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Random Transfer Integrals and the Electronic Structure of Disordered Alloys*

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Previous theories of off-diagonal disorder in the tight binding model of a binary alloy are found to be incorrect in the dilute limit. We treat this limit exactly, and discuss the extension to arbitrary impurity concentrations.

Recently, authors[1,2] have devoted a great deal of attention to the following model of the binary substitutional alloy A_xB_{1-x}:

$$H=\sum_n |n\rangle \epsilon_n \langle n| + \sum_{n\neq m} |n\rangle h_{nm} \langle m| . \tag{1}$$

The simplifying feature of the model is that the effects of the disorder do not extend over any finite distance. Thus, the local energy levels ϵ_n may take either of the two values ϵ^A or ϵ^B, but the hopping integrals h_{nm} are always periodic. On the basis of a comparison with exact results concerning the limits of the allowed energy spectrum and the values of its leading moments,[2] it has been generally agreed that an excellent mean field description of the model is provided by the coherent potential approximation (CPA). There is, however, another class of exact results that are beyond the scope of this localized perturbation model. These results, the most basic of which is the Friedel sum rule,[3] concern the choice of self-consistent atomic potentials. As Stern[4] has shown, the essential difficulty lies in the assumption of zero-range scattering forces. Accordingly, a more physical description of the alloy must include off-diagonal disorder, i.e., we must allow both h_{nm} and ϵ_n to vary randomly.

The problem of extending the CPA to treat off-diagonal disorder has been discussed by several authors.[5] In addition, their methods have recently been applied to the spin wave spectrum in alloys of Heisenberg magnets,[6] a system for which the diagonal and off-diagonal scattering must certainly be treated on an equal footing. It is important then to realize that *none* of the proposed approximations is correct in the low-density limit. Unfortunately, this is precisely the limit of interest for the Friedel sum rule in metallic alloys, and also for making contact with the exact results of Wolfram and Callaway[7] in the case of insulating magnets. The present paper is limited to a discussion of the electronic problem; the formalism however is directly applicable to magnetic systems.

We begin by considering the Hamiltonian for a single A impurity at the origin of an otherwise perfect B crystal,

$$H=H_B+|0\rangle\delta_0\langle 0| + {\sum_{n\neq 0}}' [|n\rangle \delta_1 \langle 0| + |0\rangle \delta_1 \langle n|], \tag{2}$$

$$\delta_0=(\epsilon^A-\epsilon^B), \quad \delta_1=(h^{AB}-h^{BB}); \tag{3}$$

the prime indicates that only nearest neighbors are included in the summation. h^{BB} and $h^{AB}=h^{BA}$ describe host-host and impurity-host hopping, respectively. In a momentum representation, the impurity potential $v(\vec{k},\vec{k}')$ may be written

$$v(\vec{k},\vec{k}')=\delta_0+\delta_1[s(\vec{k})+s(\vec{k}')], \tag{4}$$

where $s(\vec{k})=\sum_n{}' \exp(i\vec{k}\cdot\vec{R}_n)$ [the host E versus $\vec{k}$ relation is then $E^B(\vec{k})=\epsilon^B+h^{BB}s(\vec{k})$]. For a given (complex) energy z, Eq. (4), together with the unperturbed Green's function $G^{(0)}(\vec{k})=[z-E^B(\vec{k})]^{-1}$, permit an exact solution for the matrix elements of scattering operator $t(\vec{k},\vec{k}')=\langle\vec{k}|[1-vG^{(0)}]^{-1}v$

$\times|\vec{k}'\rangle$:

$$t(\vec{k},\vec{k}')=\frac{a_1(z)+a_2(z)[s(\vec{k})+s(\vec{k}')]+a_3(z)s(\vec{k})s(\vec{k}')}{1-D(z)},\tag{5}$$

where

$$a_1(z)=\delta_0+\delta_1{}^2F_2(z),\quad a_2(z)=\delta_1-\delta_1{}^2F_1(z),\quad a_3(z)=\delta_1{}^2F_0(z),$$

$$D(z)=\delta_0F_0(z)+2\delta_1F_1(z)-\delta_1{}^2\{[F_1(z)]^2-F_0(z)\},\quad F_n(z)=\int_{\mathrm{BZ}}G^{(0)}(\vec{k})[s(\vec{k})]^n d^3k,\quad n=0,1,2.\tag{6}$$

All information about the scatterer's effect on the electronic spectrum is contained in $t(\vec{k},\vec{k}')$. For example, fixing the values of δ_0 and δ_1, the zeros of the denominator in Eq. (5) determine the energies of the possible localized impurity states. In one dimension these energies can be evaluated analytically and the various cases are shown in Fig. 1. The situation in three dimensions is qualitatively similar. Two intersecting parabolas divide the δ_0, δ_1 plane into three regions within which there are zero, one, and two bound states, respectively. In the absence of off-diagonal scattering, $h^{AB}=h^{BB}$, and there is a single bound state for any $\delta_0>0$. We note, however, that in the case $0<h^{AB}<h^{BB}$ this bound state does not appear until δ_0 reaches a certain critical value $\delta_0{}^c$. The most interesting behavior is obtained when the scattering is purely off diagonal. If $h^{AB}>h^{BB}$ there are two roots, corresponding to the bonding and antibonding levels of the molecular cluster at the origin. Beginning on the vertical axis, as the value of δ_0 is increased, the lower root moves up and eventually merges with the continuum as we pass from region III into II.

