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General relationship between concentration derivatives and correlation functions for alloys[*]

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A general relationship is derived between the concentration derivative of any ensemble-averaged quantity and the correlation function of that quantity with fluctuations in the concentration. This relationship is then used to obtain general formulas for the concentration derivatives of the magnetization $M(\vec{\kappa})$, and of the Warren short-range order parameters, $\alpha(\vec{R})$, for the case of binary substitutional alloys. The use of these formulas in the analysis of diffuse elastic neutron-scattering data and in the analysis of the effects of short-range order is discussed briefly.

I. INTRODUCTION

Marshall[1] has derived, subject to certain restrictions, a relationship between the concentration derivative of the average magnetic moment in a ferromagnetic binary substitutional alloy and the magnetic elastic diffuse scattering cross section for neutrons in the forward direction. It is shown here that the Marshall relationship is simply a particular case of a general relationship valid without restriction. Although the explicit derivation given here is restricted for simplicity of exposition to the case of binary alloys, the resulting general relationship is given in a form which is correct for multicomponent alloys as well. The derivation of this relationship is given in Sec. II. Its use is illustrated in Secs. III and IV by considering explicitly the resultant formulas for the concentration dependence of the magnetization and of the Warren short-range order parameters for binary substitutional alloys.

II. GENERAL RELATIONSHIP

In general, any intensive quantity y, which characterizes an alloy depends not only on the chemical composition of the alloy, but also on thermodynamic variables and on the various n-site correlation functions for the alloy. Thus, in order to derive or even to define any general relationship involving a concentration derivative dy/dc (or dy/dc_i for a multicomponent alloy), it is first necessary to define precisely the meaning of that concentration derivative. One defines dy/dc operationally as the limiting value of $\delta y/\delta c$ for $\delta c \rightarrow 0$, as determined by measuring y under identical thermodynamic conditions for a series of samples of known chemical compositions prepared under identical heat and mechanical treatments. In order to formulate this definition mathematically, it is convenient to consider an ensemble of samples, each prepared in an identical manner from the same melt of fixed chemical composition c, and each having N atoms. Due to statistical fluctuations, each member of the ensemble will be characterized by a slightly different concentration $\hat{c}$, and slightly different values for each of the n-site correlation functions. The concentration derivative dy/dc can then be defined in terms of the fluctuations

$$\delta\hat{y} \equiv \hat{y} - y \equiv \hat{y} - \langle \hat{y} \rangle \tag{1}$$

and $\delta\hat{c}$, where the angular brackets $\langle \cdots \rangle$ denote an ensemble average.

To do so, it is necessary to introduce some set of intensive variables $\{\hat{\xi}_i\}$, which satisfy the condition,

$$\langle (\delta\xi_i)^2 \rangle \sim N^{-1} \tag{2}$$

for all i and which, with $\hat{c}$, form a complete set for the characterization of each sample. Such a set can be constructed from the set of all n-site correlation functions. In terms of these variables and to lowest order in N^{-1}, the expansion

$$\delta\hat{y} = \frac{\partial\hat{y}}{\partial\hat{c}}\,\delta\hat{c} + \sum_i \frac{\partial\hat{y}}{\partial\hat{\xi}_i}\,\delta\hat{\xi}_i \tag{3}$$

defines the fluctuation $\delta\hat{y}$. It is convenient to choose the variables $\hat{\xi}_i$ to be orthogonal to $\hat{c}$:

$$\langle \delta\hat{\xi}_i\,\delta\hat{c} \rangle = 0 \ . \tag{4}$$

This, together with condition (2) and the definition of our ensemble, ensures that the variables ξ_i do not change with c from sample to sample in the experimental determination of dy/dc. Thus, the experimentally measured dy/dc is defined mathematically by setting the fluctuations $\delta\hat{\xi}_i$ equal to zero in Eq. (3) and dividing by $\delta\hat{c}$. One finds the result

$$\frac{dy}{dc}=\left(\frac{\partial\hat{y}(\hat{c},\{\hat{\xi}_i\})}{\partial\hat{c}}\right)_{\delta\hat{c}=\delta\hat{\xi}_i=0}. \tag{5}$$

