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Infrared and dc conductivity in metals with strong scattering: Nonclassical behavior from a generalized Boltzmann equation containing band-mixing effects

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Metals with high resistivity (~ 100 $\mu\Omega$ cm) seem to show weaker variation of resistivity (as a function of temperature and perhaps also static disorder) than predicted by semiclassical (Bloch-Boltzmann) theory (SBT). We argue that the effect is not closely related to Anderson localization, and therefore does not necessarily signify a failure of the independent collision approximation. Instead we propose a failure of the semiclassical acceleration and conduction approximations. A generalization of Boltzmann theory is made which includes quantum (interband) acceleration and conduction, as well as a complete treatment of interband-collision effects (within the independent-collision approximation). The interband terms enhance short-time response to $\vec{E}$ fields (because the theory satisfies the exact f-sum rule instead of the semiclassical approximation to it). This suggests that the additional conductivity, as expressed phenomenologically by the shunt resistor model, is explained by interband effects. The scattering operator is complex, its imaginary parts being related to energy-band renormalization caused by the disorder. Charge conservation is respected and thermal equilibrium is restored by the collision operator. The theory is formally solved for the leading corrections to SBT, which have the form of a shunt resistor model. At infrared frequencies, the conductivity mostly obeys the Drude law $\sigma(\omega) \sim \sigma(0)(1-i\omega\tau)^{-1}$, except for one term which goes as $(1-i\omega\tau)^{-2}$.

I. INTRODUCTION

Strong-scattering metals (such as $A15$-structure metals, e.g., $\mathrm{Nb_3Sn}$) show anomalous behavior of dc electrical resistivity which theory is not yet able to explain.[1] The high-temperature (T) resistivity of metals is predicted by semiclassical Boltzmann theory (SBT) to rise linearly with disorder, i.e., $\rho_{\mathrm{SBT}} = \rho_0 + \rho_1 T$ with residual resistivity ρ_0 linear in defect density and phonon resistivity $\rho_1 T$ linear in temperature or phonon disorder. Experimental observations show that for metals with high resistivity ($\rho \sim 100$ $\mu\Omega$ cm), ρ rises less rapidly with T than predicted by SBT and seems to approach a maximum $\rho_{\max}$ as T increases. This phenomenon has been termed resistivity "saturation" by Fisk and Webb,[2] who argue as Mooij[3] that the effect is associated with the mean free path (l) decreasing toward a minimum value, the interatomic spacing (a). Wiesmann *et al.*[4] show that for several $A15$ metals, the behavior fits the phenomenological shunt resistor model

$$1/\rho_{\mathrm{expt}}(T) = 1/\rho_{\mathrm{SBT}}(T) + 1/\rho_{\max}, \tag{1a}$$

$$\sigma_{\mathrm{expt}}(T) = \sigma_{\mathrm{SBT}}(T) + \sigma_{\min} \tag{1b}$$

when temperature (and possibly also defect density) vary. Experimentally, $\rho_{\max} = 1/\sigma_{\min}$ is ~ 150 $\mu\Omega$ cm for many d-band systems. Mooij has also shown that if the $T=0$ resistivity exceeds ~ 150 $\mu\Omega$ cm, ρ will usually decrease as T increases, again approaching a saturation value ~ 150 $\mu\Omega$ cm. This latter behavior cannot be fit by Eq. (1), but must be regarded as part of the same class of phenomena. For convenience, we shall refer to these phenomena collectively as "Mooij's laws."

There is a very simple way in which Eq. (1) might arise out of microscopic theory. We must believe two things; first that the only parameter σ depends on is a/l, and second that $\sigma(a/l)$ can be represented as a simple series of powers of a/l. If so, the prediction of microscopic theory will have the form

$$\sigma = \sigma_{\min}\left[\left(\frac{a}{l}\right)^{-1} + \sum_{n=0}^{\infty} c_n \left(\frac{a}{l}\right)^{n}\right], \tag{2}$$

where c_n are dimensionless coefficients. The first term $\sigma_{\min}(a/l)^{-1}$ is σ_{SBT}, which contains the leading singular part of σ, i.e., the parts which diverge as $l \to \infty$. Corrections to Boltzmann theory appear as higher powers of a/l. As long as a/l is small, the corrections can be ignored and Boltzmann theory is correct. Equation (2) reduces to Eq. (1) if two conditions hold: $c_0 \sim 1$ and $\sum_{n>0} c_n (a/l)^n \ll 1$. It should be mentioned that (a/l) is used here as symbolic for whatever parameter in the Hamiltonian measures the strength of the disorder. For impurity scattering. (a/l) is proportional to $n_i |V|^2$, impurity density times impurity potential squared. We can imagine increasing this parameter so that (a/l) becomes 1 or larger, even though the concept of a mean free path loses meaning in this regime.[5]

Anderson[6] considered a simple model with a single band of unperturbed width W, which is perturbed by giving each site a random energy distributed in the range $(-V, V)$. Then the parameter, corresponding to a/l is $(V/W)^2$. He showed that at $T=0$ a series of the type (2) does not exist. There is an essential singularity near the critical value $(a/l)_c \sim 1$ beyond which $\sigma=0$ because the states become localized. Götze[7] has a self-consistent approximation scheme which seems to give the correct features for the metallic region $a/l < (a/l)_c$, although it is not expected to work very close to the critical point. Götze finds at $T=0$ that a remarkably good account is given of σ by using (2) with $c_0 \sim -1$ and $c_n = 0$ for $n > 0$. In other words, Götze finds a shunt resistor model with a *negative* shunt resistance. This does not necessarily contradict experiment because (1) is obeyed as a function of T and has been seldom tested in metals at $T=0$. A qualitative explanation using localization ideas has been given for the $T > 0$ resistive anomalies (Mooij's laws) by Jonson and Girvin[8] and Imry.[9] When the Fermi energy E_F is near a mobility edge E_c, the effects of temperature cannot be completely described by adding thermal disorder scattering to (a/l). There are also parameters $kT/|E_F - E_c|$ and l/ξ, where ξ is the localization length. Inelastic scattering plays a different role from elastic scattering when the states are localized or nearly localized. References 8 and 9 take approximate account of some of these new parameters. We find these theories inadequate because (1) they offer no explanation for the excellent success of Eq. (1) in clean metals (in particular they do not explain how σ can be enhanced *above* $\sigma_{\rm SBT}$), and (2) there is no evidence for an Anderson transition in dirty metals of this type. At $T=0$, ρ is seldom above 200–300 $\mu\Omega$ cm, whereas if an Anderson transition is nearby, it should be possible to make ρ diverge. We doubt that localization ideas are applicable to metals obeying Mooij's laws.

This paper proposes a completely different picture[10] for Mooij's laws, based on a different mode of failure of Bloch-Boltzmann theory. Localization is related to the failure of the independent scattering approximation when l is not large compared with a. In Sec. II we analyze the semiclassical acceleration and current approximations and show that they also fail unless $(a/l) \ll 1$. Associated with this failure is the possibility for new modes of conduction assisted by interband effects. This provides a natural explanation for the additional currents described by Eq. (1). In Sec. III, a generalized Boltzmann theory is described which completely avoids the semiclassical approximations, but continues to use the independent collision approximation. In this theory, the only parameter of obvious significance is (a/l), so the expansion (2) is expected to work, and Eq. (1) can be thus rationalized. However, no great distinction is made between elastic and inelastic scattering, so Eq. (1) should work both at $T=0$ and at $T>0$. This apparently contradicts the experimental fact that strongly disordered d-band metals can have $d\rho/dT < 0$ at $T > 0$, and $\rho(T=0)$ exceeding $\rho_{\rm max}$ (observed for the corresponding clean metal). A possible resolution of this difficulty is that $\rho_{\rm max}$ could be somewhat T dependent and larger at $T=0$ than at $T=\infty$. Within the generalized Boltzmann theory, including impurity and phonon scattering, the expression for $\rho_{\rm max}$ (worked out in Sec. V) turns out to have a form at least as complicated as

$$\rho_{\rm max} = \frac{\alpha n_i + \beta T}{\gamma n_i + \delta T} = \frac{\rho^0_{\rm max} n_i + \eta\, \rho^\infty_{\rm max} T}{n_i + \eta\, T}\,, \tag{3}$$

where α and γ are related to electron-impurity matrix elements, while β and δ are related to electron-phonon matrix elements, and $\eta = \delta/\gamma$. Thus $\rho^0_{\rm max} = \alpha/\gamma$ can exceed $\rho^\infty_{\rm max} = \beta/\delta$. This explains why very large values of $\rho(T=0)$ are not achieved in these systems. In Sec. VI the infrared conductivity is discussed. Our theory predicts that some of the additional dc currents (not contained in $\sigma_{\rm SBT}$) diminish more rapidly at finite ω than the Drude law predicts. Thus infrared experiments provide a possible method for deciding which theoretical alternative is correct.

