

The results presented here are for a single lead film. Data from two other lead films have shown qualitatively similar behavior but have not been analyzed in detail.

In conclusion, we have experimentally observed a difference in the temperature dependence of the photoelectric yield from a thin lead film between the normal and superconducting states. We believe that this is due to the presence of the superconducting energy gap. The temperature dependence is in reasonable agreement with the BCS-based calculations of Slezov,<sup>1</sup> assuming a spread in transition temperature over the surface of the film. Comparing experiment and theory on the basis of temperature dependence alone, a value of  $\Delta_0/kT_c$  between 2 and 3 is obtained, consistent with infrared absorption and tunneling measurements of other observers. The size of the effect, however, is more than an order of magnitude larger than that predicted by theory. This large discrepancy is not understood at the present time.

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<sup>1</sup>V. V. Slezov, *Fiz. Tverd. Tela* **5**, 2951 (1963) [*Sov. Phys. Solid State* **5**, 2161 (1964)]. This reference contains a typographical error in the final result on p. 2165. The radical in the denominator of each intergrand should be a factor in the exponent of  $e$ .

<sup>2</sup>J. C. McLennan, R. G. Hunter, and J. H. McLeod, *Trans. Roy. Soc. Can., Sect. 3* **24**, 3 (1930).

<sup>3</sup>J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.* **108**, 1175 (1957).

<sup>4</sup>Obtained gratis from Kawecki Chemical Co., 220 East 42nd St., New York, N.Y. 10017.

<sup>5</sup>This is a common technique in thin film technology where direct metal to metal bonds are made using local high temperature and pressure. See R. W. Berry, P. M. Hall, and M. T. Harris, *Thin Film Technology* (Van Nostrand, Princeton, N. J., 1968), p. 604.

<sup>6</sup>A colloidal dispersion of graphite obtained gratis from Acheson Colloids Co., Port Huron, Mich. 48060.

<sup>7</sup>M. Strongin, R. S. Thompson, O. F. Kammerer, and J. E. Crow, *Phys. Rev. B* **1**, 1078 (1970).

<sup>8</sup>R. D. Parks, private communication.

<sup>9</sup>P. L. Richards and M. Tinkham, *Phys. Rev.* **119**, 575 (1960).

<sup>10</sup>W. L. McMillan and J. M. Rowell, in *Superconductivity*, edited by R. D. Parks (Marcel Dekker, New York, 1969), Vol. 1, p. 596.

<sup>11</sup>W. E. Spicer, private communication.

## Influence of Quasiparticle Interactions on the Optical Effective Mass of Metallic Copper\*

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Experimental measurements of the optical mass of copper are interpreted to yield a Fermi-surface average of the Landau parameter which relates the current carried by a quasiparticle excitation to its velocity.

In this Letter we discuss the influence of quasiparticle interactions on the optical effective mass of metallic copper. An empirically adjusted nonlocal potential has been constructed which is consistent with Fermi-surface and interband absorption data and which therefore is fully renormalized by the electron-electron interaction. From the one-quasiparticle excitation spectrum derived from this potential, we calculate, neglecting quasiparticle interactions, the optical effective mass of copper. By comparing our calculated optical mass with the experimental mass, we estimate the Fermi-surface average of the Landau parameter which relates the current carried by a quasiparticle excitation to its velocity. Our result is qualitatively consistent with the results of first-

principles calculations in which band-structure effects are neglected.

From the Dyson equation of many-body theory one can show that, whenever lifetime effects are negligible, the energies of quasiparticle excitations in a metal can be derived from a single-particle-like Schrödinger equation involving a nonlocal effective potential  $V_{\text{eff}}(\vec{r}, \vec{k}, E)$  into which exchange and correlation corrections have been absorbed.<sup>1</sup> It is a convenient approximation to separate the  $\vec{k}$  dependence of the effective potential into radial and transverse components, folding the radial component into the energy dependence, and expressing the transverse component as an angular-momentum dependence so that  $V_{\text{eff}} \approx V_{\text{eff}}(\vec{r}, l, E)$ .

