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Pair interactions in alloys evaluated from diffuse-scattering data

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The theory of short-range order in alloys developed previously by the present authors is used to resolve the ambiguities existing in the problem of determination of pair potentials from diffuse-scattering measurements. It is shown that in the framework of the Krivoglaz-Clapp-Moss approximation the best results correspond to the Krivoglaz normalization. They turn out to be identical to those of the spherical model, a zero-order approximation of the theory under consideration. The origin of the self-interaction potential appearing in this case is clarified. All attempts at normalizing Krivoglaz's formula in order to preserve a sum rule or prevent the occurrence of self-interaction result in a distortion of the potentials. A higher-order approximation is used to explain the remaining disagreement between the results obtained by means of the Krivoglaz formula and the inverse Monte Carlo method.

Experimental investigation of short-range order (SRO) in disordered alloys provides information about interatomic potentials. These potentials are necessary for solving various problems, such as the determination of ground-state structures and calculation of phase diagrams. The common approach in this field is the use of the Ising model, in which a pair ordering potential

$$V_{ij}=\tfrac{1}{2}(V_{ij}^{AA}+V_{ij}^{BB}-2V_{ij}^{AB}) \quad i\neq j \;, \tag{1}$$

(V_{ij}^{AA} corresponds to the interaction between A atoms at sites i and j, etc.) plays the role of the exchange integral.[1]

For analyzing experimental data, in particular, for extracting pair potentials, the Krivoglaz-Clapp-Moss (KCM) approximation[2,3]

$$\alpha(k)=\frac{D}{1+2c(1-c)\beta V(k)} \tag{2}$$

is usually used. Here $\alpha(k)$ is the diffuse-scattering intensity in Laue units, $\alpha(k)$ and $V(k)$ are Fourier transforms of the α_{ij} and V_{ij}, respectively, α_{ij} being the Warren-Cowley SRO parameter,[1] c is the concentration, $\beta=1/k_BT$ the inverse temperature, and D the normalization factor. In the case $D=1$ Eq. (2) corresponds to the standard RPA result in the theory of magnetism[4] and has been derived by Krivoglaz.[2] However, this choice violates a well-known sum rule $\alpha_{ii}=1$ in the case of the "direct" problem of determining $\alpha(k)$ from the given $V(k)$,[5] while it leads to the appearance of a nonzero self-interaction potential V_{ii} when solving the corresponding "inverse" problem.[6-9] To eliminate these difficulties, special values of the factor D have to be used. In the former case the sum rule is satisfied by the Clapp-Moss normalization,[3] while in the latter the condition $V_{ii}=0$ is provided by the Lefebvre value[6]

$$D=\left[\Omega^{-1}\int dk\,\alpha^{-1}(k)\right]^{-1} \;; \tag{3}$$

integration is over the Brillouin zone of volume Ω.

It is generally believed that the KCM theory is only a qualitative one because of its mean-field nature.[4] Indeed, normalization (3), for instance, leads to the serious underestimation of the absolute values of potential.[6,10] On the other hand, several authors[7-9] have noted a good overall agreement between potentials obtained by using the Krivoglaz formula with $V_{ii}\neq 0$ and the recently developed inverse Monte Carlo (IMC) method.[11] Nevertheless, even in this case near-neighbor IMC potentials turn out to be somewhat greater than the corresponding KCM ones.

Recently, the present authors have developed a theory of SRO in disordered alloys[12] based on the γ-expansion method (GEM),[13] which leads to accurate results for both direct and inverse problems and gives an explicit solution for the latter. Here this theory is applied to the problem of interpreting diffuse-scattering data. Our approach allows us to understand the failure of the choice $D\neq 1$ and the relative success of the Krivoglaz normalization. In the latter case it is also able to clarify the origin of the self-interaction potential V_{ii} and to explain the above-mentioned differences between IMC and KCM potentials.

As far as the inverse problem is considered, we have[12]

$$V_{ij}=\frac{1}{2}k_BT\left[\frac{a_{ij}}{c(1-c)}+\Sigma_{ij}\right] \quad i\neq j \;, \tag{4}$$

$$a_{ii}=-c(1-c)\Sigma_{ii} \;, \tag{5}$$

where $a_{ij}=(\alpha^{-1})_{ij}$. Equations (4) and (5) reflect simply a link between the correlation function, potential, and self-energy. The main result in Ref. 12 is that the off-diagonal part of the self-energy Σ is at least of order γ^2, where γ is the small parameter of the theory. The corresponding low-order expression for this quantity in the case of cubic lattices is

$$\begin{aligned}&\Sigma_1=A\alpha_1^2+B\alpha_1^3;\ \Sigma_{2,3}=A\alpha_{2,3}^2;\ \Sigma_3=0,\ s>3\;;\\&A=\frac{1}{2}\frac{(1-2c)^2}{[c(1-c)]^2}\;,\\&B=\frac{1}{6}\frac{[1-6c(1-c)]^2-3(1-2c)^4}{[c(1-c)]^3}\;,\end{aligned} \tag{6}$$

TABLE I. Pair potentials V_{ij} as determined by the Krivoglaz-Clapp-Moss (KCM) approximation with normalization factor equal to unity using Fourier transformation (FT) and least-squares fitting (LSF) procedures, those corrected according to the γ-expansion method (GEM), and results of the inverse Monte Carlo (IMC) method. All quantities are in meV, *lmn* are Miller indices of the vector connecting sites *i* and *j*. Data have been used for samples: (1) Cu-Zn, $c_{\rm Zn}=0.311$, $T=473$ K (Ref. 7); (2)–(4) Ni-Cr, $c_{\rm Cr}=0.213$, 0.201, and 0.206; $T=741$, 828, and 973 K, respectively (Ref. 8); (5) Ni-Cr, $c_{\rm Cr}=0.11$, $T=833$ K (Ref. 9).

