PHYSICAL REVIEW B VOLUME 9, NUMBER 6 15 MARCH 1974

Electronic properties of alloy models in the dilute limit*

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(Received 18 September 1973)

It is shown rigorously that the introduction of random-hopping elements into an impurity potential in a material with a single band does not introduce any of the new phase shifts required to generally satisfy the Friedel sum rule in the dilute limit. With this proof it is now clear that the parameters required to satisfy the Friedel sum rule as suggested by Schwartz, Krakauer, and Fukuyama (SKF) are artificial in spite of the off-diagonal character of their model. Other models are suggested which give rise to phase shifts of more than one character. Also, it is demonstrated that the locator theory of Blackman, Esterling, and Berk (and hence that of Shiba) is a correct s-wave theory in the dilute limit in contrast to the claim of SKF.

I. INTRODUCTION

A great deal of useful information has been acquired over the years concerning the fundamental electronic properties of binary alloys from studies of the simple diagonal model of Koster and Slater[1] which has a single narrow band, in which the perturbation introduced by alloying is localized on a given lattice site. Nevertheless, as Stern[2] has emphasized, this model contains only s-wave scattering and hence does not have sufficient flexibility to allow satisfaction of the solid-state form of the Friedel sum rule.[3]

Several authors[4-7] have recently reported calculations on an off-diagonal hopping-disorder model in which the impurity potential is allowed to have diagonal matrix elements on the impurity site and off-diagonal elements linking the impurity site to its nearest neighbors. Schwartz *et al.*[7] (hereafter called SKF) have recently claimed that this extended potential now has sufficient flexibility to generally allow satisfaction of the Friedel sum rule.

In this comment, we show rigorously that the terms introduced into the impurity potential by this form of off-diagonality act only to modify the s-wave[8] phase shift by a single impurity, and do not introduce phase shifts associated with other partial waves. This feature is explicitly illustrated for the case of a simple cubic lattice, and the suggestion of multiple bands is made to give nonzero p and d phase shifts and allow a more general satisfaction of the Friedel sum rule than that possible with a single phase shift. In addition, we demonstrate briefly the correctness of the locator theories of Blackman *et al.*[4], and Shiba[5] in the dilute limit in contradiction to the claims of SKF.

II. NONZERO PHASE SHIFTS IN THE HOPPING-DISORDER MODEL

In the hopping-disorder model as discussed, for example, by SKF, the host has a single s band, the impurity potential V is invariant under all of the operations of the point group of the lattice, and the only nonzero matrix elements between Wannier states are when at least one of these states is that associated with the site occupied by the impurity atom.

Because of the symmetry of V, it may be block diagonalized in the bases of the irreducible representations of the lattice group that span the subspace operated on by the impurity potential. Since the Wannier state associated with the impurity site is itself one of the basis states of the s representation, it is clear from group theory that in this new basis, no matrix elements of V involving this site can occur outside of the s block (since V is block diagonal in this representation), and consequently, the hopping-disorder impurity potential has only s-wave scattering. As the Green's function on the same subspace is also block diagonalized by the same unitary transform, the t matrix also has only s-wave scattering, and the off-diagonal matrix elements in this model only modify the s-wave phase shift.

It is generally artificial to attempt to satisfy the Friedel sum rule with only a single scattering channel, and, indeed, for some values of the Fermi energy it is impossible (as has recently also been pointed out by Rudnick and Stern[9] for simple cubic materials). In addition, close to these impossible values of the Fermi energy the necessary values of the off-diagonal scattering must be so large [see, for example, Eq. (A4) of Ref. 9] that the system would be extremely susceptible to order-disorder transitions if these values occurred in real solids. A minimum requirement on V to allow higher phase shifts in a single-s-band model is to include changes in the diagonal matrix elements on sites neighboring the impurity,[9] such as would result physically from a screening charge on these sites.

