

Concentration Waves and Fermi Surfaces in Random Metallic Alloys

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On the basis of a new first-principles, electronic model for the forces driving clustering and short-range order in metallic alloys, it is argued that observed concentration-dependent peaks in the x-ray and electron diffuse scattering intensities are due to parallel sheets of flat Fermi surface. The positions of the peaks are directly related to the spanning vector \vec{k}_0 .

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It is often useful to describe inhomogeneous fluctuations in the composition of random alloys as incipient concentration waves (CW). This is a particularly fertile view when the state of order is dominated by a small number of waves with wave vectors near specific points in the Brillouin zone, say \vec{k}_0 and its star.^{1,2} For instance, the ordered state can be thought of as a thermodynamically stable CW modulating the disordered state.² In the disordered state CW's are not stable but may be long lived. They describe the short-range order (SRO) and dominant \mathcal{G} 's are directly observed as peaks at \vec{k}_0 in the x-ray, neutron, and electron diffuse scattering intensity $I(\vec{k})$, $\hbar\vec{k}$ being the momentum transfer.¹ Of special interest are the alloys, such as $\text{Cu}_c\text{Pd}_{1-c}$, $\text{Cu}_c\text{Pt}_{1-c}$,³ etc., for which \vec{k}_0 varies continuously with the average composition C . In these cases the Fermi surface is thought to play a role in singling out some particular \vec{k}_0 ,⁴ which is, therefore, not correlated with the symmetry-induced Lifshitz (special) points.¹

The conventional argument is based on the Krivoglaz-Clapp-Moss (KCM) formula for the SRO parameter $\alpha(\vec{k}) = [1 + C(1 - C)\beta W(\vec{k})]^{-1}$ where $W(\vec{k})$ is the lattice Fourier transform of a pairwise interchange potential^{1,2} and $\beta = (k_B T)^{-1}$. Since $I(\vec{k})$ is proportional to $\alpha(\vec{k})$ the diffuse scattering experiments measure the shape of $W(\vec{k})$. The suggestion of Moss⁴ is that $W(\vec{k})$ can be calculated in perturbation theory to second order in the electron-ion potential and hence is proportional to the one-electron susceptibility $\chi_0(\vec{k})$ which can peak at \vec{k}_0 's that connect parallel flat segments of the Fermi surface leading to peaks in $\alpha(\vec{k})$ and $I(\vec{k})$ at \vec{k}_0 . This would be an attrac-

tive picture since it is easy to imagine that the Fermi surface, if it existed in a random alloy,⁵ would be a sensitive function of C . However, neither low-order perturbation theory nor the assumption of pair potentials is likely to be applicable to systems with strongly nonspherical Fermi surfaces. In this Letter we present an alternative theory which is not subject to these two objections.

It turns out to be straightforward to adapt the density-functional approach for classical liquids⁶ to a lattice-gas model of alloy configurations.² The basic theorem is that, in the presence of an external field $H_{\text{ext}} = \sum_n v_n (2\xi_n - 1)$, there is a grand potential

$$\Omega(T, V, N, \nu, [C_n]) = \sum_n v_n (2C_n - 1) + F([C_n]) - \nu \sum_n (2C_n - 1) \quad (1)$$

such that the internal Helmholtz free energy $F([C_n])$ is a unique functional (independent of the external potential v_n) of the local nonequilibrium concentrations $C_n = \langle \xi_n \rangle$. Here ξ_n is an occupation variable which is 1 (0) if there is an A (B) atom on the n th site, and T , V , N , and ν are the temperature, volume, number of unit cells, and chemical potential difference $\frac{1}{2}(\mu^A - \mu^B)$, respectively. The equilibrium configuration is specified by the condition $(\partial\Omega/\partial C_n)[C^0] = 0$. Furthermore, \mathcal{Q} is a minimum at $[C_n^0]$ and equal to the thermodynamic grand potential $\bar{\Omega}(T, V, N, \nu)$. The proof follows the arguments in Ref. 6 and will be given elsewhere. With respect to the variable $u_n = \nu - v_n$,⁶ Ω is a generating function of a hierarchy of correlation functions: $\partial\Omega/\partial u_n = 2C_n$,

$$\partial^2\Omega/\partial u_n \partial u_{n'} = 4\beta q_{nn'} = 4\beta (\langle \xi_n \xi_{n'} \rangle - \langle \xi_n \rangle \langle \xi_{n'} \rangle),$$

etc. For a homogeneous system $q(\vec{k}) = C(1 - C)\alpha(\vec{k})$ is the lattice Fourier transform of $q_{nn'}$.

