

lated. The discrepancies between theory and experiment could probably be removed by adopting somewhat different values for the band parameters, without making any radical revision in Sagar's model. It should be noted, for example, that the band parameters were taken to be independent of impurity concentration. The usual decrease in electron mobility in each conduction band with increasing impurity concentration would therefore cause the observed Hall mobilities to decrease more rapidly with decreasing R_H than predicted.

For the Te-doped samples, both $R_H(300^\circ\text{K})/R_H(77^\circ\text{K})$ and $R_H\sigma(300^\circ\text{K})$ vary with $R_H(77^\circ\text{K})$ in approximately the manner predicted by theory. This agreement is to be expected, since several of the band parameter values used in the calculations were adopted by Sagar in order to fit his data on Te-doped samples. Surprisingly, however, both $\sigma(77^\circ\text{K})/\sigma(300^\circ\text{K})$ and $R_H\sigma(77^\circ\text{K})$ first increase markedly with decreasing R_H ,

rather than decreasing monotonically as predicted. At 77°K , therefore, the electron mobility in one or both conduction bands appears to increase at first with increasing Te concentration, rather than decreasing in the usual manner. No explanation has been found for this anomalous increase in mobility. Although the increase might be connected with impurity conduction, it should be noted that in the case of Ge the Hall mobility decreases continuously with increasing impurity concentration throughout the degenerate range.^{3,4}

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Friedel Sum Rule for a System of Interacting Electrons

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The Friedel sum rule is derived for a system of interacting electrons in a periodic potential.

I. INTRODUCTION

IN a recent paper¹ one of the authors (J. S. L.) has derived an expression for the impurity-resistance of a metal using as a model an interacting Fermi fluid and randomly placed scattering centers. As expected, the current-carrying excitations of the fluid had wave numbers just at the Fermi surface and were scattered by screened impurities. The usual independent-electron approximation was replaced by the assumption that these single-particle-like excitations do not interact strongly among themselves. A graphical prescription was given for calculation of the relevant impurity-scattering amplitude.

Needless to say, it is not practicable to evaluate this amplitude in perturbation theory including exchange effects and allowing for an arbitrarily strong scattering potential. Thus, it is highly desirable to know certain general relationships pertaining to this scattering process which may be useful in semi-phenomenological analyses

of metallic properties. For example, the Friedel sum rule^{2,3} relates the total charge displaced in the field of a fixed impurity to the scattering by that impurity of a free electron at the Fermi momentum k_F . In particular, the rule states that the number of displaced electrons N_D is given by

$$N_D = -\frac{2}{\pi} \sum_l (2l+1) \delta_l(k_F), \quad (1)$$

where the δ_l are the scattering phase shifts. This rule has been used by Kohn and Vosko⁴ to deduce some features of the screening of solute atoms in dilute alloys from the known residual resistivity of these materials. They then were able to explain certain results of nuclear resonance experiments and to lend support to the theory of a sharp Fermi surface in metals.

The question of the nature of the Fermi surface is

² J. Friedel, *Phil. Mag.* **43**, 153 (1952).

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¹ J. S. Langer, *Phys. Rev.* **120**, 714 (1960), hereafter referred to as I.

³ The sum rule has been proven for independent Bloch electrons in the case of spherical energy surfaces by L. M. Roth, *Tech. Rept. 267*, Cruft Laboratory, Harvard University, Cambridge, Massachusetts, 1957 (unpublished).

⁴ W. Kohn and S. H. Vosko, *Phys. Rev.* **119**, 912 (1960).

central in the present discussion. Up to now, Friedel's sum rule has been derived only for the model of independent electrons, which, of course, presupposes a well-defined Fermi level. It is the purpose of this article to show that Eq. (1) still is valid when the electrons are allowed to interact among themselves, and that the phase shifts δ_l are exactly those which determine the impurity-resistance according to I.¹ Furthermore, we shall show that an even more general form of the sum rule is

$$N_D = \frac{1}{2\pi i} \text{Tr} \ln S(\mu), \quad (2)$$

where $S(\mu)$ is the scattering matrix for single-particle-like excitations whose energy is the chemical potential μ . Equation (2) is valid for interacting electrons in a periodic potential where the Fermi surface may not be spherically symmetric. The only assumption to be made in the derivation of (2) is that the single-particle-like states of energy μ do not decay. This assumption, which seems to be provable only in perturbation theory, is made also by Luttinger and Ward,^{5,6} who conclude that the sharpness of the Fermi surface is essentially preserved in the case of interacting electrons.

