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LETTER TO THE EDITOR

A simple and accurate theory of short-range order in alloys

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Abstract. We propose a very simple method of calculating short-range order parameters α_{ij} in disordered alloys using a series expansion in powers of a parameter $\gamma = \exp(-1/\xi)$ where ξ is the dimensionless correlation length of the pair correlation function. In our approximation the sum rule $\alpha_{ii} = 1$ is satisfied exactly, unlike in previous theories. In the zeroth order our approach leads to the spherical model results. The high accuracy of the theory developed is illustrated by comparing its results with those of Monte Carlo simulation and estimating the pair interactions from diffuse scattering data. In the latter problem pair-interaction potentials are explicitly expressed in terms of experimentally determined quantities.

The problem of finding a theoretical description of short-range order (SRO) in alloys is widely discussed. One of the reasons for this is that the Fourier transform of the pair correlation function (PCF) is proportional to the directly measured intensity of x-ray or neutron diffuse scattering (see, for example, Krivoglaz 1969). To interpret the experimental data, the Krivoglaz–Clapp–Moss (KCM) theory (Krivoglaz 1969) is extensively used. However, it is essentially based on the mean-field approximation in which correlations are ignored from the very beginning (Brout 1965), and leads to quantitatively incorrect results (Gilder and Vignesoult 1984, Stark *et al* 1983). In addition, the well-known sum rule $\alpha_{ii} = 1$ where α_{ij} is the Warren–Cowley SRO parameter (Krivoglaz 1969), i and j being lattice sites, is not satisfied in the KCM approximation. At the present time there is a possibility of calculating SRO parameters or diffuse intensities more precisely in the framework of the cluster variation method (CVM) at the different levels of approximation (Kikuchi and Sato 1974, Mohri *et al* 1985) or of the cluster field method (CFM), its recently developed simplification (Vaks *et al* 1988, 1989). Unfortunately, in these fairly sophisticated calculations the sum rule is also violated.

Several authors have considered the spherical model (SM) (see, for instance, Ziman 1979) as an alternative to the KCM theory (Philhours and Hall 1968, Hoffmann 1972). Hoffmann has pointed out an interesting circumstance in which the SM results for correlations are rather good and, in particular, far exceed KCM ones in accuracy. Moreover, the SM satisfies the above-mentioned identity. Here we show that developing an approach in which the SM is obtained as the zero-order approximation and the sum rule is fulfilled is not accidental. As will be argued below, our theory leads to very accurate results.

The Hamiltonian under consideration is that of the Ising model for binary alloys,

$$H = -\frac{1}{2} \sum_{i \neq j} V_{ij} p_i p_j - \mu \sum_i p_i$$

where V_{ij} is the pair ordering potential, p_i the occupation number and μ the variable playing the role of chemical potential (de Fontaine 1979). The corresponding partition function (more precisely, the generating functional for Green functions) is (Vasil'ev 1976)

$$Z[A] = C \int D\varphi \exp(\frac{1}{2}\varphi\Delta\varphi + \beta\mu\varphi + c\Delta\varphi + F(\varphi) + \varphi A) \quad (1)$$

where

$$\exp F(\varphi) = \delta(\varphi + c - 1) + \delta(\varphi + c)$$

$\varphi(A)$ is the (source) lattice field, $\beta = 1/k_B T$ the inverse temperature and $\Delta = \beta V$. To proceed with the irreducible PCF, we have introduced the average c of the lattice field and its fluctuation φ . We have used reduced notation in which summation over site indices is implied.

From the expression (1) the following equations for m and the PCF can be derived (Tokar 1985)

$$\partial \ln R[\varphi] / \partial \varphi_i |_{\varphi=0} = 0 \quad (2)$$

$$\partial^2 \ln R[\varphi] / \partial \varphi_i \partial \varphi_j |_{\varphi=0} = 0 \quad (3)$$

where

$$R[\varphi] = \exp[\frac{1}{2}(\partial/\partial\varphi)G(\partial/\partial\varphi)] \exp(-\frac{1}{2}\varphi\Sigma\varphi + \beta\mu\varphi + c\Delta\varphi + F(\varphi))$$

is a generating functional for the S -matrix and G and Σ are, the PCF and self-energy, respectively, which are connected by the usual relation

$$G = (-\Delta - \Sigma)^{-1}. \quad (4)$$

To solve equations (2) and (3) we use the series expansion in powers of a parameter $\gamma = \exp(-1/\xi)$ where ξ is a correlation length of the PCF measured in units of distance between nearest neighbour (NN) sites (Tokar 1985). This expansion is based on the exponential decrease of the PCF away from critical points with increasing distance (see, for example, Ziman (1979), ch 1)

$$G_{ij} = F(i-j) \exp(-|i-j|/\xi) = O(\gamma^{|i-j|})$$

where $F(i)$ is a function varying at a less than exponential rate. Let us consider for simplicity the disordered phase in which all quantities depend only upon the distance between sites. Below, the subscript 's' denotes the matrix elements corresponding to the s th coordination shell. We find that the off-diagonal part of the self-energy is of order γ^2 , except for in the case of equiatomic alloys in which it is of order γ^3 . The corresponding low-order expression for Σ in the case of cubic lattices is

