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Impurity Scattering on the Fermi Surfaces: A (More) Realistic Calculation

Lee Cole and W. E. Lawrence
Department of Physics, Dartmouth College, Hanover, New Hampshire 03755

and

R. Monnier, W. Joss, and W. van der Mark
Laboratorium für Festkörperphysik, Eidgenössische Technische Hochschule Zürich, CH-8093 Hönggerberg, Switzerland

and

M. Manninen
Research Institute for Theoretical Physics, University of Helsinki, 00170 Helsinki 17, Finland

The electron-impurity scattering rate and resulting Dingle temperatures X_D are calculated for dilute AlLi. The multiple–plane-wave model of Sorbello is used, but unlike previous approaches the scattering of individual plane waves is treated self-consistently, using the Kohn-Sham density-functional method (and including the main effect of the lattice potential). Electron-phonon renormalization of X_D is included. We discuss the implications of the local approximation for the exchange and correlation.

In recent years, the de Haas–van Alphen effect has developed into a powerful technique for studying the anisotropy of the impurity-limited lifetime of Bloch electrons on the Fermi surface.[1] Theoretical progress has been somewhat slower: Although one is now able to give a realistic description of the electronic structure of the host crystal, a self-consistent treatment of the impurity is still lacking. Sorbello,[2] in his pioneering work on anisotropic lifetimes in polyvalent simple metals, describes the effective potential at the point defect by a *locally* and *linearly* screened pseudopotential, and computes scattering phase shifts in the *first Born approximation*. More recently Tomlinson, Carbotte, and Piercy[3] have extended Sorbello's method in the case of AlMg, by properly recalculating the (linearly) screened impurity pseudopotential, and including

the relaxation of the host ions around the impurity explicitly, by the method of lattice statics.[4] Their results, however, are rather sensitive to the form of dielectric function used when computing the lattice relaxation, and can only be considered as qualitative.

The basic problem with impurity calculations of the type described here is that, in most cases, the two approximations of linear screening and weak scattering *cannot be made*. In view of that, an alternative approach has been proposed[2] in which the impurity and the accompanying strain field are described by an effective t matrix, parametrized by a finite number of phase shifts *fitted* to observe Dingle temperatures, and subjected to the constraint that they satisfy the Blatt-Friedel sum rule.[5,6] A similar point of view has been taken by Coleridge, Holzwarth, and Lee[7] in their treatment of nonmagnetic impurities in a noble-metal host.

The purpose of thie Letter is to show by a direct calculation in the case of AlLi that the scattering by the impurity can be treated self-consistently. The system chosen is ideal in several respects: (i) The Fermi surface of the host is very well known; (ii) the change in lattice constant upon alloying is small enough[8] to justify the neglect of lattice relaxation effects; (iii) the

$$T_{kk'} = \frac{8\pi^2 \hbar^2}{m k_F \Omega} \sum_{l=0}^{\infty} \sum_{m=-l}^{l} \exp(i\delta_l)(\sin\delta_l) c_{lm}(\vec{k}) c_{lm}{}^*(\vec{k}'),$$

where the δ_l are phase shifts (at the Fermi energy) describing the scattering of *plane* waves from the impurity site, and the coefficients $c_{lm}(\vec{k})$ are given by

$$c_{lm}(\vec{k}) = \sum_n a_n(\vec{k}) Y_{lm}{}^*(\vec{k} - \vec{q}_n), \tag{4}$$

where Y_{lm} depends on the angular coordinates of $\vec{k} - \vec{q}_n$ with respect to some fixed axis.

To evaluate the scattering phase shifts, we use the self-consistent version of the density-functional method,[11] with the local density approximation for exchange and correlation, in the parametrization of Gunnarsson and Lundqvist.[12] Our model for the impurity consists of a point charge $Z_i = 3$ at the center of an Al vacancy. We simulate the latter by a spherical cavity in an otherwise uniform positive (jellium) background, so that the total positive charge distribution takes the form

$$n_+(\vec{r}) = Z_i \delta(\vec{r}) + n_0 \theta(r - R_{WS}), \tag{5}$$

where R_{WS} is the host Wigner-Seitz radius, n_0

absence of p states in the Li core precludes the use of a weak pseudopotential for the description of the impurity.