If instead of a single scatterer we consider a macroscopic concentration x of impurity atoms then the equilibrium properties are most conveniently described by the ensemble-averaged Green's function $G(z)\equiv\langle[z-H]^{-1}\rangle\equiv[z-H_B-\Sigma(z)]^{-1}$, where $\Sigma(z)$ is the usual electron self-energy. The preceding results for the single impurity allow us to understand the behavior of the alloy in the low-density limit $x\ll 1$. More specifically, it is well known that in this limit the self-energy is given by $\Sigma(\vec{k},z)\equiv\langle\vec{k}|\Sigma(z)|\vec{k}\rangle=xt(\vec{k},\vec{k})$, and, in addition, that each of the bound states of the single scatterer will give rise to an impurity subband of finite width. The various approximate treatments of off-diagonal disorder are *not* consistent with this result and cannot therefore be relied upon to provide an accurate description of the impurity band structure over the entire range of values of δ_0 and δ_1.[8]

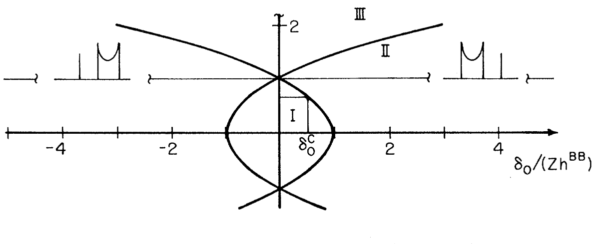

FIG. 1. The various possibilities for the bound states of a single impurity in one dimension.

As indicated at the outset, the initial motivation for examining the problem of off-diagonal disorder was to develop a theory that was consistent with the Friedel sum rule. Fortunately, this point can be understood in terms of just the low-density limit $x\to 0^+$. Indeed, the usual derivations of the Friedel sum rule[3] involve only a single impurity, with relative valence Z, in an otherwise homogeneous electron gas. Screening by the free electrons implies that the resulting perturbation is of finite range and that, asymptotically, the electronic structure is identical to that of the pure host. The final result is the familiar expression relating the valence Z to a weighted sum of phase shifts η_l. This form of the Friedel sum rule is, however, somewhat inconvenient for use in conjunction with the present model. Consideration of a single impurity in a host lattice consisting of $\sim10^{23}$ atoms is rather unsatisfying since a real system contains a finite, although possibly macroscopically infinitesimal, concentration of impurities. In addition, in a crystalline lattice the asymptotic region surrounding each impurity is certainly not spherically symmetric so that the notion of a phase shift is slightly ambiguous. It is nevertheless possible to formulate a completely general statement of the physics underlying the Friedel sum rule in terms of the purely macroscopic parameters x and μ, respectively characterizing the impurity concentration of the alloy and its chemical potential. Friedel noted[9] that, as a direct consequence of the total screening, the chemical potential is unchanged by the addition of dilute impurities. Formally, the requirement is

$$(d\mu/dx)_{x=0^+}=0. \tag{7}$$

This equation provides an important check on the choice of scattering parameters in any finite concentration alloy theory. Every such calculation must be consistent with Eq. (7) in the dilute limits $x\to 0^+$ and $x\to 1^-$. For example, if $n_A{}^0$ and $n_B{}^0$ are the constituent carrier numbers then the concentration dependence of the chemical potential $\mu(x)$ is defined by the relation

$$\begin{aligned}\langle n\rangle &= xn_A{}^0+(1-x)n_B{}^0\\ &= -2\pi^{-1}\,\mathrm{Im}\int_{-\infty}^{\mu(x)}\mathrm{Tr}G(E^+)\,dE.\end{aligned} \tag{8}$$

Combining Eq. (8) with our low-density expression for $G(z)$, differentiating with respect to x, and evaluating the resulting integral exactly, the self-consistency condition (7) is found to imply the relation

$$\begin{aligned}Z &= d\langle n\rangle/dx = n_A{}^0-n_B{}^0\\ &= -2\pi^{-1}\,\mathrm{Im}\int_{-\infty}^{\mu_B}(d/dx)[\mathrm{Tr}G(E^+)]_{x=0^+}\,dE\\ &= -2\pi^{-1}\,\mathrm{Im}\ln[1-D(\mu_B)]\\ &= 2\pi^{-1}\tan^{-1}\left[\frac{\mathrm{Im}D(\mu_B)}{1-\mathrm{Re}D(\mu_B)}\right];\end{aligned} \tag{9}$$