Several other groups have recently published work of a similar nature. Garik and Ashcroft[11] have treated the effort of collision broadening on interband conduction using a phenomenological number-conserving relaxation-time approximation. They also find new types of dc currents. However, because scattering does not directly couple intraband and interband disturbances in their model, their results are of the form $c_0 = 0$, $c_1 \sim 1$ in Eq. (2)—i.e., the corrections to $\sigma_{\rm dc}$ in their theory are weaker than ours and scale as (a/l), whereas ours are independent of a/l. Kragler and Thomas[12] have introduced equations of the same kind as Garik and Ashcroft, except specialized to the case where all bands are identical. Kragler[13] has made a microscopic transport theory similar to ours, except specialized to the same case of identical bands. He has used Green's-function methods, while we use the less reliable but more physically transparent method of truncated equations of motion. Finally, Agassi[14] has developed a related transportlike equation for the problem of the dielectric constant of a doped semiconductor.

II. SEMICLASSICAL APPROXIMATIONS

The fact that one-electron states of a crystal can be assigned a wave vector $\vec{k}$ provides an analogy between electrons in crystals and particles in a gas. This analogy is fully exploited in the Bloch-Boltzmann transport theory,[15] which assumes that the electron dynamics can be described in terms of the distribution function $F_{\vec{k}n}$, the number of electrons in quantum state $|\vec{k}n\rangle$, n being the band index. Just as in classical physics, the $\vec{E}$ field is assumed to cause a smooth acceleration of electrons (which in band theory corresponds to intraband transitions to nearby k states with n fixed). Bloch[15] gave a nice microscopic justification, except that he neglected all bands except one, which prevented an analysis of the accuracy of semiclassical approximation. Here we generalize Bloch's proof to the case of many bands. A general wave function is

$$\Psi(x,t)=\sum_{\vec{k}'n'} a_{n'\vec{k}'}(t)|\vec{k}'n'\rangle \ . \tag{4}$$

We ask how such an electronic state evolves in time under the influence of an external $\vec{E}$ field. According to standard time-dependent perturbation theory,

$$H'=e\vec{E}\cdot\vec{x}e^{-i\omega t}, \tag{5}$$

$$i\hbar\frac{da_{n\vec{k}}}{dt}=e\vec{E}\cdot\sum_{\vec{k}'n'}\langle\vec{k}n|x|\vec{k}'n'\rangle a_{n'\vec{k}'}(t) \times e^{i(\epsilon_{\vec{k}n}-\epsilon_{\vec{k}'n'}-\omega)t} \ . \tag{6}$$

To avoid the difficulty that $\vec{x}$ is unbounded, we use the identity

$$(i/\hbar)(\epsilon_{\vec{k}n}-\epsilon_{\vec{k}'n'})\langle\vec{k}n|\vec{x}|\vec{k}'n'\rangle=\vec{v}_{knn'}\delta_{\vec{k}\vec{k}'} \ , \tag{7}$$

$$\vec{v}_{\vec{k}nn'}\equiv\langle\vec{k}n|\vec{p}/m|\vec{k}n'\rangle \ . \tag{8}$$

Note that the diagonal element $\vec{v}_{\vec{k}nn}$ is just the group velocity $\vec{v}_{\vec{k}n}=h^{-1}\partial\epsilon_{\vec{k}n}/\partial\vec{k}$. After some manipulations described by Bloch, Eq. (6) becomes

$$\hbar\frac{da_{n\vec{k}}}{dt}=-e\vec{E}\cdot\frac{\partial a_{n\vec{k}}}{\partial\vec{k}}e^{-i\omega t} -e\vec{E}\cdot\sum_{n'\neq n}\left(\frac{\vec{v}_{\vec{k}n'n}}{\omega_{\vec{k}n'n}}\right)a_{n'\vec{k}}e^{i(\omega_{\vec{k}n'n}-\omega)t} \ , \tag{9}$$

where $\hbar\omega_{\vec{k}nn'}$ is $\epsilon_{\vec{k}n'}-\epsilon_{\vec{k}n}$. In Bloch's work the interband part of (9) was missing, and the remaining, purely intraband part can be integrated to give

$$a_{n\vec{k}}(t)=a_{n\vec{k}-e\vec{E}t/\hbar}(0) \ . \tag{10}$$

This is the semiclassical law[16]: Electrons remain in whatever band they start in and evolve according to $d\vec{k}/dt=-e\vec{E}/\hbar$. It relies on ignoring the second term of (9). This is quite safe in the appropriate circumstances, namely if we are concerned with either the long-time or the average behavior, and if the electron is allowed to evolve smoothly according to (9) over more than one cycle $\mathcal{T}=2\pi/|\omega_{\vec{k}n'n}|$ of the interband oscillations. Assuming $\omega\ll|\omega_{\vec{k}n'n}|$, the second term of (9) averages away at long times, but the first term remains. In a real solid with phonons or impurities, collisions will interrupt the evolution at average intervals τ. Thus we require $\tau\gg\mathcal{T}$ in order to ignore the second term of (9). This condition can be written several ways:

$$1/\tau\ll\Delta\epsilon/2\pi\hbar \ , \tag{11a}$$

$$l\gg 2\pi\hbar v_F/\Delta\epsilon \ , \tag{11b}$$

where $\Delta\epsilon$ is a typical separation of nearest bands, v_F the average Fermi velocity. In d-band compounds with many overlapping bands, repulsion of neighboring bands tends to keep v_F small. A reasonable estimate is $\hbar v_F\sim\partial\epsilon/\partial k\sim\Delta\epsilon(2\pi/a)^{-1}$. Thus (11) is equivalent to $l\gg a$, although the criterion may be stronger since we have probably underestimated $\partial\epsilon/\partial\vec{k}$ somewhat. Thus in d-band metals, the semiclassical approximation is at least as likely to fail as the independent collision approximation.

As mentioned in Sec. I, the failure of the independent collision approximation provides a likely source of enhanced resistivity (at least at $T=0$) due to incipient localization. We now argue that failure of semiclassical approximation provides a likely source of enhanced *conductivity* (independent of T) due to interband conduction, and can thus account for Eq. (1). Suppose the metal is perturbed by an impulsive $\vec{E}$ field $\delta(t)$. The response is

$$j(t)=\int d\omega\, e^{-\omega t}\sigma(\omega) \tag{12}$$

since $E(\omega)=2\pi$. The instantaneous response $j(t=0^+)$ is ne^2/m, because the classical law $m\dot{v}=-eE$ applies at very short times. This gives the f-sum rule

$$j(t=0^+)=\int_{-\infty}^{-\infty} d\omega\,\sigma(\omega)=ne^2/m=\omega_p^2/4\pi \ , \tag{13}$$

where m is the free-electron mass. The semiclassical law $\hbar\dot{k}=-eE$ gives $m\dot{v}_{k\alpha}=-(m/m_k^*)_{\alpha\beta}eE_\beta$ which predicts a smaller instantaneous current

$$\int_{-\infty}^{\infty} d\omega\, \sigma_{\mathrm{sc}}(\omega) = \left(\frac{n}{m}\right)_{\mathrm{eff}} e^2 = \frac{\Omega_p^2}{4\pi}\,, \tag{14}$$

$$\begin{aligned}\left(\frac{n}{m}\right)_{\mathrm{eff}} &\equiv 2\hbar^{-2} \sum_{k} \left(\frac{\partial^2 \epsilon}{\partial k_x^2}\right) f_k \\ &= \frac{2}{3} \sum_{\vec{k}n} v_{\vec{k}n}^2 \left(\frac{-\partial f}{\partial \epsilon_{\vec{k}n}}\right)\,,\end{aligned} \tag{15}$$

where the subscript sc means semiclassical, Ω_p is the "Drude" or infrared plasma frequency, cubic symmetry is assumed, and the factor of 2 is for spin degeneracy. The effective inverse mass $(n/m)_{\mathrm{eff}}$ is always less than the free value n/m, and in d-band systems $(n/m)_{\mathrm{eff}} \ll n/m$. For example,[17,18] in Nb$_3$Ge, $\Omega_p^2 \approx 15(\mathrm{eV})^2$ while $\omega_p^2 \approx 390(\mathrm{eV})^2$ (counting 38 valence electrons per cubic cell). The ratio $\Omega_p^2/\omega_p^2 = 0.04$ is the fraction of the $t=0$ valence electron current which is carried by the semiclassical mechanism. Thus the interband currents overwhelm the semiclassical currents at short times. This suggests that interband effects may enhance the dc current. The dc conductivity $\sigma = (2\pi)^{-1}\int_{-\infty}^{\infty} dt\, j(t)$ is the time-average response to $E = \delta(t)$. In the absence of collisions, the interband part of $j(t)$ averages to zero, but with frequent collisions it is plausible that the interband part gives a significant enhancement of σ, just as it does to $j(t=0)$.

