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Electron energy-loss spectroscopy of TiS_2

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We have made a high-resolution (0.12 eV) measurement of the electron energy-loss spectrum of the layered compound TiS_2 for energy loss E in the range 0.5–150 eV. After subtracting the contribution of plural scattering, we performed a Kramers-Kronig analysis to obtain the dielectric function. The reflectivity and absorption coefficient calculated with this dielectric function are in good agreement with direct optical measurements. Comparing our results with the band-structure calculation of Zunger and Freeman, we find substantial agreement between observed peaks and the predicted energies of the allowed transitions. A detailed comparison with theory awaits a calculation of $\epsilon_2(E)$.

I. INTRODUCTION

The layered compound TiS_2 has both unusual physical properties and a significant practical application as the cathode in a new high-energy battery.[1] Experiments on high-purity stoichiometric samples indicate a semimetallic behavior with a temperature-independent Hall coefficient, and an unusual electrical resistivity that varies purely as T^2 is observed from at least 10 to 400 K.[2] Optical experiments, however, have indicated that TiS_2 is a semiconductor. Early band-structure calculations[3,4] supported this and predicted a direct gap of 2 eV and a smaller indirect gap of 1.4 eV. A more recent self-consistent band-structure calculation by Zunger and Freeman[5] also finds TiS_2 to be a semiconductor, but with considerably smaller gaps (direct 0.8 eV, indirect 0.2–0.3 eV). Wilson[6] has argued that the experimental data are consistent with a "dirty" semiconductor model of TiS_2, and recent measurements[7] of the pressure dependence of the Hall coefficient tend to confirm this view.

The present experiment was undertaken to test the accuracy of the calculated electronic structure. Electron energy-loss spectroscopy, in the forward direction, measures the response function $g_2(E) = \mathrm{Im}[-1/\epsilon(q=0,E)]$, where $E=\hbar\omega$ is the energy lost by the scattered electron. In contrast to optical experiments, in energy-loss spectroscopy it is easy to measure the relevant quantity over a large energy range (e.g., 0–150 eV). Therefore, a Kramers-Kronig procedure may be performed without a major extrapolation, and one obtains both $\epsilon_1(E)$ and $\epsilon_2(E)$, which enables direct comparison with theory. Though inferior to that of some optical experiments, our instrumental energy resolution, 0.12 eV, is sufficient for the present task. We test our results by using our derived $\epsilon_1(E)$ and $\epsilon_2(E)$ to compute the reflectivity and the absorption coefficient, and we find good agreement with those measured optically.[8,9] The optical measurements cover the range 0–12 and 0–4 eV, respectively.

Our results are concisely summarized in Fig. 1, where we plot our derived optical conductivity $\sigma(E) = (E/\hbar)\epsilon_2(E)$ of TiS_2 from 0 to 20 eV. Since theoretical calculations of neither $\epsilon_2(E)$ nor the joint density of states exist presently, our comparison with theory can only be qualitative. It is limited to comparing to the energies of optical transitions as calculated by Zunger and Freeman. These energies are indicated in Fig. 1. At this level, the agreement between theory and experiment is excellent. In particular, our value for the direct gap, 0.8 ±0.1 eV, coincides with theory. Since we have not measured the indirect gap, we

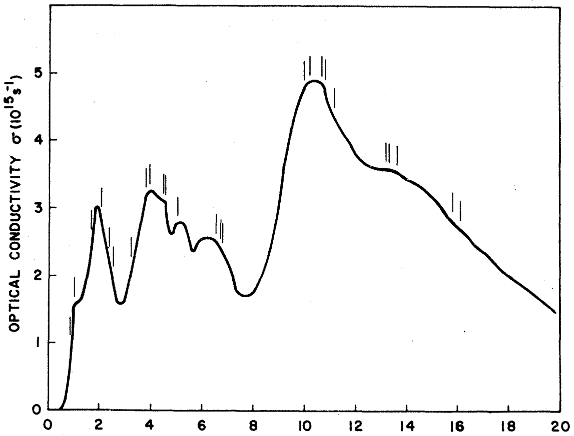

FIG. 1. Optical conductivity of TiS_2 derived from electron energy-loss data by Kramers-Kronig analysis. Threshold energies of dipole-allowed transitions calculated by Zunger and Freeman are indicated.

cannot comment on the semiconductor-semimetal controversy, but we do conclude that the results of Zunger and Freeman are superior to earlier band structures for TiS_2.