Since the Fermi surface of a metal is the surface of constant quasiparticle energy  $E_{\vec{k}} = \mu$ , its shape can be derived from the  $l$ -dependent effective potential  $V_{\text{eff}}(\vec{k}, l, \mu)$ . Studies of the Fermi surface of copper have shown that small  $l$ -dependent corrections to the local potential proposed by Chodorow<sup>2</sup> are sufficient to bring the shape of the computed Fermi surface into agreement with the experimental data.<sup>3</sup> Exchange and correlation corrections appropriate to the Fermi energy are folded into the effective potential constructed in this way.

In order to calculate the one-quasiparticle excitation spectrum, it is necessary to determine the energy dependence of the effective potential away from the Fermi surface. As a first step we establish that in the Landau-Silin approximation<sup>4</sup> the energy required to excite a quasiparticle pair is unaffected by the quasiparticle interaction. In this approximation the Hamiltonian may be written

$$H = \sum_{\vec{k}} E_{\vec{k}} (c_{\vec{k}}^{\dagger} c_{\vec{k}} - n_{\vec{k}}^0) + \frac{1}{2} \sum_{\substack{\vec{k}, \vec{k}' \\ \vec{q} \neq 0}} f_{\vec{q}}(\vec{k}, \vec{k}') c_{\vec{k}+\vec{q}}^{\dagger} c_{\vec{k}} c_{\vec{k}'-\vec{q}}^{\dagger} c_{\vec{k}'}, \quad (1)$$

where  $E_{\vec{k}}$  is the one-quasiparticle excitation spectrum,  $c_{\vec{k}}^{\dagger}$  and  $c_{\vec{k}}$  are quasiparticle field operators, and  $f_{\vec{q}}(\vec{k}, \vec{k}')$  is the Landau coefficient which describes the quasiparticle interaction; spin indices have been suppressed. The response to an external perturbation  $\sum_{\vec{k}} \rho_{\vec{k}\vec{q}}^{\dagger} U_{\vec{q}} e^{+i\omega t}$  (where  $\rho_{\vec{k}\vec{q}}^{\dagger} = c_{\vec{k}+\vec{q}}^{\dagger} c_{\vec{k}}$ ) can be calculated by solving the equation of motion of the density operator. We find that the density of quasiparticle-quasihole pairs is given by

$$\langle \rho_{\vec{k}\vec{q}} \rangle = [U_{\vec{q}} e^{+i\omega t} + \sum_{\vec{k}'} \langle \rho_{\vec{k}'\vec{q}} \rangle f_{\vec{q}}(\vec{k}, \vec{k}')] \times (n_{\vec{k}}^0 - n_{\vec{k}+\vec{q}}^0) [\omega - (E_{\vec{k}+\vec{q}} - E_{\vec{k}})]^{-1}. \quad (2)$$

Thus the transition matrix element is renormalized by the quasiparticle interaction, whereas the transition frequency remains equal to the difference between the quasiparticle energies in the initial and final states.<sup>5</sup> Therefore, provided that the lifetimes of the excited states are sufficiently long that quasiparticle excitations are well-defined, experimental measurements of optical absorption frequencies in metals can yield the quasiparticle excitation spectra. In copper the lifetime condition is satisfied for excitations of energy  $\omega \ll 7.1$  eV ( $=\mu$ ).

The band gaps corresponding to certain inter-

band transitions in copper, as calculated from the modified Chodorow potential, have been shown<sup>3</sup> to be in satisfactory agreement with the interband transition frequencies obtained experimentally by Gerhardt.<sup>6</sup> This agreement suggests that, even though the modified Chodorow potential is independent of energy, it provides a satisfactory model of the one-quasiparticle excitation spectrum.