II. DERIVATION OF THE SUM RULE

We consider a single, fixed impurity immersed in a large sample of volume Ω containing electrons which move in a periodic potential and interact among themselves. This system is to be examined at zero temperature and chemical potential μ . In order to calculate the charge displaced by the impurity, we compare the number of electrons in this system with the number in a similar system of volume Ω , temperature zero, and chemical potential μ , but containing no impurity. This comparison may be performed fairly easily by means of the techniques devised by Luttinger and Ward⁵ in their examination of the zero-temperature limit of quantum statistical mechanics. This procedure also will enable us to avoid the assumption of a spherical Fermi surface.⁷

According to Luttinger and Ward,⁵ the number of electrons in the system without the impurity is given by

$$N = \beta^{-1} \text{Tr} \sum_l \exp(\xi_l 0^+) S(\xi_l), \quad (3)$$

$$\xi_l = \mu + [\pi i (2l+1)/\beta],$$

where S is the single-particle propagator for an electron in a system of chemical potential μ and temperature $T = 1/k\beta$. S is a matrix which may be expressed in the representation of the independent single-electron eigenstates. If we are dealing with Bloch waves, for example, then S is diagonal in the wave vector and spin indices but not necessarily in the band indices. More explicitly,

⁵ J. M. Luttinger and J. C. Ward, Phys. Rev. **118**, 1417 (1960).

⁶ J. M. Luttinger, Phys. Rev. **119**, 1153 (1960).

⁷ W. Kohn and J. M. Luttinger, Phys. Rev. **118**, 41 (1960).

we may write

$$S(\xi_l) = [\xi_l - h - \Sigma(\xi_l)]^{-1}, \quad (4)$$

where h is the single-electron Hamiltonian and $\Sigma(\xi_l)$ is the sum of all proper self-energy graphs.

In similar fashion, we may compute the number of electrons in the system which does contain the impurity,

$$N' = \beta^{-1} \text{Tr} \sum_l \exp(\xi_l 0^+) S'(\xi_l). \quad (5)$$

Because of the presence of the impurity, the single-particle propagator $S'(\xi_l)$ is no longer diagonal in the wave-number indices. We may write it in the form

$$S'(\xi_l) = [\xi_l - h - \Sigma'(\xi_l)]^{-1}. \quad (6)$$

It will be convenient to separate out from Σ' those proper self-energy graphs which contain only electron-electron interactions and are thus diagonal in the wave-number indices. As in I we write

$$\Sigma'(\xi_l) = \Sigma(\xi_l) + (1/\Omega) \bar{\nu}(\xi_l), \quad (7)$$

where $\bar{\nu}(\xi_l)$ is the sum of all proper self-energy graphs containing at least one interaction with the impurity.

By comparing Eqs. (3) and (5) we have

$$N_D = \beta^{-1} \sum_l \exp(\xi_l 0^+) \text{Tr} [S'(\xi_l) - S(\xi_l)]. \quad (8)$$

We now want to perform the sum over l in this expression. To do this, note that

$$\begin{aligned} \text{Tr}(\partial/\partial \xi_l) \ln[\xi_l - h - \Sigma(\xi_l)] \\ = \text{Tr} S(\xi_l) [1 - (\partial \Sigma / \partial \xi_l)], \end{aligned} \quad (9)$$

and

$$\begin{aligned} \text{Tr}(\partial/\partial \xi_l) \ln[\xi_l - h - \Sigma'(\xi_l)] \\ = \text{Tr} S'(\xi_l) [1 - (\partial \Sigma' / \partial \xi_l)]. \end{aligned} \quad (10)$$

Here we have used the relation

$$\begin{aligned} \text{Tr}(\partial/\partial x) \ln[A + B(x)] \\ = \text{Tr}[A + B(x)]^{-1} (\partial B / \partial x), \end{aligned} \quad (11)$$

which is true for two not necessarily commuting matrices A and B . Now in Luttinger and Ward⁵ it is shown that

$$\lim_{\beta \rightarrow \infty} \sum_l \exp(\xi_l 0^+) S(\xi_l) (\partial \Sigma / \partial \xi_l) = 0. \quad (12)$$

Precisely the same argument may be used to prove that

$$\lim_{\beta \rightarrow \infty} \sum_l \exp(\xi_l 0^+) S'(\xi_l) (\partial \Sigma' / \partial \xi_l) = 0. \quad (13)$$

Thus in the zero-temperature limit we have

$$\begin{aligned} N_D &= \lim_{\beta \rightarrow \infty} \frac{1}{\beta} \text{Tr} \sum_l \exp(\xi_l 0^+) \frac{\partial}{\partial \xi_l} \\ &\quad \times \{ \ln[\xi_l - h - \Sigma(\xi_l)] - (1/\Omega) \bar{\nu}(\xi_l) \\ &\quad - \ln[\xi_l - h - \Sigma'(\xi_l)] \} \\ &= \lim_{\beta \rightarrow \infty} \frac{1}{\beta} \text{Tr} \sum_l \exp \xi_l 0^+ \frac{\partial}{\partial \xi_l} \\ &\quad \times \ln[1 - S(\xi_l)(1/\Omega) \bar{\nu}(\xi_l)]. \end{aligned} \quad (14)$$