The anomalous T-dependent resistivity of A15 metals has often[19] been ascribed to "Fermi smearing" effects, i.e., the possibility that within $\pm k_B T$ of the Fermi energy the character of classical conduction changes rapidly enough for an additional source of T dependence (beyond the usual linear behavior) to enter. There is no doubt that this effect can alter the SBT prediction to a noticeable degree in metals where structure occurs in electronic properties on a fairly narrow scale $\Delta\epsilon$. The scale $\Delta\epsilon$ for Fermi smearing is the same as the $\Delta\epsilon$ for interband effects because in both cases the determining factor is the average band separation. This can be quite small, i.e., 0.3 eV in A15 metals, since 30 d bands in a unit cell are compressed into an overall band about 10 eV wide. Fermi smearing, if computed using the Sommerfeld expansion,[20] gives corrections in powers of the small parameter $(\pi k_B T/\Delta\epsilon)^2$. This should be compared with the small parameter $(\hbar/\tau)/\Delta E$ which governs the size of the "nonclassical" corrections discussed here. In a pure metal with only electron-phonon scattering, $\hbar/\tau$ becomes $2\pi\lambda_{\mathrm{tr}} k_B T$ for $T > \Theta_D$. The coupling constant λ_{tr} equals λ in superconductivity (to about 10% accuracy). Thus, for A15 metals with $\lambda > 1$, the "nonclassical" corrections should enter at lower T than Fermi-smearing corrections.

III. THE GENERALIZED BOLTZMANN EQUATION

In a previous paper[21] we have derived a generalization of SBT which includes interband effects, and studied its predictions in the interband part of the spectrum. Unlike our present results[10] for small ω, our previous results[21] for large ω are not at all controversial; yet the same equation governs both regimes. In this section the equation is reviewed, and some new notation and previously unpublished properties presented.

The quantum-mechanical current operator can be expressed in the form

$$j_{\mathrm{op}} = -e \sum_{\vec{k}nn'} v_{\vec{k}nn'} c_{\vec{k}n}^{\dagger} c_{\vec{k}n'}\,. \tag{16}$$

From here on, $v_{\vec{k}nn'}$ and j will be written as scalars, and should be interpreted as the component of the corresponding vector in the direction of the E field. In SBT, the current is given by an unbalanced occupation $F_{\vec{k}n}$ of states each of which have a current $-ev_{\vec{k}n}$,

$$j_{\mathrm{SBT}} = -e \sum_{\vec{k}n} v_{\vec{k}n} F_{\vec{k}n}\,, \tag{17}$$

where F_{kn} can be defined as $\mathrm{tr}\rho c_{\vec{k}n}^{\dagger} c_{\vec{k}n}$. These equations suggest that a natural generalization of the ideas of Boltzmann theory begins with a matrix "distribution function,"

$$j = -e \sum_{knn'} v_{\vec{k}nn'} F_{\vec{k}n'n} \tag{18}$$

$$F_{\vec{k}nn'} \equiv \mathrm{tr}\rho c_{\vec{k}n'}^{\dagger} c_{\vec{k}n}\,. \tag{19}$$

The off-diagonal parts $F_{\vec{k}nn'}$ describe a nonequilibrium electron-hole pair amplitude which gives rise to interband currents, while the diagonal parts are the semiclassical occupation function $F_{\vec{k}n}$. A closed equation of motion can be derived for $F_{\vec{k}nn'}$ in the same way that Kohn and Luttinger[22] first "derived" the SBT by approximately closing the equation of motion for $F_{\vec{k}n'}$. Details are in Refs. 21 and 23.

To simplify the notation, $F_{\vec{k}nn'}$ will be regarded as the element $\langle \vec{k}n | F | \vec{k}'n' \rangle$ of a matrix F, with the important restriction that the physical matrices which enter at our level of approximation are all $\vec{k}$ diagonal. The standard scalar product of two matrices A, B is

$$(A,B) = \mathrm{tr} A^{\dagger} B\,. \tag{20}$$

The matrix v [Eq. (8)] is Hermitian (as F also turns out to be in the dc case), so we can write the current (18) in a compact form

$$j = -e(v,F)\,. \tag{21}$$

The equation of motion is calculated to linear order in the E field and second order in the electron-scattering matrix elements, at which stage a standard[22] decoupling approximation is made. The distribution-function matrix is written as

$$F=F^0+\Phi \ , \tag{22}$$

where F^0 is the equilibrium value and Φ is the term linear in E. In the absence of collisions, $F^0_{\vec{k}nn'}$ would be $\delta_{nn'}f(\epsilon_{\vec{k}n})$, but corrections to second order in the scattering matrix elements must be taken into account.

The resulting generalized Boltzmann equation is

$$\hat{T}(z)\Phi \equiv [-i(z-\hat{\Omega})-\hat{K}(z)]\Phi = X(z) \ , \tag{23}$$

where z is a complex external frequency to be set equal to $\omega+i\delta$; ω is real and δ is a positive infinitesimal. The notation $\hat{K}$ means that the scattering operator $\hat{K}$ is a tetradic, i.e., it operates on a matrix yielding another matrix, and in particular, $\hat{\Omega}$ is a diagonal tetradic,

$$(\hat{K}\Phi)_{12} \equiv \sum_{3,4} K_{12,34}\Phi_{34} \, , \tag{24}$$

$$(\hat{\Omega}\Phi)_{12} \equiv (\epsilon_1-\epsilon_2)\Phi_{12} \ , \tag{25}$$

where ϵ_i is the energy of the electron state i, and the shorthand i $(=1,2,3,4)$ denotes the quantum numbers $\vec{k}n$. The operator $i(z-\hat{\Omega})$ describes a sort of "inertial" effect which tends to keep the current out of phase with the field unless the external frequency ω is on resonance with a transition $\epsilon_1-\epsilon_2$. The "driving term" $X=X^{(0)}+X^{(1)}+\cdots$ is linear in E and has matrix elements $X_{knn'}$ which are expanded in powers of the scattering. The zeroth-order term is

$$\begin{aligned} X^{(0)}_{knn'} &= eE\frac{f_{\vec{k}n'}-f_{\vec{k}n}}{\epsilon_{\vec{k}n'}-\epsilon_{\vec{k}n}}\, v_{\vec{k}nn'} \\ &\equiv -eE(\hat{W}v)_{\vec{k}nn'} \ , \end{aligned} \tag{26}$$

which defines $\hat{W}$, another diagonal tetradic. The second-order term $X^{(1)}$ is given in Ref. 21. It is a function of z, and is analytic in the upper half plane, as is the scattering operator $\hat{K}(z)$. The "band-diagonal" parts $K_{11,33}(z)$ of $\hat{K}$ reduce to the semiclassical collision operator K_{13} in the small-ω limit. The semiclassical operator is real, Hermitian, and positive, which guarantees that the dc σ is real and positive. The full operator $\hat{K}(z)$ is considerably more complicated. Like the Boltzmann operator, there are scattering-out and scattering-in parts, which correspond in Feynman graphs to self-energy effects and vertex corrections. In fact, the scattering-out parts of $\hat{K}$ can be expressed entirely in terms of the (band nondiagonal) matrix self-energy $\Sigma(\vec{k}nn',z)$.[21,24] Explicit formulas for $\hat{K}$ are given in the Appendix. Various properties and symmetries of the operators and matrices are now listed.

J conjugation. There are two different tetradics (which we shall denote $\hat{Q}^J$ and $\hat{Q}^K$) which are adjoint to a given tetradic $\hat{Q}$, and generalize the notion of the Hermitian adjoint for matrices. J conjugation is defined by

$$(\hat{Q}A)^\dagger = \hat{Q}^J A^\dagger \ , \tag{27}$$

where the dagger means ordinary Hermitian conjugation of a matrix. If $\hat{Q}^J=\hat{Q}$, we shall call Q "self-J-adjoint." Such a tetradic has the property that $(\hat{Q}A)$ is Hermitian if A is (and likewise for anti-Hermitian). A specific formula for the elements of the J-adjoint tetradic is

$$Q^J_{12,34}=Q^*_{21,43} \ . \tag{28}$$

The operator $T(z)$ of Eq. (23), as well as its constituent operators iz, $i\hat{\Omega}$, and $\hat{K}(z)$, all have the property under J conjugation,

$$\hat{T}^J(\omega+i\delta)=\hat{T}(-\omega+i\delta) \ . \tag{29}$$

It is important to note that the complex conjugation [asterisk in Eq. (28)] is interpreted to operate on all quantities entering $Q_{21,43}$ including the complex variable z. In the dc limit, Eq. (29) says that $\hat{T}$ is self-J-adjoint. The operators $i\hat{\Omega}$ and $\hat{W}$, being independent of z, are always self-J-joint.

