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COMMENTS AND ADDENDA

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Far-Infrared Absorptivity of Metals

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A simple calculation of the far-infrared absorptivity of a strong-coupling metal in the normal state is presented which is valid in the anomalous-skin-effect (ASE) region. The form of the results is compared with that derived by an alternate procedure in a recent letter by the author. A discussion of electron-phonon renormalization effects in the ASE limit is then considered and, in particular, at frequencies below threshold ($\omega \ll \omega_D$), an effective mass m_P^{**} is introduced which incorporates these effects.

In a recent letter,[1] the author presented a calculation of the far-infrared absorptivity of normal lead. The calculation is based on an approximate solution of the Holstein-Boltzmann (HB) equation,[2] and the numerical results were compared to the recent measurements of Joyce and Richards.[3] The agreement is satisfactory.[1] The purpose of the present note is not to improve on the numerical calculation of the absorptivity but rather to amplify and carry out a different approach to the calculation mentioned, as an aside, at the end of the letter.

The original procedure briefly is as follows: (i) The HB equation is solved approximately in the local or $\vec{q}=0$ limit ($\vec{q}$ is the wave vector of a typical important Fourier component of the applied electromagnetic field). (ii) Using this solution, the $\vec{q}\cdot\vec{v}_k$ term of the transport equation is reintroduced and the final form for the distribution function is

$$\Phi_k(\vec{q},\omega) = v_{kx}/[i\vec{q}\cdot\vec{v}_k + i\Omega(\epsilon)] \,, \tag{1}$$

where

$$\hbar\Omega(\epsilon) \equiv -\hbar\omega - (1-\gamma'/\gamma)\{M(\epsilon) - M(\epsilon+\hbar\omega) + i[\Gamma(\epsilon)+\Gamma(\epsilon+\hbar\omega)]\} \,,$$

v_{kx} is the electron velocity in the field direction, $M(\epsilon)$ ($\Gamma(\epsilon)$) is the real (imaginary) part of the electron self-energy [due to electron-phonon (EP) interaction], and γ'/γ represents the effect of the scattering-in term of the HB equation (cf. Ref. 1). (iii) The surface impedance Z is then derived following the method of Reuter and Sondheimer.[4] (iv) For the threshold-frequency region ($\omega \approx \omega_D$, where ω_D is a typical phonon frequency, e.g., $\hbar\omega_D \approx 8.3$ meV for Pb), Z is expanded in the Dingle[5] series appropriate to the anomalous skin effect (ASE) or Pippard limit, and the final result (for the absorptivity) is contained in Eq. (10), Ref. 1.

As discussed in Ref. 1 the series parameter for the Dingle series can be written as

$$\xi = \tfrac{3}{4}(v_F/\delta_f\omega)^2[1 + i/\omega\tau_{\text{eff}}(\omega)]^{-3} \,. \tag{2}$$

Since the *minimum* value of $\omega\tau_{\text{eff}}(\omega)$ is close to unity for an EP strong-coupling metal, the magnitude of ξ is essentially determined by $v_F/\delta_f\omega$. For Pb, $v_F/\delta_f\omega_D = 3.58$, thus, the ASE limit is applicable through the threshold region and moreover, the same is probably true for most other strong-coupling metals.[6]

The main point now is that under the above conditions the HB integral equation need not be solved (as such). Only when $v_F/\delta_f\omega_D \lesssim 1$ need one solve the integral equation. Instead, as an alternative procedure, one can make an expansion in powers of q^{-1} of the conductivity $\sigma(q,\omega)$ and more directly generate the Dingle series in the ASE limit with the advantage that each term in the series will be "exact." Now, with increasing frequency, when $v_F/\delta_f\omega < 1$ for $\omega > \omega_D$, one can then iterate the HB equation in powers of ω^{-1} (in addition to the terms treated in Sec. V B, Ref. 2, one can have terms involving $\vec{q}\cdot\vec{v}_k/\omega$).