μ_B is the chemical potential of the host crystal and $D(E)$ is defined by (6). Equation (9) is the form of the Friedel sum rule relevant for the tight binding alloy Hamiltonian and is, in fact, a special case of the general S-matrix relation

$$Z=(2\pi i)^{-1}\,\mathrm{Tr}[\ln S(\mu_B)]$$

proved by Langer and Ambegaokar.[10] Equation (9) together with the corresponding result for $x=1^-$ provides an important constraint on our choice of input parameters. For example, if (in addition to the relative valence Z) we specify the values of the pure crystal hopping matrix elements h^{AA} and h^{BB} then the two Friedel sum rule equations can be used to fix the values of the "scattering parameters" $\delta_0=\epsilon^A-\epsilon^B$ and t^{AB}. In practice, however, the success of this program depends on the value of Z, the location of the host Fermi energy μ_B, and also on the shape of the density of states $\rho_B(E)$. Indeed, the effects of off-diagonal disorder are most important in the case of isovalent impurities ($Z=0$). As Stern[4] has shown, if the scattering is cell localized ($\delta_1=0$), then the Friedel sum rule immediately implies that $\delta_0=0$, i.e., that the two constituents are identical. Including the effects of off-diagonal disorder allows us to avoid this contradiction in all cases except one: when the host crystal corresponds to a half-filled symmetric band.[11] In contrast to the isovalent case, finite values of Z do not, in principle, present any difficulty. In the limit of cell-localized disorder, this problem has been discussed by Clogston.[12] If $|Z|\ll 1$, the Friedel sum rule always fixes a well-defined value of δ_0.[13] However, as $|Z|$ is increased, the conclusion of Ref. 12 is that the ability of the Friedel sum rule to determine a self-consistent value of δ_0 is limited by two factors: the use of a single band model, and the assumption of localized scattering. Since the present discussion is still based on the single band model, we again expect that well-defined solutions of Eq. (9) will be limited to small $|Z|$, although, for a given choice of μ_B and $\rho_B(E)$, the range of allowed values of $|Z|$ will most probably change.

Finally, we consider the problem of extending the theory to finite impurity concentrations. There are three minimal requirements to be satisfied by any approximation scheme. The equations should be invariant under the interchange of A and B atoms, exact to first order in the impurity concentration in both the limits $x\to 0^+$ and $x\to 1^-$, and should reduce to the usual CPA in the absence of off-diagonal disorder. Obviously, these criteria do not determine a unique description of the alloy and we present here only the simplest consistent equations. In this spirit, let us assume that the AB transfer integral is given by the average value $h^{AB}=(h^{AA}+h^{BB})/2$. *Without any further approximations*, the Hamiltonian (1) can then be rewritten as

$$H=H_B+\sum_{n\in A}\Big\{|n\rangle\,\delta_0\langle n|+\sum_{m\neq n}{}'\,\delta_1[\,|n\rangle\langle m|+|m\rangle\langle n|\,]\Big\}=H_B+\sum_{n\in A}v_n{}^A, \tag{10}$$

where δ_0 and δ_1 are defined by Eq. (3). In Eq. (10) the disordered part of H has been expressed as a sum of (finite ranged) scattering potentials associated with each of the A atoms. This description is obviously sensible in the limit of dilute A impurities in a B crystal and, in addition, is *symmetric* under the exchange of A and B atoms. Indeed, H can also be written as $H_A+\sum_{n\in B}v_n{}^B$, where $v_n{}^B=-v_n{}^A$ describes the scattering of a B atom in an A host.

Once the disordered Hamiltonian has been written as in Eq. (10), we can immediately apply the diagrammatic techniques developed by Yonezawa.[14] The electron self-energy is then calculated from the relation

$$\Sigma(\vec{k}, z) = \sum_{p=1}^{\infty} Q_p(x)\langle \vec{k}\,|\,v(Gv)^{p-1}\,|\vec{k}\rangle \tag{11}$$

and the matrix elements $v(k, k')$ are defined by Eq. (4). The renormalized cumulants $Q_p(x)$ are polynomials in x of degree p but can, in fact, always be written as symmetric functions of x and $1-x$. If there is no off-diagonal disorder, then the terms in (11) are independent of k, the summation can be evaluated exactly, and we regain the CPA. In the presence of off-diagonal disorder, the solution of Eq. (11) for specific choices of the input parameters x, δ_0, and δ_1 will be discussed in a subsequent publication. For the present, we note that [because $Q_p(x) \to x$ (all p) as $x \to 0$], Eq. (11) reduces to the exact result $\Sigma(k, z) = xt(k, k)$ in the dilute limit, and that in addition, if the scattering is weak, we obtain the virtual crystal result $G(k, z) = [z - \langle H\rangle]^{-1}$, where

$$\langle \vec{k}|\langle H\rangle|\vec{k}\rangle = (x\epsilon^A + y\epsilon^B) + [x^2 h^{AA} + 2x(1-x)h^{AB} + (1-x)^2 h^{BB}]\, s(k).$$

The first term in this equation gives a linear shift of the band center from $\epsilon^A \to \epsilon^B$, while the second term expresses the effective bandwidth as an appropriately weighted average of the various transfer integrals.

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[9] See Fig. 5 of Ref. 3, and the associated discussion.

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