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Optical conductivities of iron and nickel

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The interband optical conductivities of ferromagnetic iron and nickel have been computed using energies and wave functions obtained from recent self-consistent band calculations. The results, with the inclusion of an empirical Drude term, are compared with experiments. Incusion of substantial lifetime broadening (0.5–0.7 eV) is necessary to obtain reasonable agreement with measurements in the range of 2–6 eV. A possible self-energy correction is also discussed.

I. INTRODUCTION

The optical properties of transition metals have been the subject of investigation for many years. In particular, the optical conductivities of iron[1–8] and nickel[2,4,5,9–16] have been examined from the near infrared to the far ultraviolet. Because the optical conductivity is readily calculable in a band model, it can be used as a significant test of these models. Such tests are of great interest at the present time because results of photoemission experiments[17] have been interpreted as being in serious conflict with band calculations. Unfortunately, a first-principles calculation of photoemission is far more difficult than that of the optical conductivity.

Previously, calculations of the optical conductivities of iron[15] and nickel[16] have been reported based on band calculations employing the Kohn-Sham exchange potential and including the effects of spin-orbit coupling. However, it has become apparent that the Kohn-Sham potential leads to an overestimate of the exchange splitting in the ferromagnetic state.[18] Additional self-consistent band calculations have been performed[18,19] based on the local exchange-correlation potential of von Barth and Hedin,[20] and incorporating numerous technical improvements in the computational procedures.[21] These calculations are in good agreement with the measured charge and spin form factors and also yield rather good Fermi surfaces. The exchange splitting of the d bands was reduced in comparison with previous results but still seems to be too large in comparison with a value deduced from photoemission experiments.[17] This paper reports the results of an effort to examine further the results of the improved band-structure calculations by means of a computation of the optical conductivity for iron and nickel using energies and wave functions obtained from those calculations. Spin-orbit coupling has, however, not been included in the present studies.

II. PROCEDURE

The frequency-dependent interband optical conductivity is given by the standard formula

$$\sigma(\omega)=\frac{2\pi e^2}{3m^2\omega}\sum_{ln}\int\frac{d^3k}{(2\pi)^3}\,|\langle l\vec{k}\,|\vec{p}\,|n\vec{k}\rangle|^2 f_l(\vec{k})[1-f_n(\vec{k})]\,\delta(E_n(\vec{k})-E_l(\vec{k})-\hbar\omega)\ . \tag{1}$$

The quantities $f_l(\vec{k})$, $f_n(\vec{k})$ are the Fermi occupation probabilities for states $|l\vec{k}\rangle$ and $|n\vec{k}\rangle$, respectively; the remaining notation is conventional. Because we use a basis set of Gaussian orbitals, the matrix elements $\langle lk|\vec{p}\,|nk\rangle$ can be evaluated analytically so that we can retain the $\vec{k}$ dependence of these quantities. The integration is performed numerically, in the irreducible wedge ($\frac{1}{48}$th of the Brillouin zone) by the linear-analytic-tetrahedron method using 506 points for iron and 505 for nickel. This corresponds to a partitioning of the Γ-H line in the Brillouin zone for the body-centered cubic lattice into 20 divisions, while for the face-centered cubic lattice, the Γ-X line is partitioned into 16 divisions. The techniques employed in this integration are essentially those described in Ref. 21. An additional complication in the present case arises from the $\vec{k}$-dependent matrix elements, which are linearly interpolated through the

