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Effect of alloying on the Fermi surface*

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We obtain a theoretical expression for the change in Fermi-surface areas when dilute impurities are introduced in a nearly-free-electron-like host metal or in a d-band host metal having no resonances in the immediate vicinity of the Fermi energy. Following Stern, we obtain the Fermi surface from the real part of the self-energy. The self-energy is derived within a pseudopotential T-matrix formalism which is developed as an extension of usual scattering theory. We approximate the crystal lattice Green's function by a free-electron propagator in the T-matrix equation. The final expression for Fermi-surface changes involves impurity scattering phase shifts and pseudo-wave-function angular momentum expansion coefficients. These are the same parameters which enter the expression for the electron lifetime. The theoretical results are in agreement with recent de Haas–van Alphen measurements in dilute lead and magnesium based alloys.

I. INTRODUCTION

The concept of the Fermi surface is fundamental in the theory of metals.[1] As usually defined, the Fermi surface is meaningful only for crystals in which the one-electron Hamiltonian is perfectly periodic. When an impurity is introduced into a perfect crystal the Fermi surface formally ceases to exist, at least as far as its definition as a mathematical surface of constant energy in the space of the Bloch quantum number $\vec{k}$. The point is that $\vec{k}$ only exists as a quantum number because of the exact periodicity of the Hamiltonian, and this periodicity is destroyed when an impurity is introduced.

Nonetheless, as Stern has shown,[2-4] one can still speak in a meaningful way about Fermi-surface changes upon introducing impurities. The key to understanding this is the concept of the electron self-energy $\Sigma(\vec{k},E)$.[5,6] It has been shown by Stern that for weak scattering,[3] or more generally, when the "forward-scattering approximation" is valid,[4] it is meaningful to obtain changes in the Fermi surface from the relation

$$\Delta E(\vec{k}) = \mathrm{Re}\Sigma(\vec{k},E) \; . \tag{1}$$

Here $\Delta E(\vec{k})$ is the energy shift due to impurities for the original Bloch state $\vec{k}$ at energy E. The "forward-scattering approximation" assumes that $\mathrm{Re}\Sigma(\vec{k},E) \gg \mathrm{Im}\Sigma(\vec{k},E)$.[4] This insures that the lifetime, which is proportional to $[\mathrm{Im}\Sigma(\vec{k},E)]^{-1}$, is long enough so that the energy shift can be observed without the uncertainty principle blurring it out.

In general, $\Sigma(\vec{k},E)$ is defined through the Green's function $G=(E-H-i\epsilon)^{-1}$ by the relation[5,6]

$$\langle \psi_{\vec{k}} | G | \psi_{\vec{k}} \rangle = [E - E_0(\vec{k}) - \Sigma(\vec{k},E) - i\epsilon]^{-1} \; , \tag{2}$$

where $\psi_{\vec{k}}$ are the Bloch states in the perfect crystal (in the absence of impurities) and H is the full Hamiltonian including the impurities. $E_0(\vec{k})$ is the energy of state $\vec{k}$ in the absence of impurities. ϵ is a positive infinitesimal. In practice, the Green's function appearing in Eq. (2) is averaged over all impurity configurations since this ensemble-averaged G is simpler to work with and has the required physical content.

Equation (2) is fundamental in that $\langle \psi_{\vec{k}} | G | \psi_{\vec{k}} \rangle$, and hence $\Sigma(\vec{k},E)$, enables one to calculate relevant physical quantities *whether or not the Fermi surface "exists."* An important example is the theory of the de Haas–van Alphen effect in dilute alloys. It turns out that Green's-function calculations of the de Haas–van Alphen periods[7,8] give results identical to those obtained by naively calculating Fermi-surface area changes using Eq. (1). In this respect, even when the "forward-scattering approximation" is not valid, and therefore Fermi-surface changes are not meaningful in Stern's sense,[2-4] it is useful to pretend that a Fermi-surface change is taking place. That is the position we adopt here as we calculate Fermi-surface changes according to Eq. (1).

It is worth emphasizing that $\mathrm{Re}\Sigma(\vec{k},E)$ as determined from scattering theory does not rigorously give the energy shifts of the unperturbed states although it may enter theoretical expressions for various phenomena in a role equivalent to such a shift. In fact, it has been pointed out by Anderson and McMillan[9] and others[6,9] that the poles of Eq. (2) as determined by scattering theory do not correspond to the perturbed energy levels except in the case where the scattering phase shifts are very small. This, of course, is consistent with Stern's requirement that the "forward-scattering approximation" be valid.

To appreciate the distinction between $\mathrm{Re}\Sigma(\vec{k},E)$ and the actual energy shift one should recall how complex $\Sigma(\vec{k},E)$ comes about. One starts with the observation that the poles of the Green's function pin-point the energies of the eigenstates in the perturbed crystal, and that these energies are of course real. To show this, one can let G operate on $\sum_n |\Psi_n\rangle\langle\Psi_n| = 1$, where Ψ_n are the exact complete set of eigenfunctions in the presence of the impurities. One then obtains

$$G = \sum_n (E - E_n - i\epsilon)^{-1} |\Psi_n\rangle\langle\Psi_n| ,$$

where E_n are the eigenvalues of H. In the limit $\epsilon \to 0$ for a crystal of finite volume, the poles of G therefore occur at $E = E_n$. On the other hand, the poles of Eq. (2) occur at complex energies since $\Sigma(\vec{k}, E)$ is complex. The resolution of this apparent paradox is subtle and involves the handling of the $\epsilon \to 0$ limit and the $V \to \infty$ limit (V is the volume).[5,6] In the scattering-theory limit procedure the $V \to \infty$ limit is taken before the $\epsilon \to 0$ limit. This implicitly introduces the physical assumption that the individual discrete eigenstates are so close together that only a level density is meaningful.[10] Analytic continuation of the Green's function then gives a pole at complex energy $E = E_0(\vec{k}) + \Sigma(\vec{k}, E)$. This pole simulates the effect of the state $\vec{k}$ and its interaction with a level density of neighboring states. The complex energy is associated with the complex frequency $\omega = E/\hbar$ which describes the time development of a particle placed in the unperturbed state $|\psi_{\vec{k}}\rangle$ before the interaction is turned on. This frequency is not the real frequency associated with a particle placed in the perturbed state $|\Psi_{\vec{k}}\rangle$. However, if the damping is small enough the two frequencies must be approximately equal.

