Many-atom Correlations and the Theory of Disordered Alloys

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Abstract

Some recent theories of disordered alloys are discussed with particular emphasis on their application to short-range ordered alloys. Comparisons are made in the case when only two-atom correlations are present. The probability variation method of Clapp (1969, 1971) is applied to allow inclusion of n-atom correlations which are dependent on the experimentally observable two-atom correlations. It is suggested that the cell method of Tsukada (1969) may be extended in the same manner.

1. Introduction

It has become increasingly popular in recent times to use the coherent potential approximation (CPA) of Soven (1967) and Taylor (1967) as a basis for theories of the thermal vibrations and electronic energy structure of disordered alloys. Typical of several recent proposals for the extension of the CPA are the theories of Freed and Cohen (1971) and Takeno (1971). In such cases the authors generate a hierarchy of equations in which functions of n atoms are coupled to functions of $(n+1)$ atoms. To use these theories we require a knowledge of the $(n+1)$-atom correlation functions and, while these can be found in the case of a random distribution, generalization to short-range ordered cases is more difficult because the three(or more)-atom correlation functions cannot, in most cases, be determined experimentally. It is therefore necessary to find a method of calculation of the Green's functions which depends only on the two-atom correlation functions which may be experimentally measured. Two courses are open to us: we may terminate the theories at the second stage taking into account only the correlation of pairs of atoms, or we may use the two-atom correlations to make a 'best' prediction of the n-atom correlations.

2. Present Theories

Takeno (1971) has derived the following hierarchy of equations for the self-energies corresponding to Green's functions which have been configurationally averaged subject to certain site restrictions:

$$\sigma_{\alpha_1\alpha_2...\alpha_r} = \sum_{\alpha'} c_{r+1}(\alpha' \mid \alpha_1\alpha_2...\alpha_r)\,\varepsilon_{\alpha'}\langle D(\alpha')^{-1}\rangle_{\alpha_1\alpha_2...\alpha_r}$$
$$\times \{1 - \langle G\rangle_{\alpha_1\alpha_2...\alpha_r}(\sigma_{\alpha_1\alpha_2...\alpha_r\,\alpha'} - \sigma_{\alpha_1\alpha_2...\alpha_r})\}^{-1}. \tag{1}$$

Now, taking into account the correlations of the atoms up to pairs is equivalent to terminating the hierarchy by using the approximations

$$\langle D(\alpha')^{-1}\rangle_{\alpha\alpha'} \approx \langle D(\alpha')^{-1}\rangle_{\alpha'} \quad \text{and} \quad \sigma_{\alpha\alpha'} \approx \sigma_{\alpha'}. \tag{2}$$

Application of these results to the case of a binary alloy composed of A-type host atoms and B-type impurity atoms gives

$$\Sigma = cV\langle D(B)^{-1}\rangle_B \{1-\langle G\rangle(\Sigma_B-\Sigma)\}^{-1} \tag{3a}$$

and

$$\Sigma_B = \eta V\langle D(B)^{-1}\rangle_B, \tag{3b}$$

where V is the impurity potential and η is the matrix of the conditional atom-pair probabilities, η_{ij}, that if an impurity occupies site i there will be an impurity at site j. We note that at this stage

$$\langle D(B)^{-1}\rangle_B = \langle\{1-G(V-\Sigma)\}^{-1}\rangle_B. \tag{4}$$

Now Freed and Cohen (1971) derive an equation for the total scattering from the cluster n, which is

$$T_n = \sum_{\alpha\notin n} t_n^\alpha + \sum_{\alpha\neq\beta\notin n} t_n^\alpha \mathscr{G}_n t_n^\beta + \dots . \tag{5}$$

An exact solution of the scattering problem requires that $\langle T_n\rangle = 0$, but the coherent potential CP_n of Freed and Cohen is $\langle t_n^\alpha\rangle$ and is exact only in the random case. The solution corresponding to the CP_2 potential is thus given by a sum of the total single-site scatterings subject to a given site restriction, that is,

$$\langle T\rangle_{12}^2 = \frac{\eta(V-\Sigma_1)}{1-\langle G\rangle_1(V-\Sigma_1)} - \frac{(1-\eta)\Sigma_1}{1+\langle G\rangle_1\Sigma_1} = 0. \tag{6}$$

To determine why the CP_n breaks down, we look again at equation (5). If $|n-\alpha|$ and $|n-\beta|$ are large and $|\alpha-\beta|$ is small, the probability of α and β having given occupancy depends only to a small extent on n for the case of short-range correlations that we are considering. The approximation

$$\langle t_n^\alpha \mathscr{G}_n t_n^\beta\rangle \approx \langle t_n^\alpha\rangle\langle\mathscr{G}_n t_n^\beta\rangle \tag{7}$$

is then not valid.