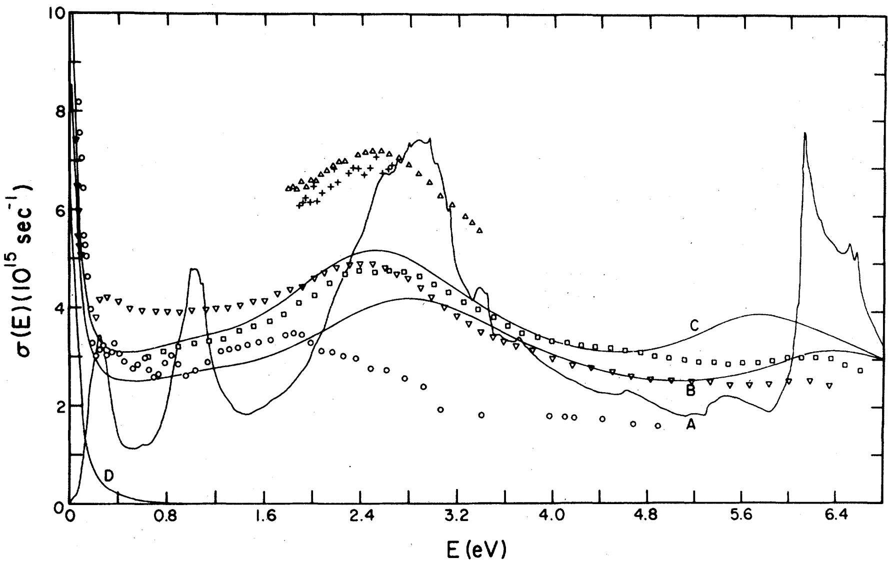

FIG. 1. Optical conductivity of iron. Curves: *A*, interband conductivity from Eq. (1); *B*, conductivity including lifetime broadening and a free-electron (Drude) contribution; *C*, including a "self-energy correction" according to Eq. (3); *D*, free-electron contribution. Symbols representing experimental points: Δ, Ref. 6; +, Ref. 4; □, Ref. 2; O, Ref. 1; ∇, Ref. 8.

tetrahedra, based on the values at the corners.

Initially, the conductivity is calculated in the sharp limit ($\tau \rightarrow \infty$) at energies between 0.001 and 0.5 Ry (0.01 and 6.8 eV). We calculate only the interband portion of the conductivity and so we must add a Drude term $\sigma_0/(1+\omega^2\tau'^2)$ to take account of the free-electron conductivity. The Drude parameters ($\sigma_0 = 6.4\times10^{15}$ sec^{-1} and $\tau' = 9.12\times10^{-15}$ sec for iron and $\sigma_0 = 18.6\times10^{15}$ sec^{-1} and $\tau' = 11.3\times10^{-15}$ sec for nickel) were obtained from Lenham and Treherne.[22] We are not aware of more recent values. These parameters yield good results for the low-energy conductivities of both elements and seem to be sufficiently accurate. The calculated conductivity (see Figs. 1 and 2) shows sharp structure which is obviously not present in the experimental observations. Presumably this is due to substantial lifetime broadening. We have therefore studied the effect of

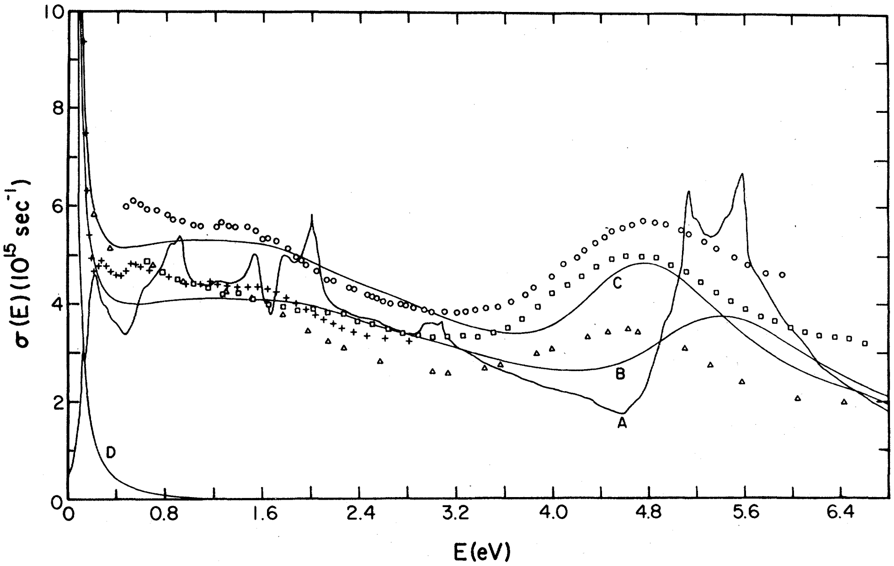

FIG. 2. Optical conductivity of nickel. Curves carry the same labeling as in Fig. 1. Symbols representing experimental points: □, Ref. 2; O, Ref. 13; Δ, Ref. 9; +, Ref. 11.

introducing an empirical relaxation time, and attempted to determine values which best reproduce the width of the major structure present. A value of $1/\tau = 0.5$ eV seemed to yield suitable results for nickel while 0.7 eV seems better for iron.