II. EXPERIMENT

TiS_2 powder was prepared by direct reaction of titanium wire with sulfur. Single crystals of TiS_2 were grown from this powder by vapor transport in a closed quartz tube containing a 5-mg/cm^3 excess of sulfur. The tube was in a temperature gradient from 700 to 600°C. After approximately a month, single crystals as large as 6 mm^2 and 0.3 mm thick were obtained. The c-axis lattice constant was found to be 5.6985 ±0.0005 Å, and the room-temperature resistivity was 1950 $\mu\Omega$ cm. Both of these values indicate a high degree of stoichiometry (i.e., $Ti_{1+x}S_2$ where $x < 0.01$). The single crystals were cleaved many times using cellotape, then floated off the tape in trichloroethylene and fished out of the solvent onto a 3-mm electron microscope grid. An electron diffraction pattern indicated good crystal quality. The sample was not uniform in thickness but consisted of a small thin region (~1000 Å) surrounded by thicker material (> 3000 Å) that did not transmit the 16-keV electrons. The sample was oriented with its c axis along the beam and only electrons scattered in the forward direction ($\theta < 0.1°$) were detected. The incident electrons had an energy of 16 keV and the overall energy resolution of the system was 0.12 eV.

In Fig. 2 we show raw data for TiS_2, consisting of points from $E = 0$ to 150 eV at intervals of 0.16 eV. The range from 0 to 10 eV, measured with a denser point spacing (0.01 eV), is shown in the inset. The fast rise below 0.5 eV is due to the tail of the strong unscattered beam (full width at half maximum 0.1 eV), and obscures any very-low-energy structure. The single scattering spectrum[10] is proportional to

$$S_1(E,\theta) = (2\pi^2 a_0 E_0)^{-1}\, g_2(E)/(\theta^2 + \theta_E^2)$$

averaged over the angular resolution of the system (0.1°). Here E_0 is the incident electron energy, a_0 is the Bohr radius, and $\theta_E = E/2E_0$. Since the response function $g_2(E) = \epsilon_2(E)/[\epsilon_1^2(E) + \epsilon_2^2(E)]$ is not simply proportional to $\epsilon_1(E)$ or $\epsilon_2(E)$, it is not generally possible to identify the origin of the features in Fig. 2. The only structures that may be readily assigned are the sharp rise at 0.8 eV (see inset to Fig. 2) which we attribute to the direct optical gap, and the large plasmonlike resonance at 21.5 eV. This resonance corresponds to the damped collective oscillation of the conduction and valence electrons. Because this resonance is so large (as it is in other layered compounds)[11] and because the sample is relatively thick, we see a significant set of plural scattering peaks at 43, 64.5, and 85 eV.[12] The peak at 43 eV is largely caused by two independent plasmon creations and it prevents a clear observation of the Ti $3p \rightarrow 3d$ core excitation seen at 45.9 eV in Ti metal.[13] The only previous energy-loss spectrum of TiS_2 (Ref. 14) had a much poorer energy resolution, a smaller total range, and was not subjected to a Kramers-Kronig analysis.

III. DATA ANALYSIS

In order to obtain the response function $g_2(E)$, we must correct the raw data for the overall energy and angular dependence of the scattering cross section, the finite angular resolution of the spectrometer, and the contributions from both plural and surface scattering. These effects are interrelated and may be treated self-consistently

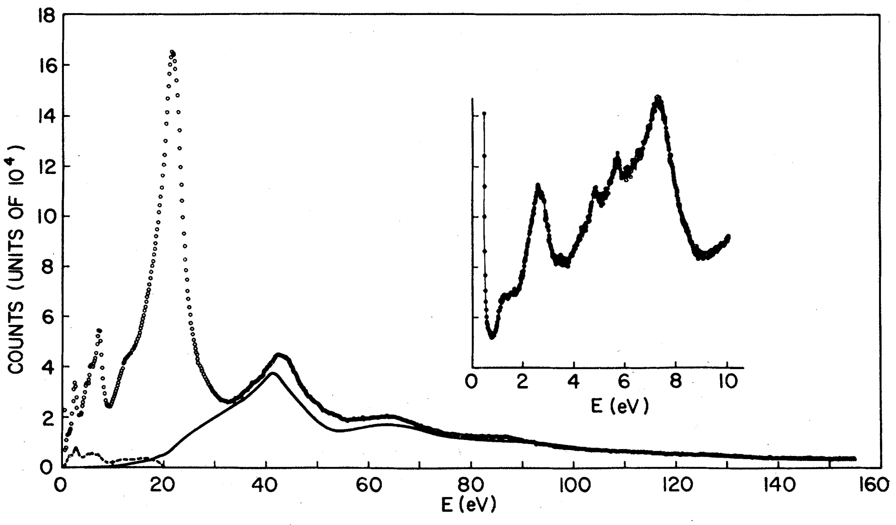

FIG. 2. Raw energy-loss data for TiS_2 (upper curve and inset). The solid and dashed curves represent our calculation of plural scattering (peaking beyond 40 eV) and surface scattering (largely confined to low E).

