\lambda^n\mu^{\frac{1}{2}m} \tag{2}$$

for the case of second approximation of quadratic lattice system, with

$$\lambda = \frac{\epsilon + x}{1 + \epsilon x}\left(\frac{\epsilon + x^2}{1 + \epsilon x^2}\right)^{\frac{1}{2}z - 1}, \text{ and } \mu = \frac{x^2(1 + \epsilon)^2}{(1 + \epsilon x^2)(\epsilon + x^2)} \tag{3}$$

Here, g_{nm} is the weighting factor of the configuration of the first characterized by the number n of wrong atoms in the shell and the number m of pairs of unequal neighbors in it. z is the coordination number, x is the Boltzmann factor $\exp(-J/kT)$, where $J = 1/2(J_{AA} + J_{BB}) - J_{AB}$ with J_{AA}, J_{BB}, and J_{AB}, the interaction energies between the atoms A A, B B, and A B, respectively. ϵ is a factor of partition function for each wrong atom in the first shell, giving long-range interaction to it.

3. Analytic thermodynamic functions

Fig. 1 shows how Bethe's second approximation works. We choose, in the atomic lattice, an arbitrary atom as a central atom, and consider the configurations of its surrounding atoms, called as "shell"s. In the Fig. 1, the crossed circle is the central atom. The squares surrounding it are the nearest neighbor atoms of the central atom, which are called as the "first shell", and the crosses and the circles surrounding the first shell are called as the "second shell", and so on. While the first approximation only utilizes the configuration of the central atom and the first shell, and consider the outer shells as a effective field, the second approximation also uses the configurations of the second shell, which makes the approximation much more realistic.
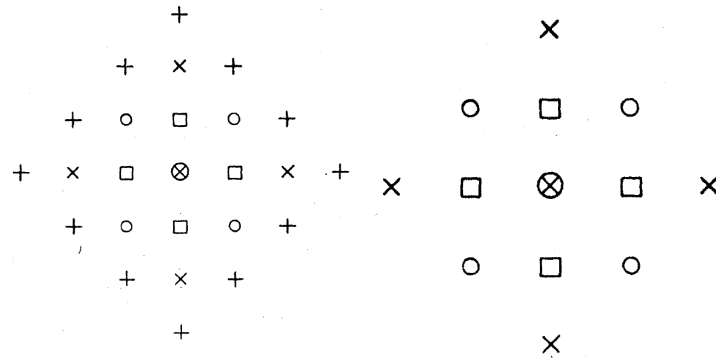

Figure 1. Bethe's approximation
in the quadratic lattice.

Figure 1. Bethe's approximation
in the quadratic lattice [2].

The analytic result of Bethe's second approximation for quadratic lattice is as in the following.

The partition function is

$$Z = \left(1 + x^4\right)\left\{1 + \left(\frac{\epsilon + x}{1 + \epsilon x}\right)^4\left(\frac{\epsilon + x^2}{1 + \epsilon x^2}\right)^4\right\} + 4x(1 + x^2)\left(\frac{\epsilon + x}{1 + \epsilon x}\right)\left\{1 + \left(\frac{\epsilon + x^2}{1 + \epsilon x^2}\right)^2\right\} \tag{4}$$

$$+ 4x^2\left(\frac{\epsilon + x}{1 + \epsilon x}\right)^2\left(\frac{x(1 + \epsilon)}{1 + \epsilon x^2}\right)^2\left\{\left(\frac{x(1 + \epsilon)}{1 + \epsilon x^2}\right)^2 + 2\left(\frac{\epsilon + x^2}{1 + \epsilon x^2}\right)\right\}$$

We obtained the explicit forms of the following thermodynamic functions calculated by:

$$F = -\frac{1}{\beta}\ln Z, \quad U = -\left(\frac{\partial \ln Z}{\partial \beta}\right)_{N, V}, \quad S = \frac{-F + U}{T}, \quad C = \left(\frac{\partial U}{\partial T}\right)_{N, V} \tag{5}$$

From these relations, the analytic form of each thermodynamic property was obtained explicitly. The details will be discussed in the presentation.

4. References

[1] W. L. Bragg and E. J. Williams. Proc. R. Soc. Lond. **A 145**. 699-730 (1934)

[2] H. A. Bethe, Proc. R. Soc. Lond. **A 150**. 552-575 (1935).

[3] J. Y. Lee *et al.*, "On the Ising Characteristic of Bragg-Williams and Bethe Alloy Models", Kor. Mag. Soc. 2012 Summer Conference.