Keeping in mind these points concerning the conceptual limitations of Eq. (1), we proceed to calculate Fermi-surface changes. Our method of calculation is based on pseudopotentials and orthogonalized plane waves (OPW's).[11,12] The OPW-pseudopotential theory has proven useful, especially in dealing with simple metals[11,12] and noble metals.[13,14] Other techniques, based on the Kohn-Korringa-Rostoker (KKR) formalism[15,16] or Wannier functions,[17] may be more useful for other metals.

The phase-shift model for the T matrix which we shall use is derived here more rigorously than it was in our earlier discussion of Dingle temperatures.[18-20] Our results are similar in structure to the results obtained through a KKR formalism by Coleridge[21] in applying the theory he developed with Holzwarth and Lee.[16]

II. FERMI-SURFACE CROSS SECTIONS

We obtain the change in Fermi-surface extremal cross sections from Eq. (1) for the case of a very dilute concentration of impurities. The impurities will change the Fermi energy from the unperturbed value E_F^0 to the perturbed value E_F where

$$E_F = E_0(\vec{k}) + \mathrm{Re}\Sigma(\vec{k}, E) . \tag{3}$$

We assume for now that there is no change in volume upon introduction of a very dilute concentration of impurities (corrections will be discussed in Sec. V B). This implies that the change in Fermi energy is zero.[22,23] We define $\delta\vec{k}$ to be the change in wave vector $\vec{k}$ in order to get to the new Fermi surface from the old Fermi surface. To lowest order in the concentration of impurities the Fermi energy change is

$$\delta E_F = \hbar \vec{v}_{\vec{k}} \cdot \delta\vec{k} + \mathrm{Re}\Sigma(\vec{k}, E_F^0) = 0 , \tag{4}$$

where $\delta E_F = E_F - E_F^0$ and $\vec{v}_{\vec{k}} = \hbar^{-1} \partial E_0 / \partial \vec{k}$ is the velocity of an electron in state $\vec{k}$.

Equation (4) allows one to solve for the change in the component of $\delta\vec{k}$ normal to the original Fermi surface. This fixes the new Fermi surface. Upon integrating around an orbit on the new Fermi surface we obtain an area change δA given by

$$\delta A = -(2\pi/\hbar^2) m_{\mathrm{BS}} \langle \mathrm{Re}\Sigma(\vec{k}, E_F^0) \rangle , \tag{5}$$

where m_{BS} is the band-structure effective mass with the sign convention that it is positive for an electronlike orbit and negative for a holelike orbit. δA is positive if an electronlike orbit area increases or a holelike orbit area decreases, and negative otherwise. The average $\langle \cdots \rangle$ is defined for any function $f(\vec{k})$ as

$$\langle f(\vec{k}) \rangle = \left(\oint \frac{f(\vec{k})\, dk}{v_\perp} \right) \Big/ \oint \frac{dk}{v_\perp} , \tag{6}$$

where $v_\perp$ is the magnitude of the component of velocity $\vec{v}_{\vec{k}}$ in the plane of the orbit and the integrals are around the orbit.

To calculate $\Sigma(\vec{k}, E)$ we use the relation that for dilute impurity concentration[5,8]

$$\Sigma(\vec{k}, E) = cN T_{\vec{k}\vec{k}} , \tag{7}$$

where c is the atomic concentration of impurities, N is the total number of atoms, and $T_{\vec{k}\vec{k}} = \langle \psi_{\vec{k}} | T | \psi_{\vec{k}} \rangle$ is the diagonal element of the T matrix for a single impurity in the unperturbed Bloch state representation. $T_{\vec{k}\vec{k}}$ will be evaluated within a pseudopotential scattering theory formalism.

III. PSEUDOPOTENTIAL SCATTERING THEORY

A. Derivation of T matrix

To evaluate $T_{\vec{k}\vec{k}}$ we introduce the pseudo-wave-function $\Phi_{\vec{k}}$, which is related to the exact wave function $\Psi_{\vec{k}}$ by[11,12]

$$\Psi_{\vec{k}} = (1 - P)\Phi_{\vec{k}} , \tag{8}$$

where $P = \sum_\alpha |\alpha\rangle\langle\alpha|$ is the projection operator onto the actual core states $|\alpha\rangle$ in the presence of the impurity.

Following pseudopotential theory[11,12] we use Eq. (8) to transform the Schrödinger equation $H\Psi_{\vec{k}} = E\Psi_{\vec{k}}$ into the corresponding pseudopotential equation

$$H_{\text{ps}}\Phi_{\vec{k}} = E\Phi_{\vec{k}} , \tag{9}$$

where H_{ps} is the total pseudo-Hamiltonian, i.e.,

$$H_{\text{ps}} = H_{\text{ps}}^0 + w , \tag{10}$$

where H_{ps}^0, the pseudo-Hamiltonian in the perfect crystal, equals $\vec{p}^2/2m + W^0$, where $\vec{p}$ is the electron momentum, m is the electron bare mass, and W^0 is the pseudopotential for the perfect crystal. w is the impurity scattering pseudopotential.

The Lippman-Schwinger equation[6] based on Eq. (9) is[24]

$$\Phi_{\vec{k}} = \phi_{\vec{k}} + (E - H_{\text{ps}} - i\epsilon)^{-1} w \phi_{\vec{k}} , \tag{11}$$

where $\phi_{\vec{k}}$ are the unperturbed pseudo-wave-functions satisfying $H_{\text{ps}}^0 \phi_{\vec{k}} = E_0(\vec{k})\phi_{\vec{k}}$. The connection between $\psi_{\vec{k}}$ and $\phi_{\vec{k}}$ is[11,12]

$$\psi_{\vec{k}} = (1 - P^0)\phi_{\vec{k}} , \tag{12}$$

where P^0 is the projection operator onto the core states of the perfect crystal.