If, instead of considering an s band, we consider a single band of Wannier states having some lower symmetry, such as a d band, the same argument carries through directly by replacing the references to the s-wave phase shift by that of the appropriate lower-symmetry representation.

III. SIMPLE CUBIC EXAMPLE

The above general arguments will now be demonstrated for an impurity in a simple cubic crystal. The impurity potential operates on the subspace of Wannier states spanned by the impurity site and the six nearest neighbors. Arranging these seven states in the order of the central site, followed by the nearest neighbor in pairs of opposing atoms, we assume the potential is of the matrix form

$$V=\begin{pmatrix} \delta_0 & \delta_1 & \delta_1 & \delta_1 & \delta_1 & \delta_1 & \delta_1 \\ \delta_1 & \delta_2 & 0 & 0 & 0 & 0 & 0 \\ \delta_1 & 0 & \delta_2 & 0 & 0 & 0 & 0 \\ \delta_1 & 0 & 0 & \delta_2 & 0 & 0 & 0 \\ \delta_1 & 0 & 0 & 0 & \delta_2 & 0 & 0 \\ \delta_1 & 0 & 0 & 0 & 0 & \delta_2 & 0 \\ \delta_1 & 0 & 0 & 0 & 0 & 0 & \delta_2 \end{pmatrix}, \qquad (1)$$

where

$$\langle 0|V|0\rangle=\delta_0, \quad \langle 1|V|0\rangle=\delta_1, \quad \langle 1|V|1\rangle=\delta_2,$$

and $|1\rangle$ is any nearest-neighbor site.

In forming this potential, diagonal perturbations on the nearest-neighbor sites have been included (δ_2) to allow the appearance of scattering in the p and d channels. The elements between the neighbor sites have been ignored.

As discussed by Wolfram and Callaway,[10] the unitary transformation S necessary to block-diagonalize this potential in terms of the irreducible representations of the group is

$$S=\begin{pmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & a & b & 0 & 0 & 0 & d \\ 0 & a & -b & 0 & 0 & 0 & d \\ 0 & a & 0 & b & 0 & c & e \\ 0 & a & 0 & -b & 0 & c & e \\ 0 & a & 0 & 0 & b & -c & e \\ 0 & a & 0 & 0 & -b & -c & e \end{pmatrix}, \qquad (2)$$

where $a=1/\sqrt{6}$, $b=1/\sqrt{2}$, $c=1/2$, $d=1/\sqrt{3}$, $e=1/\sqrt{12}$. Under this transformation, the potential becomes

$$V'=S^{\dagger}VS=\begin{pmatrix} \begin{pmatrix} \delta_0 & \sqrt{6}\,\delta_1 \\ \sqrt{6}\,\delta_1 & \delta_2 \end{pmatrix} & 0 & 0 \\ 0 & \begin{pmatrix} \delta_2 & 0 & 0 \\ 0 & \delta_2 & 0 \\ 0 & 0 & \delta_2 \end{pmatrix} & 0 \\ 0 & 0 & \begin{pmatrix} \delta_2 & 0 \\ 0 & \delta_2 \end{pmatrix} \end{pmatrix}.$$

The first block operates on the two s states (Γ_1), the second on the three p states (Γ'_{15}), and the third on the two d states (Γ_{12}). The same unitary transformation block-diagonalizes the Green's function,[11] giving

$$G'=S^{\dagger}GS=\begin{pmatrix} \begin{pmatrix} G_{00} & \sqrt{6}\,G_{01} \\ \sqrt{6}\,G_{01} & G_s \end{pmatrix} & 0 & 0 \\ 0 & \begin{pmatrix} G_p & 0 & 0 \\ 0 & G_p & 0 \\ 0 & 0 & G_p \end{pmatrix} & 0 \\ 0 & 0 & \begin{pmatrix} G_d & 0 \\ 0 & G_d \end{pmatrix} \end{pmatrix}, \qquad (3)$$