Although F is not known at this stage, it is useful to break it up into a noninteracting part

$$F_0 = \beta^{-1} \sum_n [C_n \ln C_n + (1 - C_n) \ln(1 - C_n)]$$

and an interaction function Φ defined by $F = F_0 - \Phi$. It then follows that the $[C_n^0]$ satisfy

$$\beta^{-1} \ln [C_n^0 / (1 - C_n^0)] - \beta^{-1} S_n^{(1)} + 2(\nu_n - \nu) = 0, \tag{2}$$

where $S_n^{(1)} \equiv \beta(\partial \Phi / \partial C_n)$. Clearly, $S_n^{(1)}$ is a self-energy, i.e., the contribution to the local chemical potential difference $\nu - \nu_n$ due to all the interactions. Note that Eq. (2) is a complicated equation for C_n^0 since $S_n^{(1)}$ depends on all the variables $[C_n^0]$.

With respect to the concentration variables, Φ turns out to be a generator for a new set of useful correlation functions. The first is $S_n^{(1)}$, the second

$$S_{nn'}^{(2)} = \partial S_n^{(1)} / \partial C_{n'} = \beta \partial^2 \Omega / \partial C_n \partial C_{n'},$$

and so on. To see the significance of $S_{nn'}^{(2)}$ take the derivative of Eq. (2) with respect to $C_{n'}$. The result is

$$[C_n(1 - C_n)]^{-1} \delta_{nn'} - S_{nn'}^{(2)} - \partial u_n / \partial C_{n'} = 0.$$

Noting that

$$\partial u_n / \partial C_{n'} = (\partial C_{n'} / \partial u_n)^{-1} = (2\beta)^{-1} (q^{-1})_{nn'},$$

we may rewrite this relation, for a homogeneous system, as

$$\alpha(\vec{k}) = [C(1 - C)]^{-1} q(\vec{k}) = [1 - C(1 - C)S^{(2)}(\vec{k})]^{-1}. \tag{3}$$

This identifies $S^{(2)}(\vec{k})$ as a close relative of the Ornstein-Zernike direct correlation function for our lattice model.⁷ For a model with pair potentials, within the random-phase approximation (RPA), $S^{(2)}(\vec{k}) = -\beta W(\vec{k})$, which leads to the KCM result. Here, however, Eq. (3) is exact and $S^{(2)}(\vec{k})$ has been defined without reference to pair potentials.

In the present concentration-functional approach, the mean-field theory is to take $\Phi_{MF} = -\langle H([\xi_n]) \rangle$, where angular brackets denote the average with respect to the inhomogeneous distribution function $P([\xi_n]) = \prod_n P_n(\xi_n)$ where $P_n(1) = C_n$ and $P_n(0) = 1 - C_n$. For pair potentials this yields the RPA result for $S^{(2)}(\vec{k})$ and Eq. (2) becomes the Bragg-Williams equation of state. To go further one must add to Φ_{MF} fluctuation corrections. However, our aim here is to calculate the self-energy $S_n^{(1)}$ and the direct correlation function $S_{nn'}^{(2)}$ in the mean-field approximation on the basis of electronic forces which cannot be represented as pairwise interactions.