The structure of Eqs. (9)–(11) is identical to the equations in which H_{ps} is replaced by a real Hamiltonian. Therefore, in analogy to that case we can define a pseudo-T-matrix T^{ps} by

$$\langle \phi_{\vec{k}'} | T^{\text{ps}} | \phi_{\vec{k}} \rangle = \langle \phi_{\vec{k}'} | w | \Phi_{\vec{k}} \rangle \tag{13}$$

and obtain

$$T^{\text{ps}} = w + wG^{\text{ps}}w + wG^{\text{ps}}wG^{\text{ps}}w + \cdots , \tag{14}$$

where $G^{\text{ps}} = (E - H_{\text{ps}}^0 - i\epsilon)^{-1}$ plays the role of the Green's function for the pseudo-Hamiltonian.[25]

Since $T_{\vec{k}\vec{k}} = \langle \psi_{\vec{k}} | w | \Psi_{\vec{k}} \rangle$, assuming a Hermitian w, it follows from Eqs. (8) and (12) that

$$T_{\vec{k}\vec{k}} = \langle \phi_{\vec{k}} | w | \Phi_{\vec{k}} \rangle + \langle \phi_{\vec{k}} | P^0 w P - P^0 w - wP | \Phi_{\vec{k}} \rangle . \tag{15}$$

Now according to pseudopotential theory, the plane-wave matrix elements of P or P^0 are regarded as small compared to unity[11] (generally $\langle \vec{k} | P | \vec{k}' \rangle \leq 0.1$, where $|\vec{k}\rangle$ stands for a plane-wave state). Therefore, since $\phi_{\vec{k}}$ is generally plane-wave-like in OPW-pseudopotential theory,[11] we can ignore the second term in Eq. (15), and write to a good approximation

$$T_{\vec{k}\vec{k}} = \langle \phi_{\vec{k}} | T^{\text{ps}} | \phi_{\vec{k}} \rangle . \tag{16}$$

Equation (16) is a generalization of a result obtained by Austin, Heine, and Sham[26] for weak pseudopotentials. In their work T^{ps} was replaced by w since the Born approximation was used.

B. Approximation scheme

Our next approximation restricts us to metals with small energy gaps near the energy E_F^0. We propose replacement of G^{ps} in Eq. (14) by the free-electron propagator $G_0^{\text{ps}} = (E_F^0 - \vec{p}^2/2m - i\epsilon)^{-1}$. This replacement is valid for small band gaps since only electrons scattered by w into the relatively few states in the immediate vicinity of the gaps are exposed to the crystal-lattice scattering effects contained in G^{ps} but not in G_0^{ps}. Mathematically one can see this by inserting the complete set of intermediate states[27] $\{|\psi_{\vec{k}}\rangle, |\alpha\rangle\}$ between the G^{ps} and w operators in Eq. (14). For small gaps, the contribution is dominated by matrix elements of G^{ps} between free-electron-like (one-OPW) states $|\psi_{\vec{k}}\rangle$, and these matrix elements are very close to the matrix elements of G_0^{ps} between these states. This implies G^{ps} may be replaced by G_0^{ps} in Eq. (14).

Clearly a large domain of non-free-electron-like states in the neighborhood of E_F and within scattering range of w would spoil this approximation scheme. We are thus restricted to nearly-free-electron-like metals and to noble metals or other d-band metals with resonances well removed from E_F. The d-band metal case can be handled within the framework of Harrison's transition-metal pseudopotential.[13] This would lead to extra d orbitals contributing to Eq. (8) and to Eq. (15). It can easily be verified that these corrections are of order $\Delta/(E_F - E_d)$, where Δ is the d bandwidth and E_d is the position of d band. The corrections are therefore negligible provided that E_F is sufficiently removed from resonance.

It is important to realize that our approximation does not require that the individual atomic pseudopotentials of the host lattice are weak. We only require that the energy gaps are small, i.e., that the full pseudopotential is weak at a reciprocal-lattice vector. This does not imply that the atomic phase shifts are small.[28]

Our approximation then replaces (14) by

$$T^{\text{ps}} = w + wG_0^{\text{ps}}w + wG_0^{\text{ps}}wG_0^{\text{ps}}w + \cdots , \tag{17}$$

which is equivalent to the T matrix of a scatterer w placed in a free-electron gas. Assuming spherical symmetry for w, the plane-wave matrix elements between plane-wave states on an energy shell is therefore[29]

$$\langle \vec{k} | T^{\text{ps}} | \vec{k}' \rangle = \frac{-2\pi\hbar^2}{mk_F\Omega} \sum_{l=0}^{\infty} (2l+1) e^{i\delta_l} \sin\delta_l P_l(\cos\theta) , \tag{18}$$

where k_F is the Fermi wave vector, Ω is the crystal volume, and θ is the angle between $\vec{k}$ and $\vec{k}'$ on the one-OPW Fermi sphere $|\vec{k}| = |\vec{k}'| = k_F$. The phase shifts δ_l are at the Fermi energy. The P_l are Legendre functions.

We now expand $\phi_{\vec{k}}$ in plane waves, by writing

$$|\phi_{\vec{k}}\rangle = \sum_n a_n(\vec{k}) |\vec{k} - \vec{q}_n\rangle \ ,$$

where $\vec{q}_n$ are the reciprocal-lattice vectors, and use Eqs. (7), (16), and (18) to obtain

$$\Sigma(\vec{k}, E) = \frac{-2\pi\hbar^2 c}{m k_F \Omega_0} \sum_{l=0}^{\infty} (2l+1) F_l e^{i\delta_l} \sin\delta_l \ , \tag{19}$$

where

$$F_l = \sum_{n,n'} a_n^*(\vec{k}) a_{n'}(\vec{k}) P_l(\cos\theta_{nn'}) \ , \tag{20}$$

and where $\Omega_0 = \Omega/N$ and $\theta_{nn'}$ is the angle between $\vec{k} - \vec{q}_n$ and $\vec{k} - \vec{q}_{n'}$. In obtaining (19) by using (18) we have had to assume that the appreciable $a_n(\vec{k})$ coefficients occur for $|\vec{k} - \vec{q}_n|$ very near k_F. This "on-Fermi-sphere approximation" is a good one if the energy gaps are small near the Fermi energy.[12]

We remark that the basic idea of using a plane-wave T-matrix expression similar to (18) for describing scattering between Bloch states $\psi_{\vec{k}}$ was originally suggested by Ziman along heuristic lines.[30] In our derivation we have shown how the approximation can be justified within pseudopotential theory.