Now, the desired relationship between dy/dc and $\langle\hat{y}\delta\hat{c}\rangle$ follows immediately. Substituting Eq. (3) into Eq. (1), multiplying both sides by $\delta\hat{c}$, taking an ensemble average, and using Eq. (5) and the orthogonality condition (4), one finds the result

$$\langle\hat{y}\delta\hat{c}\rangle=\frac{dy}{dc}\langle(\delta\hat{c})^2\rangle\ . \tag{6}$$

For the case of a multicomponent alloy Eq. (6) assumes the very similar form

$$\langle\hat{y}\delta\hat{c}_i\rangle=\frac{dy}{dc_i}\langle(\delta\hat{c}_i)^2\rangle\ . \tag{7}$$

Here, due to the nonorthogonality of the partial concentrations $\hat{c}_i$, dy/dc_i is not equal to $\partial y/\partial c_i$ but instead is given by the equation

$$\frac{dy}{dc_i}=\frac{\partial y}{\partial c_i}+\sum_{j\neq i}\frac{\langle\delta\hat{c}_j\delta\hat{c}_i\rangle}{\langle(\delta\hat{c}_i)^2\rangle}\frac{\partial y}{\partial c_j}\ , \tag{8}$$

where $\partial y/\partial c_i$ is defined as is dy/dc for a binary alloy:

$$\frac{\partial y}{\partial c_i}\equiv\left\langle\frac{\partial\hat{y}\{\hat{c}_j\},\{\hat{\xi}_j\})}{\partial\hat{c}_i}\right\rangle. \tag{9}$$

Thus, for an n-component alloy, Eq. (8) assumes the form

$$\langle\hat{y}\delta\hat{c}_i\rangle=\sum_{j=1}^{n-1}\frac{\partial y}{\partial c_j}\langle\delta\hat{c}_j\delta\hat{c}_i\rangle\ . \tag{10}$$

By explicitly calculating the mean-square fluctuation $\langle(\delta\hat{c})^2\rangle$ and the quantities $\langle\delta\hat{c}_j\delta\hat{c}_i\rangle$, one can reduce Eqs. (6) and (10) to forms more meaningful to the experimentalist. For this purpose we consider only ensembles of single-crystal samples. Polycrystalline and powder specimens as well as single-crystal specimens are well represented as ensemble averages over such samples. Nonsubstitutional alloys can be treated simply by considering vacancies as an additional chemical species.

First, consider the case of binary substitutional alloys. For that case, it is convenient to introduce the chemical order parameters

$$\hat{\alpha}(\vec{n})=\sum_{\vec{m}}\frac{(\hat{p}_{\vec{n}+\vec{m}}-c)(\hat{p}_{\vec{m}}-c)}{Nc(1-c)}\ , \tag{11}$$

their Fourier transform

$$\hat{S}(\vec{\kappa})=\sum_{\vec{n}}\hat{\alpha}(\vec{n})e^{i\vec{\kappa}\cdot\vec{n}}\ , \tag{12}$$

and the corresponding ensemble averages $\alpha(\vec{n})$ and $S(\vec{\kappa})$. Here, for an alloy $A_{1-c}B_c$,

$$\hat{p}_{\vec{n}}=\begin{cases}1 & \text{if an atom of type } B \text{ is on site } \vec{n},\\ 0 & \text{otherwise}\end{cases} \tag{13}$$

is a site-occupation number. For the random alloy one finds the simple results $\alpha(\vec{n})=\delta_{\vec{n}\vec{0}}$ and $S(\vec{\kappa})=1$. In the presence of only short-range order, the $\alpha(\vec{n})$ are the usual Warren short-range order parameters and yield an additional diffuse contribution to $S(\vec{\kappa})$. Long-range order introduces superlattice Bragg peaks in $S(\vec{\kappa})$. From Eqs. (11) and (12) and the equation