In the adiabatic approximation $\Phi_{MF} = -\langle H_{II} \rangle - \langle \Omega_e \rangle$ where H_{II} is the bare ion-ion interaction and Ω_e is the grand potential of the electrons for a specific configuration. In the density-functional theory for the electrons, Ω_e can be written as a "band-structure" contribution Ω_e^0 plus corrections for double counting. The latter can be lumped together with H_{II} and the result is a sum over short-ranged, repulsive, pairwise forces as in the phonon problem.⁸ In what follows we shall confine our attention to the attractive long-ranged forces governed by Ω_e^0 . We take the effective one-electron potential to be of the muffin-tin form. We consider only two kinds of potential wells characterized by the partial-wave scattering amplitudes $f_{A,l}(\epsilon)$ and $f_{B,l}(\epsilon)$ and assume that they do not change during rearrangements. That this is a sound basis for our present discussion follows from the success of Korringa-Kohn-Rostoker-coherent-potential-approximation (KKR-CPA) method of calculating electronic states in random alloys.⁵ Thus, following the lead of Ducastelle and Gautier⁹ in the context of tight-binding models, we shall study $\langle \Omega_e^0 \rangle$ within an inhomogeneous generalization of the KKR-CPA.

The coherent-potential lattice is described by the effective partial-wave scattering amplitudes $f_{c,n;LL'}(\epsilon)$ (the index c designates quantities calculated in CPA) which for an arbitrary $[C_n]$ are off-diagonal in the angular-momentum indices $L (=l, m)$ and are different on every site. They are the solutions of the generalized KKR-CPA equation:

$$\underline{t}_{c,n}^{-1} = C_n \underline{t}_A^{-1} + (1 - C_n) \underline{t}_B^{-1} + (\underline{t}_A^{-1} - \underline{t}_{c,n}^{-1}) T^{c,nn'} (\underline{t}_B^{-1} - \underline{t}_{c,n}^{-1}), \tag{4}$$

where $\underline{t}_{c,n}$, \underline{t}_A , and \underline{t}_B , are "on-the-energy-shell" t matrices ($\underline{f} = -\epsilon^{1/2} \underline{t}$) and $\tau_{L,L'}^{c,nn'}(\epsilon)$ is the inverse of the real-space KKR matrix

$$t_{c,n;LL'}^{-1} \delta_{mm'} - G_{LL'}(\vec{R}_n - \vec{R}_{n'}; \epsilon)$$

with the usual free-electron structure constants $G_{LL'}(\vec{R}_n - \vec{R}_{n'}; \epsilon)$. The grand potential Ω^{CPA} is given by $-2\beta \int_{-\infty}^{\infty} d\epsilon N^{\text{CPA}}(\epsilon) f(\epsilon)$. The stationarity of N^{CPA} with respect to variations in $t_{c,n}^{-1}$ means that in the disordered state ($C_n = C$ for all n)

$$S_n^{(1)} = -\beta \partial \Omega^{\text{CPA}} / \partial C_n = 2\beta \int d\epsilon f(\epsilon) (\ln \|D_A\| - \ln \|D_B\|),$$

where $\|D_{\alpha,n}\|$ ($\alpha = A, B$) is the determinant of the matrix $[\underline{1} + (t_{\alpha}^{-1} - t_{c,n}^{-1}) \underline{\tau}^{c,nn}]^{-1}$ in angular momentum space. After a KKR-CPA calculation has been performed this is a simple formula to evaluate. Its consequences for the equation of state, Eq. (3), will be discussed elsewhere.

To calculate $S_{n,n'}^{(2)}$ we need to take another derivative of Ω^{CPA} . This involves $\partial t_{c,n}^{-1} / \partial C_n$ for which we can derive an integral equation from Eq. (4). In the disordered state the solution of this yields

$$S^{(2)}(\vec{k}) = [2\beta/n^{\text{CPA}}(\mu)] [\Delta Z - \Delta(\mu)] \Delta(\mu) \delta_{\vec{k},0} + 2\beta \int_{-\infty}^{\infty} d\epsilon f(\epsilon) \sum_{LL'} M_{LL'}(\epsilon) [1 + \gamma_L X_{LL'}(\vec{k}, \epsilon)]^{-1} X_{LL'}(\vec{k}, \epsilon), \quad (5)$$