The expansion of $\sigma(q,\omega)$ in powers of q^{-1} is facilitated by an examination of the contribution of the ladder diagrams (Fig. 6, Ref. 2) to the conductivity. Holstein[2] has discussed these diagrams in considerable detail and using part of his analysis, it can be shown that if $\vec{q}\cdot\vec{v}_k > \omega$, $\Gamma(\epsilon)$, each additional "rung" yields a contribution $\sim\Gamma(\epsilon)/\vec{q}\cdot\vec{v}_k$. Thus, to expand $\sigma(q,\omega)$ up to second order in q^{-1}, it suffices to consider the zero- and one-rung diagrams; explicitly,

$$\sigma^{(2)}(q,\omega)=\frac{2e^2}{\mathcal{V}}\sum_k\left(\frac{f^{(-)}(\epsilon)-f^{(-)}(\epsilon+\hbar\omega)}{\hbar\omega}\right)\left[\frac{v_{kx}^2}{i\vec{q}\cdot\vec{v}_k+i\Omega_s}+\frac{\pi/\hbar}{i\vec{q}\cdot\vec{v}_k+i\Omega_s}\sum_{k',\pm}\frac{|V_{kk'}|^2v_{kx}v_{k'x}\{\,\}}{i\vec{q}\cdot\vec{v}_{k'}+i\Omega_s'}\right] \tag{3}$$

with

$$\{\,\}=\{\delta(\epsilon-\epsilon'\pm\hbar\omega_{kk'})[f^{(\mp)}(\epsilon'+\hbar\omega)+f^{(\mp)}(\epsilon')]$$
$$+(i/\pi)P(\epsilon-\epsilon'\pm\hbar\omega_{kk'})^{-1}[f^{(\mp)}(\epsilon'+\hbar\omega)-f^{(\mp)}(\epsilon')]\}$$

and Ω_s, Ω_s' the same as $\Omega(\epsilon)$, $\Omega(\epsilon')$ with, however, $\gamma'/\gamma=0$. The expression for $\sigma^{(2)}(q,\omega)$ in (3) can, equivalently, be derived by an iteration in the HB equation, with

$$\Phi_k^{(0)}=v_{kx}/(\vec{q}\cdot\vec{v}_k+i\Omega_s)\ , \quad \text{etc.}$$

The k, k' sums are converted into integrals with the q direction chosen as the polar axis for the k integration and k direction as the polar axis for the k' integration. The angular integration of the first term (in the square bracket) is performed and the result expanded to q^{-2},

$$\sigma^{(2)}(q,\omega)\simeq\frac{3}{4}\left(\frac{\omega_p^2}{4\pi}\right)\int_{\epsilon_F-\hbar\omega}^{\epsilon_F}\frac{d\epsilon}{\hbar\omega}\left[\frac{\pi}{qv_F}+\frac{4\Omega_s}{i(qv_F)^2}-\frac{1}{(qv_F)^2}\int_{-1}^{+1}\frac{d\mu}{\mu+(\Omega_s/qv_F)}\int_0^{2\pi}d\phi\sum_{k'\pm}\frac{|V_{kk'}|^2\hat{v}_{kx}\hat{v}_{k'x}\{\,\}}{i\hat{q}\cdot\hat{v}_{k'}+(\Omega_s'/qv_F)}\right], \tag{4}$$

where ω_p is suitably averaged over the Fermi surface.

The third term (the contribution from the one-rung ladder diagram) is of order q^{-2}, however, Ω_s/qv_F and Ω_s'/qv_F are retained and considered as small negative imaginary quantities in order to define the angular integrals and are set equal to zero after the integration has been completed.

In order to carry out the integration, it is necessary to assume that the EP matrix element $V_{kk'}$ and the phonon frequencies $\omega_{kk'}$ depend only on $|\vec{k}-\vec{k}'|$. After some messy, but straightforward manipulation, the final result for the third term is

$$\frac{4}{i(qv_F)^2}\frac{i\pi^2}{\hbar}\frac{\mathcal{V}}{(2\pi)^3}\sum_\pm\int dk'\,k'^2\int_0^{2\pi}\sin\theta'\,d\theta'$$
$$\times|V_{kk'}|^2\{\,\}\left[\frac{\cos\theta'}{\sin\theta'}\left(\frac{\pi}{2}-\left|\frac{\pi}{2}-\theta'\right|\right)+1\right]\ . \tag{5}$$