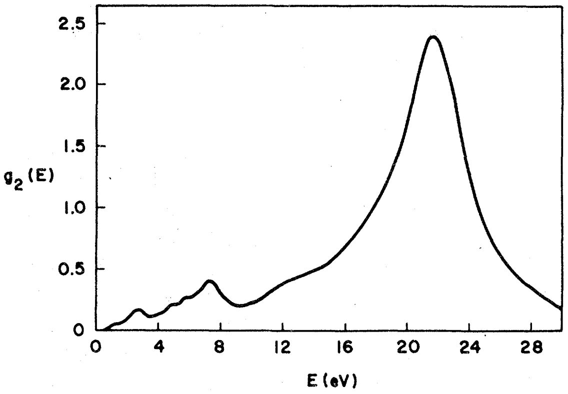

FIG. 3. Response function $g_2(E)$ for TiS_2.

by a procedure described in Ref. 10. The plural and surface scattering corrections are shown in Fig. 2. Because the plural scattering is strong and the correction only approximate[15] (e.g., it assumes an isotropic medium), the corrected data beyond 25–30 eV are correspondingly approximate. However, the plural scattering correction is small at small E, where the data exhibits the most structure. Because of the uncertainty in the data at high energy, the oscillator-strength sum rule [Ref. 10, Eq. (2.4)] which depends strongly on $g_2(E)$ or $\epsilon_2(E)$ at high E can be used only approximately. This lack of self-consistency should only affect overall normalizations, but not the structure obtained in the Kramers-Kronig analysis.

The corrected data, $g_2(E)$, are shown in Fig. 3 in the range from 0 to 30 eV. From $g_2(E)$ over the range 0–150 eV, we have derived by Kramers-Kronig analysis[10,16]: $\epsilon_1(E)$ and $\epsilon_2(E)$ (Fig. 4), the absorption coefficient (Fig. 5), the normal-incidence reflectivity (Fig. 6), and the optical con-

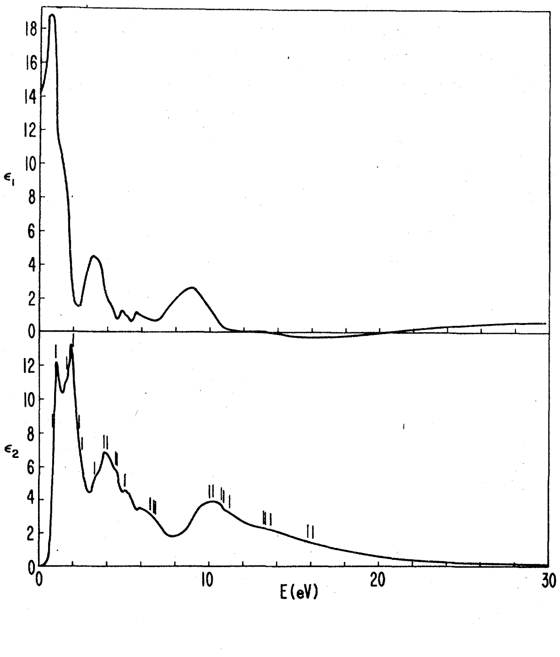

FIG. 4. Derived real and imaginary parts of the dielectric constant $\epsilon(E)$ for TiS_2. Threshold energies for dipole-allowed transitions calculated by Zunger and Freeman are indicated.

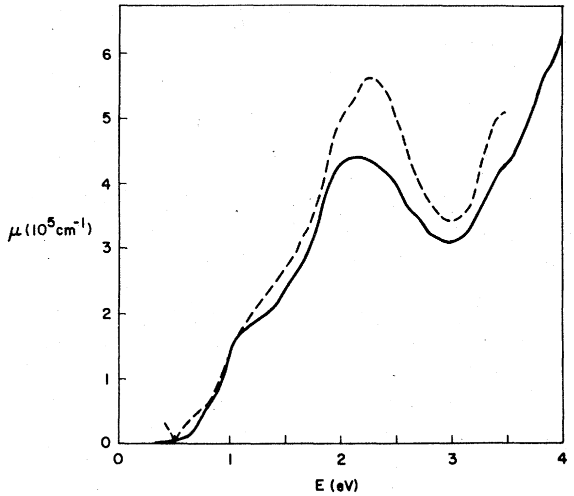

FIG. 5. Derived absorption coefficient for TiS_2 (solid curve) compared to direct measurement (dashed curve) of Ref. 9.

