On the Mooij Rule

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Abstract

Weak localization leads to the same correction to both the conductivity and the electron-phonon coupling constant $\lambda$ (and $\lambda_{tr}$). Consequently the temperature dependence of the (thermal) electrical resistivity is decreasing as the conductivity is decreasing due to weak localization, which results in the decrease of the temperature coefficient of resistivity (TCR) with increasing the residual resistivity. When $\lambda$ is approaching zero, only residual resistivity part remains and gives rise to the negative TCR. Accordingly, the Mooij rule is a manifestation of weak localization correction to the conductivity and the electron-phonon interaction. This study may provide a new means of probing the phonon-mechanism in exotic superconductors.

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I. INTRODUCTION

Although weak localization has greatly deepened our understanding of the normal state of disordered metals, its effect on superconductivity and electron-phonon interaction has not been understood well. Recently, it has been shown that weak localization leads to the same correction to the conductivity and the phonon-mediated interaction. It is then anticipated that the electron-phonon interaction will also be influenced strongly by weak localization. For instance, phonon-limited electrical resistance, attenuation of a sound wave, thermal resistance, and a shift in phonon frequencies may change due to weak localization.

In fact, the Mooij rule in strongly disordered metallic systems seems to be a manifestation of the effect of weak localization on the electron-phonon interaction and the conductivity. In early seventies, Mooij found a correlation between the residual resistivity and the temperature coefficient of resistivity (TCR). In particular, TCR is decreasing with increasing the residual resistivity. Then it becomes negative above 150$\mu\Omega cm$. There are already several theoretical works on this problem. Jonson and Girvin performed numerical calculations for an Anderson model on a Cayley tree and found that the adiabatic phonon approximation breaks down in the high-resistivity regime producing the negative TCR. Imry pointed out the importance of incipient Anderson localization (weak localization) in the resistivities of highly disordered metals. He argued that when the inelastic mean free path, $\ell_{ph}$, is smaller than the coherence length, $\xi$, the conductivity increases with temperature like $\ell_{ph}^{-1}$ and thereby leads to the negative TCR. On the other hand, Kaveh and Mott generalized the Mooij rule. Their results are as follows: The temperature dependence of the conductivity of a disordered metal as a function of temperature changes slope due to weak localization effects, and if interaction effects are included, the conductivity changes its slope three times. Götze, Belitz, and Schirmacher introduced a theory with phonon-induced tunneling. There is also the extended Ziman theory.

In this paper, we propose an explanation of the Mooij rule based on the effect of weak localization on the electron-phonon interaction. If we assume the decrease of the electron-phonon interaction due to weak localization, we can understand the decrease of TCR with increasing the residual resistivity. The negative TCR is therefore due to weak localization correction to the Boltzmann conductivity, since when TCR is approaching zero there is no temperature-dependent resistivity left. (This latter point is similar to Kaveh and Mott’s interpretation.) Matthiessen’s rule seems to remain intact to a large extent even in the highly disordered systems. In Sec. II, we briefly describe the Mooij rule. In Sec. III, weak localization correction to the electron-phonon coupling constant $\lambda$ and $\lambda_w$ is calculated. A possible explanation of the Mooij rule is given in Sec. IV, and its implication is briefly discussed in Sec. V. In particular, this study may provide a means to probe the phonon-mechanism in exotic superconductors.

II. THE MOOIJ RULE

According to Matthiessen’s rule, resistivity $\rho(T)$ caused by static and thermal disorder is additive, i.e.,

$$\rho(T) = \rho_o + \rho_{ph}(T), \quad (1)$$
where $\rho_{ph}$ is mostly due to electron-phonon scattering. Mooij found (at high temperatures) that the size and sign of the temperature coefficient of resistivity (TCR) in many disordered systems correlate with its residual resistivity $\rho_o$ as follows:

$$
\frac{d\rho}{dT} > 0 \quad \text{if} \quad \rho_o < \rho_M
$$

$$
\frac{d\rho}{dT} < 0 \quad \text{if} \quad \rho_o > \rho_M.
$$

(2)

Thus, TCR changes sign when $\rho_o$ reaches the Mooij resistivity $\rho_M \approx 150 \mu \Omega \text{cm}$. Figure 1 shows the temperature coefficient of resistance $\alpha$ versus resistivity for transition-metal alloys obtained by Mooij. It is clear $\alpha$ (and TCR) is correlated with the residual resistivity. Note that above $150 \mu \Omega cm$ most $\alpha$’s are negative. Figure 2 shows the resistivity as a function of temperature for pure Ti and TiAl alloys containing 3, 6, 11, and 33% Al. TCR is decreasing as the residual resistivity is increasing. For TiAl alloy with 33% Al shows the negative TCR. Since this behavior is generally found in strongly disordered metals and alloys, amorphous metals, and metallic glasses, it is called the Mooij rule. However, the physical origin of this rule has remained unexplained until now.