where

$$G_s(E)=\frac{6}{N}\sum_k \frac{\gamma_k^2}{E-E_k}, \quad G_{00}=\frac{1}{N}\sum_k \frac{1}{E-E_k}, \quad G_p(E)=\frac{1}{N}\sum_k \frac{(1-\gamma_{2k})}{E-E_k}, \quad G_{01}=\frac{1}{N}\sum_k \frac{\gamma_k}{E-E_k},$$

$$G_d(E)=\frac{1}{N}\sum_k \frac{\frac{3}{2}(1+\gamma_{2k}-2\gamma_k^2)}{E-E_k},$$

and $\gamma_k=\frac{1}{3}(\cos k_x a+\cos k_y a+\cos k_z a)$.

The t matrix may now be written in block diagonal form, with the three blocks

$$t_s(E)=\left[\begin{pmatrix}1&0\\0&1\end{pmatrix}-\begin{pmatrix}\delta_0&\sqrt{6}\,\delta_1\\\sqrt{6}\,\delta_1&\delta_2\end{pmatrix}\begin{pmatrix}G_{00}&\sqrt{6}\,G_{01}\\\sqrt{6}\,G_{01}&G_s\end{pmatrix}\right]^{-1}\begin{pmatrix}\delta_0&\sqrt{6}\,\delta_1\\\sqrt{6}\,\delta_1&\delta_2\end{pmatrix}, \tag{4a}$$

$$t_p(E)=[1-\delta_2G_p(E)]^{-1}\delta_2\begin{pmatrix}1&0&0\\0&1&0\\0&0&1\end{pmatrix}, \tag{4b}$$

$$t_d(E)=[1-\delta_2G_d(E)]^{-1}\delta_2\begin{pmatrix}1&0\\0&1\end{pmatrix}. \tag{4c}$$

Now it can be seen that when δ_2 is set to zero, as in the hopping-disorder model, only the s-wave scattering is nonzero and the diagonal element of the t matrix in k space becomes

$$t^s_{kk}=\frac{\delta_0+6\delta_1^2G_s+12\delta_1(1-6\delta_1G_{01})\gamma_k+36\delta_1^2G_{00}\gamma_k}{1-\delta_0G_{00}-12\delta_1G_{01}+36\delta_1^2G_{01}^2-6\delta_1^2G_{00}G_s}. \tag{5}$$

This term, which is the negative of the correction to the inverse Green's function to first order in impurity concentration, is just the result obtained by Blackman *et al.*[4] in their locator theory of s-wave scattering.

IV. DILUTE LIMIT OF THE THEORY OF BLACKMAN, ESTERLING, AND BERK

Since the accuracy of the theory[4] of Blackman *et al.* (BEB) in the dilute limit has been strongly questioned by SKF,[7] we shall carefully expand their inverse Green's function to first order in concentration of A impurities to demonstrate the accuracy of their result. The main result obtained by Blackman *et al.* for a binary alloy is expressed in the 2×2 matrix equations

$$\tilde{G}_k(E)=\begin{pmatrix}\dfrac{E-E_A-C_BU_1-C_AW_k^{AA}}{C_A}&U_3-W_k^{AB}\\U_3-W_k^{AB}&\dfrac{E-E_B-C_AU_2-C_BW_k^{BB}}{C_B}\end{pmatrix}^{-1}, \tag{6a}$$

$$\frac{1}{N}\sum_k\tilde{G}_k(E)=\begin{pmatrix}\dfrac{C_A}{E-E_A-U_1}&0\\0&\dfrac{C_B}{E-E_B-U_2}\end{pmatrix}, \tag{6b}$$

where E_A and E_B are the cell-localized potentials associated with A and B atoms, which occur at concentrations C_A and C_B, respectively. W_k^{AA} and W_k^{BB} are the hopping matrix elements between the atoms indicated in the superscripts, and U is the renormalized interactor defined in Ref. 4 and determined by Eq. (6b).