K conjugation. The K-adjoint tetradic $\hat{Q}^K$ is defined by

$$(A,\hat{Q}B)=(\hat{Q}^K A,B). \tag{30}$$

An explicit formula for the elements of Q^K is

$$Q^K_{12,34}=Q^*_{34,12} \ . \tag{31}$$

The operators iz, $i\hat{\Omega}$, $\hat{K}$, and $\hat{T}$ have the property

$$\hat{T}^K(\omega+i\delta)=-\hat{T}(\omega-i\delta), \tag{32}$$

while $\hat{W}$ is self-K-adjoint, i.e., $\hat{W}^K=\hat{W}$. In the dc limit, $\hat{K}$ and $\hat{T}$ are neither self-K-adjoint nor anti-self-K-adjoint, whereas $i\hat{\Omega}$, being independent of z, is anti-self-K-adjoint for all values of z.

Charge conservation. Collisions can alter electronic energy (because of phonons) and momentum (because of the lattice) but must leave charge conserved. The expectation value of the $\vec{Q}$th Fourier component of the charge density is

$$n(\vec{Q})=\mathrm{tr}\,\rho \sum_{\vec{k}\vec{k}'nn'} \langle \vec{k}'n'|e^{i\vec{Q}\cdot\vec{x}}|\vec{k}n\rangle c^\dagger_{\vec{k}'n'}c_{\vec{k}n} \, . \tag{33}$$

The law $\vec{\nabla}\cdot\vec{j}+\partial n/\partial t=0$ must be satisfied. For homogeneous external fields $(\vec{Q}=0)$ this reduces to $\partial n(\vec{Q}=0)/\partial t=0$. Using (19) this becomes

$$\sum_{\vec{k}n} \frac{\partial F_{\vec{k}nn}}{\partial t} = 0 = -i\,\omega \sum_{i} F_{ii}\,. \tag{34}$$

To prove this, we must prove

$$\sum_{i} \left(\frac{\partial F_{ii}}{\partial t}\right)_{\text{coll}} = 0 = \sum_{ijk} K_{ii,jk} F_{jk}\,, \tag{34a}$$

$$\sum_{1} \left(\frac{\partial F_{ii}}{\partial t}\right)_{\text{field}} = 0\,. \tag{34b}$$

A detailed inspection of the operator $\hat{K}$ (Refs. 21, 23, and the Appendix) shows that

$$\sum_{1} K_{11;23}(z) = 0\,, \tag{35}$$

$$\sum_{1} X_{11}(z) = 0\,. \tag{36}$$

These establish (34a) and (34b), respectively, and thus guarantee charge conservation, Eq. (34). Relation (35) derives from a cancellation of scattering-in terms against scattering-out terms, just as in SBT. As a consequence of these relations, it is apparent that the matrices Φ, X, V, are all traceless.

Negativity. A fundamental property of the scattering operator in Boltzmann theory is that in the absence of external forces, it should always drive the system towards thermal equilibrium. This property remains true when interband effects are included. That is, if the distribution F differs by an arbitrary small amount Φ from equilibrium F_0, then

$$\frac{d}{dt}(\Phi,\Phi)\bigg|_{\text{coll}} = (\hat{K}\Phi,\Phi) + (\Phi,\hat{K}\Phi) \leqslant 0\,. \tag{37}$$

Since there is no external force, the external frequency z is here $i\delta$. In other words, the operator $\hat{K}+\hat{K}^K$ is negative definite, i.e., for arbitrary Φ,

$$(\Phi, (\hat{K}+\hat{K}^K)\Phi) \leqslant 0\,. \tag{38}$$

A proof of this property is given in Ref. 23. From this it also follows that

$$(\Phi,\hat{K}\Phi) \leqslant 0 \tag{39}$$

provided Φ is a Hermitian matrix. We had hoped to be able to use this property to develop a variational principle for the dc current. (In the dc limit, the true distribution Φ is Hermitian.) However, we have not been able to find a way to do this.

Reality of response. A physical restriction on a response function like $\sigma(\omega)$ is that $\sigma(-\omega) = \sigma(\omega)^*$. This condition guarantees that the response to a real field $E\cos(\omega t)$ will be a real current $\sigma'(\omega)E\cos\omega t + \sigma''(\omega)E\sin\omega t$. Using (21) and (22), a sufficient condition to guarantee this is

$$\Phi^\dagger(\omega+i\delta) = \Phi(-\omega+i\delta)\,. \tag{40}$$

Specifically, in the dc limit, (40) says that the distribution function should be Hermitian, which is sufficient to guarantee that the dc conductivity is real. The property (40) follows from the J-conjugation symmetry (29) of $\hat{T}$, plus the property

$$X^\dagger(\omega+i\delta) = X(-\omega+i\delta)\,. \tag{41}$$

Property (41) follows by inspection of the form of $X(z)$; property (40) then follows from (23) and (29). A tetradic with the property (29) conserves the property (40) of the matrices it operates on.

The solution of Eqs. (21) and (23) for the conductivity is derived in Ref. 21 and can be written

$$\sigma(z) = -i(e/E) \sum_{\vec{k}nn'} X_{\vec{k}n'n}(z) v_{\vec{k}nn'} \times [z + \epsilon_{\vec{k}n} - \epsilon_{\vec{k}n'} + M_{\vec{k}nn'}(z)]^{-1}\,. \tag{42}$$

This expression is very similar to the usual Kramers-Heisenberg dispersion relation, differing only in the appearance of the memory term $M_{\vec{k}nn'}$ and the terms in $X_{\vec{k}n'n}$ which are higher order than $X^0_{\vec{k}n'n}$. The memory function satisfies a nonlinear integral equation [Eq. (19) of Ref. 21], which has the advantage that good leading-order solutions can be obtained in various limits, although exact solutions are difficult. In the special case when the external frequency ω is equal to an interband frequency $\epsilon_{\vec{k}n'} - \epsilon_{\vec{k}n}$, the memory function $M_{\vec{k}nn'}(z)$ becomes, to excellent approximation, the self-energy difference $\Sigma_{\vec{k}n'} - \Sigma^*_{\vec{k}n}$ [Eq. (23) of Ref. 21]. This result confirms (and extends) earlier work on this problem and demonstrates that vertex corrections do not alter the intuitive one-electron interpretation of optical spectroscopy (Coulombic vertex corrections leading to exciton effects are omitted from our theory). In the case where ω equals an indirect interband frequency $\epsilon_{\vec{k}+\vec{Q}n'} - \epsilon_{\vec{k}n}$, $M_{\vec{k}nn'}$ has been shown[21] to contain the usual theory of indirect optical absorption. These results have been summarized in the hope of convincing the reader that Eq. (23) is both powerful and correct (at the familiar level of approximation which treats collisions as independent events). Before proceeding to the new results for dc and infrared properties in Secs. V and VI, a brief further digression on the interpretation of Eq. (23) is made.

IV. RELATION BETWEEN NONCLASSICAL CURRENTS AND BAND RENORMALIZATION

There are two ways to describe qualitatively the problem we are addressing. The surprising thing is that they seem intuitively to be different problems, but they turn out to be the same. The first has already been mentioned, namely the problem of including interband currents and band mixing due to the $\vec{E}$ field in the description of transport. The second was our initial aim, namely to include in transport theory a recognition of the fact that at high T or in the presence of impurities, conduction occurs in electronic states which have been altered or renormalized by the disorder [as contained in the memory function $M_{\vec{k}nn'}$ of Eq. (42)]. The approach we have taken unifies these two problems. This does not seem to us an accident of the method, but an inescapable fact. The renormalization which shifts bands with n_i or T, and the scattering which affects transport, are real and imaginary parts of the same object, $i\hat{K}(z)$ in our theory. In semiclassical theory, which keeps only intraband parts of $i\hat{K}$, all important real parts of $i\hat{K}$ cancel in the dc limit. This includes the large electron-phonon mass enhancement, which appears in specific heat, and can also be seen in $\sigma(\omega)$ at low T for ω in the infrared,[25,26] but not for $\omega = 0$. Holstein[25] has shown that this theory is accurate to the level of Migdal's approximation, i.e., $\hbar\omega_D/E_F$, and mentions that interband effects are negligible at the same level. Our analysis is consistent with his. The new contributions to σ are "smaller" than σ_{SBT} by a/l or $\hbar/\tau\Delta\epsilon = 2\pi\lambda kT/\Delta\epsilon$, and this is just the high-T, narrow-band analog of the Migdal parameter $\hbar\omega_D/E_F$, but it is no longer small. The renormalization effects contained in our theory are the high-T band shifts[24] of order $dE/dT \sim 2-4\ k_B$ as seen by optical spectroscopy in semiconductors.[27] These corrections are ignored in low-temperature physics, having a *relative* (but not absolute) effect smaller by $\hbar\omega_D/E_F$ than the nonadiabatic mass enhancement. For high-T transport, we claim that the priorities are reversed, and effects which were of order $\hbar\omega_D/E_F$ at low T have become significant.

