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Mooij correlation in disordered metals

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We point out that the Mooij correlation follows naturally from a dynamically disordered tight-binding Hamiltonian with random modulations of both the diagonal and the off-diagonal matrix elements which are known to act in opposition. The dynamic disorder is treated exactly while the static disorder is incorporated approximately as an effective additional time-dependent disorder affecting the diffusive electron. Such a time translation of static disorder is known to manifest itself in certain limits as a renormalization of the diffusion coefficient. The calculated conductivity exhibits the Mooij correlation at high temperatures, where quantum coherence associated with the static disorder can be ignored.

Operationally, the metallic state is often characterized by a positive temperature coefficient of resistance (TCR) in the temperature range of interest. A change of sign of the TCR is then taken as the transition from the metallic to the insulating state. Perhaps a more fundamental view is that the "metallic" resistance should extrapolate to a finite residual resistance (RR) at the absolute zero of temperature. Many random alloys show an anomalous TCR. Mooij[1] was the first to observe on empirical grounds that there exists a correlation between the sign of the TCR and the absolute magnitude of the RR, i.e., $\rho_{(T=0)} \gtrless \rho_c$ implies $(d\rho/dT)_{T=0} \lesseqgtr 0$. This correlation is quite universal, holding for glassy and liquid metals, amorphous alloys and the highly resistive $A15$ compounds, both in bulk samples and thin films.[2] The magnitude of ρ_c is, however, not universal.[3] It can have values ranging from 30 to 400 $\mu\Omega$ cm. In certain transition-metal oxides values for $\rho_c \sim (2\text{–}3)\times 10^3$ $\mu\Omega$ cm have been reported.[4] A typical value is 150 $\mu\Omega$ cm.

Most theoretical approaches[3,5,6] to the Mooij correlation are based on quantum-mechanical coherence effects, namely, the incipient Anderson localization. This is suggested by the fact that the observed ρ_c is not too far from the value of Mott's[6] maximum metallic resistance $\rho_{\max} \sim 1000$ $\mu\Omega$ cm, where incipient localization sets in above the mobility edge. It has been argued that the breakdown of the adiabatic approximation, even in the metallic phase due to incipient localization, leads to phonon-assisted tunneling and, therefore, to a negative TCR.[7] Using the scaling theory of localization,[8] Imry has argued that just above the mobility edge the coherence length ξ, which represents the length scale beyond which conductance becomes Ohmic, determines the conductivity which is given by $\sigma = c(e^2/\hbar\xi)$. Here c is a constant and $\xi < L$, the sample size. This is for $T = 0$ K. At a finite temperature, however, the inelastic scattering due to phonons (or electrons) makes the quantum motion incoherent, suppressing the quantum interference necessary for the incipient localization. Then the length-scale-dependent localization effects are cut off beyond the inelastic diffusion length l_i [or more precisely the Thouless length $L_T = (l_e l_i)^{1/2}$] and, in the regime where $l_i < \xi$, the conductivity is given by $\sigma = c'(e^2/\hbar l_i)$. Usually l_i is proportional to $T^{-p/2}$, where p can assume any value between 1 and 4 depending on the temperature regime and the dimensionality of the sample. This results in the increase of conductivity as we increase temperature (negative TCR). It may be noted that $p \to 1$ as $T \to$ Debye temperature for all dimensions. The above treatment is in the regime of marginal metallicity. In a highly metallic regime, where the elastic mean free path $l_e \gg a$, the interatomic spacing, the conventional Boltzmann transport takes over, leading to a positive TCR. Similar results are obtained by Mott and Kaveh[6] who consider diffusion correction to the Boltzmann conductivity in a perturbative calculation to the order of $1/(k_F l_e)^2 < 1$.

The above theories assume $l_e < l_i$. Inasmuch as Mooij correlation persists even above room temperature where l_i becomes quite small, it is not clear if the ideas based on quantum coherence (localization) continue to hold at these temperatures (see, however, Tsuei[3]). In this note we point out that even without localization as a dominant effect, Mooij-type correlation is possible at high temperatures. This arises naturally from the competition between the diagonal and the off-diagonal matrix element modulations by thermal phonons for a tight-binding degenerate electron system. The temperatures considered are high (comparable to Debye temperature Θ_D) to ensure stochasticity, but low compared to the Fermi temperature T_F to ensure degeneracy. Our treatment is based on the exact result known[9-12] for the dynamically disordered systems. Static disorder is, however, treated in an approximate way.