In the collisionless regime ( $\omega\tau \gg 1$ ) the real part of the dielectric function of a metal can be expressed in the form

$$\epsilon_1(\omega) = 1 - 4\pi N e^2 / m_{\text{opt}} (\omega^2 + \tau^{-2}) + \epsilon_{1i}(\omega), \quad (3)$$

where  $N$  is the number of conduction electrons per unit volume and  $\epsilon_{1i}(\omega)$  is the contribution due to interband transitions. Neglecting the interaction between quasiparticle excitations, the optical mass can be expressed in terms of Fermi-surface parameters by<sup>7</sup>

$$m_{\text{opt}}/m = S_F^0 v_F^0 / S_F \langle v_{\vec{k}}^c \rangle, \quad (4)$$

where  $S_F$  is the surface area of the Fermi surface,  $\langle v_{\vec{k}}^c \rangle$  is the Fermi-surface average of the Coulomb-renormalized quasiparticle velocity, and  $S_F^0$  and  $v_F^0$  are the free-electron Fermi-surface area and velocity, respectively. For typical values of  $\tau$ , experimental frequencies in the collisionless regime satisfy the further condition  $\omega \gg \omega_D$  (the Debye frequency), so the experimental value of the optical mass is not expected to be affected by the electron-phonon interaction.<sup>8</sup> We have used the values of  $S_F$  and  $v_{\vec{k}}^c$  deduced from the modified Chodorow potential to calculate the optical mass of copper. We find that

$$m_{\text{opt}}/m = 1.29 \pm 0.01 \quad (5)$$

which may be compared with an earlier by Segall<sup>9</sup> obtained from the Chodorow potential:  $m_{\text{opt}}/m = 1.3 \pm 0.1$ .

When the interactions between quasiparticle excitations are taken into account, the optical mass is given by

$$m_{\text{opt}}/m = S_F^0 j_F^0 / S_F \langle j_{\vec{k}} \rangle, \quad (6)$$

where  $j_{\vec{k}}$  is the current associated with the states of wave vector  $\vec{k}$ . For a metal whose Fermi surface is derived from a single band, the quasiparticle current  $j_{\vec{k}}$  is related to the Coulomb-renormalized quasiparticle velocity  $v_{\vec{k}}^c$  by<sup>10</sup>

$$j_{\vec{k}} = v_{\vec{k}}^c + \sum_{\vec{k}'} f_{\text{eff}}(\vec{k}, \vec{k}') v_{\vec{k}'}^c \delta(E_{\vec{k}'} - \mu). \quad (7)$$

If in evaluating the second term we neglect the Fermi-surface anisotropy and the anisotropy of

Table I. Comparison of estimates of the experimental optical effective mass of copper.

Source	$m_{\text{opt}}/m$
Roberts (Ref. 12)	1.44(1)
Schulz (Ref. 13)	1.45(6)
Myers, Walldén, and Karlsson (Ref. 6)	1.46(?)
Beaglehole (Ref. 15)	1.46(5) <sup>a</sup>
Ehrenreich and Philipp (Ref. 11)	1.42(5) <sup>a</sup>
Present work	1.39(6) <sup>a</sup>

<sup>a</sup>Includes correction for interband transitions.

$v_{\vec{k}}^c$ , we find that

$$j_{\vec{k}}^c = v_{\vec{k}}^c (1 + A_1^c), \quad (8)$$

where  $A_1^c$  is the  $l=1$  component of the Legendre polynomial expansion of the effective quasiparticle interaction  $f_{\text{eff}}(\vec{k}, \vec{k}')$ . The optical mass is then given by

$$m_{\text{opt}}/m = S_F^0 v_F^0 / S_F \langle v_{\vec{k}}^c \rangle (1 + A_1^c)^{-1}. \quad (9)$$

Experimentally, the optical mass is determined from measurements of  $\epsilon_1(\omega)$ . However, the data must first be corrected for the frequency dependence of the interband contribution  $\epsilon_{1i}(\omega)$ . Ehrenreich and Philipp<sup>11</sup> have shown that such a correction can be carried out by Kramers-Kronig inversion of interband absorption data. Correcting experimental measurements of  $\epsilon_1(\omega)$  by Roberts<sup>12</sup> and Schulz,<sup>13</sup> they found  $m_{\text{opt}}/m = 1.42 \pm 0.05$ . Recent absorption data by Pells and Shiga<sup>14</sup> suggest that the earlier data may have underestimated the interband correction. We have therefore computed the interband correction from both sets of absorption data. Using Ehrenreich and Philipp's data to correct the value of the optical mass obtained by Schulz at 0.62 eV, we find that  $m_{\text{opt}}/m \approx 1.14$ , whereas Pells and Shiga's data give  $m_{\text{opt}}/m \approx 1.38$ . This correction, when applied to the average optical mass obtained by Ehrenreich and Philipp, yields our preferred value of the experimental optical mass of copper:

$$m_{\text{opt}}/m = 1.39 \pm 0.06. \quad (10)$$

Our preferred value is compared with other estimates<sup>15,16</sup> of the optical mass in Table I.

In the isotropic approximation, the experimental optical mass is related to parameters of the Fermi surface by Eq. (9). Therefore, by comparing the experimental mass with the mass calculated from Eq. (4) (i.e., neglecting quasiparticle interactions), one can determine a Fermi-surface average of the Landau parameter  $A_1^c$ .

Table II. Comparison of first-principles calculations of the Landau parameter  $A_1^c$  for  $r_s = 2.66$  with the result derived from the optical mass of copper.

Pines and Nozieres approximation (Ref. 17)	+0.03
Hubbard approximation (Ref. 17)	0.00
Screened exchange (Ref. 18)	-0.045
Rice (Ref. 18)	+0.020
Expansion method (Ref. 18)	-0.031
Present work	-0.07 $\pm$ 0.05

Combining our calculated value of the optical mass of copper in Eq. (5) with the experimental value in Eq. (10), we find that

$$A_1^c = -0.07 \pm 0.05. \quad (11)$$

Our approximation of isotropy is likely to be adequate for the contribution of the belly region of the Fermi surface to the optical mass. The approximation is likely to overestimate the correction on the necks, but their area is small, and their contribution to the optical mass is further reduced by the low quasiparticle velocity on this region of the Fermi surface. Our result indicates that on the belly of the Fermi surface of copper the quasiparticle current is reduced by backflow.

Several authors have estimated the Landau parameters of the quasiparticle interaction from microscopic theory.<sup>17,18</sup> Values of  $A_1^c$  for a uniform electron gas having the same density as in copper ( $r_s = 2.66$ ) are set out in Table II. The results of the first-principles calculations vary widely among themselves, but are qualitatively consistent with our result. Quantitative agreement cannot be expected because the first-principles calculations neglect band structure effects.

The uncertainty in our estimate of the Landau parameter  $A_1^c$  is dominated by experimental error in the optical mass. More accurate measurements of the infrared dielectric constant of copper are needed to determine this parameter with greater precision.

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<sup>1</sup>See, for example, M. J. G. Lee, Phys. Rev. **178**, 953 (1969).

<sup>2</sup>M. I. Chodorow, thesis, Massachusetts Institute of Technology, 1939 (unpublished).

<sup>3</sup>M. J. G. Lee, Phys. Rev. **187**, 901 (1969).

<sup>4</sup>V. P. Silin, Zh. Eksp. Teor. Fiz. **33**, 495 (1957) [Sov.

Phys. JETP 6, 387 (1958)).

<sup>5</sup>This result has been obtained independently by R. A. Craig and J. W. McClure, Bull. Amer. Phys. Soc. 13, 92 (1968), and to be published.

<sup>6</sup>U. Gerhardt, Phys. Rev. 172, 651 (1968).

<sup>7</sup>M. H. Cohen, Phil. Mag. 3, 762 (1958).

<sup>8</sup>J. W. Wilkins, in "Lectures on Observable Many-Body Effects in Metals," NORDITA, Copenhagen, 1968, (unpublished), pp. 11-28.

<sup>9</sup>B. Segall, Phys. Rev. 125, 109 (1962).

<sup>10</sup>D. Pines and P. Nozières, *The Theory of Quantum Liquids* (Benjamin, New York, 1966), pp. 35, 195.

<sup>11</sup>H. Ehrenreich and H. R. Philipp, Phys. Rev. 128,

1622 (1962).

<sup>12</sup>S. Roberts, Phys. Rev. 118, 1509 (1960).