$$\delta\hat{c}=N^{-1}\sum_{\vec{n}}\hat{p}_{\vec{n}}-c\ , \tag{14}$$

one finds the result

$$\langle(\delta\hat{c})^2\rangle=N^{-1}c(1-c)S(0)\ , \tag{15}$$

and hence the form

$$\langle\hat{y}\delta\hat{c}\rangle=N^{-1}c(1-c)S(0)\frac{dy}{dc} \tag{16}$$

for Eq. (6). It should be noted that as defined here $S(\vec{\kappa})$ approaches its limiting value $S(0)$ continuously and gradually as $\kappa\to0$.[2] Both the diffuse and the Bragg contributions to $S(\vec{\kappa})$ can be measured by the elastic scattering of neutrons or x rays.

For the case of crystalline multicomponent alloys of any type, one can introduce the generalized order parameters

$$\hat{\alpha}_{ij}(\vec{n})=\sum_{\vec{m}}\frac{(\hat{p}^{(i)}_{\vec{n}+\vec{m}}-c_i)(\hat{p}^{(j)}_{\vec{m}}-c_j)}{Nc_i[c_j+\delta_{ij}(1-2c_j)]}\ , \tag{17}$$

and their Fourier transforms $\hat{S}_{ij}(\vec{\kappa})$, in terms of the partial concentrations c_i and the corresponding site-occupation numbers

$$\hat{p}^{(i)}_{\vec{n}}=\begin{cases}1 & \text{if an atom of type } i \text{ is on site } \vec{n},\\ 0 & \text{otherwise}\ .\end{cases} \tag{18}$$

One finds the result

$$\langle\delta\hat{c}_j\delta\hat{c}_i\rangle=N^{-1}c_i[c_j+\delta_{ij}(1-2c_j)]S_{ij}(0)\ , \tag{19}$$

and hence the forms

$$\frac{dy}{dc_i}=\frac{\partial y}{\partial c_i}+\sum_{j\neq i}\frac{c_jS_{ij}(0)}{(1-c_i)S_{ii}(0)}\frac{\partial y}{\partial c_j} \tag{20}$$

and

$$\langle\hat{y}\delta\hat{c}_i\rangle=N^{-1}c_i\sum_j\left([c_j+\delta_{ij}(1-2c_j)]\,S_{ij}(0)\frac{\partial y}{\partial c_j}\right) \tag{21}$$

for Eqs. (8) and (10), respectively. Note that for the random alloy, $S_{ij}(0)$ is equal to $2\delta_{ij}-1$ and that in all cases, $S_{ij}(0)$ has the sign of $2\delta_{ij}-1$.

There is one very useful generalization of our fundamental equations (6), (10), (16), and (21). As is done in Eqs. (1), (11), (14), and (17) for $\delta\hat{y}$, $\delta\hat{c}$, $\hat{\alpha}(\vec{n})$, and $\hat{\alpha}_{ij}(\vec{n})$, it is often convenient to define a quantity $\hat{y}$ as an explicit function of c or of the c_i's as well as of $\hat{c}$ or of the $\hat{c}_i$'s. In that case one must equate dy/dc to $\langle \partial\hat{y}/\partial\hat{c}+\partial\hat{y}/\partial c\rangle$ rather than just to $\langle \partial\hat{y}/\partial\hat{c}\rangle$. This leads to the replacement of the derivative dy/dc by the quantity $dy/dc - \langle \partial\hat{y}/\partial c\rangle$ in Eqs. (6) and (16), yielding the results

$$\langle \hat{y}\delta\hat{c}\rangle = \left(\frac{dy}{dc} - \left\langle \frac{\partial\hat{y}}{\partial c}\right\rangle\right)\langle(\delta\hat{c})^2\rangle \tag{22}$$