Takeno's (1971) method does not allow such a simple analysis except when we further approximate $\langle D(B)^{-1}\rangle_B$. If we ignore atom correlations in finding $\langle D(B)^{-1}\rangle_B$, we have

$$\langle D(B)^{-1}\rangle_B \approx \{1-\langle G\rangle_B(V-\Sigma_B)\}^{-1}, \tag{8}$$

and we arrive at the same solution as the CP_2 of Freed and Cohen (1971) that was discussed above. In fact $\langle D(B)^{-1}\rangle_B$ is dependent on the three(and more)-atom correlations and considerations similar to those applicable to equation (5) apply.

For completeness we now look at a method which is a direct generalization of the coherent potential approximation (designated GCPA). Following the notation of Freed and Cohen (1971), the equation

$$\langle\mathscr{G}\rangle = G = g+g\langle V\mathscr{G}\rangle \tag{9}$$

for the configurationally averaged Green's function can be written

$$G = g +g\sum_1 \langle V_1 G_{\{1\}}\rangle^1, \tag{10}$$

and similarly

$$G_{\{1\}} = g + g \sum_2 \langle V_2 G_{\{2\}} \rangle^2 . \tag{11}$$

The hierarchy of equations

$$G_{\{n-1\}} = g + g \sum_n \langle V_n G_{\{n\}} \rangle^n \tag{12}$$

can then be developed, and this leads to the following expression for G

$$G = g + g \sum_{\{1\}} \langle V_1 g \rangle^1 + g \sum_{\{2\}} \langle V_1 g \langle V_2 g \rangle^2 \rangle^1$$

$$+ g \sum_{\{3\}} \langle V_1 g \langle V_2 g \langle V_3 g \rangle^3 \rangle^2 \rangle^1 + \dots$$

$$\dots + g \sum_{\{n\}} \langle V_1 g \langle V_2 g \langle \dots \langle V_n G_{\{n\}} \rangle^n \rangle^{n-1} \dots \rangle^2 \rangle^1 . \tag{13}$$

We may terminate the hierarchy at any stage by determining $G_{\{n\}}$. In the exact treatment $G_{\{n\}}$ depends on the $(n+1)$ and higher order site-occupation probabilities but, since these are not known, approximations must be made. The simplest solution is to put $G_{\{2\}} \approx G_{\{1\}}$. In the random case this corresponds to the CPA proposed by Soven (1967) and applied to disordered alloys by Taylor (1967). The solution for two-atom correlations has been investigated by Towers (1971).

3. *n*-particle Correlations from Two-particle Data

None of the methods discussed in the previous section are entirely satisfactory when employed in the non-random case. The GCPA solution places an atom in an averaged scattering potential or virtual crystal which is determined by a pair distribution function. Freed and Cohen (1971) consider correlated pairs of atoms placed in a random crystal, and they find a coherent cluster potential such that the average of the scattering from all such pairs is zero. Takeno's (1971) work is similar to Freed and Cohen's in some approximations.

A different approach to the problem is proposed here. By using the probability variation method (PVM) of Clapp (1969, 1971) we develop a system for the extension of these theories to include up to n-atom correlations (where n can be 10 or more) and consider its application to the cell method of Tsukada (1969).

(a) Probability Variation Method

Clapp (1969) has devised a general theoretical method for inferring the higher order cluster probabilities from the pair probability data. He has recently (1971) applied the method to the calculation of the probability distribution of nearest-neighbour configurations for a number of cubic binary alloys from their experimentally determined short-range order parameters.

To apply the PVM we first choose the n-site cluster to be studied, and then assign to this cluster a probability, $P_k(n)$, that if it is chosen randomly in the lattice it should have a configuration of type k. Subject to a series of linear constraints that ensure that the composition and short-range order parameters of the alloy remain fixed, the $P_k(n)$ are varied to maximize the function

$$I(P_k(n)) = -\sum_k P_k(n) \ln P_k(n) .$$

Information theory tells us that any other solution implies that we have more information about the $P_k(n)$ than has been given. The method is based upon the physical assumption that the configurational energy of the lattice does not depend on three(or more)-body interactions and is a function only of the composition and the short-range order parameters.

A further postulate is made that the maximal entropy point of the real lattice ensemble of configurational states always coincides with the maximal point of the artificial ensemble used in the calculations. Clapp (1971) was unable to prove the assumption generally but was able to show that it is valid for a number of cases where the exact result is known.