<sup>13</sup>L. G. Schulz, J. Opt. Soc. Amer. 44, 540 (1954).

<sup>14</sup>G. Pells and M. Shiga, J. Phys. C: Proc. Phys. Soc., London 2, 1835 (1969).

<sup>15</sup>D. Beaglehole, Proc. Phys. Soc., London 87, 461 (1966).

<sup>16</sup>H. P. Myers, L. Walldén, and A. Karlsson, Phil. Mag. 18, 725 (1968).

<sup>17</sup>Ref. 10, p. 332.

<sup>18</sup>L. Hedin and S. Lundqvist, in *Solid State Physics*, edited by H. Ehrenreich, F. Seitz, and D. Turnbull (Academic, New York, 1969), Vol. 23, p. 102.

## Far-Ultraviolet Reflectance Spectra of Ionic Crystals\*

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Synchrotron radiation has been used to measure the reflectance spectra of KCl, KBr, RbCl, CsCl, CsBr, CaF<sub>2</sub>, SrF<sub>2</sub>, and BaF<sub>2</sub> for photon energies  $6 < \hbar\omega < 36$  eV at temperatures  $90 < T < 400$  K. Excitations of both valence and core electrons show sharp structure and strong  $T$  dependence. Analysis of the data in terms of excitonic and interband transitions from core states is made with regard to  $T$  dependence, crystal structure, and chemical composition.

Our understanding of the electronic band structure of ionic crystals is not as advanced as for many other solids, even though the alkali halides were among the first materials studied in solid-state physics. This situation arises because the large energy gaps of these crystals place their fundamental absorption spectra in the vacuum ultraviolet, a region not easily accessible for experiments. This paper reports the normal-incidence reflectance spectra of several ionic crystals for photon energies  $6 < \hbar\omega < 36$  eV and temperatures  $90 < T < 400$  K. Low- $T$  measurements beyond 12 eV, the transmission cutoff of LiF windows, were made possible for the first time by the use (without windows) of synchrotron radiation as a light source. A number of new structures have been observed, particularly at low  $T$ .

Synchrotron radiation from the 240-MeV electron storage ring at the University of Wisconsin was used. The experimental system<sup>1</sup> employs the rotating-light-pipe scanning-reflectometer technique<sup>2</sup> to obtain detailed reflectance spectra directly. Before measurement, bulk samples are heated to 400 K in the ultrahigh vacuum to remove absorbed gases from the surface.

Figure 1 shows the reflectance spectra of KCl, KBr, RbCl, CsCl, CsBr, CaF<sub>2</sub>, SrF<sub>2</sub>, and BaF<sub>2</sub>. Correction was made for second-order light from the grating. Reflectance shifts separate the spectra at different temperatures, placing the 90-K

curves above and the 400-K curves below the 300-K measurements. The wavelength resolution is  $\Delta\lambda = 5$  Å.

The spectra have been divided by dashed vertical lines into three regions. Structure in region I arises from electronic excitation of the valence bands, which originate predominately from the filled  $p$  states of the negative ions. Region II begins with the onset of excitations from flat core bands which lie below the valence bands and originate from the  $p$  states of the positive ions. This core threshold may be determined for K<sup>+</sup>( $3p$ ) and Cs<sup>+</sup>( $5p$ ) at 19.9 and 13.2 eV, respectively, by observing which structures are insensitive to changes of the halide. Atomic x-ray levels<sup>3</sup> help to determine the onset in the other crystals. Region II, several eV wide, is composed of very sharp peaks (width  $< 0.2$  eV) which also characterize the core threshold. Their width is resolution limited. We believe, in agreement with others,<sup>4-8</sup> that these sharp peaks correspond to core excitons. The present analysis uses this interpretation. It should be noted, however, that the experimental results do not exclude the possibility that the sharp peaks are caused by interband transitions. An abrupt change to much broader minimum at  $X_3$ . The  $A_1'$  peak may be the first excited state of the  $A_1$  exciton.<sup>10</sup> most likely arises from interband transitions between core and conduction bands.