We consider an electron moving on a lattice (L) coupled to phonons. The appropriate Hamiltonian in a tight-binding one-band model can be written as

$$H_L = \sum_{n,\delta} J \,|n\rangle\langle n+\delta| + \sum_{n,\delta} V_{n,n+\delta}(t)\,|n\rangle\langle n+\delta| + \sum_{n} (\Delta_n + \epsilon_n(t)\,|n\rangle\langle n| \ . \tag{1}$$

J is the off-diagonal matrix element connecting nearest neighbors (δ) separated by lattice spacing a and $|n\rangle$ is the nondegenerate Wannier orbital associated with the site n. Δ_n is the random-site energy representing static disorder. $\epsilon_n(t)$ and $V_{n,n+\delta}(t)$ are, respectively, the diagonal and the

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off-diagonal matrix elements, evolving stochastically in time and are c-number variables. Such a time dependence arises from the random modulation of crystal potential by thermal lattice vibrations (phonons). Thus in our treatment we have replaced the dynamical degrees of freedom (phonons) by classical c-number variables. A Gaussian approximation is made for such variables, which is valid at high temperatures $T \gtrsim \Theta_D$. Statistical properties of these random variables are taken as

$$\langle V_{n,n+\delta}(t)\rangle = \langle \epsilon_n(t)\rangle = 0 \ , \tag{2a}$$

$$\langle V_{n,n+\delta}(t) V_{n,n+\delta}(t')\rangle = 2\Gamma_1 \delta(t-t') \ , \tag{2b}$$

$$\langle \epsilon_n(t)\epsilon_n(t')\rangle = 2\Gamma_0 \delta(t-t') \ , \tag{2c}$$

and all other correlations zero. For the static disorder we take

$$\langle \Delta_n \rangle_s = 0 \ , \tag{3a}$$

$$\langle \Delta_n \Delta_{n'} \rangle_s = 2\Delta^2 \delta_{n,n'} \ . \tag{3b}$$

Here $\langle \cdots \rangle$ and $\langle \cdots \rangle_s$ represent ensemble averages over all the realizations of the dynamic and static randomness, respectively. Γ_1 and Γ_0 can be expressed in terms of phonons[10,12] (mean-squared displacements) and deformation potentials Λ_1 and Λ_0:

$$2\Gamma_0 = \pi^2 \Lambda_0^2 k_B T / 12 a^2 m \Omega_D^3$$

and

$$2\Gamma_1 = \pi^2 \Lambda_1^2 k_B T / 12 a^2 m \Omega_D^3 \ ,$$

where Ω_D is the Debye frequency. The Hamiltonian in Eq. (1) has been studied extensively[9-14] in the absence of static disorder, the motivation being the current interest in the problem of charge and energy transport[9-16] in molecular solids and also the diffusion of light atoms[17] absorbed on solid surfaces. Essentially, in all these treatments one deals with quantum-mechanical dynamics of quasiparticles (electrons, excitons, etc.) coupled to phonons. In the absence of static disorder one can show analytically that in the long-time limit the motion of the quasiparticle is diffusive and an exact expression for the diffusion constant D_0 is obtained through the calculation for the mean-squared displacement[9-12]

$$D_0 = a^2 \left[\frac{J^2}{\Gamma_0 + 3\Gamma_1} + \frac{2\Gamma_1}{\hbar^2} \right] \ . \tag{4}$$

Note that the diagonal and the off-diagonal fluctuations contribute to the diffusion constant in qualitatively different ways. The strength of the diagonal fluctuations Γ_0 appears only in the denominator of the first term in Eq. (4), indicating that the diagonal fluctuations disfavor the diffusion. That is understandable from the fact that these fluctuations create mismatch of the nearest-neighbor site energies which in turn reduces the tunneling and hopping probabilities. However, the strength of the off-diagonal fluctuations Γ_1 appears in the denominator of the first term and in the numerator of the second. These fluctuations not only disrupt the coherent band motion but also accelerate the particle motion favoring diffusion. One can readily appreciate the latter in the limit $J = 0$.