### III. Weak Localization Correction to Electron-Phonon Interaction

Since the electron-phonon interaction in metals gives rise to both the (high temperature) resistivity and superconductivity, these properties are closely related, which was noticed by many workers. In this Section, we show that weak localization leads to the same correction to the conductivity and the electron-phonon coupling constant $\lambda$ and $\lambda_{tr}$.

#### A. High Temperature resistivity

At high temperatures, the phonon limited electrical resistivity is given by

$$
\rho_{ph}(T) = \frac{4\pi m k_B T}{ne^2 \hbar} \int \frac{\alpha_{tr}^2 F(\omega)}{\omega} d\omega,
$$

$$
= \frac{2\pi m k_B T}{ne^2 \hbar} \lambda_{tr},
$$

(3)

where $\alpha_{tr}$ includes an average of a geometrical factor $1 - \cos\theta_{kk'}$ and $F(\omega)$ is the phonon density of states. On the other hand, in the strong-coupling theory of superconductivity, the electron-phonon coupling constant is defined by

$$
\lambda = 2 \int \frac{\alpha^2(\omega) F(\omega)}{\omega} d\omega.
$$

(4)

Assuming $\alpha_{tr}^2 \approx \alpha^2$, we obtain

$$
\rho_{ph}(T) = \frac{2\pi m k_B T}{ne^2 \hbar} \lambda_{tr}
$$

$$
\approx \frac{2\pi m k_B T}{ne^2 \hbar} \lambda.
$$

(5)
Consequently the electron-phonon coupling constant \( \lambda \) determines also the size and sign of TCR. Table I shows the comparison of \( \lambda_{tr} \) and \( \lambda \) for various materials.\(^{20,21}\) The overall agreement between \( \lambda_{tr} \) and \( \lambda \) is impressive.

**B. Weak localization correction to \( \lambda \) and \( \lambda_{tr} \)**

Now we need to calculate the electron-phonon coupling constant \( \lambda \) for highly disordered systems. We follow the approach by Park and Kim.\(^{5}\) (For simplicity we consider an Einstein model with frequency \( \omega_D \)). Note that \( \lambda \) can be written as\(^{19}\)

\[
\lambda = 2 \int \frac{\alpha^2(\omega)F(\omega)}{\omega} d\omega
\]

\[
= N_o \frac{< I^2 >}{M < \omega^2 >},
\]

where \( M \) is the ionic mass and \( N_o \) is the electron density of states at the Fermi level. \( < I^2 > \) is the average over the Fermi surface of the square of the electronic matrix element and \( < \omega^2 > = \omega_D^2 \). In the presence of impurities, weak localization leads to a correction to \( \alpha^2 \) or \( < I^2 > \), (disregarding the changes of \( F(\omega) \) and \( N_o \)).

The equivalent electron-electron potential in the electron-phonon problem is given by,\(^{22,23}\)

\[
V(x - x') \rightarrow \frac{I_o^2}{M\omega_D^2} D(x - x'),
\]

where \( x = (r, t) \) and \( I_o \) is the electronic matrix element for the plane wave states. The Fröhlich interaction at finite temperatures is then obtained by

\[
V_{nn'}(\omega, \omega') = \frac{I_o^2}{M\omega_D^2} \int d\mathbf{r} d\mathbf{r}' \psi^*_n(\mathbf{r}) \psi^*_n(\mathbf{r}') D(\mathbf{r} - \mathbf{r}', \omega - \omega') \psi_n(\mathbf{r}') \psi_n(\mathbf{r})
\]

\[
= \frac{I_o^2}{M\omega_D^2} \int |\psi^*_n(\mathbf{r})|^2 |\psi_n(\mathbf{r})|^2 d\mathbf{r} \frac{\omega_D^2}{\omega_D^2 + (\omega - \omega')^2}
\]

\[
= V_{nn'} \frac{\omega_D^2}{\omega_D^2 + (\omega - \omega')^2},
\]

where\(^{23}\)

\[
D(\mathbf{r} - \mathbf{r}', \omega - \omega') = \sum_q \frac{\omega_D^2}{(\omega - \omega')^2 + \omega_D^2} e^{i \mathbf{q} \cdot (\mathbf{r} - \mathbf{r}')}
\]

\[
= \frac{\omega_D^2}{(\omega - \omega')^2 + \omega_D^2} \delta(\mathbf{r} - \mathbf{r}').
\]

Here \( \omega \) means the Matsubara frequency and \( \psi_n \) denotes the scattered state. Subsequently, the strong-coupling gap equation can be easily obtained.\(^{5}\) Note that the spatial part of the phonon Green’s function \( D(\mathbf{r} - \mathbf{r}', \omega - \omega') \) becomes the Dirac delta function, since the phonon frequency does not depend on the momentum. Accordingly, the electron-phonon interaction coupling constant \( \lambda \) is given by
\[ \lambda = N_o < V_{nn'}(0,0) > = N_o \frac{I_o^2}{M \omega_D^2} < \int |\psi_n(r)|^2 |\psi_n'(r)|^2 dr >. \] (11)

This result agrees with the BCS theory with a point interaction \( V \delta(r_1-r_2) \), i.e.,

\[ \lambda_{eff} = N_o V < \int |\psi_n(r)|^2 |\psi_n'(r)|^2 dr >, \] (12)

where \( V = \frac{I_o^2}{M \omega_D^2} \).