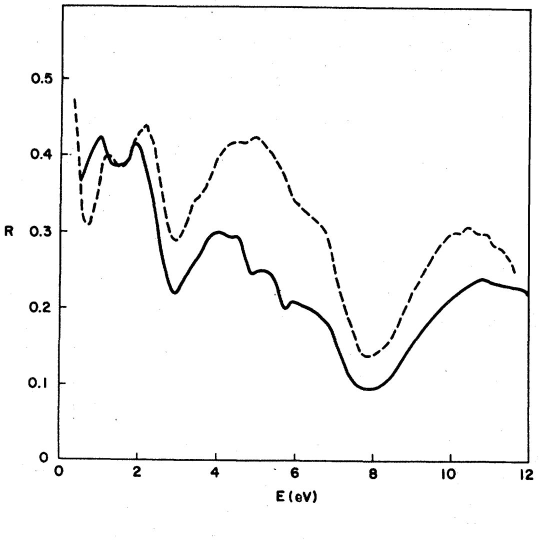

FIG. 6. Derived normal-incidence reflection coefficient for TiS_2 (solid curve) compared to direct measurement (dashed curve) of Ref. 8.

ductivity (Fig. 1). A direct measurement of the absorption coefficient by Beal, Knights, and Liang[9] has also been plotted in Fig. 5. We find good agreement with our derived values. The absolute magnitudes differ by less than 20% even though Beal *et al* only claim accuracy within a factor of 2. The direct measurement had a higher resolution and was performed at liquid-helium temperature, and the results show slightly more fine structure. The reflectivity measured by Greenaway and Nitsche[8] is plotted together with our derived result in Fig. 6. The two agree in terms of the energies of the principal features, but the absolute and relative magnitudes differ by 25%. The direct measurements also extend to lower energies (< 0.5 eV), where the effect of the free carriers begin to play a role. The direct gap at 0.8 eV is clearly seen in ϵ_2 and σ, as well as in the raw data and $g_2(E)$. The energies of dipole-allowed transitions at symmetry points calculated by Zunger and Freeman[5] are indicated in Figs. 1 and 4.

IV. CONCLUSIONS

The Kramers-Kronig analysis of our high-resolution electron energy-loss data has provided us with the fundamental optical properties, $\epsilon_1(E)$ and $\epsilon_2(E)$, of TiS_2 from $E = 0.5$ to 30 eV. Future calculations of the electronic structure of TiS_2 which include the matrix elements may be tested against these results.

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[1] M. S. Whittingham, Science 192, 1126 (1976).

[2] A. H. Thompson, Phys. Rev. Lett. 35, 1786 (1975).

[3] R. B. Murray and A. D. Yoffe, J. Phys. C 5, 3038 (1972).

[4] H. W. Myron and A. J. Freeman, Phys. Rev. B 9, 481 (1974).

[5] A. Zunger and A. J. Freeman, Phys. Rev. B 16, 906 (1977).

[6] J. A. Wilson, Solid State Commun. 22, 551 (1977); Phys. Status Solidi B 86, 11 (1978).

[7] R. H. Friend, D. Jerome, W. Y. Liang, J. C. Mikkelsen, and A. D. Yoffe, J. Phys. C 10, L705 (1977).

[8] D. L. Greenaway and R. Nitsche, J. Phys. Chem. Solids 26, 445 (1965).

[9] A. R. Beal, J. C. Knights, and W. Y. Liang, J. Phys. C 5, 3531 (1972).

[10] L. A. Feldkamp, L. C. Davis, and M. B. Stearns, Phys. Rev. B 15, 5535 (1977).

[11] M. G. Bell and W. Y. Liang, Adv. Phys. 25, 53 (1976).

[12] The strength of the nth order of multiple scattering goes as $[t g_2(E)]^n$, where t is the thickness of the sample. The plasmon peak in TiS_2 has $g_2(E) \approx 2.5$, compared with <1 for Cu and ~16 for Al.

[13] B. Sonntag, R. Haensel, and C. Kunz, Solid State Commun. 7, 597 (1969); C. Wehenkel and B. Gauthe, Phys. Status Solidi B 64, 515 (1974).

[14] R. Vilanove, C. R. Acad. Sci. B 271, 1101 (1970).

[15] An electron detected in the forward direction could have been scattered out of this direction and then back. Our plural and surface scattering corrections take such processes into account. We include the angular dependence of the cross section, but ignore any possible variation of $g_2(E)$ or $\epsilon_2(E)$ with wave vector. We also ignore the fact that TiS_2 does not have cubic symmetry.

[16] Because our very-low-energy data (≤ 0.5 eV) are obscured by the tail of the unscattered beam, we do not observe any effect of the free carriers in TiS_2. In our Kramers-Kronig analysis we treat TiS_2 as an insulator with $\epsilon_1 \rightarrow 14$ as $E \rightarrow 0$ [G. Lucovsky, W. Y. Liang, and R. M. White, Solid State Commun. 19, 303 (1976)]. The free carriers have a plasma oscillation in the infrared and would lead to a narrow peak in $g_2(E)$. Ignoring this peak in $g_2(E)$ causes negligible error for all E away from the immediate vicinity of the plasma energy. Neglect of this plasma oscillation causes our derived absorption and reflection coefficients to lack the characteristic low-energy structure observed in the direct measurements.