Next we incorporate the static disorder in the above treatment by the following physical *Ansatz*. If the static disorder is weak compared to the dynamic disorder, we expect the quantum-coherence effects to become unimportant except at short distances and times. In such a situation an electron diffusing incoherently will see the spatial randomness Δ_n's time translated as an approximately Gaussian random process $\epsilon_n^s(t)$ with

$$\langle \epsilon_n^s(t)\rangle = 0 \ , \tag{5a}$$

$$\langle \epsilon_n^s(t)\epsilon_n^s(t')\rangle = 2\Delta^2 \tau \delta(t-t') \ , \tag{5b}$$

where τ is the transit time between the neighboring sites and is of the order of $\hbar/W$. Here W is the bandwidth of the system given by $W = 2ZJ$, with Z the coordination number. We will return to the physical basis of this *Ansatz* later. We would like to point out, however, that this does not necessarily require that the Debye temperature be large compared to the bandwidth (or the Fermi energy). It, however, does imply large electron-phonon coupling, i.e., large depth of modulation. Now we can incorporate the effect of static disorder on the diffusion constant by the replacement $\Gamma_0 \rightarrow \Gamma_0 + \Delta^2 \tau$ in Eq. (4). Thus the bare diffusion constant D_0 gets modified to D given by

$$D = a^2 \left[\frac{J^2}{\Gamma_0 + \Delta^2 \tau + 3\Gamma_1} + \frac{2\Gamma_1}{\hbar^2} \right] \ . \tag{6}$$

This is our central result. Now the Einstein-Nernst relation between conductivity $\sigma(T)$ and the diffusion constant for a degenerate system is

$$\sigma(T) = e^2 D (dn/dE)_F \ , \tag{7}$$

where $(dn/dE)_F$ is the density of states at the Fermi energy and is given by[6] $(dn/dE)_F = 1.75 \times 2/Wa^3$ for a half-filled band and simple cubic lattice. From Eqs. (6) and (7), we get

$$\sigma(T) = C \left[\frac{1}{(2Z)^2(\delta^2 + a_0 t + 3a_1 t)} + 2a_1 t \right] \ , \tag{8}$$

where $C = 3.5(e^2/\hbar a)$ and we have introduced the dimensionless variables $t = k_B T/W$ the reduced temperature, $\delta^2 = \Delta^2/W^2$ representing the static disorder, $a_0 = \Gamma_0/\hbar k_B T$ and $a_1 = \Gamma_1/\hbar k_B T$. In our model Γ_0 and Γ_1 are linearly proportional to the temperature.

In Fig. 1 we have plotted the normalized resistivity $\rho_N (= C/\sigma)$, as a function of reduced temperature for some typical values of δ. We have chosen $a_0 = a_1 = 0.5$ and various values of $\delta^2 (= 0.05, 0.08, 0.12, 0.16$, and $0.19)$. From Fig. 1 we can see explicitly the Mooij-type behavior. Strictly speaking, the plots are meaningful only in the high-temperature regime as discussed earlier and the extrapolation to zero temperature is obviously suspect. It is to be noted, however, that while the assumption of white-noise stochasticity, i.e., delta-correlated random potential modulations in Eq. (2) indeed requires $T \gtrsim \theta_D$, the results for the *dc conductivity* are more general and hold even for colored noise that obtains for lower temperatures when the correlation time for the stochastic force is finite. In fact what enters the dc conductivity is essentially the integrated strength of the noise auto correlation func-