Note that in the presence of impurities, the correlation function has a free-particle form for \( t < \tau \) (scattering time) and a diffusive form for \( t > \tau \). As a result, for \( t > \tau \) (or \( r > \ell \)), one finds

\[ R = \int_{t>\tau} |\psi_n(r)|^2 |\psi_n'(r)|^2 dr \]

\[ = \sum_\tilde{q} |<\psi_n| e^{i \tilde{q} \cdot r} |\psi_n'>|^2_{AV} \]

\[ = \frac{1}{2\pi hN_o D \tilde{q}^2} \sum_{\pi/L < \tilde{q} < \pi/\ell} \]

\[ = \frac{3}{2(k_F \ell)^2} (1 - \frac{\ell}{L}). \] (13)

Here \( \ell \) is the mean free path and \( L \) is the inelastic diffusion length. Whereas the contribution from the free-particle-like density correlation for \( t < \tau \) is\(^5\),\(^25\)

\[ V_{nn'} = V \int_{t<\tau} |\psi_n(r)|^2 |\psi_n'(r)|^2 dr \]

\[ \approx V [1 - \frac{3}{(k_F \ell)^2} (1 - \frac{\ell}{L})]. \] (15)

Since the phonon-mediated interaction is retarded for \( t_{ret} \approx 1/\omega_D \), only the free-particle-like density correlation contributes to the pairing matrix element. Thus, we obtain

\[ \lambda = N_o V [1 - \frac{3}{(k_F \ell)^2} (1 - \frac{\ell}{L})] \]

\[ = \lambda_o [1 - \frac{3}{(k_F \ell)^2} (1 - \frac{\ell}{L})]. \] (16)

Here \( \lambda_o \) is the BCS \( \lambda \) for the pure system. Subsequently, one finds

\[ \lambda_{tr} = 2 \int \frac{\alpha^2_n(\omega) F(\omega)}{\omega} d\omega \]

\[ \approx \lambda_o [1 - \frac{3}{(k_F \ell)^2} (1 - \frac{\ell}{L})] \]

\[ = \lambda_o [1 - \frac{3}{(k_F \ell)^2}]. \] (17)

We have used the fact that \( L \) is effectively infinite at \( T = 0 \). Note that the weak localization correction term is the same as that of the conductivity.
IV. EXPLANATION OF THE MOOIJ RULE

The high temperature resistivity is then

\[ \rho_{ph}(T) \approx \frac{2\pi mk_B T}{ne^2\hbar} \lambda \]

\[ \approx \frac{2\pi mk_B T}{ne^2\hbar} \lambda_o \left[ 1 - \frac{3}{(k_F\ell)^2} \right]. \]  

(18)

On the other hand, the conductivity and the residual resistivity are given by

\[ \sigma = \sigma_B \left[ 1 - \frac{3}{(k_F\ell)^2} \left( 1 - \frac{\ell}{L} \right) \right], \]  

(19)

and

\[ \rho_o = \frac{1}{\sigma_B \left[ 1 - \frac{3}{(k_F\ell)^2} \left( 1 - \frac{\ell}{L} \right) \right]}, \]  

(20)

where \( \sigma_B = ne^2\tau / m \). According to Matthiessen’s rule, we may add both resistivities,

\[ \rho \approx \rho_o + \rho_{ph}(T) \]

\[ = \frac{1}{\sigma_B \left[ 1 - \frac{3}{(k_F\ell)^2} \left( 1 - \frac{\ell}{L} \right) \right]} + \frac{2\pi mk_B T}{ne^2\hbar} \lambda_o \left[ 1 - \frac{3}{(k_F\ell)^2} \right]. \]  

(21)

As the disorder parameter \( 1/k_F\ell \) is increasing, the system is more disordered and the residual resistivity is getting higher. It is remarkable that the slope of the high temperature resistivity is decreasing concomitantly, in good agreement with experiment. Note that the slope varies as \( \sim 1/(k_F\ell)^2 \). This point has not been noticed before. When \( 1/k_F\ell \) becomes comparable to \( \sim 1 \), the magnitude and slope of \( \rho_{ph}(T) \) is becoming too small. In that case, only the residual resistivity will play an important role. Therefore, the observed negative TCR may be understood from the residual part. With decreasing \( T \), since the inelastic diffusion length \( L \) increases, the residual resistivity will also increase, leading to the negative TCR.