For the alloy problem, the coherent potential approximation (CPA)(Ref. 28) seems to give a good account of the band renormalization; that is, it gives a good treatment of $\overline{G}$, the average Green's function. Transport properties are determined by $\overline{GG}$, the average of the product of two Green's functions. There is some hope[29] that the approximation $\overline{GG} \sim \overline{G}\,\overline{G}$ will allow CPA theory to describe transport beyond the regime of Boltzmann theory, and attempts have been made to extend this to $T > 0$ phonon effects.[30] The counterargument is that $\overline{GG} - \overline{G}\,\overline{G}$ describes vertex corrections, which are necessary for charge conservation (they give the scattering-in term in the Boltzmann limit) and are crucial for localization. Nevertheless, it is possible that $\overline{GG} \sim \overline{G}\,\overline{G}$ works reasonably well for *d*-band metals at high alloy concentration or high T. After all, neglecting scattering-in terms in Boltzmann theory, although very bad at low T, is accurate to about 10% at high T. So far, most CPA theories have been model theories with a single band. However, Stocks and Butler[31] have recently reported a calculation for $\sigma(T = 0)$ in concentrated AgPd alloys based on a full Korringa-Kohn-Rostoker (KKR)-CPA band theory.[28] Agreement with experiment is impressive, and suggests that the method should be tested for stronger-scattering systems. The relation between such a theory and our formalism is complicated. Many-band CPA theory keeps many of the interband renormalization effects to higher accuracy than our theory and thus describes, at least in part, the effects we call nonclassical conduction *via* interband channels.

V. dc CONDUCTIVITY

In order to put the generalized theory in perspective, a brief discussion of the standard dc theory is presented, with special emphasis on the validity of the assumptions usually made. The semiclassical Boltzmann equation is written as

$$0 = -eEv_k \frac{\partial f}{\partial \epsilon_k} + \sum_{k'} K_{kk'}\Phi_{k'} \,. \tag{43}$$

Here Φ_k is the correction to first order in E to the equilibrium distribution function F_k^0 for electrons in state k (short for $\vec{k}n$) with energy ϵ_k and velocity $\epsilon_k = \partial\epsilon_k/\partial k_x$. The solution to this equation is

$$\begin{aligned}\Phi_k &= eE\sum_{k'} (K^{-1})_{kk'} v_{k'} \frac{\partial f}{\partial \epsilon_{k'}} \\ &= eE\, v_k\tau_k \frac{\partial f}{\partial \epsilon_k} \,,\end{aligned} \tag{44}$$

where τ_k is defined by this set of equations. The resulting conductivity is

$$\sigma_{\text{SBT}} = e^2 \sum_k v_k^2 \tau_k \left(\frac{-\partial f}{\partial \epsilon_k}\right) . \tag{45}$$

In principle τ_k can be evaluated only by solving Eq. (43). For most cases, however, the assumption of τ_k being independent of k works surprisingly well.[32] The optimum value of τ is then determined by a variational principle.[33]

Our aim in this section is to show how the generalized equation (23) can be used to derive systematic corrections to the result (45). The lowest corrections will have the same form as the "shunt resistor model," Eq. (1), and provide a novel but natural interpretation for the shunt resistor, $\rho_{\max}$, as a nonclassical conduction channel. The method of derivation used in this section is chosen because it assists in the interpretation of the new results. The same results will also emerge in a different way in the next section by taking the dc limit of the infrared results.

We now write the tranport equation in a form where the presence of two conduction channels, intra and interband, is evident. The distribution function can be separated into band-diagonal and nondiagonal parts ϕ and ψ, respectively;

$$\begin{aligned} \phi &= \hat{\Delta}\Phi\,, \\ \psi &= (\hat{1} - \hat{\Delta})\Phi\,, \\ \Delta_{\vec{k}nn';\vec{p}mm'} &= \delta_{\vec{k},\vec{p}}\,\delta_{n,m}\,\delta_{n',m'}\,\delta_{nn'}\,, \end{aligned} \tag{46}$$

where $\hat{1}$ is the unit tetradic and $\hat{\Delta}$ is a "diagonal projection operator." The function ϕ is the semiclassical component of Φ. It is useful to consider $X_{\vec{k}nn'}$ and $\Phi_{\vec{k}nn'}$ as elements of column vectors with the band-diagonal parts occupying the first $N\nu$ entries and the nondiagonal parts the remaining $N(\nu^2 - \nu)$ entries, where N is the number of $\vec{k}$ states and ν the number of bands. In this representation, the dc version of the generalized transport equation [Eq. (23)] becomes

$$\begin{pmatrix} P & R \\ R^{\dagger} & Q - i\Omega \end{pmatrix} \begin{pmatrix} \phi \\ \psi \end{pmatrix} = -eE \begin{pmatrix} x \\ y \end{pmatrix}, \tag{47}$$

where the scattering operator has been divided into diagonal, nondiagonal, and coupled terms, as follows:

$$\begin{aligned} \hat{P} &= \hat{\Delta}\hat{K}(i\delta)\hat{\Delta}\,, \\ \hat{R} &= \hat{\Delta}\hat{K}(\hat{1} - \hat{\Delta})\,, \\ \hat{Q} &= (\hat{1} - \hat{\Delta})\hat{K}(i\delta)(\hat{1} - \hat{\Delta})\,. \end{aligned} \tag{48}$$

The new tetradics (48) are written in matrix form in (47), so the caret is omitted. The generalized driving term $X_{\vec{k}nn'}$ has also been divided into diagonal and nondiagonal parts,

$$\begin{aligned} -eEx &= \hat{\Delta}X\,, \\ -eEy &= (\hat{1} - \hat{\Delta})X\,. \end{aligned} \tag{49}$$

In what follows, the symbol d will be used to denote the degree of disorder; for example, d will stand for the number of impurities in the case of impurity disorder, and k_BT in the case of high-temperature phonon disorder. The operators $\hat{P}, \hat{Q}, \hat{R}$ are all of order d^1 and in the limit of small disorder can be neglected compared to $i\hat{\Omega}$, which is of order d^0. But because of the otherwise singular nature of the equation when $\omega = 0$, $\hat{P}$ should be retained. The resulting transport equation for small disorder is

$$\begin{pmatrix} P & 0 \\ 0 & -i\hat{\Omega} \end{pmatrix} \begin{pmatrix} \phi \\ \psi \end{pmatrix} = -eE \begin{pmatrix} x^{(0)} \\ y^{(0)} \end{pmatrix}. \tag{50}$$

In this equation the intraband and interband part are completely decoupled. Using the various definitions (48), (49), (25), (26), the two parts of Eq. (50) can be written out explicitly. The intraband part of (50) is identical to SBT, Eq. (43). The interband term is

$$-i(\epsilon_{\vec{k}n} - \epsilon_{\vec{k}n'})\psi_{\vec{k}nn'} = -eE\,v_{\vec{k}nn'}\,\frac{f_{\vec{k}n} - f_{\vec{k}n'}}{\epsilon_{\vec{k}n} - \epsilon_{\vec{k}n'}}\,. \tag{51}$$

The corresponding intraband conductivity $\sigma_{\mathrm{ra}}(0)$ is σ_{SBT} [Eq. (45)], while the interband part is

$$\sigma_{\mathrm{er}}(0) = i \sum_{\vec{k}nn'}^{n \neq n'} \frac{|v_{\vec{k}nn'}|^2}{(\epsilon_{\vec{k}n} - \epsilon_{\vec{k}n'})^2}\,(f_{\vec{k}n} - f_{\vec{k}n'}) \tag{52}$$

which is pure imaginary, and in fact, zero. There is no dc interband conductivity in a collisionless theory. Nevertheless, we shall see that when collisions are added, an interband conductivity which is formally of order d^0 will appear.

