

## Localized-Perturbation Model for Alloys\*

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The strongly localized model of disordered alloys, where the random perturbations are localized to a single lattice site, is shown not to have much applicability to real systems when the self-consistency requirement on the potential is included.

A particularly simple model has played a central role in the development of the theory of alloys.<sup>1-13</sup> This model assumes that the perturbation introduced by alloying is localized on a given lattice site and does not extend to its neighboring sites. In terms of some appropriate localized set of wave functions centered around each atom, this perturbation is assumed diagonal. One of the more successful techniques for approximately solving the alloy problem has been the coherent-potential approximation (CPA).<sup>2,3</sup> All of the applications of the CPA which have yielded numerical results have utilized this model of a strongly localized perturbation.<sup>3-8,11</sup> Detailed calculations based on this model have yielded numerical data on many properties as a function of composition, electron-per-atom ratio, and size of the perturbation. In these calculations the aforementioned variables have been assumed to be independent of one another.

As has been extensively discussed elsewhere,<sup>1,14-16</sup> self-consistency requirements on the alloy perturbations add an additional restraint which has been neglected in the CPA calculations. The purpose of this Letter is to point out that the addition of this restraint causes a drastic restriction on the applicability of the localized model to real alloys. In fact, it is not an exaggeration to state that the localized-perturbation model has essentially no applicability to real systems.

Consider a dilute alloy where the various impurities are, on the average, many atomic spacings apart. In this case the effect of each impurity can be considered independent of the other impurities. Let us therefore consider a single impurity in an otherwise pure host. This impurity introduces a perturbation which, because of the shielding of the conduction electrons, is localized in its vicinity. We assume in this discussion that the impurity perturbation does not change the volume of the alloy. The actual perturbation present is a function of two factors: one the ion-core perturbation, and the other the perturbation introduced by the rearranged distribution of conduction electrons. The conduc-

tion electrons are distributed around the impurity in such a manner as to shield it completely. This requirement places a restriction on the potential produced by the perturbation. If the host is a free-electron gas, this restriction can be expressed as the Friedel sum rule,<sup>14</sup>

$$Z = (2/\pi) \sum_l (2l+1) \delta_l. \quad (1)$$

Here  $Z$  is the increased number of electrons added to the host by the impurity to maintain charge neutrality,  $l$  is the angular momentum of the spherical partial wave, and  $\delta_l$  is the phase shift in this partial wave introduced by the perturbation. It is assumed that the perturbation has spherical symmetry. Another consequence of the complete shielding of the impurity is that the Fermi level remains unchanged by the addition of dilute impurities.<sup>14</sup>

The important thing to note is that the perturbation is not a completely independent variable but has the condition (1) placed on it.

The self-consistency condition on a potential in a dilute alloy will have to be modified from (1) when the host is not a free-electron gas. We consider the strongly localized model which has been extensively studied in the CPA, namely, a single-band tight-binding alloy whose Hamiltonian is given by

$$H = \sum_n \epsilon_n |n\rangle \langle n| + W \sum_{n,\beta} |n\rangle \langle n+\beta|. \quad (2)$$

Here  $\epsilon_n$  has the value  $\epsilon_1$  or  $\epsilon_2$  depending on whether a type-1 atom or a type-2 atom, respectively, is at the  $n$ th site at  $\vec{R}_n$ . The atomic state centered at  $\vec{R}_n$  is denoted by  $|n\rangle$ . The second sum on the right of (2) is, for fixed  $n$ , over nearest neighbors, and then summed over sites.  $W$  is an overlap integral assumed the same regardless of the type of neighbor.