and

$$\langle \hat{y}\delta\hat{c}\rangle = N^{-1}c(1-c)S(0)\left(\frac{dy}{dc} - \left\langle \frac{\partial\hat{y}}{\partial c}\right\rangle\right) \tag{23}$$

for binary alloys. Similarly, for multicomponent alloys one must equate $\partial y/\partial c_i$ to $\langle \partial\hat{y}/\partial\hat{c}_i + \partial y/\partial c_i\rangle$ rather than just to $\langle \partial\hat{y}/\partial\hat{c}_i\rangle$. This leads to the replacement of the partial derivative $\partial y/\partial c_i$ by the quantity $\partial y/\partial c_i - \langle \partial\hat{y}/\partial c_i\rangle$ in Eqs. (10) and (21), yielding the results

$$\langle \hat{y}\delta\hat{c}_i\rangle = \sum_j\left(\frac{\partial y}{\partial c_j} - \left\langle \frac{\partial\hat{y}}{\partial c_j}\right\rangle\right)\langle \delta\hat{c}_j\delta\hat{c}_i\rangle \tag{24}$$

and

$$\langle \hat{y}\delta\hat{c}_i\rangle = N^{-1}c_i\sum_j\Bigg[[c_j+\delta_{ij}(1-2c_j)] \times S_{ij}(0)\left(\frac{\partial y}{\partial c_j} - \left\langle \frac{\partial\hat{y}}{\partial c_j}\right\rangle\right)\Bigg]\,. \tag{25}$$

Equations (22)–(25) constitute the primary results of this paper expressed in a general form. However, there remains one more general result to be given. If one chooses the variables $\hat{\xi}_i$ to satisfy the orthogonality conditions

$$\langle \delta\hat{\xi}_i\delta\hat{\xi}_j\rangle = \delta_{ij}\langle(\delta\hat{\xi}_i)^2\rangle \tag{26}$$

for all i and j, as well as the condition (4), then by a derivation exactly analogous to that of Eq. (22), one finds the result

$$\langle \hat{y}\delta\hat{\xi}_i\rangle = \left(\frac{dy}{d\xi_i} - \left\langle \frac{\partial\hat{y}}{\partial \xi}\right\rangle\right)\langle(\delta\hat{\xi}_i)^2\rangle\,, \tag{27}$$

where $dy/d\xi_i = \partial y/\partial\xi_i$ is defined in exact analogy with dy/dc, and where $\hat{\xi}_i$ is any quantity which satisfies Eqs. (4) and (26). The choice $\hat{\xi}_i=\hat{c}$ reduces Eq. (27) to form (22); the choice of $\hat{\xi}_i$ as an orthogonalized order parameter yields the result

$$\begin{aligned}\langle \hat{y}\delta\hat{\alpha}(\vec{n})\rangle ={}& \langle[\delta\hat{\alpha}(\vec{n})]^2\rangle\left(\frac{\partial y}{\partial\alpha(\vec{n})} - \left\langle \frac{\partial\hat{y}}{\partial\alpha(\vec{n})}\right\rangle\right) \\ &+ N^{-1}c(1-c)S(0)\left[\left(\frac{d}{dc}+\frac{1-2c}{c(1-c)}\right)\alpha(\vec{n})\right] \\ &\times\left[\frac{dy}{dc} - \left\langle\frac{\partial\hat{y}}{\partial c}\right\rangle - \left(\frac{\partial y}{\partial\alpha(\vec{n})} - \left\langle \frac{\partial\hat{y}}{\partial\alpha(\vec{n})}\right\rangle\right)\right. \\ &\left.\times\left(\frac{d}{dc}+\frac{1-2c}{c(1-c)}\right)\alpha(\vec{n})\right]\end{aligned} \tag{28}$$

or, for the case of long-range order, the analogous equation with $\hat{\alpha}(\vec{n})$ and $\alpha(\vec{n})$ replaced by $\hat{S}(\vec{\kappa}_i)$ and $S(\vec{\kappa}_i)$, respectively, with $\vec{\kappa}_i$ a superlattice reciprocal vector. Such equations are of less interest than Eqs. (22)–(25) because such higher-order correlation functions as $\langle \hat{y}\delta\hat{\alpha}(n)\rangle$ or $\langle \hat{y}\delta\hat{S}(\vec{\kappa}_i)\rangle$ cannot be measured directly, whereas $\langle \hat{y}\delta\hat{c}\rangle$ can be measured directly in many cases, such as those discussed in Sec. III.