As the disorder is increased, it is no longer justified to neglect $\hat{R}$ and $\hat{Q}$. From the structure of Eq. (47) it is evident that the two conduction channels get coupled by $\hat{R}$. The exact formal solution of (47) does not seem to us to yield much insight into the theory. We exhibit instead a perturbative solution, where the small parameter which we have been calling d will turn out to be $1/\tau\Delta\epsilon$ as mentioned in Sec. I. The distribution function is expanded in powers of the disorder with $\phi^{(n)}$ and $\psi^{(n)}$ denoting functions of order d^n. Since the Boltzmann result $\phi^{(-1)}$ is of order d^{-1}, the relevant corrections are of order d^0. To get some understanding of the physical processes involved, it is useful to write the matrix Eq. (47) expanded to order d^0, as a set of two coupled equations;

$$P\,\phi^{(0)} + R\psi^{(0)} = -eEx^{(1)}\,, \tag{53}$$

$$R\,\phi^{(-1)} - i\Omega\psi^{(0)} = -eEy^{(0)}\,, \tag{54}$$

where $\hat{Q}$ has been left out because it contributes only in higher order. Focusing on (53), the main difference with semiclassical theory is the appearance of an extra driving term, $-R\psi^{(0)}$. The function ψ can be thought of as an interband polarization, arising from processes contained in (54). The sources of the polarization ψ are (i) the direct effect of the electric field represented by, e.g., $E\Omega^{-1}y^{(0)}$ (this part gives zero dc current as already mentioned), and (ii) an induced effect $i\Omega^{-1}R\phi^{(-1)}$ (with $\phi^{(-1)} = -eEP^{-1}x^{(0)}$). The physics of the induced effect is that the electric field creates an intraband imbalance $\phi^{(-1)}$, with the real scatterings (P^{-1}) counteracting; then virtual scatterings (R) excite electron-hole pairs out of this shifted distribution, with the "inertia" Ω^{-1} counteracting. This part of ψ contributes in order d^0 to σ. Both parts of ψ have a further effect on σ in order d^0: they alter the intraband distribution ϕ because of virtual interband scatterings represented by R. (This is a phonon-mediated recombination process.) A typical scattering-out term in $R\psi$ is

$$(R\psi)_{\vec{k}n} = \sum_{\vec{p}nm'} \frac{V^{(1)}_{\vec{k}n,\vec{p}m'} V^{(1)}_{\vec{p}m',\vec{k}m} \psi_{\vec{k}mn}}{\epsilon_{\vec{k}n} - \epsilon_{\vec{p}m'} + \omega_{\vec{k}-\vec{k}} + i\delta} \times [f(\epsilon_{km}) + N(\omega_{\vec{k}-\vec{p}})] \,. \tag{55}$$

The electron-hole pair (km, kn) has an amplitude $\psi_{\vec{k}mn}$ which the phonons can reduce by scattering the electron from $|\vec{k}m\rangle$ to $|\vec{k}n\rangle$ via $|\vec{p}m'\rangle$. This recombination results in altering the semiclassical distribution ϕ for electrons in state $|kn\rangle$. In other words, the scattering operator R drives ψ toward equilibrium, but this has the effect of driving the semiclassical distribution ϕ back away from equilibrium. The disorder therefore acts in two different ways, resulting in an extra contribution to the dc current which is formally independent of the disorder. These processes are only relevant in metals. In a semiconductor there is no leading term $\phi^{(-1)}$ which can initiate the chain leading to $\sigma \sim d^0$.

A new dc conduction channel thus opens up because of virtual interband scatterings. The picture that results is very suggestive of the shunt resistor model. The interband channel offers an extra path for the current to flow through, and so the total resistivity does not increase with disorder as rapidly as it would have if only the intraband channel were present. This mechanism is more complicated, and more powerful, than the one described in Refs. 11 and 12.

The Boltzmann result was obtained when the disorder was small enough for $\hat{R}$ to be neglected compared to $\hat{\Omega}$. Since $\hat{R}$ like $\hat{P}$ is of the order of $1/\tau$ while $\hat{\Omega}$ is of order $\Delta\epsilon$, the effective expansion parameter is $1/\tau\Delta\epsilon$. The corrections due to the opening of this new conduction channel are unimportant when this parameter is much less than one. The final result for the conductivity $\sigma(0)$ to zeroth order in d is

$$\sigma(0) = \sigma_{\mathrm{SBT}}(0) + \sigma^{(0)}(0) \,, \tag{56}$$

$$\sigma^{(0)}(0) = e^2\left(\sum_{\vec{k}n} v_{\vec{k}n}[(P^{-1}x^1)_{\vec{k}n} - i(P^{-1}R\Omega^{-1}y^0)_{\vec{k}n} + i(P^{-1}R\Omega^{-1}R^\dagger P^{-1}x^0)_{kn}] - i\sum_{\vec{k}nn'n\neq n'} v_{kn'n}(\Omega^{-1}R^\dagger P^{-1}x^0)_{knn'}\right) \tag{57a}$$

$$\equiv \sigma_1(0) + \sigma_2(0) + \sigma_3(0) + \sigma_4(0) \,. \tag{57b}$$

A more explicit expression for $\sigma^{(0)}$ will be presented in the next section when the dc result is derived as a special case of infrared. The four parts $\sigma_i(0)$ refer to the four terms and will be discussed separately. These equations are now just a step away from the shunt resistor formula; identifying $\sigma^{(0)}(0)$ with $\sigma_{\min} = 1/\rho_{\max}$ gives Eq. (1). Numerical calculations of $\rho_{\max}$ have not been attempted. It can be seen, however, that $\sigma^{(0)}(0)$ has the right order of magnitude; $\sigma^{(0)}(0) \sim \Omega_P^2/4\pi\Delta\epsilon$, where Ω_P^2 is the Drude plasma frequency. For aluminum, using free-electron parameters and setting $\Delta\epsilon$ to E_F the deduced value of $\rho_{\max}$ is ~350 $\mu\Omega$ cm. This is much larger than the observed ρ for Al and thus a negligible effect, in agreement with experiment. For the A15's both Ω_P^2 and ΔE are much smaller than their free-electron values, and the experimental value of $\rho_{\max}$ for these materials is of the order of 150 $\mu\Omega$ cm, the same order of magnitude as the room-temperature resistivity, and thus a very important correction. Since the operators R, P, and the driving term x' in (57) are linear sums of impurity and phonon terms, it is clear that all terms of (57) have the form of Eq. (3) except for the third which looks like (3) squared.

It is not warranted to claim that the theory presented here provides a complete description of Mooij's laws. We believe there is little doubt[1] that the parameters a/l and $1/\tau\Delta E$ have increased to values near 1 in the physically accessible range of disorder in highly disordered d-band alloys and even in clean A15 metals[17] with $T \gtrsim 300$ K. Therefore it is insufficient to solve our generalized equation (20) only to order d^0, and impossible to justify the independent collision approximation. Nevertheless we believe it likely that the explanation given here for saturation is qualitatively correct. With greater confidence we claim that the results found here are significant and should be included in any attempt at a full theory.

VI. INFRARED OPTICAL PROPERTIES

Infrared measurements can provide valuable additional insight into transport processes. In this section we show how band-mixing effects alter the infrared response and how this in principle can be used to get some independent information about the nonclassical conduction mechanisms.

In the usual ($l \gg a$) theory, optical response in the infrared is given by

$$\epsilon(\omega) = \epsilon_{\mathrm{er}}(\omega) + 4\pi i \sigma_{\mathrm{ra}}(\omega)/\omega \qquad (58\mathrm{a})$$

$$\sigma_{\mathrm{ra}}(\omega) = \sigma_{\mathrm{dc}}/[1 - i\omega\tau(1+\Lambda)] \,. \qquad (58\mathrm{b})$$

The factor $(1+\Lambda)$ is a many-body correction factor which disappears from the theory in the dc limit. The electron-phonon interaction makes a large contribution (of order 1) to Λ at low temperatures,[25, 26, 34] but this is a nonadiabatic effect and goes away at temperatures higher than Θ_D. Coulomb interactions can also contribute to Λ, as predicted by Landau Fermi-liquid theory, but the effect appears to be quite small (less than 10%) in alkali metals.[35] The term $\epsilon_{\mathrm{er}}(\omega)$ in (58a) represents the interband dielectric response. If ω lies well below the interband excitation energies, then this term is real and independent of ω. However, metals like $A15$'s have interband transitions and structure in $\epsilon_{\mathrm{er}}(\omega)$ at energies $\lesssim 0.1$ eV. Even in this case, the term $\epsilon_{\mathrm{er}}(\omega)$ can be neglected if the second term dominates. Supposing a dc resistivity of 100 $\mu\Omega$ cm and a photon energy $\omega \sim 0.1$ eV, the factor $4\pi\sigma_{\mathrm{dc}}/\omega$ is ~ 600 while $\omega\tau$ can be expected to be of order 1. Thus it seems safe to drop $\epsilon_{\mathrm{er}}(\omega)$ if $\omega < 0.1$ eV.