We limit ourselves to the dilute case which is equivalent to solving for an isolated impurity. Let the host be of type-1 atoms and the impurities of type 2. Then as shown by Mann,<sup>15</sup> the self-consistency requirement becomes

$$Z = \left(\frac{2}{\pi}\right) \tan^{-1} \left( \frac{\pi \epsilon_{21} \rho_0(E_F)}{1 - \epsilon_{21} G_{E_F}} \right), \quad (3)$$

where  $Z$  is the difference in valence between the type-2 impurities and the type-1 host,  $E_F$  is the Fermi energy, and  $\epsilon_{21} \equiv \epsilon_2 - \epsilon_1$ ; also,

$$\rho_0(E) = \Omega(2\pi)^{-3} \int_{E=E_F} dS_k / |\nabla E(\vec{k})|, \quad (4)$$

where  $\Omega$  is the atomic volume,  $dS_k$  is an element of a constant energy surface in  $k$  space, and

$$G_{E_F} = P \int \rho_0(E) dE / (E_F - E), \quad (5)$$

with  $P$  symbolizing the principle value.

We note that the self-consistency condition (3) prevents  $\epsilon_{21}$  from being an independent variable, contrary to the usual assumption in CPA calculations. For example, consider (3) for the case where the host and impurity have the same valence ( $Z=0$ ). If we assume that the host is metal-

lic so that  $\rho_0(E_F) \neq 0$ , the only possible value is

$$\epsilon_{21} = 0, \quad Z = 0. \quad (6)$$

Since when  $\epsilon_{21} = 0$  we have no alloy, we immediately note that the model (2) cannot apply to a metallic alloy composed of components with the same valence.

If we assume that the host is insulating or semiconducting so that  $\rho_0(E_F) = 0$ , then  $\epsilon_{21}$  is not defined by (3). Equation (3) assumes that the solid is in its ground state. To determine  $\epsilon_{21}$  we must consider the self-consistency requirement for the solid in an excited state. If we consider the excited state where all the electrons in the energy interval  $E_1$  to  $E_1 + \Delta E_1$  are excited from a completely occupied band to occupy fully the energy interval  $E_2$  to  $E_2 + \Delta E_2$  in an initially empty band, the self-consistency requirement leads to

$$Z = \left(\frac{2}{\pi}\right) \tan^{-1} \left( \frac{\pi \epsilon_{21} \rho_0(E_F)}{1 - \epsilon_{21} G_{E_F}} \right) - \frac{2\epsilon_{21} \Delta E_1}{\pi} \text{Im} \left[ \frac{g_{E_2}' \rho_0(E_1)}{(1 - \epsilon_{21} g_{E_2}) \rho_0(E_2)} - \frac{g_{E_1}'}{1 - \epsilon_{21} g_{E_1}} \right], \quad (3')$$

where

$$g_E = G_E - i\pi\rho_0(E) \text{ and } g_E' = dg_E/dE.$$

Here we used the relationship that  $\Delta E_1 \rho_0(E_1) = \Delta E_2 \rho_0(E_2)$ . For  $Z=0$ , (3') is satisfied for all possible  $E_1$  and  $E_2$  only when  $\epsilon_{21} = 0$ , even when  $\rho_0(E_F) = 0$ . Thus, even for an insulating semiconducting host,  $Z=0$  requires that  $\epsilon_{21} = 0$ .

Consider (3) for the case where the host and impurity have a valence differing by one ( $Z = \pm 1$ ). In that case the only possible value is

$$\epsilon_{21} = G_{E_F}^{-1}. \quad (7)$$

If  $Z = +1$ , we expect that  $\epsilon_{21} < 0$ , while for  $Z = -1$  we expect that  $\epsilon_{21} > 0$ . Requirement (7) does not permit both of these possibilities to exist simultaneously. Depending on the details of the host, which determines whether  $G_{E_F}$  is positive or negative, the model of (2) can apply to either  $Z = 1$  or  $Z = -1$  but not both simultaneously. If reasonable host properties are assumed, then the condition (7) leads to a bound state for the impurity. For no values of  $\epsilon_{21}$  can condition (3) be satisfied if  $Z$  has any other integer values. Thus the model can be used only for one of the possibilities  $Z = 1$  or  $-1$  and then only for a potential so strong that a bound state occurs. Physically both  $Z = \pm 1$  can occur for a given host, and it appears that the strongly localized model is not physical because it cannot describe this.