III. CONCENTRATION DERIVATIVES OF THE MAGNETIZATION

It is useful in studying magnetic alloys to establish relations between magnetization measurements and neutron-scattering measurements. The basic quantities to be related are the ensemble average μ of the sample average magnetic moments

$$\hat{\mu} = N^{-1}\sum_{\vec{n}}\hat{\mu}_{\vec{n}} \tag{29}$$

and, for binary substitutional alloys, the ensemble average of the quantity

$$\hat{\mathfrak{M}}(\vec{\kappa}) = [Nc(1-c)]^{-1}\sum_{\vec{m},\vec{n}}\hat{\mu}_{\vec{m}}\hat{f}_{\vec{m}}(\vec{\kappa})(p_{\vec{m}+\vec{n}}-c)e^{i\vec{\kappa}\cdot\vec{n}}\,. \tag{30}$$

Here, $\hat{\mu}_{\vec{n}}$ is the z component of the total moment associated with the site $\vec{n}$, and $\hat{f}_{\vec{n}}(\vec{\kappa})$ is the form factor associated with that moment. The quantity $\mathfrak{M}(\vec{\kappa})$ is directly measured by the magnetic diffuse elastic scattering of polarized neutrons[3] and also can be determined approximately from an analysis of the scattering cross section for unpolarized neutrons.[1] Noting that Eq. (30) yields the result

$$\mathfrak{M}(0) = N\langle\hat{\mu}\delta\hat{c}\rangle/[c(1-c)]\,, \tag{31}$$

and that $\hat{f}_{\vec{m}}(0)=1$ by the definition of the form factor, one finds that the relation

$$\frac{d\mu}{dc} = \frac{\mathfrak{M}(0)}{S(0)} \tag{32}$$

follows immediately from Eq. (16). Equation (32) is just the Marshall relation, but is derived here without assuming chemical randomness, ferromagnetic ordering, or the linearity of the dependence of any moment $\hat{\mu}_{\vec{n}}$ on its local environment.

In common practice, the quantities $\mathfrak{M}(\vec{\kappa})$ and $S(\vec{\kappa})$ are measured only down to some minimum value of κ, $\kappa_{\min} \gtrsim 0.1$ Å, and the values $\mathfrak{M}(0)$ and $S(0)$ are determined by extrapolation. Relationship (32) allows one to check the validity of one's data analysis, in particular, the validity of the theoretical or phenomenological curves used for the extrapolations to $\kappa = 0$. In at least one case, that of concentrated Ni-Cr and Ni-V alloys,[3] Eq. (32) establishes the existence of important long-range effects not seen by neutron scattering. Such effects could arise from band saturation, which can lead to long-range charge transfer.

Useful relations also exist between the higher-order concentration derivatives $d^n\mu/dc^n$ and the quantities

$$\mathfrak{M}_n(\vec{\kappa}) = \sum_{\vec{n}_1, \ldots, \vec{n}_{n-1}} \Psi_n(\vec{\kappa}; \vec{n}_1, \ldots, \vec{n}_{n-1}) \tag{33}$$

for $\vec{\kappa} = 0$. Here,

$$\Psi_n(\vec{\kappa}; \vec{n}, \ldots, \vec{n}_{n-1}) = \langle \hat{\eta}_n(\vec{\kappa}; \vec{n}_1, \ldots, \vec{n}_{n-1}) \delta\hat{\mathfrak{M}}(-\vec{\kappa}) \rangle \tag{34}$$