The Green's function G_k is given by the sum of the four elements of the matrix $\tilde{G}_k$, and thus the inverse Green's function is given by

$$G_k^{-1}=\frac{(E-E_A-C_BU_1-C_AW_k^{AA})(E-E_B-C_AU_2-C_BW_k^{BB})-C_AC_B(U_3-W_k^{AB})^2}{C_B(E-E_A-C_BU_1-C_AW_k^{AA})+C_A(E-E_B-C_AU_2-C_BW_k^{BB})-2C_AC_B(U_3-W_k^{AB})}. \tag{7}$$

To first order in the concentration of A atoms, this becomes

$$G_k^{-1}=E-E_B-W_k^{BB}-C_A\left(\frac{(E-E_B-U_3+W_k^{BB})^2}{E-E_A-U_1}+E_B+U_2-E\right). \tag{8}$$

Letting $W_k^{AB}-W_k^{BB}=6\delta_1\gamma_k$, $E_A-E_B=\delta_0$, and using the values of the U_i to zeroth order in C_A, given by

$$(E-E_B-U_3)G_{00}=1-6\delta_1G_{01}, \tag{9a}$$

$$(E-E_B-U_2)G_{00}=1, \tag{9b}$$

$$(E-E_B-U_1)G_{00}=(1-6\delta_1G_{01})^2-6\delta_1^2G_sG_{00}, \tag{9c}$$

then, the inverse Green's function becomes

$$G_k^{-1}(E)=E-E_B-W_k^{BB}-C_A\,\frac{\delta_0+6\delta_1^2G_s+12\delta_1(1-6\delta_1G_{01})\gamma_k+36\delta_1^2G_{00}\gamma_k^2}{1-\delta_0G_{00}-12\delta_1G_{01}+36\delta_1^2G_{01}^2-6\delta_1^2G_{00}G_s}\ ,$$

which, from Eq. (5), is the exact dilute limit for this model. Although this proof was formulated in terms of Callaway's formalism with only nearest-neighbor hopping, the proof can rather trivially be extended to arbitrary forms of W_k^{AA}, W_k^{AB}, and W_k^{BB}. Furthermore, Blackman[12] has recently shown that this theory of BEB reduces exactly, for the special case of separable hopping elements, to Shiba's locator theory for a binary alloy. Hence Shiba's theory is also an exact s-wave theory in the dilute limit (in contrast to the claim in Ref. 7). Perhaps it should be said, however, that a proof that Shiba's theory has the correct dilute limit is easily formulated in Shiba's notation which is not restricted to that of a binary alloy.[13] Finally, the further approximation by Brouers *et al.*[6] on Shiba's theory does not have the correct dilute value for G_k^{-1} since $\Sigma(k)$ is truncated to first order in γ_k although this approximation happens to preserve the correct dilute limit for G_{00}.

V. DISCUSSION OF THE MODELS

So far in this paper, the discussion has centered on a single narrow-band model for a metal, and how Friedel's sum rule might best be satisfied. Since the sum rule is a property of the whole system, and not just of a particular band on which we are concentrating, it is instructive to remember that when narrow bands occur in tight-binding metals, there are generally bands of other symmetries also present, such as hybridized s-d bands in transition-metal alloys, where one might wish to concentrate only on the d bands. In this case, even a cell-localized potential will create as many different phase shifts as there are bands of different symmetry at the Fermi surface and thus a many-band-type of potential might conceivably satisfy the sum rule without any extension to off-diagonal disorder. Certainly, in discussing the importance of off-diagonal disorder for satisfying Friedel's sum rule for the d bands in transition metals, the effects of the s bands should be explicitly included if one wishes to make quantitative comments.

ACKNOWLEDGMENT

The authors are grateful to Dr. Joseph Sak for stimulating conversations.

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*Work supported in part by the National Science Foundation.

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