Other models of a strongly localized perturbation besides (2) have been employed.<sup>6,12</sup> They all have in common the case that the perturba-

tion occurs in the diagonal portion of the Hamiltonian as in (2). The same conclusion holds for them too. Their nonphysical behavior is related to the fact that the self-energy induced by the perturbation is independent of  $\vec{k}$ , i.e.,

$$\Sigma(z, \vec{k}) = \Sigma(z). \quad (8)$$

The self-energy  $\Sigma(z, \vec{k})$  is defined by

$$G_z(\vec{k}) = [z - E_k - \Sigma(z, \vec{k})]^{-1}, \quad (9)$$

where  $G_z(\vec{k})$  is the diagonal element for the  $\vec{k}$  Bloch state of the Green's function of the alloy averaged over all impurity positions,  $E_k$  is the unperturbed energy of the  $\vec{k}$  Bloch state, and the Green's function is defined by

$$G_z = (z - H)^{-1}. \quad (10)$$

In (10),  $H$  is the Hamiltonian of the alloy.

If we take the special case of the free-electron host, then the strongly localized model reduces to the condition that only  $\delta_0 \neq 0$ . The self-consistency condition (1) adds the additional restriction  $\delta_0 = 0$  when  $Z = 0$ . Thus all these shifts are equal to zero in the strongly localized model, and we can no longer have a perturbing impurity. If the perturbation is more extended so that more than one phase shift is nonzero, we can satisfy the self-consistency condition (1) for  $Z = 0$  without requiring that all phase shifts be zero.

Numerical results for alloys calculated in the CPA have only been obtained for the strongly localized perturbation model.<sup>3-8,11</sup> As indicated

above, this model has no applicability to alloys for  $Z$  even, and only extremely limited applicability to alloys where  $Z$  is  $\pm 1$ . The self-consistency requirement on the potential requires that the perturbation of an impurity be more extended than allowed by the strongly localized model. Although calculations in the CPA have been closely tied in with the strongly localized perturbation model, the inapplicability of this model does not mean that the CPA is not applicable nor does it necessarily mean that all conclusions on the properties of alloys obtained from this model are incorrect. One would expect that the model cannot be trusted to give quantitative results, and qualitative results should be treated with some caution. To conform better with reality, the model used will have to employ a more extended perturbation, requiring a reformulated form<sup>17,18</sup> of the CPA or a new approach.<sup>19</sup> In addition, the self-consistency of the perturbation must also be solved simultaneously with the rest of the calculation. It is not possible to treat the perturbation as an independent variable to be varied at will.

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## Logarithmic Field Dependence of the Susceptibility of a Paramagnetic Fermi Liquid—the Pd Problem

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The susceptibility  $\chi(H)$  of a paramagnetic Fermi liquid in a magnetic field is shown to have the logarithmic form  $\chi(H) = \chi(0)(1 - bH^2 \ln H)$ , and hence the free energy of the system cannot be expanded in powers of  $H$  or in powers of the magnetization. Contrary to the result of the band model, this prediction is consistent with the experimental field dependence observed in Pd.

Among various metals, palladium is one of the most intractable and hence the most fascinating from the standpoint of studying magnetism. Recently, for Pd, the magnetic field dependence of the paramagnetic susceptibility  $\chi(H)$  (or nonlinear magnetization) has been measured,<sup>1</sup> the result being expressed approximately in the form  $\chi(H) = \chi(0)(1 + \beta H^2)$  with  $\beta = 6.0 \times 10^{-14} \text{ Oe}^{-2}$ . Prior

to this experiment Wohlfarth<sup>2</sup> gave an expression for  $\beta$  on the basis of the band theory with consideration for the effect of exchange enhancement. Most recent data<sup>3</sup> on the band structure of Pd give us the theoretical value of  $\beta$  as negative:  $\beta = -2.5 \times 10^{-13}$  or  $-1.1 \times 10^{-12} \text{ Oe}^{-2}$ , which apparently contradicts experiment.

Here we shall give a clue as to how this dis-