

Infrared study of the electronic instabilities in tantalum disulfide and tantalum diselenide

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Reflectivity spectra of the $1T$ form of TaS_2 and the $2H$ form of $TaSe_2$ have been measured over the spectral range 0.04–5.0 eV. Spectra were taken at temperatures above and below the phase transitions which have been associated with charge-density waves. Kramers-Kronig analysis shows a metallic-type conductivity at high temperatures in TaS_2 . This conductivity is removed below 0.5 eV by the phase transitions but no sharp gap structure appears. In $TaSe_2$, an absorption peak appears at 0.3 eV. The spectra are related to the charge-density-wave picture of the transitions.

I. INTRODUCTION

There has been widespread interest in the past few years in chalcogenide layered compounds such as TaS_2 , $TaSe_2$, and related crystals. Members of this group of compounds range in behavior from superconducting through metallic to semiconducting and often individually show transitions as a function of temperature, pressure, or doping. The structure and physical properties of this broad group of materials have been reviewed by Wilson and Yoffe.¹ Wilson *et al.*² have emphasized the two-dimensional nature of the Fermi surface in the d^1 compounds and its tendency to be unstable to distortions (electronic instabilities) connected with the Fermi-surface shape. The $1T$ polytype of TaS_2 is somewhat unique in that it undergoes two phase transitions as its temperature is varied. At temperatures above 350 K the conductivity is temperature independent and comparable in magnitude to many metallic d -band compounds. On cooling through each of the phase transitions the conductivity drops abruptly. Arguments based on the conductivity sum rule show that there should be optical-absorption peaks connected with these phase transitions.³ The $2H$ polytype of $TaSe_2$ shows only a bend in its conductivity near 120 K; however, recent electron-diffraction and neutron-scattering studies indicate a phase transition in this material also. The work reported here is a reflectivity study of $1T$ - TaS_2 and $2H$ - $TaSe_2$ made at temperatures near the phase transitions in the wavelength range of 0.2 through 30 μm . Previous reflectivity studies of chromium metal^{3,4} and of α -NiS showed absorption peaks near 10 μm which correlated with phase transitions in these materials. The present study shows absorption structure in both of these tantalum compounds; however, there are considerable differences between them. Only the $2H$ - $TaSe_2$ shows a well-defined absorption peak.

II. EXPERIMENTAL

The crystals used for this study were prepared by iodine-vapor transport with excess chalcogen in a sealed quartz tube.⁶ The method of preparation yielded crystals of a size (approximately 4 \times 6 mm) and surface quality that allowed us to make reflectivity measurements with the infrared electric field parallel to the layer direction with no special surface preparation. Prior to making reflectivity measurements one-half of the crystal surface was covered with an evaporated layer of Al. This was done in order to obtain a reference surface to allow absolute reflectivity measurements. Reflectivity measurements of the as-grown surface of the crystal were made with reference to the reflectivity of the Al evaporated surface and also with reference to a separate plane front-surface mirror. This double reference was made in order to verify the optical quality of the as-grown crystal surface. At all wavelengths the reflectivities obtained using either the Al evaporated on the grown surface or the plane mirror as the reference agreed to within $\pm 1\%$. Reflectivity measurements were made continuously from 0.2 through 1.5 μm at room temperature using a Beckman DK-2A ratio recording spectrometer. Point-by-point reflectivity measurements were made from 0.55 through 30 μm with the crystals held at various temperatures near the phase transitions using a prism spectrometer. Temperature was maintained constant to ± 2 K. In addition, continuous temperature scans were made at a fixed wavelength of 8 μm for the TaS_2 .