where the first term is due to changes in the chemical potential μ for the electrons, ΔZ is the valence difference $Z^A - Z^B$, $n^{\text{CPA}}(\mu) = \partial N^{\text{CPA}} / \partial \mu$, the matrix element

$$M_{L,L'}(\epsilon) = D_L^A (t_{A,L}^{-1} - t_{B,L}^{-1}) D_L^B D_{L',A} (t_{A,L'}^{-1} - t_{B,L'}^{-1}) D_{L',B},$$

the vertex function

$$\gamma_L(\epsilon) = D_L^A (t_{A,L}^{-1} - t_{c,L}^{-1}) D_L^B (t_{B,L}^{-1} - t_{c,L}^{-1})$$

and the "susceptibility"

$$X_{LL'}(\vec{k}, \epsilon) = -\sum_{\vec{k}'} \bar{\tau}_{LL'}^c(\vec{k}', \epsilon) \tau_{L',L}^c(\vec{k}' + \vec{k}; \epsilon)$$

with $\tau_{LL'}^c(\vec{k}, \epsilon)$ being the Fourier transform of $\tau_{L,L'}^{c,nn'}(\epsilon)$ in the homogeneous KKR-CPA. Again evaluation of Eq. (5) is a tractable way of investigating the influence of the band structure on the distribution of the diffuse scattering intensity $I(\vec{k})$ in a first-principles calculation. Here we are concerned with the possible role of the Fermi surface.

For $\gamma_L = 0$ and $M_{LL'}$ constant, the second term in Eq. (5) may be rewritten as

$$\sum_{\vec{k}} \int d\epsilon \int d\epsilon' \{f(\epsilon) - f(\epsilon')\} (\epsilon - \epsilon')^{-1} \text{Im} \tau_{LL'}(\vec{k}', \epsilon) \text{Im} \tau_{L',L}(\vec{k}' + \vec{k}; \epsilon).$$

Since $\text{Im} \tau_{L,L'}(\vec{k}, \epsilon)$ is closely related to the spectral function $A_B(\vec{k}, \epsilon)$ which has sharp peaks in regions of \vec{k} and ϵ where there are well defined bands, this term will peak at \vec{k} vectors which connect well defined flat sheets of Fermi surfaces. It is now our suggestion that the full $S^{(2)}(\vec{k})$ in Eq. (5) will also have this structure.

To check the above hypothesis we have evaluated Eq. (5) for a number of the one-dimensional alloys studied by Gonis and Stocks.^{10, 11} The results are shown in Fig. 1. For alloys with $C=0.9$ and 0.7 the peak is at " $2k_F$ " and it is seen to vary with concentration. This is an ordering analog of the Peierls transition. In the alloy with $C=0.5$ the peak is at the special point of one dimension, $k_0 = \pi/a$.

We have not yet studied $S^{(2)}(\vec{k})$ for three dimensional systems but our KKR-CPA calculations indicate that many alloys of noble and transition metals such as $\text{Ag}_C \text{Pd}_{1-C}$ (Ref. 5) and $\text{Cu}_C \text{Pd}_{1-C}$ do have flat portions to their Fermi surfaces perpendicular to the 110 directions; moreover, these

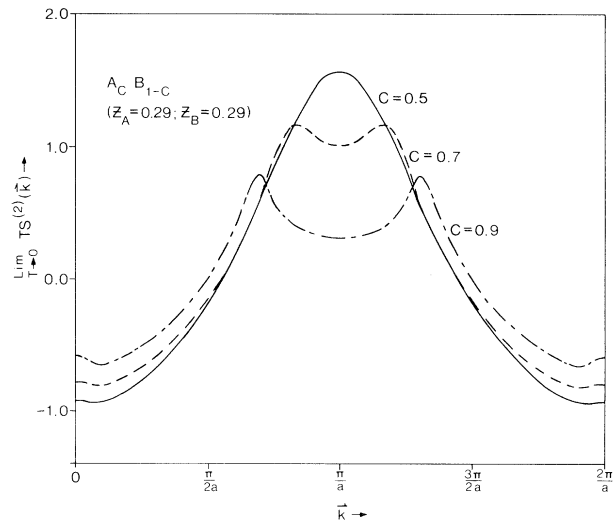


FIG. 1. Calculated values of $S^{(2)}(\vec{k})$ for three concentrations of a one-dimensional random alloy (Refs. 10 and 11). The chemical potential is determined with the assumption that both the A and B species contribute 0.29 states atom⁻¹.