$$\begin{aligned} \Sigma_1 &= A\alpha_1^2 + B\alpha_1^3 \\ \Sigma_s &= A\alpha_s^2 \quad s = 2, 3 \\ \Sigma_s &= 0 \quad s > 3 \end{aligned}$$

$$A = \frac{1}{2}(1-2c)^2/[c(1-c)]^2 \quad B = \frac{1}{6}\{[1-6c(1-c)]^2 - 3(1-2c)^4\}/[c(1-c)]^3$$

where c is the concentration, $\alpha_s = G_s/c(1-c)$.

In the case under consideration equation (4) becomes

$$\alpha_s = \Omega^{-1} \int d^3k \left[\lambda_s(k) / \left(a_0 + \sum_{r \neq 0} Z_r a_r \lambda_r(k) \right) \right] \quad (5)$$

where

$$a_0 = -c(1-c)\Sigma_0 \quad a_s = -c(1-c)(\Delta_s + \Sigma_s) \quad s \geq 1 \quad (6)$$

and the elements of the α^{-1} matrix, and

$$\lambda_s(k) = Z_s^{-1} \sum_{(s)} \exp(ikj) \quad \lambda_0(k) = 1. \quad (7)$$

Integration in (5) and summation in (7) is over the Brillouin zone of volume Ω and over the s th shell of which Z_s is the coordination number. The identity $\alpha_0 = 1$ in our approximation turns out to be simply a consequence of the equations (2) and (3) at $i = j$. It completes the set of equations for quantities α_s and a_0 (or Σ_0). An explicit expression for the latter quantity can be obtained by inserting the sum rule into the exact relation

$$1 - a_0 \alpha_0 - \sum_{s \neq 0} Z_s a_s \alpha_s = 0 \quad (8)$$

which immediately follows from (5). Inserting, in turn, (8) into (5) we obtain the set of equations for SRO parameters with the level of approximation being determined by the expression for the off-diagonal part of Σ . We have already seen above that this quantity is at least of order γ^2 . Setting, therefore, $\Sigma_s = 0$ in the zeroth order for all $s \geq 1$ we obtain the SM result. To obtain the KCM result, the last term in the left-hand side of equation (8) has to be neglected completely, so the sum rule is violated.

Our approach leads to particularly simple results when setting $\Delta_s = \Sigma_s = 0$ for all $s > 1$. In this case one can easily derive, from (5), the expression $\alpha_s = P_0^{-1}(x)P_s(x)$, where the auxiliary variable x is found from the equation

$$P_0(x) = Z_1 c(1-c)(\Delta_1 + \Sigma_1)$$

and

$$P_s(x) = \Omega^{-1} \int d^3k \frac{\lambda_s(k)}{x - \lambda_1(k)}$$

is the NN interaction Green function, which can be expressed for the cubic lattices in terms of the complete elliptic integral (Morita and Horiguchi 1971).

In figure 1 we show the temperature dependence of the NN SRO parameter for three concentrations in the case of NN interaction on FCC and BCC lattices calculated according to (5) and (8). Our results are compared with those of a Monte Carlo simulation (Bichara *et al* 1982). Here, three successive approximations have been used:

(i) a spherical model in which the off-diagonal part of the self-energy is neglected (zero order in γ),

(ii) $\Sigma_1 = A\alpha_1^2$, $\Sigma_s = 0$ for all $s > 1$ (second order in γ),

(iii) $\Sigma_1 = A\alpha_1^2 + B\alpha_1^3$, $\Sigma_2 = A\alpha_2^2$, $\Sigma_s = 0$ for all $s > 2$ (third order in γ).