In both iron and nickel, as well as a recent study of vanadium,[23] the major structure in the calculated conductivities appears to be shifted to higher energy in comparison with experiment as well as broadened. This result was also obtained in our previous studies.[15,16] It has not been changed through the introduction of an expanded orbital basis for the wave functions, which should produce substantially improved excited-state wave functions. It is possible that there is some defect or omission in the local-density potential employed which tends to produce d bands which are too broad. In the case of nickel, this conclusion has been deduced from the results of photoemission experiments.[17]

In the present work we have examined this situation empirically through a procedure introduced by Janak *et al.* in a study of the optical conductivity of Cu.[24] They noted that the local-density approximation may not give the energies of excited states (electron or hole) correctly. They modified the energies of the band states by including an electron self-energy correction based on the work of Sham and Kohn.[25] After many simplifying approximations are introduced, an expression is obtained for corrected band energies $\tilde{E}_n(k)$ which involves a single empirical parameter λ

$$\tilde{E}_n(\vec{k}) = E_n(\vec{k}) + \lambda[E_n(\vec{k}) - E_F] \quad . \tag{2}$$

Substitution of Eq. (2) in Eq. (1) leads to a revised conductivity $\tilde{\sigma}(\omega)$ which is given by

$$\tilde{\sigma}(\omega) = \frac{1}{(1+\lambda)^2}\,\sigma\left(\frac{\omega}{1+\lambda}\right) \quad . \tag{3}$$

Janak *et al.* found that the choice $\lambda = 0.08$ gave a good match between calculated and observed conductivities. In the present case, we find that negative values of λ are needed to produce agreement: $\lambda = -0.1$ for iron and -0.12 for nickel work reasonably well. The negative value of λ has the effect of reducing energy-level differences.

III. IRON

The optical conductivity of iron is shown in Fig. 1 and includes both calculated and experimental results. We will consider first curve A which shows sharp structure and which represents the interband conductivity only with no modifications due to lifetime or other self-energy effects. Peaks are found near 0.25 and 4.0 eV, a major (and broad) peak near 2.8 eV, and another broad structure with a peak and a shoulder near 6.0 eV. Most of the conductivity is due to transitions within the minority-spin bands. The majority-spin d bands contribute very little to the conductivity in the energy range shown on the graph, since these states are almost entirely occupied.

We also determined the regions in the Brillouin zone which give rise to the larger contributions to the conductivity. The maximum at 0.25 eV arises mainly from transitions along the Δ axis near the Γ point, while transitions near the N point are responsible for the 1 eV peak. A large region contributes to the 2.8 eV peak but transitions near the P point and the N point are between relatively low-lying bands (Λ_3, Σ_1) and those lying just above the Fermi energy (Λ_1, Σ_4), while transitions near the H point are between bands just below $E_F(\Delta_5)$ and relatively high-energy bands (Δ_1). The peak near 6 eV coincides with the onset of transitions from very low-lying bands (Σ_1) near the N point to those just above $E_F(\Sigma_4)$.

Curve B of Fig. 1 shows the sum of the interband conductivity and the Drude intraband conductivity (curve D), including lifetime broadening with a choice of reciprocal lifetime of 0.7 eV. This value was chosen so that the width of the calculated peak at 2.8 eV would agree reasonably well with that of the 2.4 eV peak as observed by Johnson and Christy.[2] This broadening destroys much of the structure of the conductivity in a sharp limit, and leaves only a barely noticeable bump at 1 eV plus the more substantial maxima near 2.8 and 6.3 eV. The Drude term becomes important below 0.4 eV. Since the parameters for this term were chosen empirically, agreement with experiment is expected, and does seem to occur at low energies.