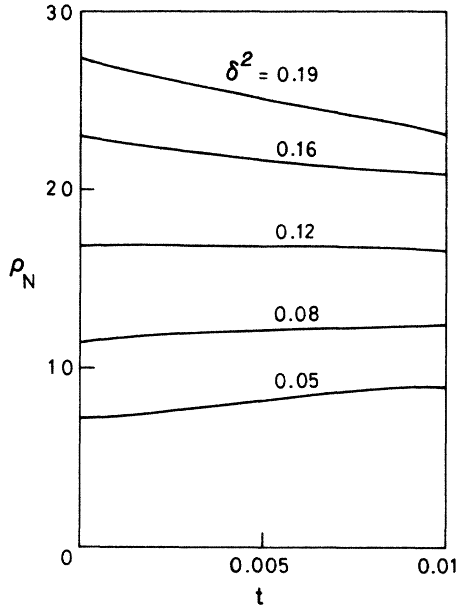

FIG. 1. Plot of normalized resistivity ρ_N against reduced temperature for various values of disorder δ^2 and $\alpha = 0.5$.

tion.[18] This amounts to redefining our parameter Δ. What really limits the domain of validity at low temperatures is the requirement that the inelastic mean free path l_i (or L_T) be less than the coherence length ξ. This happens typically for temperatures less than θ_D, extending thus the domain of validity of the present treatment to lower temperatures for the high resistivity samples for which ξ is expected to be large.

From the expression (7) we can evaluate the critical value of the conductivity (or RR) at which TCR changes sign, i.e., at which $(d\sigma/dT)_{T=0} = 0$. One gets

$$\sigma_c(t=0) = (3.5/2Z)(e^2/\hbar a)\sqrt{2\alpha_1/(\alpha_0+3\alpha_1)} \ . \quad (9)$$

This shows that the Mooij value depends on many parameters (not universal). For typical values of parameters $a = 2$ Å, $\alpha_1 = \alpha_0$, and $Z = 6$, we obtain the Mooij value of RR $\rho_c \sim 500$ $\mu\Omega$ cm. Again we have used Eq. (8) extrapolated to zero temperature to evaluate critical residual resistance ρ_c at which TCR changes sign. In fact we could have used a higher temperature (room temperature, say) as a reference temperature for the discussion of Mooij correlation. This would be operationally more appropriate for comparison with experimental results. For the purpose of this discussion of the basic ideas, however, we have found it more appealing to present our results in terms of the *extrapolated* residual resistance, which is well defined.

It is interesting to note in passing here that for many highly resisitive but metallic transition-metal oxides and related systems[10] where the transport is by a small density (n) of holes in the otherwise half-filled band (odd-electron Hubbard insulator), the holes can form a nondegenerate system at operating temperature. In such a case the relation (6) is replaced by usual Einstein relation $\sigma = e^2nD/k_BT$. This gives resistance saturation at high temperatures. This explanation is, of course, not applicable to metallic alloys and other highly resistive systems where the degeneracy temperature is much higher.

We now return to our treatment of static disorder. Consider the Brownian motion defined by a bare diffusion constant D_0. The effect of weak static disorder varying slowly (i.e., weak dilute limit) in space is readily treated in an effective field approximation leading to a renormalized, smaller diffusion constant. The problem is equivalent to that of diffusion in a fluid in the presence of random potential (irrotational) flow.[19] In the present case, however, the disorder is fluctuating on the atomic length scale and local bare diffusion constant is not defined. Motion on this length scale is essentially controlled by the transfer matrix element J (or bandwidth W) giving rise to a local oscillatory motion on the time scale $\tau \sim \hbar/W$, superimposed on the slow diffusive motion controlled by D_0. Now, the local oscillation will make the expectation value of the disordered site potential Δ itself fluctuate on the short time scale $\tau \sim \hbar/W$. This will be seen by the diffusing particle as an additional time-dependent disorder of strength $\Delta^2\tau$ which simply adds to Γ_0. It is reassuring to see that the form of our expression (5) is similar to that obtained by Belitz and Schirmacher[20] so far as the temperature dependence is concerned. It seems to us that our off-diagonal modulation corresponds to their phonon coupling to the electron momentum density.

In conclusion, we have shown that the Mooij correlation can arise entirely from strong electron-phonon interaction provided that one takes into account qualitatively different roles of the diagonal and the off-diagonal modulations. The static disorder is incorporated approximately as translated into the dynamic disorder due to the incoherence caused by the electron-phonon interaction. The treatment is appropriate to the high-temperature regime and does complement the low-temperature behavior described by the incipient localization effects. However, the range of validity of our treatment of static disorder needs a closer analysis, which is in progress.

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