The k' sum in (5) is restored and combined with the self-energy terms in Ω_s, so that the final form for $\sigma^{(2)}$ to order q^{-2} is

$$\sigma^{(2)}(q,\omega)\simeq\frac{3}{4}\left(\frac{\omega_p^2}{4\pi}\right)\left[\frac{\pi}{qv_F}+\frac{4\bar{\Omega}_P}{i(qv_F)^2}\right]\ , \tag{6}$$

with

$$\bar{\Omega}_P\equiv\int_{\epsilon_F-\hbar\omega}^{\epsilon_F}\frac{d\epsilon}{\hbar\omega}\,\Omega_P(\epsilon)\equiv\int_{\epsilon_F-\hbar\omega}^{\epsilon_F}\frac{d\epsilon}{\hbar\omega}\Bigg\{-\omega-\frac{i\pi}{\hbar}\sum_{k'\pm}$$

$$\times|V_{kk'}|^2\{\,\}\ [1-g(\psi_{kk'})]\Bigg\}\ , \tag{7}$$

where

$$g(\psi_{kk'})\equiv\frac{1}{2}\left[\frac{\cos\psi_{kk'}}{\sin\psi_{kk'}}\left(\frac{\pi}{2}-\left|\frac{\pi}{2}-\psi_{kk'}\right|\right)+1\right] \tag{8}$$

and $\psi_{kk'}\equiv\theta'$, the angle between $\vec{k}$, $\vec{k}'$.

The calculation for the absorptivity can now be completed by inserting expression (6) for the conductivity in the Fourier transform of Maxwell's equation and solving for the surface impedance.[4] The integral in the expression for Z is then appropriately expanded, and one has for the absorptivity

$$A=\frac{c}{\pi}\operatorname{Re}Z$$
$$=\frac{8}{3}\sqrt{3}\left(\frac{4\omega^2v_F}{3\pi\omega_p^2c}\right)^{1/3}+\frac{8}{9}\sqrt{3}\left(\frac{4\omega^2v_F}{3\pi\omega_p^2c}\right)^{2/3}\frac{16c}{3\pi v_F}$$
$$\times\operatorname{Re}\left[\frac{i\bar{\Omega}_Pe^{-i\pi/6}}{\omega}\right]\ . \tag{9}$$

In comparing (9) with Eq. (10) in Ref. 1, one observes that the only difference appears in the replacement of $\bar{\Omega}$ by $\bar{\Omega}_P$. The $1-\gamma'/\gamma$ factor in $\bar{\Omega}$ is a result of an approximate treatment of the $1-\cos\psi_{kk'}$ velocity transfer factor familiar to transport theory. Thus, the upshot of the present approach is to replace $\cos\psi_{kk'}$ by $g(\psi_{kk'})$ in the scattering-in contribution in the ASE limit. In addition, since this second term of the Dingle series (9) is "exact," one has further confirmation of the *form* of the approximate solution to the HB equation obtained both in Ref. 1 and, in an interesting way, by Allen.[7]

At frequencies below threshold ($\omega \ll \omega_D$), the square brackets in the second term in (9) can be replaced by $-m_P^{**}/2m_{op}$, where

$$\frac{m_P^{**}}{m_{op}} = 1 + 2 \sum_{k',\pm} \frac{|V_{kk'}|^2}{\hbar\omega_{kk'}} [1 - g(\psi_{kk'})]\delta(\epsilon_{k'} - \epsilon_F) \ . \tag{10}$$

Although a mass does not explicitly appear in (9), for a spherical Fermi surface the product of (10) and v_F^{-1} can be written as v_F^{*-1}, a renormalized Fermi velocity (the ratio v_F/ω_p^2 is independent of EP renormalization).

To the extent that the two terms of the Dingle series in (9) are an accurate expression of A at the lower frequencies [ξ in (2) is increasing as ω^{-2}], all the EP effects are contained in m_P^{**}, the effective mass appropriate to the ASE or Pippard limit. In comparing m_P^{**} to m^{**}, derived in Sec. V C, Ref. 2, the only difference is again the replacement of $\cos\psi_{kk'}$ by $g(\psi_{kk'})$. The mass m^{**} is operative in the London limit: $\omega \ll \omega_D$, $\omega\tau_{eff} \gg 1$, and $\omega \gg v_F q$. The region of applicability for m_P^{**} also has $\omega \ll \omega_D$, $\omega\tau_{eff} \gg 1$ but the opposite of the last condition, i.e., $\omega \ll v_F q$.