Structure in the energy range 0.4–2.0 eV has been reported by some authors.[1,3,7,8] In particular, Weaver *et al.*[8] find that after a Drude term is subtracted the interband conductivity has a shoulder at 0.8 eV. Thermoreflectance measurements also show structure near this energy.[8] Serious disagreements between different experimental groups are obvious at higher energies. However, in the range of 2–5 eV, all except one of the experiments report a smooth maximum with a peak near 2.5 eV which corresponds to the maximum in the calculated conductivity at 2.75 eV. There is an indication of our maximum near 6 eV in the results of Johnson and Christy[2] while it clearly appears in the work of Moravec *et al.*[5]

In curve C, we show the result of including in addition to lifetime broadening, a "self-energy" correction of the sort discussed by Janak *et al.*[24] [Eq. (3)] with $\lambda = -0.1$. While this simple type of correction must be considered to be rather speculative in nature, it does appear to improve the agreement with experiment in regard to the position of the 2.4 eV maximum and also in regard to its magnitude. However, the maximum at 6.4 eV appears in contrast to be shifted to too low an energy in comparison with that observed by Moravec *et al.*[5] The magnitude of the peak also becomes too large.

IV. NICKEL

The optical conductivity of nickel is shown in Fig. 2. The calculated interband conductivity, curve *A*, exhibits a series of peaks at 0.2, 0.9, 1.5, 2.0, and 3.1 eV, plus a large maximum with two peaks at 5.15 and 5.55 eV. We have not been able to interpret the structure in terms of transitions near symmetry points: a detailed examination of the transitions which contribute to each peak shows participation from several regions of the Brillouin zone.

The analysis shows that most of the low-energy optical conductivity is due to transitions within the minority-spin band. The large structure in the 5–6 eV range has contributions from both spins, and is strongly dominated by transitions from the lowest *d* band to states close to the Fermi level. Hence, the displacement of the observed peak from the calculated one may be an indication that the computed *d* bands are too wide, as has been asserted on the basis of photoemission measurements.[17]

Although there is rather good agreement between the theoretical and observed conductivity in regard to the general shape and order of magnitude, there is little indication of sharp structure in the experimental results except possibly at low energy. As in the case of iron, we believe that substantial lifetime broadening is present. Curve *B* shows the conductivity including the Drude free-electron contribution and with a broadening of the interband conductivity corresponding to $\tau^{-1}=0.5$ eV. This seems to be reasonably satisfactory, although a somewhat larger value (0.7 eV, say) would produce results of the same quality. What is clear is that the broadening can not be as large as the 2.0 eV suggested by Pendry and Hopkinson[26] for states at the bottom of the *d* band, since this would essentially wash out all of the structure in the 5–6 eV range.

As in the case of iron, we have examined the effect of including a "self-energy correction" according to Eqs. (2) and (3). In this case, a value of $\lambda=-0.12$ produces curve *C*. This value of λ displaces the high-energy maximum of the broadened conductivity from 5.45 to 4.8 eV where it is then in reasonable agreement with observation.

Structure in thermoreflectance measurements in the low-energy range (0.2–0.4 eV) has been reported.[27] There is also a peak at 0.3 eV in one of the optical conductivity measurements.[11] One would certainly expect that lifetime broadening is much smaller at these energies. This structure may be associated with the peak in the calculated conductivity at 0.2 eV. However, if the exchange splitting in nickel is about 0.3 eV, as has been proposed,[17] then this peak could be associated with a transition across the gap between $\uparrow$ and $\downarrow$ states near the top of the *d* band, which becomes weakly allowed when spin-orbit coupling is considered.[16]

V. CONCLUSIONS

The optical conductivity obtained straightforwardly from band calculations agrees in regard to general order of magnitude with the observed conductivities of both iron and nickel. Large systematic discrepancies between the results of different experiments exist, and allow only a cautious statement about magnitudes. The absence of sharp structure in the observed conductivities, at least for photon energies of 1 eV or greater, appears to be the result of lifetime broadening. This is probably mainly associated with the *d* band hole. The broadening seems to be of the order of 0.5–0.7 eV. Agreement between theory and experiment is improved over most of the energy range considered if an energy-dependent "self-energy" correction is made to the band energies; but the fundamental basis of this correction requires further investigation. Furthermore, the values of the parameter λ [Eq. (2)] correspond to approximately a 10% narrowing of the *d* band compared to the original band calculation. This is a change in the same direction as suggested by Eastman *et al.*[17] for nickel, but of a considerably smaller magnitude. In the case of iron, the introduction of band narrowing moves the 6.2 eV peak to too low an energy. This suggests that there is no strong evidence for overall band narrowing in that element.

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