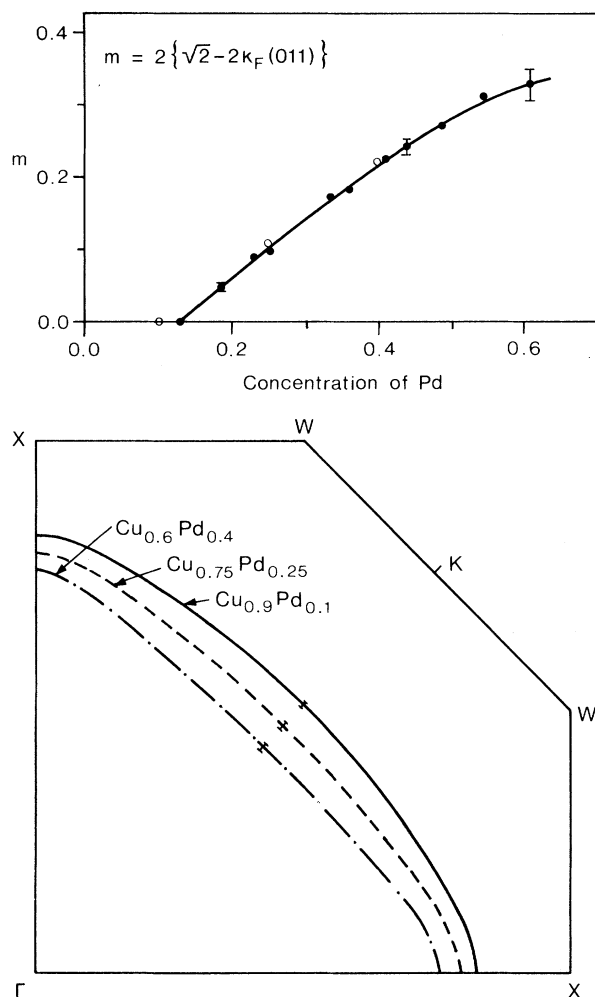


FIG. 2. Upper frame: Calculated (open circles) and experimental (dots) values of the diffuse scattering spot separation for $\text{Cu}_c\text{Pd}_{1-c}$ [in units of the distance between the $(0,0,0)$ and $(0,0,2)$ Bragg maximal]. Lower frame: Calculated Fermi surfaces in the $\Gamma X K$ plane for three $\text{Cu}_c\text{Pd}_{1-c}$ alloys showing the increasing flattening of the Fermi surface with increasing Pd content. The bars indicate the degree of disorder broadening.

Fermi surfaces are rather sharp. In Fig. 2 we show Fermi surfaces and values of $m = 2[(\sqrt{2} - 2k_F(110))]$ obtained on the basis of self-consistent-field-KKR-CPA¹² calculations for the experimentally relevant $\text{Cu}_c\text{Pd}_{1-c}$ system. The

quantity m is the separation along the (110) direction between the diffuse scattering spots defined by Ohshima and Watanabe.³ The experimental results for m obtained from electron diffraction measurements are also shown in Fig. 2 and are in excellent agreement with our calculated values. We note that the occurrence of this flat Γ -centered piece of Fermi surface in this and similar alloys is a robust phenomenon since this sheet of Fermi surface must change from a convex shape in the noble metal to a concave one in the late transition metal in a continuous fashion. Hence, it is almost forced to be flat for some concentration. Thus, we suggest that when $S^{(2)}(\vec{k})$ is evaluated for these systems it will show structure due to this sheet and so provide an explanation for the concentration-dependent features in the diffuse scattering intensities.¹

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