Now we calculate Eq. (21) numerically to see the detailed temperature dependence of the resistivity of disordered systems. Figure 3 shows the resistivity as a function of temperature. We used \( k_F = 0.8\,\text{Å}^{-1} \), \( n = k_F^2 / 3\pi^2 \), and \( \lambda = 0.5 \). Since it is difficult to evaluate \( k_F\ell \) up to a factor of 2,\(^{26}\) we assume that \( \rho = 100\mu\Omega\text{cm} \) corresponds to \( k_F\ell = 3.2 \). We also used \( L = \sqrt{D\tau_i} = \sqrt{\ell} \times 350/T(\text{Å}) \). Here \( D \) is the diffusion constant and \( \tau_i \) denotes the inelastic scattering time. For low temperatures \( \tau_i \) is determined by electron-electron scattering while for high temperatures it is determined by the electron-phonon scattering. Since we are interested in rather high temperatures, we assumed \( \tau_i \sim T^{-1} \) corresponding to the electron-phonon scattering. Considering the crudeness of our calculation, the overall behavior is in good agreement with experiment.
V. DISCUSSION

It is clear that weak localization effect on the electron-phonon interaction needs more theoretical and experimental studies. In particular, weak localization effect on the attenuation of a sound wave, shear modulus, thermal resistance, and a shift in phonon frequencies will be very interesting. Since superconductivity is also caused by the electron-phonon interaction, comparative study of the normal and superconducting properties of the metallic samples will be beneficial. There is already compelling evidence that this is the case. For instance, Testardi and his coworkers\textsuperscript{27–30} found the universal correlation of $T_c$ and the resistance ratio. They also found that decreasing $T_c$ is accompanied by the decrease of the thermal electrical resistivity.\textsuperscript{27}

Note that this study may provide a means of probing the phonon-mechanism in exotic superconductors, such as, heavy fermion superconductors, organic superconductors, fullerene superconductors, and high $T_c$ cuprates. For superconductors caused by the electron-phonon interaction we expect the following behavior. As the electrons are weakly localized by impurities or radiation damage, the electron-phonon interaction is weakened. As a result, both $T_C$ and TCR are decreasing at the same rate. When $\lambda$ is approaching zero, both $T_c$ and TCR drops to zero almost simultaneously. When this happens we may say that the electron-phonon interaction is the origin of the pairing in the superconductors. This behavior was already confirmed in A15 superconductors\textsuperscript{27–30} and Ternary superconductors.\textsuperscript{31} More details will be published elsewhere.

VI. CONCLUSION

It is shown that weak localization decreases both the conductivity and the electron-phonon interaction at the same rate and thereby leads to the Mooij rule. As the residual resistivity is increasing due to weak localization, so the thermal electrical resistivity is decreasing, producing the decrease of TCR. When the electron-phonon interaction is near zero, only the residual resistivity is left and therefore the negative TCR is obtained. Matthiessen’s rule seems to be intact to a large extent even in highly disordered systems. This study may provide a means of probing the phonon-mechanism in exotic superconductors, such as, heavy fermion superconductors, organic superconductors, fullerene superconductors, and high $T_c$ superconductors.

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Table I. Comparison of $\lambda_{tr}$ and $\lambda$ as given in Ref. 20.

| Metal | $\lambda_{tr}$ | $\lambda$   | Metal | $\lambda_{tr}$ | $\lambda$   |
|-------|----------------|-------------|-------|----------------|-------------|
| Li    | .40            | .41±.15     | Na    | .16            | .16±.04     |
| K     | .14            | .13±.03     | Rb    | .19            | .16±.04     |
| Cs    | .26            | .16±.06     | Mg    | .32            | .35±.04     |
| Zn    | .67            | .42±.05     | Cd    | .51            | .40±.05     |
| Al    | .41            | .43±.05     | Pb    | 1.79           | 1.55        |
| In    | .85            | .805        | Hg    | 2.3            | 1.6         |
| Cu    | .13            | .14±.03     | Ag    | .13            | .10±.04     |
| Au    | .08            | .14±.05     | Nb    | 1.11           | .9±.2       |
FIGURES

FIG. 1. The temperature coefficient of resistance $\alpha$ versus resistivity for bulk alloys (+), thin films (●), and amorphous (X) alloys. Data are from Mooij, Ref. 7.

FIG. 2. Resistivity versus temperature for Ti and TiAl alloys containing 0, 3, 6, 11, and 33% Al. Data are from Mooij, Ref. 7.

FIG. 3. Calculated resistivity versus temperature for $k_F\ell = 15, 5, 3.4, 2.8, 2.4,$ and $2.3$. 