IV. CALCULATION OF FERMI-SURFACE CHANGES

The self-energy (19) leads via Eq. (5) to a relative change in the Fermi-surface cross-sectional area A which is given by

$$\frac{\delta A}{A} = \frac{2\pi^2 m_{\text{BS}} c}{m k_F \Omega_0 A} \sum_{l=0}^{\infty} (2l+1) \langle F_l \rangle \sin 2\delta_l \ . \tag{21}$$

Note that in the free-electron limit $\langle F_l \rangle = 1$, and we obtain a result identical to Soven's for the relative change in area, or equivalently, in de Haas–van Alphen frequencies.[7] In the weak-scattering limit ($|\delta_l| \ll \frac{1}{2}\pi$) we recover the perturbation theory result based on replacing $\text{Re}\Sigma(\vec{k}, E_F^0)$ by $\langle \phi_{\vec{k}} | w | \phi_{\vec{k}} \rangle$ in Eq. (5). The free-electron weak-scattering limit of (21) gives the rigid-band-model result[31] except that the band-structure density of states $n(E_F^0)$ in the rigid-band model is replaced by its free-electron value $m k_F / \pi^2 \hbar^2$. The rigid-band-model result is[31]

$$\left(\frac{\delta A}{A}\right)^{\text{rbm}} = \frac{2\pi m_{\text{BS}} c \Delta Z}{\hbar^2 \Omega_0 n(E_F^0) A} \ , \tag{22}$$

where ΔZ is the nominal valence difference between impurity and host atoms. ΔZ can be related to the phase shifts δ_l through the Friedel sum rule[23]

$$\Delta Z = \frac{2}{\pi} \sum_l (2l+1) \delta_l \ ,$$

provided that lattice distortion is neglected.

Equation (21) gives the area changes on alloying in terms of the parameters $\langle F_l \rangle$ and δ_l. These are the same parameters needed to calculate the Dingle temperature X^* which enters the de Haas–van Alphen effect.[18-20]

The relation between X^* and the self-energy is

$$X^* = -(m_{\text{BS}}/m^* \pi k_B) \langle \text{Im}\Sigma(\text{k}, E_F^0) \rangle \ ,$$

where m^* is the phonon enhanced electron mass and k_B is Boltzmann's constant.[16] From Eq. (19) we then obtain our earlier result[20]

$$X^* = \frac{2\hbar^2 c m_{\text{BS}}}{m k_F \Omega_0 k_B m^*} \sum_{l=0}^{\infty} (2l+1) \langle F_l \rangle \sin^2\delta_l \ . \tag{23}$$

The $\langle F_l \rangle$ factors can easily be determined for each orbit of interest from an OPW calculation. This has been done for Al,[18] In,[18] Pb,[18,20] and Mg.[32] The only undetermined parameters are the δ_l characterizing the impurity scattering. These phase shifts can be obtained from first-principles pseudopotentials or model potentials. It is easier, however, to obtain the δ_l by fitting to experimental data.

In the numerical calculations reported here for Pb and Mg alloys we used the $\langle F_l \rangle$ values which we have calculated for Pb,[18,20] and the $\langle F_l \rangle$ values which Fung and Gordon have recently calculated for Mg.[32] These values are listed in Table I along with effective masses and cross sections of the various orbits.

One set of phase shifts which we used were those previously obtained from a local rescreening[18] of published form factors. For Pb alloys, the form factors used are those of Heine-Abarenkov-Animalu.[11,20] For Mg alloys, Fung and Gordon[32] have calculated δ_l using a similar procedure based on the model potential of Appapillai and Williams.[35] These first principles δ_l were computed within the Born approximation (as in Ref. 18). For consistency, when using these δ_l in Eqs. (21) or (23) we treat them as small and replace $\sin 2\delta_l$ by $2\delta_l$ and $\sin^2\delta_l$ by δ_l^2 in the respective equations. The results for X^* and $\delta A/A$ are shown in Tables II and III for Pb alloys and Tables IV and V for Mg alloys. (Values are labeled with superscript b in the tables.)

A second set of phase shifts which we used were obtained by a three phase-shift fit to experimental data. The three phase-shift fit assumes that only δ_0, δ_1, and δ_2 are nonvanishing. There are only two fitting parameters δ_0 and δ_1; the third shift δ_2 is determined from the Blatt-Friedel sum rule[23,37]

TABLE I. Cross-sectional areas A, effective-mass ratios m_{BS}/m and m^*/m_{BS}, and amplitude factors $\langle F_l \rangle$ for orbits on the Fermi surfaces of Pb and Mg.

Metal	Orbit	$[A\,(\text{a.u.})]$[a]	(m_{BS}/m)[a]	(m^*/m_{BS})[a]	$\langle F_0\rangle$[b]	$\langle F_1\rangle$[b]	$\langle F_2\rangle$[b]
Pb	$\alpha[110]$[c]	0.425	−0.576	1.92	1.380	1.456	0.449
Pb	$\beta[100]$[c]	0.137	0.570	2.13	0.484	1.396	1.049
Pb	$\gamma[110]$[c]	0.048	0.228	2.44	0.041	1.097	1.578
Mg	$\mu_1^1(0°)$	0.0022	−0.085	1.30	0.807	0.854	1.298
Mg	$\mu_1^1(30°)$	0.0019	−0.080[d]	1.30[d]	0.778	0.869	1.302
Mg	$\mu_1^5(90°)$	0.0072	−0.107	1.29	1.432	0.589	1.090
Mg	$\mu_2^1(45°)$	0.0020	−0.080[d]	1.30[d]	0.490	1.109	1.215
Mg	$\gamma_1^1(0°)$	0.0597	0.080	1.25	1.031	0.969	1.000

[a] Values from Ref. 33 for Pb and Ref. 34 for Mg (negative m_{BS}/m indicate hole orbits).