Following Sorbello,[2] we calculate the pseudo wave functions $\varphi_k(\vec{r})$ of the pure host, within the four-OPW (orthogonalized-plane-wave) model:

$$\varphi_k(\vec{r}) = \sum_n a_n(\vec{k}) \exp[i(\vec{k} - \vec{g}_n) \cdot \vec{r}], \tag{1}$$

where $\vec{g}_n$ are reciprocal-lattice vectors. The mixing coefficients $a_n(\vec{k})$ are computed from the four-OPW secular equation, whose Fermi energy and matrix elements are fitted (by least squares) to recently published de Haas–van Alphen frequencies for ten extremal orbits.[9] In terms of these pseudo wave functions, the scattering rate (per impurity) from state $\vec{k}$ to $\vec{k}'$ is[2]

$$P_{kk'} = 2\pi\hbar^{-1} |T_{kk'}|^2 \delta(E_k - E_{k'})$$

$$= 2\pi\hbar^{-1} |\langle \varphi_k | T^{ps} | \varphi_k \rangle|^2 \delta(E_k - E_{k'}), \tag{2}$$

where the superscript ps indicates that electron propagation between impurity-scattering events is governed by the Green's function G^{ps} for the pseudo Hamiltonian of the pure crystal. We approximate the t matrix by replacing G^{ps} with the free-electron (one-OPW) propagator (this neglects "lattice backscattering") and assume that the scattering takes place "on the Fermi sphere."[10] This leads to[2]

$$\tag{3}$$

is the bulk density of valence electrons, and θ is the step function.

Recent calculations of vacancy formation energies[13] show that for polyvalent simple metals the pure-jellium approach is insufficient. This is best seen as follows: Assume that the host crystal is made up of neutral Wigner-Seitz spheres and that the ions, of charge Z, are described by an empty-core potential with a core radius r_c. The average of the difference between this "true" ionic potential in the sphere, and that of a uniform distribution of positive charge of density n_0 is then

$$\langle \delta V_{WS} \rangle_{av} = -\tfrac{3}{10}(Z/R_{WS})[1 - 5(r_c/R_{WS})^2] \tag{6}$$

in atomic units. For Al ($Z = 3$, $r_c = 1.12$, $R_{WS} = 2.98$) this is more than one-fifth of the Fermi energy in absolute value. If we now remove a Wigner-Seitz sphere from the crystal in order to create a vacancy, it is essential to subtract $\langle \delta V_{WS} \rangle_{av}$ for that sphere as well, which means

adding to the effective potential appearing in the Kohn-Sham[11] equations the extra term

$$V_{vac}(r) = - \langle \delta V_{WS} \rangle_{av} \theta(R_{WS} - r). \tag{7}$$

In this way we include the main effect of the discreteness of the lattice in the self-consistent calculation, the remainder being a small perturbation of zero average. The effect of the additional potential on the phase shifts is substantial, as shown in Table I, where they are compared with those of the jellium [$V_{vac}(r) = 0$] treatment.[14] It is interesting to note that among all density profiles generated by an effective potential containing a term of the form $C\theta(R_{WS} - r)$, the one with $C = - \langle \delta V_{WS} \rangle_{av}$ minimizes the total energy of the system.

Scattering by impurities manifests itself as a temperature-independent reduction in amplitude of the de Haas–van Alphen signal, due to the lifetime broadening of electron states on the extremal orbit under study. This is described in terms of an effective (Dingle) temperature X_Γ, defined for the orbit Γ by

$$(2\pi/\hbar)k_B X_\Gamma = \langle 1/\tau_0(\vec{k}) \rangle_\Gamma / \langle 1 + \lambda_k \rangle_\Gamma, \tag{8}$$

where λ_k is the effective mass enhancement for state $\vec{k}$ due to the electron-phonon interaction, and $\langle \rangle_\Gamma$ means a weighted average over the orbit

$$\langle f(\vec{k}) \rangle_\Gamma = \frac{\oint_\Gamma dk_\Gamma [f(\vec{k})/v_\perp(\vec{k})]}{\oint_\Gamma dk_\Gamma [1/v_\perp(\vec{k})]}. \tag{9}$$