is a correlation function of the Fourier transform

$$\delta\hat{\mathfrak{M}}(\vec{\kappa}) = \sum_{\vec{n}} [\hat{\mu}_{\vec{n}} f_{\vec{n}}(\vec{\kappa}) - \langle \hat{\mu} \hat{f}(\vec{\kappa}) \rangle] e^{i\vec{\kappa}\cdot\vec{n}} \tag{35}$$

of fluctuations in the magnetization with the quantity $\hat{\eta}_n(\vec{\kappa}; \vec{n}_1, \ldots, n_{\vec{n}-1})$, which reduces to an ordinary n-site chemical order parameter for $\kappa = 0$, is equal to zero if $\vec{n}_i = \vec{n}_j$ for any $i \neq j$, and is given by the equation

$$\begin{aligned} \hat{\eta}_n(\vec{\kappa}; \vec{n}_1, \ldots, \vec{n}_{n-1}) &= [Nc(1-c)]^{-1} \\ &\times \sum_{\vec{m}} (\hat{p}_{\vec{n}_1+\vec{m}} - c) \cdots (\hat{p}_{\vec{n}_{n-1}+\vec{m}} - c)(\hat{p}_{\vec{m}} - c)\, e^{i\vec{\kappa}\cdot\vec{m}} \end{aligned} \tag{36}$$

otherwise. Choosing $\hat{y}$ to be given by the quantity

$$\frac{d\hat{\mu}}{dc} = [Nc(1-c)S(0)]^{-1} \sum_{\vec{n}, \vec{m}} (\hat{p}_{\vec{n}} - c)\hat{\mu}_{\vec{m}} \tag{37}$$

in Eq. (23), so that y is equal to $d\mu/dc$, one finds the result

$$\begin{aligned} \mathfrak{M}_2(0) = S(0) \frac{d\mu}{dc} \left((1-2c)[S(0)-1] + c(1-c) \frac{dS(0)}{dc} \right) \\ + c(1-c)S(0)^2 \frac{d^2\mu}{dc^2} \,. \end{aligned} \tag{38}$$

Similar but more complicated relations are found for higher n. For the case of random alloys, $S(0)$ is equal to one, the coefficient of $d\mu/dc$ in Eq. (38) vanishes, the quantities Ψ_n are proportional to $[c(1-c)]^{n-1}$, and one can prove, by induction, the result

$$\mathfrak{M}_n(0) = [c(1-c)]^{n-1} \frac{d^n\mu}{dc^n} \,. \tag{39}$$

As will be discussed elsewhere, the quantities $\Psi_n(\vec{\kappa}; \vec{n}_1, \ldots, \vec{n}_{n-1})$ are useful parameters in the analysis of neutron-scattering data. In particular, the quantitiy $\mathcal{T}(\vec{\kappa})$, which is directly proportional to the cross section for the magnetic diffuse elastic scattering of unpolarized neutrons is given exactly by the infinite series

$$\begin{aligned} \mathcal{T}(\vec{\kappa}) = \sum_{n=1}^{\infty} (n!)^{-1} \sum_{\vec{n}_1, \ldots, \vec{n}_{n-1}} \Psi_n(\vec{\kappa}; \vec{n}_1, \ldots, \vec{n}_{n-1}) \\ \times \Phi_n(-\vec{\kappa}; \vec{n}_1, \ldots, \vec{n}_{n-1}) \,, \end{aligned} \tag{40}$$

where $\Phi_n(\vec{\kappa}; \vec{n}, \ldots, \vec{n}_{n-1})$ is the value assumed by the quantity

$$[c(1-c)]^{1-n} \Psi_n(\vec{\kappa}; \vec{n}_1, \ldots, \vec{n}_{n-1}) \,,$$

in the limit of a perfectly random alloy.