III. RESULTS

Figure 1(a) shows the phase transitions which occur in TaS_2 ($1T$) as abrupt changes in reflectivity while heating or cooling the sample. These results show the higher temperature transition to be centered at 352 K with a hysteresis of 3 K and the lower transition to be centered near 200 K with a

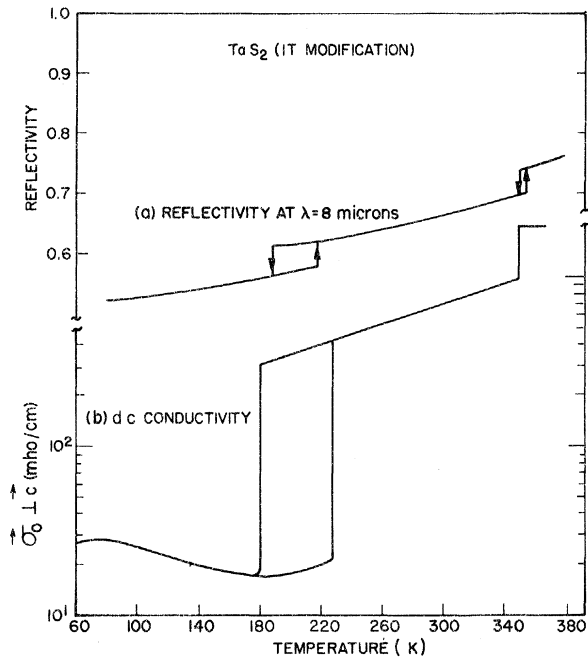


FIG. 1. (a) Infrared reflectivity at 8- μm wavelength measured as a function of temperature for the electric field perpendicular to the c axis. Two abrupt transitions with hysteresis are detected. (b) dc conductivity of a different sample grown in the same manner as the sample in (a).

hysteresis of 30 K. Figure 1(b) shows the dc conductivity measured on a different sample over the same temperature range. Slightly different transition temperatures were obtained. Similar temperature scans for $2H\text{-TaSe}_2$ at $\lambda = 5 \mu\text{m}$ showed very small and smooth reflectivity changes with a slight knee at 120 K.

Kramers-Kronig analysis has been performed on the reflectivity spectra to obtain the optical constants. The results for $1T\text{-TaS}_2$ are plotted in Fig. 2. We show the real part of the optical conductivity σ' . The dashed portions indicate some uncertainty due to the extrapolation methods used. Since little temperature dependence was observed for wavelengths shorter than $1 \mu\text{m}$, we have appended our 300-K visible and ultraviolet spectrum to all the different temperature spectra for the Kramers-Kronig procedure. Figure 3 shows the results of Kramers-Kronig analysis of the $2H\text{-TaSe}_2$ reflectivity spectra. A significant (but weak) peak appears near 0.3 eV at low temperatures. This feature is seen more clearly in the original reflectivity spectra shown in Fig. 4.

IV. DISCUSSION

A. Low-temperature phases of $1T\text{-TaS}_2$

The dc conductivity of $1T\text{-TaS}_2$ has been measured for current parallel to the crystalline layers

by Thompson *et al.*⁷ and by DiSalvo *et al.*⁸ Their results are similar to Fig. 1. The present results and those of DiSalvo *et al.* on similar samples find lower conductivities in the two low-temperature phases than obtained by Thompson *et al.* These lower values are listed near each curve in Fig. 2. The 80-K reflectivity we measure agrees closely with the 4.2-K measurements of Benda.⁹ He has not measured to wavelengths longer than $4 \mu\text{m}$, however, nor calculated the optical conductivity. We find that the infrared conductivity extrapolates towards the dc values though there may be spectral structure below our frequency range for the low-temperature phases. Thompson *et al.* suggest that the low-temperature phase is semiconducting and deduce an activation energy of 10^{-4} eV. This result must be questioned since the energy gap implied by this result is many times smaller than kT . Their activation energy is 2000