[b] Values from Ref. 20 for Pb and Ref. 32 for Mg.

[c] In Refs. 20 and 33 the orbits corresponding to the α, β, γ oscillations are denoted by ψ, ν, and ζ, respectively.

[d] Assumed value based on taking electron-phonon enhancement to be isotropic.

$$\Delta Z^* = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1)\delta_l , \qquad (24)$$

where ΔZ^* is the effective-valence difference. According to continuum model prescription[37]

$$\Delta Z^* = \Delta Z - Z(\delta\Omega/\Omega_0) , \qquad (25)$$

where Z is the host valance and $\delta\Omega$ is the local volume change due to the impurity as estimated from lattice distortion data.[38] The calculated X^* and $\delta A/A$ values using the fitted δ_l are shown in Tables II–V with superscript c.

Finally a third set of phase shifts were obtained by treating all phase shifts as independent parameters *not* subject to the Blatt-Friedel sum rule. This procedure, used previously in noble-metal studies,[16,21] generates a set of phase shifts which can then be used to calculate ΔZ^* from Eq. (24). The resulting X^* and $\delta A/A$ values and the corresponding ΔZ^* are also given in Tables II–V. (The X^* and $\delta A/A$ values are labeled with superscript d.)

TABLE II. Dingle temperatures X^* and Fermi-surface area changes $\delta A/A$ in dilute Pb-Tl alloys per at.% Tl (X^* in K/at.%).

Orbit		Calc.				Expt.
$\alpha[110]$	X^*	5.7[a]	7.6[b]	10.1[c]	10.2[d]	10.4[e]
	$\delta A/A$	0.58[f]	0.35[b]	0.50[c]	0.51[d]	0.50[e]
$\beta[100]$	X^*	5.1[a]	3.8[b]	8.6[c]	8.1[d]	5.5[e]
	$\delta A/A$	−1.8[f]	−1.02[b]	−1.36[c]	−1.25[d]	−1.25[e]
$\gamma[110]$	X^*	4.5[a]	1.7[b]	5.9[c]	5.9[d]	5.9[e]
	$\delta A/A$	−2.0[f]	−1.07[b]	−1.15[c]	−1.00[d]	−1.9[e]

[a] Free-electron values obtained by setting $\langle F_l \rangle = 1$ in Eq. (23) and using Born-approximation phase shifts computed in Ref. 20 from Heine-Abarenkov-Animalu model potential ($\delta_0 = -0.4430, \delta_1 = -0.1514, \delta_2 = -0.0581$).

[b] Full calculation using Born-approximation δ_l given above.

[c] Calculated from best two-parameter fit with δ_l subject to Blatt-Friedel sum rule and ΔZ^* taken from Ref. 20 ($\delta_0 = -0.135, \delta_1 = -0.345, \delta_2 = -0.033, \Delta Z^* = -0.85$).

[d] Calculated from best three-phase-shift fit without Blatt-Friedel sum-rule constraint ($\delta_0 = -0.330, \delta_1 = -0.285, \delta_2 = -0.124, \Delta Z^* = -1.15$).

[e] Reference 33. There is significant experimental uncertainty in X^* and $\delta A/A$. The latter were estimated from the figures in Ref. 33 and typically contain a ±20% experimental uncertainty.

[f] Calculated from rigid-band-model expression (22).

TABLE III. Dingle temperatures X^* and Fermi-surface area changes $\delta A/A$ in dilute Pb-Bi alloys per at.% Bi (X^* in K/at.%).

Orbit		Calc.				Expt.
$\alpha[110]$	X^*	6.4[a]	9.1[b]	10.8[c]	10.2[d]	···
	$\delta A/A$	−0.58[f]	−0.53[b]	−0.52[c]	−0.50[d]	···
$\beta[100]$	X^*	5.8[a]	5.8[b]	8.9[c]	8.7[d]	6.7[e]
	$\delta A/A$	1.8[f]	1.33[b]	1.38[c]	1.36[d]	1.4[e]
$\gamma[110]$	X^*	5.0[a]	3.4[b]	5.9[c]	5.9[d]	5.9[e]
	$\delta A/A$	2.0[f]	1.15[b]	1.17[c]	1.16[d]	1.2[e]

[a] Free-electron values obtained by setting $\langle F_l \rangle = 1$ in Eq. (23) and using Born-approximation phase shifts computed in Ref. 20 from Heine-Abarenkov-Animalu model potential ($\delta_0 = 0.3719, \delta_1 = 0.2519, \delta_2 = 0.0252$).

[b] Full calculation using Born-approximation δ_l given above.

[c] Calculated from best two-parameter fit with δ_l subject to Blatt-Friedel sum rule and ΔZ^* taken from Ref. 20 ($\delta_0 = 0.175, \delta_1 = 0.350, \delta_2 = 0.010, \Delta Z^* = 0.81$).

[d] Calculated from best three-phase-shift fit without Blatt-Friedel sum-rule constraint ($\delta_0 = 0.130, \delta_1 = 0.345, \delta_2 = 0.034, \Delta Z^* = 0.85$).

[e] Reference 33 (see Table II).

[f] Calculated from rigid-band-model expression (22).

TABLE IV. Dingle temperatures X^* and Fermi-surface area changes $\delta A/A$ in dilute Mg-Li alloys per at.% Li (X^* in K/at.%).

Orbit		Calc.				Expt.
$\mu_1^1(0°)$	X^*	24^a	16^b	12.4^c	9.6^d	9.1^e
	$\delta A/A$	21^f	15^b	21^c	17^d	17^g
$\mu_1^1(30°)$	X^*	24^a	15^b	12.5^c	9.6^d	9.6^e
	$\delta A/A$	23^f	16^b	24^c	19^d	17^g
$\mu_1^5(90°)$	X^*	24^a	27^b	11.1^c	10.6^d	10.6^e
	$\delta A/A$	8.2^f	7.2^b	7.3^c	6.4^d	7.2^g
$\mu_2^1(45°)$	X^*	24^a	11^b	13^c	9.5^d	9.4^e
$\gamma_1^1(0°)$	$\delta A/A$	-7.3^f	-5.8^b	-7.0^c	-6.0^d	-6.9^g

[a] Free-electron values obtained by setting $\langle F_l \rangle = 1$ in Eq. (23) and using Born-approximation phase-shifts computed in Ref. 32 from Appapillai-Williams model potential ($\delta_0 = -0.699, \delta_1 = -0.136, \delta_2 = -0.025$).