IV. SUM RULES FOR CHEMICAL ORDER PARAMETERS

For the case of binary substitutional alloys, the general relationship (23) with $\hat{y}$ set equal to $\hat{\alpha}(n)$ immediately yields a useful sum rule for the parameters

$$\begin{aligned} \eta(\vec{n}, \vec{m}) &= \langle \hat{\eta}_3(0; \vec{n}, \vec{m}) \rangle \\ &= [c(1-c)]^{-1} (1 - \delta_{\vec{n}\vec{m}})(1 - \delta_{\vec{n}\vec{0}})(1 - \delta_{\vec{m}\vec{0}}) \\ &\quad \times \langle (\hat{p}_{\vec{n}} - c)(\hat{p}_{\vec{m}} - c)(\hat{p} - c) \rangle \,. \end{aligned} \tag{41}$$

Direct evaluation of the correlation function $\langle \hat{\alpha}(\vec{n}) \delta\hat{c} \rangle$ yields the result

$$\begin{aligned} \langle \hat{\alpha}(\vec{n}) \delta\hat{c} \rangle = N^{-1} \Big((1-2c)[2(1-\delta_{\vec{n}\vec{0}})\alpha(\vec{n}) + \delta_{\vec{n}\vec{0}} S(0)] \\ + \sum_{\vec{m}} \eta(\vec{n}, \vec{m}) \Big) . \end{aligned} \tag{42}$$

Substituting this result into Eq. (25), one finds the sum rule,

$$\begin{aligned} \sum_{\vec{m}} \eta(\vec{n}, \vec{m}) = (1 - \delta_{\vec{n}\vec{0}}) \Big((1-2c)[S(0) - 2] \\ + c(1-c)S(0) \frac{d}{dc} \Big) \alpha(\vec{n}) \,. \end{aligned} \tag{43}$$

For the case of chemical ordering or clustering induced by pairwise forces and for only weak short-range order, the sum rule assumes the simple form

$$\sum_{\vec{m}} \eta(\vec{n}, \vec{m}) = 2(1 - 2c)(1 - \delta_{\vec{n}\vec{0}})[S(0) - 1]\alpha(\vec{n}) \qquad (44)$$

in the usual approximation that $\alpha(\vec{n})$ is proportional to $c(1-c)$ for $n \neq 0$.

Using the methods of Sec. III, one can obtain corresponding sum rules for all of the n-site chemical order parameters in terms of higher-order concentration derivatives of the order parameters $\alpha(\vec{n})$. Also, similar sum rules can be obtained for the case of multicomponent alloys, using Eqs. (17)–(20) and (25). The n-site order parameters cannot be directly measured for $n \geq 3$, yet a knowledge of the n-site order parameters is necessary for the analysis of unpolarized neutron-scattering data for some alloys and is necessary for many alloy calculations. Thus, sum rules such as Eqs. (43) and (44) serve as useful adjuncts to approximate calculations of the n-site order parameters.

V. SUMMARY

A general thermodynamic relation, valid for all alloy systems, has been derived. This relation connects the derivatives of any intensive quantity with respect to chemical composition and long- and short-range order to the appropriate correlations between that quantity and fluctuations in chemical composition or long- or short-range order. That relation has been used to derive specific equations which relate the concentration derivatives of the bulk magnetization of a binary alloy to correlation functions measured by magnetic diffuse neutron scattering. The simplest of those relations has been previously derived, but only under special restrictive conditions. Sum rules relating the three-site chemical order parameters to concentration derivatives of the measurable two-site order parameters have also been derived. Finally, it has been made clear how other such relations can be obtained.

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[1] W. Marshall, J. Phys. C 1, 88–101 (1968).

[2] Although Marshall (Ref. 1) claims that $S(0)$ is equal to zero with $S(\vec{\kappa})$ discontinuous or changing abruptly as $\kappa \to 0$, that result, which contains no useful physical information, holds only if one considers an ensemble of samples with no fluctuations in the concentration, not if one considers a grand canonical ensemble as is done here. This question is discussed in detail by S. C. Moss and P. C. Clapp, Phys. Rev. 171, 764 (1968).

[3] J. W. Cable and R. A. Medina, Phys. Rev. B 13, 4868–4874 (1976).