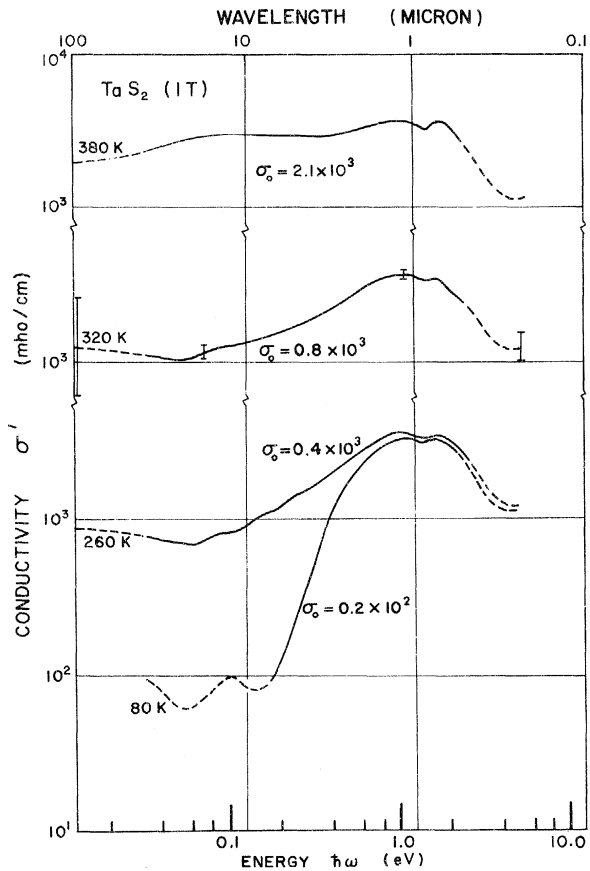


FIG. 2. Real part of the infrared conductivity for four temperatures in $1T\text{-type TaS}_2$. These spectra were obtained by Kramers-Kronig analysis of reflectivity spectra taken with the beam parallel to the c axis of the crystals. Typical uncertainties are shown by bars. The dashed regions are more uncertain since they depend on extrapolation of the measured data to higher and lower energies.

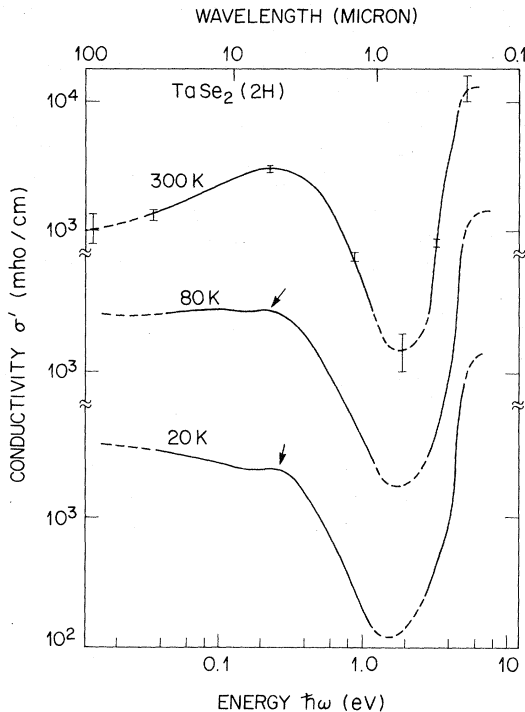


FIG. 3. Conductivity spectra for three temperatures in 2H-type TaSe₂ using the same geometry and procedures of Fig. 2. Typical uncertainties are shown as in Fig. 2. The weak features marked by arrows are discussed in the text and are shown expanded in Fig. 4.

times smaller than the energy of the prominent absorption edge we see near 7 μm ($T = 80\text{ K}$). If the lowest-temperature phase was a normal semiconductor, then the broad band which begins near 7 μm (0.18 eV) and peaks near 1 μm (1.2 eV) arises from transitions between states far removed from the band gap.