[b] Full calculation using Born-approximation phase shifts given above.

[c] Calculated from best two-parameter fit with δ_l subject to Blatt-Friedel sum rule and ΔZ^* computed from data in Ref. 38 ($\delta_0 = -0.215, \delta_1 = -0.235, \delta_2 = -0.130, \Delta Z^* = -1.00$).

[d] Calculated from best three-phase-shift fit without Blatt-Friedel sum-rule constraint ($\delta_0 = -0.310, \delta_1 = -0.195, \delta_2 = -0.088, \Delta Z^* = -0.85$).

[e] Reference 32.

[f] Calculated from rigid-band-model expression (22).

[g] Reference 36.

V. DISCUSSION

A. Comparison with experiment

We note from Tables II–V that the fitted phase shifts give good agreement with the experimental values for both X^* and $\delta A/A$. The calculations based on first-principles pseudopotentials do not agree with experiment. This lack of agreement is to be expected in view of the crude determination of impurity scattering phase shifts through the Born approximation. (See Sec. V C for further discussion.)

It is encouraging that the values of δ_l obtained from the fitting procedures based on independent phase shifts without the constraint imposed by the Blatt-Friedel sum rule (24) are close to the δ_l values obtained by the fitting procedure in which the sum rule (24) is imposed as a constraint. An exception is the case of *Mg*Li where the ΔZ^* for optimal fit is -0.85 rather than -1.00. The -0.85 value is in better agreement with the ΔZ^* value of -0.93 estimated by Fung and Gordon[32] using the method of Tripp and Farrell.[39] [Unfortunately the ΔZ^* value for *Mg*In estimated by this method is[32] 0.85 and this gives a considerably poorer phase-shift fit to experimental data than the ΔZ^* value of 1.01 computed from Eq. (25).] It turns out that for *Pb*Bi, *Mg*Li, and *Mg*In the agreement with experiment is spoiled by attempting to use a two-parameter fit with ΔZ^* fixed at a value appreciably different from the optimal ΔZ^* (typically a 20% change in ΔZ^* leads to at least a doubling of the total error). This sensitivity implies that lattice-distortion effects need to be accurately known in a fitting scheme which uses the Blatt-Friedel sum rule.

Although the rigid-band-model expression (22) gives reasonable agreement with experimental data for $\delta A/A$ on several orbits, we note that there are some significant departures from rigid-band behavior in Tables II–V. One can expect such departures on orbits where an $\langle F_l \rangle$ differs considerably from unity and the corresponding phase shift δ_l is appreciable. This is the case on the γ orbits of Pb where $\langle F_0 \rangle = 0.04$. This small $\langle F_0 \rangle$ value leads to a reduced s-like contribution to $\delta A/A$ and hence a smaller $\delta A/A$ than expected within the rigid-band model. This effect is somewhat evident in *Pb*Bi and is in agreement with experiment. However, the same effect apparently worsens the agreement for *Pb*Tl.

The s-like reduction in $\delta A/A$ may also explain the observed failure of the rigid-band model in the

TABLE V. Dingle temperatures X^* and Fermi-surface area changes $\delta A/A$ in dilute Mg-In alloys per at.% In (X^* in K/at.%).

Orbit		Calc.				Expt.
$\mu_1^1(0°)$	X^*	27^a	21^b	20^c	20^d	21^e
	$\delta A/A$	-21^f	-16^b	-17^c	-18^d	-18^g
$\mu_1^1(30°)$	X^*	27^a	20^b	20^c	20^d	21^e
	$\delta A/A$	-23^f	-17^b	-19^c	-20^d	-19^g
$\mu_1^5(90°)$	X^*	27^a	35^b	22^c	22^d	22^e
	$\delta A/A$	-8.2^f	-7.9^b	-6.4^c	-6.8^d	-7.4^g
$\mu_2^1(45°)$	X^*	27^a	16^b	21^c	21^d	21^e
$\gamma_1^1(0°)$	$\delta A/A$	7.3^f	6.4^b	6.6^c	6.9^d	6.6^g

[a] Free-electron values obtained by setting $\langle F_l \rangle = 1$ in Eq. (23) and using Born-approximation phase shifts computed in Ref. 32 from Appapillai-Williams model potential ($\delta_0 = 0.804, \delta_1 = 0.183, \delta_2 = 0.004$).

[b] Full calculation using Born-approximation phase shifts given above.

[c] Calculated from best two-parameter fit with δ_l subject to Blatt-Friedel sum rule and ΔZ^* computed from data in Ref. 38 ($\delta_0 = 0.470, \delta_1 = 0.345, \delta_2 = 0.016, \Delta Z^* = 1.01$).

[d] Calculated from best three-phase-shift fit without Blatt-Friedel sum-rule constraint ($\delta_0 = 0.465, \delta_1 = 0.345, \delta_2 = 0.030, \Delta Z^* = 1.05$).

[e] Reference 32.

[f] Calculated from rigid-band-model expression (22).

[g] Reference 36.

case of Pb impurities in In, where it was found that the rigid-band-model value is too high for orbits in the third-band corner of the In Fermi surface.[40] For these orbits $\langle F_0\rangle = 0.05$.[18] A similar effect may have been observed in the β orbits of Al upon addition of Ge.[41] We have calculated $\langle F_0\rangle = 0.38$ for this orbit[18] and have estimated a large δ_0 for Ge impurity in Al.[18] Based on this picture for *Al*Ge we have predicted[18] a sign change in the low-field Hall coefficient as impurities are added. This has been subsequently confirmed experimentally.[42]

B. Effects of lattice distortion

It is straightforward to modify our $\delta A/A$ results to take into account the volume change upon alloying. Following Stern,[43] we can correct our results by simply changing the volume of the crystal matrix to its appropriate final value. This value $\Delta V'$ is determined from the continuum theory to be $(\frac{2}{3}\Delta V)(1-2\sigma)/(1-\sigma)$, where ΔV is the total volume change upon alloying and σ is the Poisson ratio[43,44] (the local volume change at the impurity is $\delta\Omega = \Delta V - \Delta V'$).