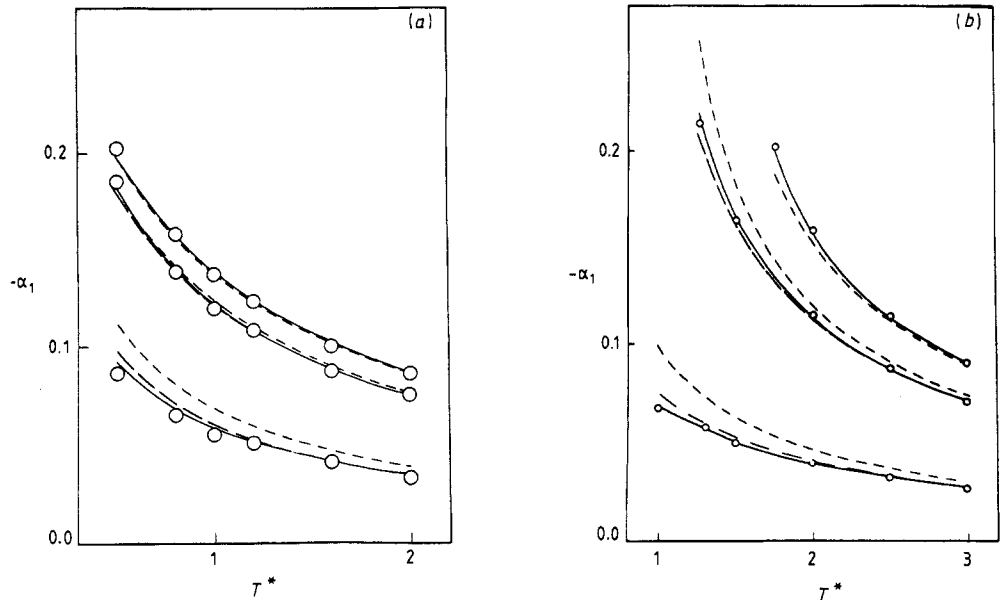


Figure 1. Variation of the NN SRO parameter α_1 versus reduced temperature $T^* = \Delta^{-1}$ in the case of a NN interaction on (a) FCC and (b) BCC lattices for concentrations $c = 0.5$ (upper group of curves), $c = 0.3$ (middle group) and $c = 0.1$ (lower group). Circles denote Monte Carlo results (Bichara *et al* 1982); data have been read off from their figures. Approximations (i)–(iii) (see text) have been used (short-dashed, long-dashed, and full curves, respectively). In the case $c = 0.5$ approximations (i) and (ii) give identical results.

It is seen that even zero-order approximation leads to reasonable agreement with the simulation data, especially when the concentration is large. The results obtained in the following two approximations demonstrate rapid convergence and agree remarkably well with the Monte Carlo ones.

The inverse problem, namely the determination of the pair interactions from diffuse scattering data, is also of considerable interest. Our theory gives the explicit expression for these interactions (see equation (6))

$$V_s = -k_B T (a_s / c(1 - c) + \Sigma_s) \quad s \geq 1. \quad (9)$$

The right-hand side of this relation is a combination of quantities α_s and $a_s = (\alpha^{-1})_s$, which can be determined experimentally, as explained by Vaks *et al* (1988). To illustrate this result, we apply it to the interpretation of neutron measurements of Lefebvre *et al* (1981) for the $\text{Ni}_{0.765}\text{Fe}_{0.235}$ alloy and compare the results obtained with those of the CFM. Corresponding values of pair potentials are given in table 1. The results appear to be very close. The discrepancy between those for V_2 is probably connected with the fairly large α_2 values (see Lefebvre *et al* 1981). Taking into account that the agreement between the CFM and the best available octahedron–tetrahedron CVM approximation (Mohri *et al* 1985) is quite good, as has been argued elsewhere (Vaks *et al* 1988), we have further evidence of the high accuracy of our approach.

In conclusion, we have developed the theory of SRO in disordered alloys which leads to the simple equations for SRO parameters and provides an explicit solution for the

Table 1. Pair potentials V_s (in K) as obtained in the CFM and in the present work at the different levels of approximation. Our approximations are denoted as SM ($\Sigma_s = 0$ for all s), α^2 ($\Sigma_s = A\alpha_s^2$), and α^3 ($\Sigma_s = A\alpha_s^2 + B\alpha_s^3$). For those of CFM, see Vaks *et al* (1988).

CFM	γ		T_1		T_2		T_3		T_4		T_5	
	KCM	SM										
$\frac{1}{2}$	α^2	T_1										
$\frac{1}{6}$	α^3	658 K	745 K		780 K		808 K		958 K			
$-V_1$		432	635	511	664	494	622	476	647	568	676	
		766	684	781	717	720	671	746	690	765	713	
		678	694	711	727	663	680	690	698	717	719	
V_2		225	331	195	253	225	283	226	307	155	184	
		311	232	242	170	271	206	292	240	180	155	
		258		205		238		254		159		
$-V_3$		12	18	38	49	34	43	19	26	56	67	
		17	19	50	50	43	43	26	26	67	67	
		17		49		42		25		66		
$-V_4$		8	12	11	14	21	26	6	8	39	46	
		12		15		27		9		46		
		13		16		27		9		47		
V_5		0	0	19	25	17	21	-4	-5	10	12	
		0		24		22		-5		12		
		-1		25		22		-6		12		
V_6		5	7	20	26	15	19	20	27	-7	-8	
		7		26		19		27		-8		
$-V_7$		19	28	1	1	12	15	10	14	4	5	
		28		1		15		14		5		
V_8		-13	-19	16	21	7	9	2	3	-16	-19	
		-19		21		9		3		-19		
V_{9a}		-10	-15	6	8	-6	-8	10	14	7	8	
		-15		8		-8		14		8		
V_{9b}		-20	-29	4	5	6	8	-3	-4	9	-11	
		-30		5		8		-4		-11		

inverse problem of restoring pair potentials from diffuse scattering data. Both problems are solved with high accuracy.

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