As the temperature is increased to 260 K, Thompson *et al.* find a change in activation energy to 0.02 eV ($\lambda = 62\ \mu\text{m}$).⁷ This energy is below our spectral range. If this phase (between 220 and 350 K) was a simple well-behaved semiconducting phase, then the measured activation energy would suggest a gap near or above 0.04 eV. Even with thermal population changes, we would expect little temperature variation in the spectra above 0.1 eV ($\lambda = 12\ \mu\text{m}$). The substantial measured changes between 260 and 320 K show that considerable band rearrangement must be occurring in this temperature range and that an interpretation in terms of a simple semiconductor phase was incorrect.

B. High-temperature phase

We now discuss the high-temperature (most metallic) phase and the nature of the transitions. If we assign 1 free electron per Ta atom, the carrier density is 1.7×10^{22} electrons/cm³. Mat-

theiss has performed augmented-plane-wave (APW) band calculations for 1T-TaS₂.¹⁰ He finds a manifold of *d*-state bands separated by approximately 1.3 eV from a group of filled bands derived primarily from the sulphur 3*p* orbitals. The Fermi level cuts through portions of the lowest *d* band, giving Fermi surfaces centered on zone-boundary faces which are parallel to the *c* axis. The conductivity sum rule may be applied to these mobile carriers which provide conductivity perpendicular to the *c* axis. The data of Fig. 2 show that above 3000 cm⁻¹ (0.37 eV) σ is approximately independent of temperature. If we attribute $\sigma_F \sim 1500$ mho/cm to those carriers at 380 K which are removed by the phase transition, then we find

$$\int_0^{3000\text{ cm}^{-1}} \sigma_F d\omega = 4.5 \times 10^6 \text{ mho/cm}^2. \quad (1)$$

This value is 7.5 times smaller than would be given by 1 free (i. e., $m^* = m_e$) electron per Ta

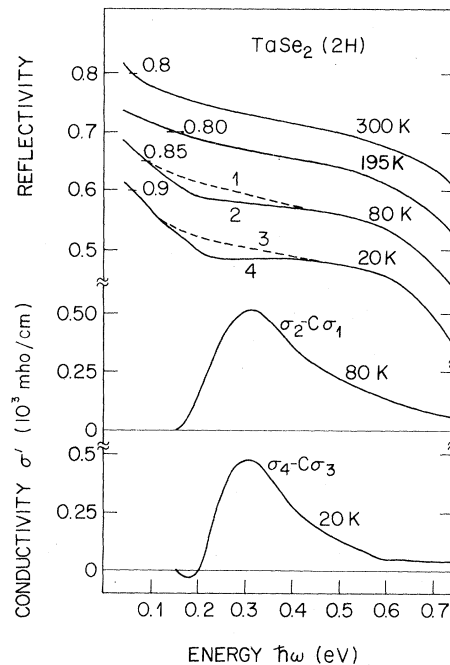


FIG. 4. Reflectivity spectra of TaSe₂ showing the gap feature near 0.3 eV at low temperatures. To subtract the background the reflectivity was interpolated as shown by the dashed curves. Kramers-Kronig analysis was done on these curves to yield σ_1 and σ_3 . This procedure does not allow for broad (frequency independent) level shifts connected with CDW formation. σ_1 and σ_3 are therefore scaled by *c* (about 0.86) to give zero conductivity near 0.15 eV when subtracted as shown at the bottom of the figure. The magnitude of the net absorption is probably uncertain by a factor of 2 using these procedures. The resultant conductivity peak at 0.3 eV shows a distinct broadening as the transition temperature is approached from below.

atom. This result implies that the electrons have a large mass for motion in the basal plane, or that even at $T = 380$ K there are already gaps in the bands which are not included in the Mattheiss calculation. Such gaps would certainly be consistent with electron-diffraction results.² The major peak near 1 eV in Fig. 2 may be the direct gap between the p and d states, which suggests that the APW calculation should be adjusted to reduce the calculated p - d separations.