The volume change then adds to our $\delta A/A$ expression (21) an amount $(\Delta V'/A)(dA/d\Omega)$, where the volume derivative of the Fermi surface area is that associated with hydrostatic pressure deformations. This derivative is known experimentally for a number of pure metals.[45] Using experimental values for the Pb,[46] and Mg,[47] orbits under consideration we find that the correction to $\delta A/A$ is negligible (less than two percent in all cases).

The local distortion field is more difficult to treat. It was included in our analysis through the Blatt-Friedel sum rule (24) and the continuum-model expression (25). This approximation seems to work well since the fitted δ_l are very similar whether or not the sum rule (24) is imposed as an additional constraint. However as mentioned earlier, the continuum expression (25) is suspect in the case of *Mg*Li. It has also been challenged in the case of noble metals,[21] where more realistic treatments of lattice distortion were shown to be necessary.[21,48]

We remark that our calculations may be extended to treat more realistic models of lattice distortion as well as complex anisotropic scattering centers such as di-vacancies and impurity clusters. To do this we must go back to Eq. (17) and find the T matrix for the multiple-scattering problem consisting of only defects in a free-electron gas. The T matrix is then expressed in the Bloch representation through the expansion coefficients $a_n(\vec{k})$. This is a much more tractable problem than one would consider within KKR formalism where one needs to treat lattice atoms and defects simultaneously.

C. Calculations from first-principles pseudopotentials

The failure of the first-principles pseudopotential calculations may be due to the highly simplified method of constructing the pseudopotentials used here. Specifically, the local screening procedure is suspect. We are also ignoring additional corrections in the nonlocal energy-dependent part of the solute pseudopotential when it is placed in the solvent lattice. More sophisticated pseudopotential constructions are needed.

A more fundamental difficulty may lie in the use of the Born approximation for obtaining phase shifts. In the view of Heine and Weaire, for example, the Born approximation is not valid for defects except perhaps in the case of isovalent substitutional impurities, where the phase shifts are generally small.[49] Although for all the dilute alloys considered here the fitted phase shifts are not very large ($\delta_l \leqslant 0.5$), this does not insure the validity of the Born-approximation formula[49,50]

$$\delta_l = -\frac{2mk}{\hbar^2}\int_0^\infty r^2 j_l(kr)\,w(r)\,j_l(kr)\,dr\ , \qquad (26)$$

where j_l is the spherical Bessel function.

The exact phase shifts satisfy the equation[29]

$$\sin\delta_l = -\frac{2m}{\hbar^2}\int_0^\infty j_l(kr)\,w(r)\,y_l(r)\,r\,dr\ , \qquad (27)$$

where $r^{-1}y_l(r)$ is the solution of the radial Schrödinger equation with normalization such that

$$y_l(r) \to \sin(kr - \tfrac{1}{2}l\pi + \delta_l) \quad \text{as } r \to \infty\ .$$

Now for δ_l values up to 0.5 one can replace $\sin\delta_l$ on the left-hand side of Eq. (27) by δ_l with an error of only a few percent. (Even for $\delta_l = 0.8$, the error is only ten percent.) This leads to an equation like (26) except that the pseudopotential w is replaced by an effective pseudopotential $w_{\text{eff}}(r)$ which equals $w(r)y_l(r)/krj_l(kr)$. The important point is that the Born-approximation phase shifts of w_{eff} are very close to the exact phase shifts of w despite the fact that the Born-approximation phase shifts of w may be very different from the exact phase shifts.[51]

We therefore suggest that our fitted δ_l can differ significantly from the first-principles δ_l computed within the Born approximation because the fitted δ_l are essentially the Born-approximation phase shifts of w_{eff} rather than of w. As far as we know the distinction between w and w_{eff} for first-principles pseudopotentials has not been investigated. Obviously, the distinction arises from the distortion of the pseudo-wave-function from the unperturbed plane-wave form since if $y_l(r) = krj_l(kr)$ then $w_{\text{eff}}(r) = w(r)$. The quantitative effect of this distortion will be better understood when accurate first-principles pseudopotentials are constructed for impurity scattering and the appropriate phase shifts are obtained by numerical computation. If the distortion effect is negligible then the objection of Heine and Weaire[49] concerning the use of the Born approximation can be rejected and Harrison's approach[11,50] to impurity scattering would be vindicated.

VI. CONCLUSION

A pseudopotential-based scattering theory has led to expressions for Fermi surface area changes [Eq. (21)] and Dingle temperatures [Eq. (23)] which are similar in structure to the corresponding KKR expressions. We have not invoked the muffin-tin assumption, however, and hence we can handle more realistic defect complexes and distortion fields in a more consistent way. In exchange for this advantage our results are restricted to nearly-free-electron-like host metals or to d-band host metals with relatively small gaps and no d-band resonances close to the Fermi energy. For the case of weak scatterers (e.g., iso-valent impurities) our results reduce to first order perturbation theory using pseudopotentials and multiple-plane-wave pseudo-wave-functions.

We have been able to fit experimental data for Pb and Mg alloys using a two-parameter phase-shift model. Departures from rigid-band-model behavior can be traced to non-free-electron-like amplitude factors $\langle F_l \rangle$ combining with appreciable phase shifts for that l value. Phase-shift calculations from known pseudopotentials using a local rescreening within the Born approximation do not give good agreement with experiment. It is suggested that further effort be made in determining phase shifts from first-principles pseudopotentials without using the Born approximation or linear screening.

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[1] See, for example, J. M. Ziman, *Electrons and Phonons* (Oxford, U.P., London, 1960).

[2] E. A. Stern, Phys. Rev. 168, 730 (1968).

[3] E. A. Stern, Phys. Rev. 188, 1163 (1969).

[4] E. A. Stern, Phys. Rev. B 7, 1303 (1973).

[5] See, for example, S. Doniach and E. H. Sondheimer, *Greens Functions for Solid State Physicists* (Benjamin, Reading, Mass., 1974).