First we digress a little on the status of (58b). This classical Drude result is not an exact solution of the semiclassical theory, but is based on some relatively accurate approximations which we review so that we can justify similar approximations in our generalized theory. The right-hand side of the SBT [Eq. (43)] must be augmented by the term $\partial\Phi/\partial t = -i\omega\Phi$. The exact solution is then

$$\sigma_{\mathrm{ra}}(\omega) = -e^2 \sum v_{\mathbf{k}} [i\omega(1+\Lambda_{\mathrm{op}}) - K_{\mathrm{op}}]^{-1} v_{\mathbf{k}} \frac{\partial f(\epsilon)}{\partial \epsilon} \,, \qquad (59)$$

where an additional operator Λ_{op} has been added phenomenologically. We then approximate (59) by

$$\sigma_{\mathrm{ra}}(\omega) \simeq -e^2 \sum v_k^2 \frac{\partial f}{\partial \epsilon_k} \left(i\omega(1+\Lambda_k) + \frac{1}{\tau_k} \right)^{-1} . \qquad (60)$$

This step may be regarded as a definition of Λ_k and τ_k, except that in order to be exact, different values of Λ_k and τ_k would have to be used at each frequency ω. In practice it seems safe (except at low T where strong ω-dependent electron-phonon effects occur) to use the dc values since (a) Λ_{op} and K_{op} are probably both approximate constants giving Λ_k and τ_k only weak k and ω dependence, and (b) what k and ω dependence there is will be washed out by the final k sum in Eq. (60). Consistent with this, we replace λ_k and τ_k by their average dc values Λ and τ, thus recovering the Drude result (58b).

When we examine our generalized theory, it is no longer possible to make a unique separation of $\sigma(\omega)$ into intra- and interband parts because of the coupling between the two channels. We shall use a separation based on Eq. (42), namely,

$$\sigma_{\mathrm{ra}}(\omega) = -ie^2 \sum_{1} X_1 v_1 [\omega + M_1(\omega + i\delta)]^{-1} \,, \qquad (61)$$

$$\sigma_{\mathrm{er}}(\omega) = -ie^2 \sum_{1\neq 2} X_{12} v_{12} [\omega + \omega_{12} + M_{12}(\omega + i\delta)]^{-1} . \qquad (62)$$

In this notation, v_1 is short for v_{kn} and v_{12} for $v_{knn'}$, and so forth. The coupling between the intra and interband channels manifests itself through the interdependence of the inter and intra- and interband channels manifests itself through the interdependence of the inter- and tained from the equation for $M_{\vec{k}nn'} = M_{12}$ presented in Ref. 21, Eq. (19), are

$$M_1 = M_1^a + M_1^b \,, \qquad (63)$$

$$M_1^a = i \sum_{3} K_{1,3}(-z) \frac{v_3}{v_1} \frac{z+M_1}{z+M_3} \,, \qquad (64\mathrm{a})$$

$$M_1^b = i \sum_{3\neq 4} K_{1,34}(-z) \frac{v_{34}}{v_1} \frac{z+M_1}{z+\omega_{34}+M_{34}} \qquad (64\mathrm{b})$$

$$\equiv (z+M_1)\mathbf{\Gamma}_1 \,, \qquad (64\mathrm{c})$$

$$\mathbf{\Gamma}_1 = i \sum_{3\neq 4} K_{1,34}(-z) \frac{v_{34}}{v_1} \frac{1}{z+\omega_{34}+M_{34}} \,, \qquad (65)$$

$$M_{12} = M_{12}^a + M_{12}^b \,, \qquad (66)$$

$$M_{12}^a = i \sum_{3\neq 4} K_{12,34}(-z) \frac{v_{34}}{v_{12}} \frac{(z+\omega_{12}+M_{12})}{(z+\omega_{34}+M_{34})} \,, \qquad (67\mathrm{a})$$

$$M_{12}^b = i \sum_{3} K_{12,3}(-z) \frac{v_3}{v_{12}} \frac{(z+\omega_{12}+M_{12})}{(z+M_3)} \qquad (67\mathrm{b})$$

$$\equiv (z+\omega_{12}+M_{12})\mathbf{\Gamma}_{12} \,, \qquad (67\mathrm{c})$$

$$\mathbf{\Gamma}_{12} = i \sum_{3} K_{12,3}(-z) \frac{v_3}{v_{12}} \frac{1}{z+M_3} . \qquad (68)$$

The equations (64c) and (67c) which define $\mathbf{\Gamma}$ can be rewritten

$$z + M_1 = (z + M_1^a)(1 - \mathbf{\Gamma}_1)^{-1} \,, \qquad (69)$$

$$z + \omega_{12} + M_{12} = (z + \omega_{12} + M_{12}^a)(1 - \mathbf{\Gamma}_{12})^{-1} . \qquad (70)$$

Equations (61) and (62) for the conductivity then become

$$\sigma_{\mathrm{ra}}(\omega) = -ie^2 \sum_{1} X_1 \bar{v}_1 [\omega + M_1^a(\omega + i\delta)]^{-1} \,, \qquad (71)$$

$$\sigma_{\mathrm{er}}(\omega) = -ie^2 \sum_{1\neq 2} X_{12} \bar{v}_{12} [\omega + \omega_{12} + M_{12}^a(\omega + i\delta)]^{-1} \,, \qquad (72)$$

where renormalized velocities $\bar{v}$ are defined as

$$\bar{v}_1 = v_1(1-\Gamma_1)\,, \tag{73a}$$

$$\bar{v}_{12} = v_{12}(1-\Gamma_{12})\,. \tag{73b}$$

The coupled equations for M_1^a and M_{12}^a [(64a) and (67a)] can be written in a form in which M^b no longer explicitly appears:

$$M_1^a = i\sum_3 K_{1,3}(-z)\frac{\bar{v}_3}{\bar{v}_1}\frac{(z+M_1^a)}{(z+M_3^a)}\,, \tag{74a}$$

$$M_{12}^a = i\sum_{3\neq 4} K_{12,34}(-z)\frac{\bar{v}_{34}}{\bar{v}_{12}}\frac{(z+\omega_{12}+M_{12}^a)}{(z+\omega_{34}+M_{34}^a)}\,. \tag{74b}$$

Equations (71)–(74) represent an *exact* transformation of the equations of Ref. 21; no approximation except independent collisions has been made. These equations appear to have no coupling between intraband and interband channels because the coupling is now hidden in the functions Γ, which obey Eqs. (65) and (68), or alternately

$$\Gamma_1 = i\sum_{3\neq 4} K_{1,34}(-z)\frac{\bar{v}_{34}}{v_1}\frac{1}{z+\omega_{34}+M_{34}^a}\,, \tag{75a}$$

$$\Gamma_{12} = i\sum_3 K_{12,3}(-z)\frac{\bar{v}_3}{v_{12}}\frac{1}{z+M_3^a}\,. \tag{75b}$$

Equations (73)–(75) are a complicated set of nonlinear coupled equations. However, approximate solutions can be easily formulated for the weak-scattering limit. We will treat $\hbar/\tau\Delta\epsilon$ and $\hbar\omega/\Delta E$ as small parameters. Equations (74) show that M_1 is of order K or d to the first power, and M_{12}/ω_{12} is of order $\hbar/\tau\Delta E$. Thus to first order, $\omega_{12}+M_{12}^a$ can be replaced by ω_{12} in (74b) (numerator *and* denominator) and (75a) (denominator). Thus Γ_1 is also of order d^1, while Γ_{12} [Eq. (75b)] is of order $K/(z+M)$ which is of order d^0. The part of $\sigma_{er}(\omega)$ [Eq. (72)] which is of order d^0 can be written explicitly as

$$\sigma_{er}(\omega) \simeq ie^2\sum_{1\neq 2}|v_{12}|^2\frac{f_1-f_2}{\epsilon_2-\epsilon_1}\frac{1-\Gamma_{12}}{\omega+\omega_{12}}\,, \tag{76}$$

where Eq. (26) has been used for X_{12} in lowest order. The corresponding result for $\sigma_{ra}(\omega)$ is

$$\begin{aligned}\sigma_{ra}(\omega) \simeq{}& ie^2\sum_1\frac{-\partial f}{\partial\epsilon_1}v_1^2(\omega+M_1^a)^{-1}\\ &-ie^2\sum_1 x_1^{(1)}v_1(\omega+M_1^a)^{-1}\\ &-ie^2\sum_1\frac{-\partial f}{\partial\epsilon_1}v_1^2\Gamma_1(\omega+M_1^a)^{-1}\,.\end{aligned} \tag{77}$$