The proposed method shows considerable improvement over previous methods which involved analytical probability determinations (such as the 'superposition approximation of Kirkwood' (Hill 1956) and the approximation of Hartmann (1968)), for it gives a set of cluster probabilities that are consistent with the composition and short-range order data of the alloy.

(b) Application of PVM to Coherent Potential Theories

We have discussed how the PVM allows the determination of n-atom correlations from the composition and short-range order data of the alloy. In other words, we have the correlation function

$$\langle \sigma_1^A \sigma_2^B \dots \sigma_n^X \rangle = f_{A_1 B_2 \dots X_n}(c, \{\alpha_{ij}\}), \tag{14}$$

where

$$\sigma_i^{\text{host}} = (1, 0) \qquad \text{for a (host, defect) on site } i,$$

$$\sigma_i^{\text{defect}} = 1 - \sigma_i^{\text{host}},$$

c is the concentration of defects and $\{\alpha_{ij}\}$ is the set of Warren short-range order parameters.

It is now a simple process to extend the theories described in Section 2 to include the effects of up to n-particle correlations. The function c_{r+1} of Takeno (1971) becomes

$$c_{r+1}(\alpha' \mid \alpha_1 \alpha_2 \dots \alpha_r) = \frac{f_{\alpha' \alpha_1 \alpha_2 \dots \alpha_r}(c, \{\alpha_{ij}\})}{f_{\alpha_1 \alpha_2 \dots \alpha_r}(c, \{\alpha_{ij}\})}. \tag{15}$$

Taking into account the correlation of up to n atoms is equivalent to terminating the hierarchy by using the approximations

$$\langle D(\alpha')^{-1} \rangle_{\alpha' \alpha_1 \alpha_2 \dots \alpha_{n-1}} \approx \langle D(\alpha')^{-1} \rangle_{\alpha' \alpha_2 \dots \alpha_{n-1}} \tag{16a}$$

and

$$\sigma_{\alpha' \alpha_1 \alpha_2 \dots \alpha_{n-1}} \approx \sigma_{\alpha' \alpha_2 \dots \alpha_{n-1}}. \tag{16b}$$

The extension can be similarly applied to the theory of Freed and Cohen (1971) and to the GCPA. Use of this method has one basic advantage. It allows for the inclusion of experimentally observable short-range order effects but does not require the construction of a coherent potential which includes only the pair correlations. The influence of up to n-atom correlations can be included in the coherent potential by expressing them in terms of the experimentally observable pair correlations. In this

manner we can find a coherent potential which includes n-atom correlation effects but which is a function only of the observable two-atom correlations.

(c) The Cell Method

In the so-called cell method proposed by Tsukada (1969) for the calculation of the electronic structure of a random lattice, the crystal is divided into cells and the Green's function in a cell is calculated for each atomic configuration in it. The influence of the other cells in the crystal is approximated by an average which is determined self-consistently so that the translational symmetry of the Green's function in this configurationally averaged lattice is preserved.

We may use the method to include the microscopic configuration effects of up to n-atom clusters by determining the probabilities of the n-atom configurations using the PVM. We expect that the solution will become better as n becomes larger, since Tsukada (1969) has shown that the approximations improve as n increases. The self-consistency relation (Tsukada's equation (2.17))

$$N^{-1} \sum_k \frac{1}{\mathscr{A} - J_k} = \sum_{p=1}^{2^n} \omega_p \left\{ z - H_0^{(p)} - \mathscr{A} + N \bigg/ \left(\sum_k \frac{1}{\mathscr{A} - J_k} \right) \right\}^{-1} \qquad (17)$$

is already in the form required for applying the PVM. Here ω_p is the probability of the cell configuration p and $H_0^{(p)}$ is the Hamiltonian for that configuration. The PVM may be used to find the value of $\omega_p = P_p(n)$ for substitution into equation (17). Thus n-atom correlation effects may then be included in an analysis based upon the measured short-range order parameters. It should be noted that this method gives analytic solutions for the self-energy, unlike some CPA extensions for which solutions cannot generally be found (Nickel and Butler 1973).

4. Conclusions

We have seen how the probability variation method of Clapp (1969) may be used in the calculation of the Green's functions of an alloy with short-range order. Previously, theories have either been truncated after an allowance for two-particle correlations or have only included approximations to the n-particle correlations. The present work has shown that use of the probability variation method allows the n-particle correlations to be determined from experimentally observable two-particle correlations. Ways in which the method may be applied to existing theories of disordered alloys have been outlined.

Acknowledgment

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