[6] M. I. Goldberger and K. M. Watson, *Collision Theory* (Wiley, New York, 1964), Chap. 8. [In this reference, the self-energy is called the "level-shift operator" and is denoted by $R(E)$.]

[7] P. Soven, Phys. Rev. B 5, 260 (1972).

[8] E. Mann, Phys. Kondens. Mater. 12, 210 (1971).

[9] P. W. Anderson and W. L. McMillan, in *Rendiconti della Scuola Internazionale di Fisica "Enrico Fermi," XXXVII Corso*, edited by W. Marshall (Academic, New York, 1967), and references cited therein.

[10] For further discussion see Ref. 5, pp. 106–109; Ref. 6; and A. L. Fetter and J. D. Walecka, *Quantum Theory of Many-Particle Systems* (McGraw-Hill, New York, 1971), Chap. 3.

[11] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966).

[12] V. Heine, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1970), Vol. 24.

[13] W. A. Harrison, Phys. Rev. 181, 1036 (1969).

[14] J. A. Moriarty, Phys. Rev. B 5, 2066 (1972).

[15] R. Harris, J. Phys. F 3, 89 (1973), and references cited therein.

[16] P. T. Coleridge, N. A. W. Holzwarth, and M. J. G. Lee, Phys. Rev. B 10, 1213 (1974).

[17] A. Seeger, in *Metallic Solid Solutions*, edited by J. Friedel and A. Guinier (Benjamin, New York, 1963), paper VII.

[18] R. S. Sorbello, J. Phys. F 4, 1665 (1974).

[19] R. S. Sorbello, Phys. Kondens. Mater. 19, 251 (1975).

[20] R. S. Sorbello, Phys. Rev. B 12, 3500 (1975).

[21] P. T. Coleridge, J. Phys. F 5, 1307 (1975).

[22] E. A. Stern, Phys. Rev. B 5, 366 (1972).

[23] J. Friedel, Adv. Phys. 3, 446 (1954).

[24] X. A. da Silva, A. A. Gomes, and J. Danon, Phys. Rev. B 4, 1161 (1971).

[25] Our G^{ps} is not identical with the "pseudo-Green's-function" constructed from an over-complete basis set using d orbitals as in Ref. 14.

[26] B. J. Austin, V. Heine, and L. J. Sham, Phys. Rev. 127, 276 (1962).

[27] Diagonality of G^{ps} is assured if $|\psi_{\vec{k}}\rangle$ and $|\alpha\rangle$ are eigenstates of H^0_{ps}. This is the case for the important class of pseudopotentials of the form $W = V + (E - H)P$, where V is the potential energy. Diagonality cannot be assumed for the most general class of pseudopotential, which is of the form $W = V + PQ$, where Q is any arbitrary operator.

[28] In our approach we use the fact that W^0 is weak at a reciprocal-lattice vector. This weak scattering is the result of simultaneous (coherent) scattering by the atomic pseudopotentials of all the host atoms in a perfect lattice. This scattering is weak even if the scattering by a *single* host-atom potential is strong (i.e., host-atom phase shifts are large, modulo π) and even if the true total potential for the perfect lattice is large (i.e., of order E_F) at $\vec{q}_n$.

[29] A. Messiah, *Quantum Mechanics* (North-Holland, New York, 1962).

[30] J. M. Ziman, Proc. R. Soc. A 252, 63 (1959).

[31] V. Heine, Proc. Phys. Soc. Lond. 69, 505 (1956).

[32] W. K. Fung and W. L. Gordon, Phys. Rev. B 4, 1770 (1976).

[33] J. R. Anderson, J. Y. M. Lee, and D. R. Stone, Phys. Rev. B 11, 1308 (1975).

[34] J. C. Kimball, R. W. Stark, and F. M. Mueller, Phys. Rev. 162, 600 (1967); R. W. Stark, *ibid.* 162, 589 (1967).

[35] M. Appapillai and A. R. Williams, J. Phys. F 3, 759 (1973).

[36] L. J. Hornbeck, W. K. Fung, W. L. Gordon, and J. H. Tripp, Phys. Lett. A 54, 463 (1975).

[37] F. J. Blatt, Phys. Rev. 108, 285 (1957); see also, W. A. Harrison, *ibid.* 110, 14 (1958).

[38] W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals* (Pergamon, New York, 1958); see p. 818, Vol. I for Pb alloys, and pp. 1017 and 1057, Vol. II for Mg alloys.

[39] J. H. Tripp and D. E. Farrell, Phys. Rev. B 7, 571 (1973).

[40] A. J. Hughes, J. P. G. Shepherd, and D. F. Gauton, J. Phys. C 3, 2461 (1970).

[41] J. P. G. Shepherd and W. L. Gordon, Phys. Rev. 169, 541 (1968). See Fig. 5.

[42] K. Böning, K. Pfänder, P. Rosner, and M. Schlüter, J. Phys. F 5, 1176 (1975).

[43] E. A. Stern, Phys. Rev. 157, 544 (1967).

[44] J. D. Eshelby, J. Appl. Phys. 25, 255 (1954).

[45] A. P. Cracknell, *The Fermi Surfaces of Metals* (Taylor and Francis, London, 1971).

[46] J. R. Anderson, W. J. O'Sullivan, and J. E. Schirber, Phys. Rev. 153, 721 (1967).

[47] G. M. Beardsley, J. E. Schirber, and J. P. Van Dyke, Phys. Rev. B 6, 3569 (1972).

[48] M. T. Béal-Monod and W. Kohn, J. Phys. Chem. Solids 29, 1877 (1968).

[49] V. Heine and D. Weaire, Ref. 12, p. 346.

[50] W. A. Harrison, *Solid State Theory* (McGraw-Hill, New York, 1970), p. 186.

[51] The Born approximation phase-shift may differ from the exact δ_l even if the δ_l are very small since small δ_l is not a sufficient condition for reducing Eq. (27) to Eq. (26). For example, in low-energy scattering ($ka \ll 1$) by a spherical well (of radius a) the δ_l are very small but cannot be correctly obtained within the Born approximation (see Ref. 29 for the standard analysis).