In the last step we have used

$$\text{Tr} \ln A + \text{Tr} \ln B = \text{Tr} \ln AB, \quad (15)$$

which again is true for two not necessarily commuting matrices.⁸

Following Luttinger and Ward, we transform the sum in (14) into an integral by writing

$$N_D = \lim_{\beta \rightarrow \infty} \frac{1}{2\pi i} \int_{\Gamma} d\zeta \exp(\zeta 0^+) f_{\zeta}^-(\mu, \beta) \times \text{Tr} \frac{\partial}{\partial \zeta} \ln [1 - S(\zeta)(1/\Omega)\tilde{v}(\zeta)], \quad (16)$$

where f_{ζ}^- is the Fermi function of complex argument ζ , namely,

$$f_{\zeta}^-(\mu, \beta) = (e^{\beta(\mu - \zeta)} + 1)^{-1}. \quad (17)$$

f_{ζ}^- has simple poles at each $\zeta = \zeta_i$; and the contour Γ encloses these poles in the negative sense with two separate loops, one above the real axis and the other below. [See the diagram in Appendix A of Luttinger and Ward.⁵] The factor $\exp(\zeta 0^+)$ allows us to distort Γ into the contour Γ_0 which surrounds the entire real axis but encloses none of the poles of f_{ζ}^- . Integrating (16) by parts, we have

$$N_D = -\lim_{\beta \rightarrow \infty} \frac{1}{2\pi i} \int_{\Gamma_0} d\zeta \left[\frac{\partial}{\partial \zeta} f_{\zeta}^-(\mu, \beta) \right] \times \text{Tr} \ln \left[1 - S(\zeta) \frac{1}{\Omega} \tilde{v}(\zeta) \right]. \quad (18)$$

Since

$$\lim_{\beta \rightarrow \infty} \frac{\partial}{\partial \zeta} f_{\zeta}^-(\mu, \beta) = -\delta(\zeta - \mu), \quad (19)$$

we may perform the ζ integration immediately to obtain

$$N_D = \lim_{\eta \rightarrow 0} \frac{1}{2\pi i} \text{Tr} \left\{ \ln \left[1 - S(\mu - i\eta) \frac{1}{\Omega} \tilde{v}(\mu - i\eta) \right] - \ln \left[1 - S(\mu + i\eta) \frac{1}{\Omega} \tilde{v}(\mu + i\eta) \right] \right\}. \quad (20)$$

Next we must make the assumption mentioned in the

⁸ We are grateful to Dr. A. A. Maradudin for providing us with a simple proof of this result.

Introduction that the single-particle-like state at the Fermi surface does not decay; i.e., the self-energy $\Sigma(\mu)$ is real. According to the discussion following Eq. (7.7) of I, this assumption implies that $\Sigma'(\mu)$ also is real as long as the impurity potential does not shift the bottom of the continuum of free-electron states. Using this assumption we may write, for infinitesimal η ,

$$S(\mu - i\eta) = S(\mu + i\eta) + 2\pi i \delta(h + \Sigma(\mu) - \mu); \quad (21)$$

$$\tilde{v}(\mu - i\eta) = \tilde{v}(\mu + i\eta) = \tilde{v}(\mu). \quad (22)$$

On substituting (21) and (22) into (20) and using the matrix relation (15) we have

$$N_D = \frac{1}{2\pi i} \text{Tr} \ln \{ 1 - 2\pi i \delta(h + \Sigma(\mu) - \mu)(1/\Omega)\tilde{v}(\mu) \times [1 - S(\mu + i\eta)(1/\Omega)\tilde{v}(\mu)]^{-1} \}. \quad (23)$$

The argument of the logarithm in Eq. (23) is just the S matrix which describes the process in which eigenstates of the Hermitian operator $h + \Sigma(\mu)$ at energy μ are scattered by the screened impurity potential $\tilde{v}(\mu)$. This is precisely the same scattering system which was relevant to the calculation of impurity resistance as discussed in I. According to Lippmann and Schwinger,⁹ the exact scattering states $\psi_a^{(+)}$ satisfy the equation

$$\psi_a^{(+)} = \phi_a + S(\mu + i\eta)(1/\Omega)\tilde{v}(\mu)\psi_a^{(+)}, \quad (24)$$

where ϕ_a is an eigenstate of $h + \Sigma(\mu)$. The T matrix corresponding to this process is

$$T_{b,a} = [\phi_b, (1/\Omega)\tilde{v}(\mu)\psi_a^{(+)}] = \{ (1/\Omega)\tilde{v}(\mu)[1 - S(\mu + i\eta)(1/\Omega)\tilde{v}(\mu)]^{-1} \}_{b,a}; \quad (25)$$

and

$$S_{b,a}(\mu) = \delta_{b,a} - 2\pi i \delta(E_b - \mu) T_{b,a}. \quad (26)$$

Thus

$$N_D = (1/2\pi i) \text{Tr} \ln S(\mu). \quad (27)$$

In the special case of spherical symmetry, the eigenvalues of $S(\mu)$ are $e^{2i\delta_l(k_F)}$, where the δ_l are the scattering phase shifts. Using this form of S , we have immediately

$$N_D = \frac{1}{2\pi i} \sum_{l,m,\sigma} 2i\delta_l(k_F) = \frac{2}{\pi} \sum_l (2l+1)\delta_l(k_F), \quad (28)$$

which is the usual form of the Friedel sum rule.

⁹ B. A. Lippmann and J. Schwinger, Phys. Rev. **79**, 469 (1950).