It has been asserted in the literature[2,8] that there are no EP renormalization effects in the ASE limit, so that some clarification here is essential. The first term of (9) represents the familiar extreme ASE absorptivity and it contains no EP effects (cf. Sec. V A, Ref. 2); the quantity ω_p^2/v_F is simply proportional to the area of the Fermi surface. *The EP effects occur in the frequency-dependent corrections to the extreme ASE result* [the second term or q^{-2} term of (9)]. More to the point, it is not just the retention of the q^{-2} term in the conductivity (6) but the frequency dependence of that term that leads to EP renormalization. The statement of no EP effects in the ASE limit does not merely refer to a lack of higher q-dependent corrections to the conductivity but rather to conditions (e.g., finite temperature) such that $\omega\tau \ll 1$ (τ is the relaxation time associated with higher-temperature resistivity). When $\omega\tau \ll 1$, ω can essentially be set equal to zero in the transport equation (cf. footnote 89, Ref. 2), and the second term in (6) would be $-4/[(qv_F)^2\tau]$ [of course, assuming here that τ^{-1} is not so large that it is greater than qv_F where q in this case is $\sim \delta_{cl}^{-1}$, $\delta_{cl} = \delta_f/(\omega\tau)^{1/2}$]. In the present physical context, $\omega\tau_{eff}(\omega) \gtrsim 1$ so that the ω-dependent term in the conductivity is retained and leads to measurable EP-renormalization effects to the extent that the second term in (9) is a correction to the first. In Pb this is the case and the extent of EP renormalization can be seen by comparing the theoretical A below 30 cm^{-1} in Fig. 2, Ref. 1, to the theoretical A below 30 cm^{-1} in Fig. 1, Ref. 3. The latter, multiplied by $\frac{8}{9}$ (to account for the difference in boundary condition assumptions) is larger than the former above 10 cm^{-1}. It is 20% larger at 30 cm^{-1} and 10% larger at 20 cm^{-1}. As a result of its slower variation with frequency below 30 cm^{-1} the former curve passes through the experimental points in this region, the latter does not (the experimental points are normalized in both comparisons to coincide with the theoretical curve at threshold).

As a final consideration, an estimate (for Pb) is made of the change due to the replacement of $\cos\psi_{kk'}$ by $g(\psi_{kk'})$. In Fig. 1 both functions are plotted along with $Q^2v_Q^2$ (normalized to the peak value, where v_Q is the dressed electron-ion pseudopotential[9] and $Q/2k_F = \sin(\frac{1}{2}\psi_{kk'})$. The function $Q^2v_Q^2$ divided by the phonon frequency ω_Q is proportional to the absolute square of the EP matrix element. It can be observed that with $g(\psi_{kk'})$ the contribution of the scattering-in term is enhanced.[10] By comparing the integrals of $\sin\psi_{kk'}\cos\psi_{kk'}Q^2v_Q^2$ and $\sin\psi_{kk'}g(\psi_{kk'})Q^2v_Q^2$ and in estimating the effect of ω_Q, the term γ'/γ is

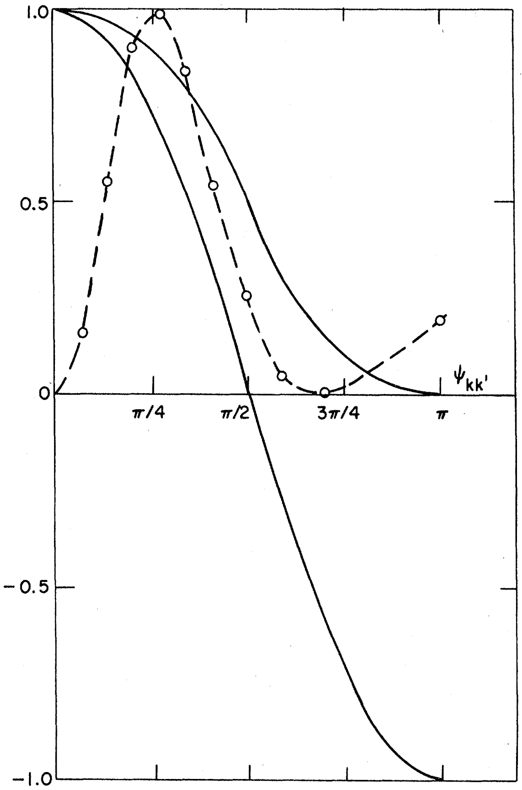

FIG. 1. The functions $g(\psi_{kk'})$ and $\cos\psi_{kk'}$ are the upper and lower (solid) curves, respectively. The dashed curve is the normalized $Q^2v_Q^2$ with $Q/2k_F = \sin(\frac{1}{2}\psi_{kk'})$.

found to be approximately increased by $\approx 30\%$. Therefore, the factors $1-\gamma'/\gamma \approx 0.43$ and $m_P^{**}/m_{op} \approx 1.65$. The change in $1-\gamma'/\gamma$ will, of course, cause a modification in the numerical results for the calculated absorptivity (Fig. 2, Ref. 1), however, the change will be small (on the order of 10%) as the two parts of the second term in (9) have opposite sign (the part proportional to Γ being positive).

