Quasiparticle interactions in the optical properties of Nb and Mo†

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The optical masses of Nb and Mo are calculated within one-electron theory and are found to disagree with the reported experimental values. Large Fermi-liquid effects provide a probable resolution of the discrepancy. The effects of quasiparticle interactions and low-energy interband transitions on the optical properties are discussed and further experiments are suggested.

It is well known[1] that the optical mass of a metal can be altered from its band-theoretical value by quasiparticle interaction effects. In this paper we present the first detailed calculations of the band-theoretic prediction for transition metals. We find evidence that the corrections to band theory are very large for Nb and Mo. This supports a semiquantitative estimate for Mo by Bolotin, Mayevskii, and Charikov,[2] and provides a strong counterexample to the careful work of Lee and Nowak[3] which found only a small correction for Cu. For Nb we suggest that the interactions may well be large enough that Nb is close to an electronic instability.

The optical mass is inversely proportional to the square of the plasma frequency Ω_p which is determined by measurement of the conductivity $\sigma(\omega)$ for frequencies ω below the onset of interband transitions. For cubic symmetry, σ is a scalar and, in the collision time (τ) approximation, can be written

$$\sigma(\omega)=\frac{i}{4\pi}\frac{\Omega_p^2}{\omega+i/\tau}. \tag{1}$$

One-electron theory gives

$$\Omega_p^2=\tfrac{4}{3}\pi e^2\sum_k v_k^2\delta(\epsilon_k)=\tfrac{4}{3}\pi e^2 N(0)\langle v_F^2\rangle, \tag{2}$$

where ϵ_k is the electron energy of the state k, which is shorthand for wave vector $\vec{k}$, band index n, and spin, $\vec{v}_k=\partial\epsilon_k/\partial\vec{k}$ is the electron velocity (we set $\hbar=1$), energies are measured relative to the Fermi energy, and $N(0)$ is the density of states at the Fermi energy.

Our calculation of Ω_p^2 for Nb and Mo is part of a continuing study of the wave vector ($\vec{Q}$) and frequency (ω) dependent susceptibility $\chi(\vec{Q},\omega)$ of these metals, where

$$\chi(\vec{Q},\omega)=\sum_{\substack{k\\ nn'}}\frac{F_{kn}-F_{k+Q,n'}}{\epsilon_{k+Q,n'}-\epsilon_{kn}-\omega-i\delta}. \tag{3}$$

Here F is the Fermi function and δ is a positive infinitesimal quantity. In evaluating Eq. (3) we have used Slater-Koster parameterizations[4] of the nonrelativistic augmented-plane-wave (APW) energy-band calculations of Mattheiss[5] for Nb and of Petroff and Viswanathan[6] for Mo. The APW bands of Nb were found[5] to agree with experimental Fermi-surface data,[7] and the $Q=0$ interband contributions to the imaginary part χ_2 of the susceptibility have been found[8] to give good agreement with the measured optical properties above 1 eV.

In the $\tau\to\infty$ approximation assumed in Eq. (3), the intraband part of χ_2 for $Q=0$ is proportional to $\delta(\omega)$ and is not easily calculated. Instead we use the fact that $N(0)\langle v_F^2\rangle$ is given by the intraband part of the F sum on χ_2 in the limit $Q\to 0$:

$$\lim_{Q\to 0}\int_{-\infty}^{\infty}\omega\,\chi_2^{\text{intra}}(Q,\omega)\,d\omega=\tfrac{1}{3}\pi N(0)\langle v_F^2\rangle Q^2+O(Q^4), \tag{4}$$

where again cubic symmetry is assumed. In addition we have found $N(0)$ separately from the real part χ_1 using the relation

$$\lim_{Q\to 0}\chi_1(Q,\omega\simeq 0)=N(0)+O(Q^2). \tag{5}$$

The results of two separate numerical methods of calculation were found to be very similar. The methods for doing the $Q\neq 0$ calculations are in an unpublished technical report[9] and relevant details will be published elsewhere.

The $Q\to 0$ extrapolations indicated in Eqs. (4) and (5) were carried out along the [100] direction using $Q=\frac{1}{32}m(1,0,0)(2\pi/a)$, $m=1,2$, and along the [111] direction using $Q=\frac{1}{32}m(1,1,1)(2\pi/a)$, $m=1,2$. Each of the values of $N(0)$, $v_F=\langle v_F^2\rangle^{1/2}$, and Ω_p listed in Table I is the average of the two extrapolations, with the number in parentheses giving one-half the difference. In most cases the results of the extrapolations in fact differed little from the values which would have been obtained from the smallest wave vectors, and are in good agreement with the requirement of cubic symmetry that $Q\to 0$ extrapolations of these quantities be independent of the direction of $\vec{Q}$. In addition, the total density of states and the average Fermi velocity $v_F=0.61\times10^8$ cm/sec of Nb are within 1% of the values found by Mattheiss[5] using the original APW calculations. The resulting values of Ω_p are 9.1

TABLE I. Values of the density of states $N(0)$, Fermi velocity v_F, and one-electron plasma frequency Ω_p for Mo and Nb, calculated as described in the text. For comparison, the experimental plasma frequency ω_p (and reference) and the resulting value of the Silin parameter A are included.