Here $v_\perp(\vec{k})$ is the *band* velocity (component perpendicular to the applied magnetic field), whose renormalization is accomplished by the factor $(1 + \lambda_k)^{-1}$. The *product* $v_\perp(\vec{k})\tau_0(\vec{k})$ is unrenormalized, as discussed in this context by Poulsen, Randles, and Springford.[15] The inverse lifetime is given in terms of the scattering rate per impurity (2), in the dilute limit, by

$$\tau_0^{-1}(\vec{k}) = Nc \int_{F.S.} P_{kk'} d^3k', \tag{10}$$

where c is the impurity concentration and N is

the total number of atoms in the crystal. The integral over the Fermi surface on the right-hand side of (10) is related to the diagonal element of the *exact* single-site t matrix by the optical theorem:

$$\int_{F.S.} P_{kk'} dk' = - 2\hbar^{-1} Im T_{kk}. \tag{11}$$

We have computed Dingle temperatures for three extermal orbits with the above formalism. The integrals over the Fermi surface were performed with the method described in a recent study of the electron-phonon interaction in pure Al.[16] The results are given in Table II. Note the close agreement between the values yielded by the "full" calculation and those obtained by applying the optical theorem (11), which provides an *a posteriori* justification for our approximation to the t matrix.

Preliminary measurements on the α and γ orbits yield Dingle temperatures of about 50 K/at.% for both cases.[17] Our apparent overestimate of the anisotropy can be traced back to the large s-wave phase shift, which is heavily weighted on the γ orbit.[2] This large (negative) s-wave phase shift suggests that the self-consistent potential from which the (quasi-) electron scatters is not attractive enough.[18] A number of possible explanations come to mind. As mentioned previously we have dismissed lattice relaxation effects on the basis of Refs. 3 and 8. Other explanations relate to the use of the local-density approximation (LDA), both for the description of the impurity site itself, and for the scattering of conduction electrons from it. We may detail the situation as follows: The quasiparticle states are obtained from a Schrödinger-like equation whose potential is replaced by an energy-dependent, nonlocal self-energy,[19]

$$\Sigma(\vec{r}, \vec{r}'; E) = V(\vec{r})\delta(\vec{r} - \vec{r}') + M(\vec{r}, \vec{r}'; E). \tag{12}$$

TABLE I. Phase shifts at the Fermi level for a substitutional Li ion in Al. The first row is for the jellium model; the second row is for the improved approach described in the text. δ_0 is given module π since there are two bound s electrons.

δ_0	δ_1	δ_2	δ_3
-1.0780	-0.2419	-0.1607	-0.0519
-1.214	-0.341	-0.148	-0.033

TABLE II. Average mass enhancements and Dingle temperatures for three extremal orbits on the Fermi surface of AlLi.

Zone	Orbit	λ	X [a] (K/at.%)	X [b] (K/at.%)
Second	(110)	0.42	45	49
Third	α (100)	0.48	54	51
Third	γ (110)	0.38	81	90

[a]"Full" calculation.
[b]Calculation using the optical theorem with the approximate t matrix.

$V(\vec{r})$ is the sum of the external and Hartree potentials, and M is the nonlocal term describing exchange and correlation. M is not known exactly, and a standard approximation for it at the Fermi level μ is

$$M(\vec{r},\vec{r}';E=\mu)\approx M_h(\vec{r}-\vec{r}';\mu_h[n(\vec{r}_0)];n(\vec{r}_0)), \quad (13)$$

where M_h is the self-energy operator for a uniform electron gas of density $n(\vec{r}_0)$, $\vec{r}_0=\frac{1}{2}(\vec{r}+\vec{r}')$, and $\mu_h(n)$ is the chemical potential of a uniform electron gas of density n. One further approximation that is usually made (and which we have used here) is to replace the right-hand side of (13) by the local potential

$$M_h(\vec{r}-\vec{r}';\mu_h[n(\vec{r}_0)];\ n(\vec{r}_0))$$
$$\rightarrow \mu_{xc}(n(\vec{r}))\delta(\vec{r}-\vec{r}'), \quad (14)$$

where $\mu_{xc}(n)$ is the exchange-correlation contribution to μ_h; this is nothing else but the local-density approximation (LDA) for ground-state properties.[20] While the LDA is rigorously correct in the limit of slowly varying or high density, it is known to break down for a metallic surface, where it gives the wrong asymptotic form for the exchange-correlation potential at large distances. The surface density profiles are nevertheless believed to be given accurately.[21] Similar arguments should apply to the outer regions of the Wigner-Seitz sphere containing the impurity. In the central region where the potential is dominated by the Coulomb contribution from the point charge, and the electron density is high, the LDA is a good approximation. Overall, then, the LDA is probably accurate for the impurity-induced charge distribution, but not for the potential. In a recent calculation for Li, Rasolt and co-workers[22] found it essential to preserve the nonlocality of M_h in order to obtain agreement with de Hass–van Alphen measurements (extremal Fermi-surface areas). We believe that nonlocality is at least as important in our case, where the impurity causes rapid variations in charge density. This could be checked by a calculation along the lines drawn by Vinter[23] for a proton in jellium. However, in view of the difficulties he encountered in going beyond $Z=1$, and the uncertainties associated with the present theory and measurement, such an effort seems premature.