As stated above the main consideration in the present note is to present an alternate and simpler approach to the calculation of the far-infrared absorptivity of a metal in the ASE limit in the frequency range of greatest interest ($\omega \approx \omega_D$). With the present approach it may be feasible to consider, more explicitly, the band structure and phonon anisotropy of the metal.

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[1] H. Scher, Phys. Rev. Letters 25, 759 (1970).

[2] T. Holstein, Ann. Phys. (N. Y.) 29, 410 (1964).

[3] R. R. Joyce and P. L. Richards, Phys. Rev. Letters 24, 1007 (1970).

[4] G. E. H. Reuter and E. H. Sondheimer, Proc. Roy. Soc. (London) A195, 336 (1948).

[5] R. B. Dingle, Physica (Utrecht) 19, 311 (1953).

[6] The band parameters one needs to determine $v_F/\delta_f\omega$ can be derived from a measurement of the surface impedance of a pure metal ($\omega\tau_{\text{Res}} \gg 1$, where τ_{Res} is the relaxation time associated with the residual resistance) at very low temperature. In addition, one must have $\omega \lll \omega_D$, so that there are no EP effects (to be discussed below) on the value of σ/l or $\omega_p^2/4\pi v_F$ obtained from the measurement.

[7] P. B. Allen, Phys. Rev. B 3, 305 (1971).

[8] S. Nakajima and M. Watabe, Progr. Theoret. Phys. (Kyoto) 29, 341 (1963).

[9] W. A. Harrison, *Pseudopotentials in the Theory of Metals* (Benjamin, New York, 1966), p. 314.

[10] In the ASE limit it is well known that the scattering-in contribution is negligible. As seen in (4) only the scattering-out (zero-rung diagram) contributes to the *leading* (q^{-1}) *term*. However, the scattering-in enters the q^{-2} term. Now the question is, why in the ASE limit is this scattering-in term larger than the usual transport ($\cos\psi_{kk'}$) term? A study (with T. Holstein) on this point is in progress.

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Hellmann-Feynman Theorem and Uniform Expansion of Crystals

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The applicability of the Hellmann-Feynman theorem under periodic boundary conditions is discussed. The recent result of Wannier, Misner, and Schay on the instability of metals toward uniform expansion is shown to result not so much from the inapplicability of this theorem as from the improper evaluation of a sum.

Wannier, Misner, and Schay[1] (WMS) recently used the Hellmann-Feynman theorem[2] (HFT) to consider the stability of a metal against uniform expansion. They claimed that their results showed the inadequacy of recent electronic wave-function calculations and of the nearly free-electron approach to such calculations.

Kleinman[3] (K) criticized their procedure on the basis that the HFT can be applied only to finite systems, since uniform expansion would violate the periodic boundary conditions (PBC) normally employed. He then argued that in a finite metal the structure near the surface would be distorted from the purely periodic arrangement in the interior in such a way as to provide the necessary confining force.

I believe that Kleinman has pointed out a significant inadequacy in WMS's argument, but that to see clearly where their error lies, it is more instructive to use PBC as far as possible.

Let us suppose that we have a Hamiltonian $H(p, r, R)$, where p, r stand for all the momenta and coordinates which are treated dynamically (in this case, those of the electrons: $\vec{p}_i$, $\vec{r}_i$), and R stands for all other coordinates which enter as parameters (say the positions $\vec{R}_\alpha$ of the nuclei).

Now let us consider a few independent changes in the Hamiltonian: (i) Move the nuclei from $\vec{R}$ to $\vec{R}/\eta$:

$$H(p, r, R) \to H(p, r, R/\eta) .$$

As Kleinman says, this cannot be done in PBC. (ii) Transform the coordinates $\vec{r}_i/\eta$ by a canonical transformation:

$$H(p, r, R) \to H(\eta p, r/\eta, R) .$$

This also cannot be done in PBC. (iii) Change the