The only approximations made so far are omission of second-order terms such as the cross term involving $X_1^{(1)}\Gamma_1$ in Eq. (77), the term involving $X_{12}^{(1)}$ in Eq. (76), and replacing $\omega_{12}+M_{12}^a$ by ω_{12} in the denominator of (76). Consistent with this, we can approximate Eqs. (75) for Γ and Eq. (74a) for M_1^a by

$$\Gamma_1 \simeq i\sum_{3\neq 4}K_{1,34}(-z)\frac{v_{34}}{v_1}\frac{(1-\Gamma_{34})}{z+\omega_{34}}\,, \tag{78a}$$

$$\Gamma_{12} \simeq i\sum_3 K_{12,3}(-z)\frac{v_3}{v_{12}}\frac{1}{z+M_3^a}\,, \tag{78b}$$

$$M_1^a \simeq i\sum_3 K_{1,3}(-z)\frac{v_3}{v_1}\frac{z+M_1^a}{z+M_3^a}\,. \tag{79}$$

The only remaining difficulty with these equations is that (79) is still an integral equation for M_1^a; everything else is simple integrals. There is no avoiding this difficulty—it is an ac generalization of the semiclassical theory, and our guiding principle has been to construct a theory which reduces properly to SBT in the weak-scattering limit. We can, however, use our experience with SBT to approximate the solution of Eq. (79), following the procedure of Eqs. (59) and (60). In the dc limit, the solution is

$$v_3(z+M_3^a)^{-1} \rightarrow -iv_k\tau_k = -i(P^{-1}v)_3\,, \tag{80}$$

where the operator P, defined in Eqs. (48), is the dc limit of $K_{1,3}(z)$, or the SBT scattering operator. The approximate ac generalization is

$$(z+M_3^a)^{-1} \cong [\omega(1+\Lambda)+i/\tau]^{-1}\,, \tag{81}$$

where τ is (roughly) the dc τ_k and Λ is a renormalization defined implicitly through Eqs. (79) and (81). The exact answer can always be written in the form of Eq. (81), but we propose that the k and ω dependence of the exact Λ, τ is probably not very significant, at least in dirty metals or at $T \gtrsim \Theta_D$. If this approximation is accepted, the infrared results can be expressed simply in terms of the dc results. For example, consider Eq. (76), which separates into two parts, the second containing Γ_{12} and the first being the collisionless interband response. In the dc limit, the first part becomes Eq. (52) which is zero. At finite ω, this term is nonzero, but we have already argued that we can neglect it in the region $\hbar\omega \lesssim 0.1$ eV. The second term can be written out using Eqs. (78b) and (81). In the dc limit, Eq. (78b) becomes

$$v_{12}\Gamma_{12} \cong [R^\dagger(P^{-1}v)]_{12} \tag{82}$$

[where Eq. (40) defines $K_{12,3}$ as an element of $R^\dagger$]. Thus the corresponding conductivity (76) corresponds to the second term of Eq. (57a), i.e., σ_2. The result can be written

$$\sigma_{er}(\omega) \simeq \sigma_2(0)(1-i\omega\tau^*)^{-1}\,, \tag{83}$$

$$\tau^* = \tau(1+\Lambda)\,. \tag{84}$$

The ac intraband conductivity, Eq. (77), has three parts. The first is clearly $\sigma_{SBT}(0)(1-i\omega\tau^*)^{-1}$, and the second corresponds to $\sigma_1(0)(1-i\omega\tau^*)^{-1}$. The third term of (77) involves Γ_1. In the dc limit, Eq. (78a) for Γ_1 can be written as

$$v_1\Gamma_1 \cong i\sum_{34} R_{1,34}(\Omega^{-1})_{34,34}v_{34} - i\sum_{3}(R\Omega^{-1}R^{\dagger}P^{-1})_{13}v_3\,, \tag{85}$$

where the second term comes from the part of (78a) involving Γ_{34} [Eq. (82)] and corresponds to $\sigma_3(0)$, while the first term corresponds to $\sigma_4(0)$. In the ac case, σ_3 involves $(z+M)^{-1}$ twice (once explicitly and once through Γ_{34}) and thus becomes $\sigma_3(0)(1-i\omega\tau^*)^{-2}$, while σ_4 becomes $\sigma_4(0)(1-i\omega\tau^*)^{-1}$. Collecting all the terms, the final answer is

$$\sigma(\omega)\cong\frac{\sigma_{\text{SBT}}+\sigma_1(0)+\sigma_2(0)+\sigma_4(0)}{1-i\omega\tau^*}+\frac{\sigma_3(0)}{(1-i\omega\tau^*)^2}\,. \tag{86}$$

Of the four nonclassical terms of order d^0 in the dc theory, three have Drude-type infrared response, while one decays more rapidly than Drude. We have no numerical estimates of the relative sizes of the four terms $\sigma_i(0)$, and can only suggest that there seems to us no reason why $\sigma_3(0)$ should be particularly different in magnitude from the other terms (i.e., presumably of order $\sigma_{\text{min}}/4$).

The predicted behavior of Eq. (86) is in sharp contrast to the expected behavior of a metal with E_F near a mobility edge E_c. The only results we know of for this problem are theoretical results by Götze[7] which predict an ac conductivity peak instead of Drude inertial falloff of $\text{Re}[\sigma(\omega)]$. Thus infrared measurements could in principle help clarify the physics of resistivity in metals with resistivities ~100 $\mu\Omega$ cm. Preliminary results by Yao and Schnatterly[36] seem consistent with neither scheme, but could be nicely explained if part of the dc conductivity remained constant in the infrared while the remainder exhibited Drude inertial falloff. At an earlier stage of our work, we believed that our theory yielded such a result,[1(b),23] but this preliminary conclusion turned out to be incorrect.

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APPENDIX

In Sec. III the scattering operator $\hat{K}$ was introduced and described abstractly. A concrete representation of this operator, for the case of impurity scattering, is given here for the convenience of the reader. These formulas were derived in Ref. 21, but it is necessary to use also Ref. 24 in order to find all the pieces explicitly. The result in a Bloch-state basis $|1\rangle=|\vec{k}n\rangle$ is

$$iK_{12,34}(\omega+i\delta)=\Xi_{12,34}(\omega+i\delta)-\Xi_{21,43}(-\omega+i\delta)^*\,. \tag{A1}$$

Here the complex conjugation operates on all quantities entering $\Xi_{21,43}$, including the argument $-\omega+i\delta$. From Eq. (A1) the property (29) of $\hat{K}$ can be verified. The subsidiary operator $\hat{\Xi}$ has two parts corresponding to scattering in and scattering out:

$$\hat{\Xi}=\hat{\Xi}^{\text{out}}+\hat{\Xi}^{\text{in}}\,, \tag{A2}$$

$$\Xi^{\text{in}}_{12,34}(z)=-n_i\frac{\langle 1|V|3\rangle\langle 4|V|2\rangle}{z+\epsilon_4-\epsilon_1}\,, \tag{A3}$$

$$\Xi^{\text{out}}_{12,34}(z)=n_i\delta_{24}\left(\langle 3|V|1\rangle+\sum_5\frac{\langle 1|V|5\rangle\langle 5|V|3\rangle}{z+\epsilon_2-\epsilon_5}\right), \tag{A4}$$

where n_i is impurity density and V is the electron-impurity scattering operator or T matrix. Charge conservation, Eq. (35), can now be verified. When the sum $\sum_1\Xi_{11,34}$ is constructed, scattering in cancels the second-order part of scattering out, leaving only a term $n_i\langle 3|v|4\rangle$. This piece cancels when $\sum_1 K_{11,34}$ is constructed from Eq. (A1).

The electron-phonon part of $\hat{K}$ is somewhat messier because of the appearance of $\pm\omega_Q$ in the denominators to (A3) and (A4), and Fermi functions in the numerator. However, at high T it is accurate to make the adiabatic approximation, i.e., neglect $\pm\omega_Q$ in the denominators, which corresponds to neglecting the explicit time dependence of the phonons. Then Fermi functions cancel, and formulas completely analogous to (A3) and (A4) result. In the second-order terms, the operator V is replaced by $\vec{u}\cdot\nabla\vec{V}$ and in the first-order term of (A4), V is replaced by $\frac{1}{2}u^2\nabla^2V$, where ∇V is the change in crystal potential felt by an electron due to atomic motion, and u is the displacement. The impurity concentration n_i is replaced by phonon density $2N(\omega_Q)+1$. Finally, the correct momentum transfer Q must be used both for $\vec{u}_Q=(\hbar/2M\omega_Q)^{1/2}\vec{\epsilon}$ and for $N(\omega_Q)=[\exp(\beta\omega_Q)-1]^{-1}$.

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