In summary, we have computed Dingle temperatures for three extremal orbits on the Fermi surface of AlLi, without invoking the usual approximations of linear screening and weak scattering, and including electron-phonon mass-enhancement

effects explicitly. The order of magnitude predicted by our calculations is correct, but the anisotropies are too large. We interpret this as a failure of the local approximation for the self-energy to describe quasiparticles on the Fermi surface, in accord with recent findings of Ref. 22.

We are indebted to R. M. Nieminen for many helpful conversations. This work has benefitted from support by the Swiss National Science Foundation, and by the U. S. Department of Energy through Grant No. EY-76-S-02-2315.

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Evidence for Strong Coulomb Correlations in an Organic Conductor

P. M. Chaikin and J. F. Kwak[a]

Department of Physics, University of California, Los Angeles, California 90024

and

A. J. Epstein

Xerox Webster Research Center, Rochester, New York 14644

(Received 6 October 1978)

The thermopower of highly conducting quarter-filled–band TCNQ (tetracyanoquinodimethane) salts corresponds to an entropy per carrier of $k\ln2$. We have measured the change of the thermoelectric power upon application of a magnetic field for quinolinium ditetracyanoquinodimethane. We find an isotropic shift which agrees with the entropy change of a free-spin system. Coupled with the observation of a negligibly small magnetoresistance, this provides definite evidence that the conducting electrons are correlated as in the strong-coupling Hubbard model.

One of the most lingering questions which has concerned researchers in the area of quasi–one-dimensional conductors is the role played by the Coulomb interaction between electrons as compared with the electronic bandwidth.[1] Several authors have analyzed susceptibility,[2-4] nuclear magnetic resonance,[5,6] and x-ray[7] data in a number of TCNQ (tetracyanoquinodimethane) salts and conclude that the Coulomb interaction is either dominant, comparable to bandwidth, or small.

In this Letter, we present the results of our study of magnetoresistance and magnetothermopower of quinolinium ditetracyanoquinodimethane [denoted hereafter as Q(TCNQ)$_2$]. These results show that the electrons involved in transport retain their spin degrees of freedom. This is the first hard evidence that in at least one compound, Q(TCNQ)$_2$, the Coulomb interaction is sufficiently strong to correlate the electrons apart so that they behave as free spins. We also believe this system to be the first compound (organic or not) in which this strong correlation has been experimentally demonstrated. A strong-coupling Hubbard model therefore seems appropriate.[8]

Buravov, Fedutin, and Schegolev[9] were the first to point out the similarity between the thermoelectric power (TEP) of a number of 1:2 TCNQ salts. As temperature was increased to-ward 300 K, the thermopower tended to saturate to a value of ~ –60 μV/K. More recently it has become apparent that the saturation toward –60 μV/K is a more general phenomenon for 1:2 TCNQ salts than was originally envisioned. A compilation of data from several authors is shown in Fig. 1.[9-12]

To date all quarter-filled–band (one electron per two sites on the conducting chain) TCNQ salts which exhibit "metallike" conductivity at room temperature have a thermopower of –60 μV/K. In this context we take "metallike conductivity" to merely signify that the conductivity is not apparently strongly activated. Note that Fig. 1 also contains data from (N-methylphenozinium)$_{0.54}$-(phenozine)$_{0.46}$-TCHQ, [abbreviated as (NMP)$_{0.54}$-(Phen)$_{0.46}$-TCNQ],[13] which achieve a quarter-filled–band situation by partial substitution of a poor donor (Phen) for a good donor (NMP) in the cation chain.

Buravov, Fedutin, and Schegolev[9] were able to fit their data on three of the 1:2 salts by a model in which the spin degrees of freedom were quenched and the thermopower was due to the motion of bonds formed between near-neighbor and next-near-neighbor molecules along the conducting chain. An alternative approach was suggested in several papers by Beni[14] and by Kwak