	Mo	Nb
$N(0)$ (states/Ry spin)	4.21 (0.22)	9.96 (0.37)
v_F (10^8 cm/sec)	0.71 (0.02)	0.61 (0.01)
$\hbar\Omega_p$ (theory) (eV)	7.4 (0.1)	9.1 (0.1)
$\hbar\omega_p$ (experiment) (eV)	5.9	4.8, 5.7, 7.9
Reference	2, 10, 11	12, 13, 14
A	−0.36	−0.7, −0.6, −0.2

eV for Nb and 7.4 eV for Mo. This result for Mo is in agreement with an estimate $\Omega_p \gtrsim 7.7$ eV by Bolotin, Mayevskii, and Charikov,[2] using an early Fermi-surface parameterization.

Three different optical studies[2,10,11] on Mo give a plasma frequency $\Omega_{p,\mathrm{exp}} = 5.9$ eV. The normalized difference Δ between the theoretical and experimental optical masses, defined by

$$\Delta = (m^{-1}_{\mathrm{opt,th}} - m^{-1}_{\mathrm{opt,exp}})/m^{-1}_{\mathrm{opt,th}} = (\Omega^2_{p,\mathrm{th}} - \Omega^2_{p,\mathrm{exp}})/\Omega^2_{p,\mathrm{th}}, \tag{6}$$

of $\Delta(\mathrm{Mo}) = 0.36$ represents a large discrepancy between one-electron theory and experiment. The experimental situation in Nb is much less clear, with optical experiments in the near-infrared region leading to reported values of Ω_p of 4.8 eV,[12] 5.7 eV,[13] and 7.9 eV,[14] with corresponding values of $\Delta(\mathrm{Nb}) \approx 0.7, 0.6, 0.2$, respectively. The difficulty of extracting the experimental plasma frequency deserves further discussion.

Part of the problem in experimentally determining Ω_p arises because the experimental data for Nb are not well described by the simple Drude form of Eq. (1). In Ref. 12 the data were interpreted in terms of the anomalous skin effect and in Ref. 11 discrepancies were discussed in terms of two types of carriers. Recent calculations of the interband contributions[8] to the dielectric constant indicate that very-low-frequency interband transitions will be a more likely cause of deviation from the Drude formula. In Fig. 1 we have reproduced the joint density of states $G(\omega)$ for interband transitions in both Nb and Mo in the low-frequency region $\omega < 1$ eV as calculated in Ref. 8; the details of the calculation are given in that paper. In Mo the onset of interband transitions occurs at $\omega = 0.2$ eV and the Drude formula should be sufficient below the onset. This is reflected in consistent experimental results.

Figure 1 shows that interband transitions in Nb are already strong at $\omega = 0.1$ eV. We use the constant momentum matrix element approximation to estimate the effect of these transitions. Within this approximation we can write

$$\epsilon_2(\omega) = (2A/\omega^2)G(\omega), \tag{7}$$

where 2 accounts for the spin and $A \simeq 1.2\times10^{-2}$ Ry^3 results in agreement with the measured value at $\omega \simeq 0.2$ Ry. Equation (7) gives an interband contribution to ϵ_2 at $\omega \simeq 0.1$ eV (the lower limit of the experiments quoted above) of the same order of magnitude as the Drude term. Relativistic effects should not be important here, as Koelling *et al.*[15] have shown for Mo that bands 2 and 3 near the Σ and Λ directions of the Brillouin zone, which give rise to the low-energy transitions, are not split by relativistic corrections.

With a simple model we can show that low-energy interband transitions are not likely to resolve the optical mass discrepancy. Consider a single transition at frequency ω_0; the contribution $\Delta\epsilon_1$ to the real part of the dielectric function from this transition is

$$\Delta\epsilon_1 = F_0/(\omega_0^2 - \omega^2), \tag{8}$$

where F_0 is proportional to the oscillator strength.