		KCM		GEM		
No.	*lmn*	FT	LSF	FT	LSF	IMC
	110	18.1	15.5	18.7	16.1	18.6
1	200	−7.4	−7.8	−6.7	−7.1	−6.6
	211	−1.4	−1.6	−1.4	−1.6	−1.3
	110	23.4	23.1	25.9	25.6	26.1
2	200	−17.3	−16.9	−15.8	−15.4	−16.0
	211	−4.3	−4.8	−4.0	−4.5	−4.0
	110	25.6	27.4	28.6	30.4	29.3
3	200	−19.8	−18.2	−18.0	−16.4	−17.9
	211	−4.0	−3.2	−3.7	−2.9	−3.3
	110	25.8	25.1	27.9	27.2	28.0
4	200	−12.6	−13.7	−11.5	−12.6	−11.7
	211	0.1	−1.3	0.2	−1.2	0.1
	110		22.7		27.1	26.1
5	200		−10.9		−9.2	−10.5
	211		−1.6		−1.5	−1.6

where *s* is the coordination shell number. The diagonal part Σ_{ii} is determined from the sum rule $\alpha_{ii}=1$, one of the GEM equations. The zero-order approximation ($\Sigma_{ij}=0$ for $i\neq j$) is equivalent to the spherical model (SM) for alloys.[14]

From Eqs. (2), (4), and (5) it is easily seen that exact potentials are connected with KCM ones by simple relations:

$$V_{ij}=\frac{1}{D}V_{ij}^{\rm KCM}+\frac{1}{2}k_BT\Sigma_{ij}\quad i\neq j\ , \tag{7}$$

$$V_{ii}^{\rm KCM}=-\frac{1}{2}k_BT\left[\frac{1}{c(1-c)}+D\Sigma_{ii}\right] . \tag{8}$$

Therefore several important conclusions can immediately be drawn:

(i) When using the KCM approximation (2) to calculate pair interactions from diffuse-scattering data, the best values of the corresponding potentials are to be expected in the case $D=1$. They turn out to be identical to those of the SM. The quantity $V_{ii}^{\rm KCM}$ in this case is actually not a self-interaction potential; it is related directly to the SM self-energy.

(ii) The term $A\alpha_{ij}^2$ being the first correction to the SM value of the near-neighbor potential V_{ij} is always positive. This fact may lead to the elimination of discrepancy between the SM (KCM theory with $D=1$) and IMC results.

(iii) In the case $D\neq 1$ the potentials obtained are distorted depending on the particular value of *D*. Actually, their absolute values are underestimated since both Clapp-Moss and Lefebvre normalizations lead to *D* being less than unity.

(iv) Correct potentials can be calculated according to Eqs. (6) and (7) using only data existing in literature, namely, KCM results, normalization factor *D*, and the set of SRO parameters.

To verify the statements above, we will analyze available diffuse-scattering data. In the experimental studies of neutron diffuse scattering from $\rm Cu_{0.689}Zn_{0.311}$,[7] $\rm Ni_{0.80}Cr_{0.20}$,[8] and $\rm Ni_{0.89}Cr_{0.11}$,[9] alloy pair potentials have been determined using the KCM approximation and the IMC method. In all three cases Krivoglaz normalization has been used. In Refs. 7 and 8 two procedures were exploited; (i) direct Fourier transformation (FT) of the set $\{\alpha_{ij}\}$, and (ii) least-squares fitting (LSF) to the measured diffuse intensity, while the authors of the Ref. 9 used only LSF. The agreement between FT, LSF, and IMC results was stated to be good. However, all near-neighbor IMC potentials have turned out to be greater than the corresponding KCM ones. All these potentials are listed in Table I, along with our results obtained by means of Eqs. (6) and (7). It is seen that GEM corrections lead to an excellent agreement with IMC results when added to FT potentials; this agreement slightly worsens in the LSF case.

Normalization (3) was used for $\rm Ni_{0.80}Cr_{0.20}$ (Ref. 8) and $\rm Ni_{0.765}Fe_{0.235}$ (Ref. 6) alloys. In the first case it has been noted that absolute values of potentials are approximately 20% smaller compared to those for $D=1$, and do not agree with IMC results. In the second case the underestimation is about from 20 to 30%. Corrected potentials for this case are presented in Ref. 12, together with those of the cluster field method (CFM),[10] a simplified version of the cluster variation method (CVM).[1] The results turn out to be very close.

In summary, our theory of SRO appears to be able to clarify such controversial points in diffuse-scattering data treatment as the correct choice of normalization factor *D* in the KCM approximation (2), the nature of the self-interaction potential V_{ii}, and underestimation of the potentials when using the Krivoglaz value $D=1$.

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