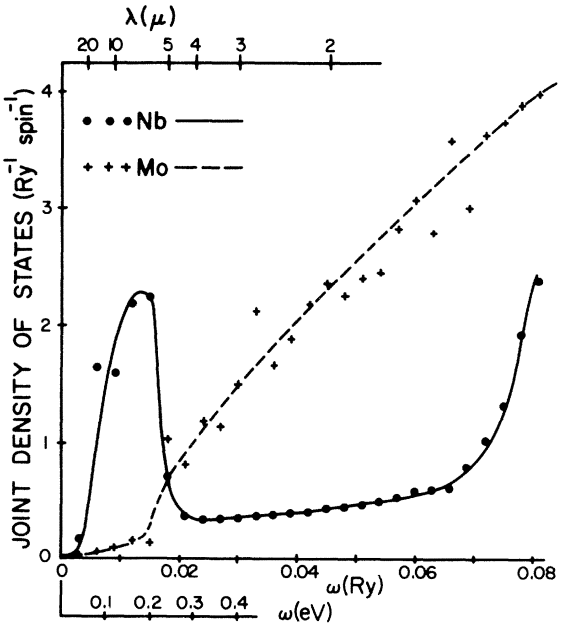

FIG. 1. Joint density of states for interband optical ($Q = 0$) transitions at low frequency $\omega > 1$ eV, for both Nb and Mo. The symbols mark the calculated values; the lines are only guides for the eye. Strong low frequency transitions in Nb are evident. The upper scale gives the wavelength (λ) in microns (μ).

The observed ϵ_1 in the region $\omega > \omega_0$, $\omega > 1/\tau$ will be

$$\epsilon_1(\omega) = 1 + 4\pi i\sigma/\omega + \Delta\epsilon_1 \simeq -(\Omega_p^2 + F_0)/\omega^2. \quad (9)$$

Thus transitions below the region of observation result in an apparent decrease in the optical mass, rather than an enhancement as noted above.

Another consideration which is important in transition metals is that of local field effects arising from the lack of translational invariance of the electron system. The dielectric function (or conductivity) then becomes a matrix $\epsilon(\vec{Q}, \vec{Q}', \omega)$ in momentum space. Wiser[16] has shown however, that within the random phase approximation the inclusion of such crystalline local field effects cannot affect the intraband contribution to ϵ.

A correction to Ω_p which goes beyond the one-electron theory is that due to Fermi-liquid effects. In the Landau theory[17] of Fermi liquids it is assumed that the energy ϵ_k of a quasiparticle is changed by an amount

$$\delta\epsilon_k = \sum_{k'} f_{kk'}\, \delta n_{k'} \quad (10)$$

when a distribution $\delta n_{k'}$ of quasiparticles is excited, where $f_{kk'}$ represents the interaction energy of quasiparticles in states k and k'. The inclusion of the interaction energy leads to a total electric current $\vec{J}$ given by [18,19]

$$\vec{J} = e\sum_k \left(\vec{v}_k + \sum_{k'} f_{kk'}\vec{v}_{k'}\,\delta(\epsilon_{k'})\right)\delta n_k. \quad (11)$$

Writing the Landau-Boltzmann equation in the collision time approximation, the quasiparticle distribution in the presence of an applied electric field $\vec{E}$ is found to be

$$\delta n_k = (-i\omega + 1/\tau)^{-1} e\vec{v}_k \cdot \vec{E}\,\delta(\epsilon_k). \quad (12)$$

The conductivity then has the classical Drude form

$$\sigma(\omega) = (i/4\pi)\,\omega_p^2/(\omega + i/\tau), \quad (13)$$

where the squared plasma frequency ω_p^2 is given by

$$\omega_p^2 = \tfrac{4}{3}\pi e^2\left(\sum_k v_k^2\delta(\epsilon_k) + \sum_{kk'} f_{kk'}\vec{v}_k\cdot\vec{v}_{k'}\,\delta(\epsilon_k)\delta(\epsilon_{k'})\right), \quad (14a)$$

$$\omega_p^2 = \Omega_p^2(1 + A). \quad (14b)$$

The Silin parameter[20] A gives the optical mass enhancement due to quasiparticle interaction. Identifying ω_p with the observed plasma frequency and comparing Eqs. (6) and (14b) leads to $A = -\Delta$. Confirming the conclusions of Bolotin, Mayevskii, and Charikov,[2] we find that a Fermi-liquid correction $A = -0.36$ for Mo will account for the enhanced optical mass which is observed.

For $A = -1$ the quasiparticle interactions make the Fermi surface unstable under small translations. If low-energy interband transitions are indeed causing an over estimate of the plasma frequency in Nb, it may be possible that Nb is approaching this stability limit. Although it is likely to require measurement substantially below 0.1 eV (say, wavelengths in the 10–40-μm range) to determine unambiguously the intraband behavior, such measurements would provide important information on Fermi-liquid effects. In addition, Hopfield[21] has pointed out the usefulness of infrared optical measurements in transition metals in other contexts, particularly that of determining the electron-phonon coupling constant λ from values of the electronic collision time, as well as listing complications which can arise in interpreting the parameters determined by the experiments. The possibility of low-energy interband transitions is an additional complication, and since materials having high superconducting transition temperature T_c have a large density of states $N(0)$, these transitions can be expected to be most prevalent in the high-T_c materials. Since Nb is such a material ($T_c = 9.2\,^\circ$K) and λ is known with some confidence, the measurements proposed here will provide a test of how useful the Hopfield idea will be in this interesting class of materials.

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