As the sample is cooled through the 350-K transition, there is a distinct drop both in the dc and the infrared conductivities. Since the sum-rule integral over the entire spectrum must remain constant, we expect the loss of 4.5×10^6 mho/cm² given by Eq. (1) to be made up by a peak or other excess absorption elsewhere in the spectrum at 320 K. This amount could be made up by a very small rearrangement of the tremendous optical strength in the peak above 1 eV. Experience with other systems showing transitions suggests that the peak may occur at lower frequencies, however. In Cr metal there is a transition at $T_N = 312$ K which occurs because of electron-hole interactions which result in a spin-density wave (SDW). The SDW causes small gaps to open in the Fermi surface of energy⁴

$$\hbar\omega_g = 5.1 kT_N. \quad (2)$$

This gap has a very sharp optical-absorption edge which has been measured at 0.125 eV.⁴ In α -NiS there is a phase transition at $T_t = 260$ K.⁵ Reflectivity measurements have shown a rather broad absorption feature rising above 0.13 eV and reaching a peak near 0.37 eV. For both Cr and NiS the strength of the absorption corresponds to the loss in integrated conductivity given by Eq. (1), and moreover is of the same magnitude as the numerical value given by Eq. (1) for TaS₂. The energy gap [Eq. (2)] and the corresponding optical-absorption peak is predicted by a weak-coupling theory of interactions among the conduction electrons.⁴

Wilson *et al.* have made a series of electron-diffraction studies of 1T- and 2H-TaS₂, TaSe₂, and NbSe₂.² These studies show that new periodicities occur in the real lattice of the 1T materials on cooling through the onset temperature $T_0 \approx 550$ K. The authors interpret these as arising from charge-density waves (CDW). In 1T-TaS₂ at 350 K this periodic disturbance locks into a value close to but not quite commensurate with a reciprocal-lattice vector. If a free-electron approximation is used then the gaps produced by the CDW should obey an equation like Eq. (2), with a prefactor of the same order of magnitude (i. e., ~ 5.1). The 550-K onset temperature suggests on this basis a gap at 0.24 eV. We find no sharp gap structure

at this energy but note a very broad weak structure around 0.1 eV at 380 K. Unfortunately, this small bulge is within the experimental uncertainty. On cooling there is a gradual removal of absorption strength at and below 0.5 eV. Figure 1(a) indicates that the strength is removed in a continuous manner with jumps at the transition temperatures. Wilson *et al.* find that the new periodicities below T_0 are somewhat temperature dependent, though vectors \vec{q} characterizing the periodicity remain approximately constant and parallel to the hexagonal basal-plane vectors a_0^* of the high-temperature phase.² At 350 K \vec{q} abruptly adopts a value 11.5 deg off a_0^* . With further cooling \vec{q} rotates slightly and continuously, and then near 200 K abruptly locks into a commensurate superlattice value which is 13.9° from the original hexagonal lattice direction. We expect the new periodicity to produce gaps in portions of the Fermi surface as was the case in Cr. Unlike Cr, however, the Fermi surface of 1T-TaS₂ does not have the special property of nesting, so that \vec{q} opens gaps only over a restricted region of the surface with the possibility of the gap decreasing to zero away from the strongly coupled regions. The optical absorption σ' would measure an average over these regions and would probably show no sharp structure. With this interpretation our data suggest gaps ranging from below 0.04 to about 0.5 eV.

C. Gap in 2H-TaSe₂

The measured dc conductivity of 2H-TaSe₂ shows a monotonic increase on cooling from 300 to 4 K. There is however a weak feature near 120 K below which the slope is larger.² Unlike 1T-TaS₂ or the cases of Cr and NiS mentioned above, there is no measurable abrupt rise in conductivity signaling the sudden formation of an energy gap in parts of the Fermi surface. Electron-diffraction² and neutron-scattering¹¹ studies show, however, that similar to 1T-TaS₂, superlattice Bragg reflections do develop via an incommensurate phase. This lattice distortion accompanying the CDW should certainly open gaps in some region of the band structure. We interpret the peak shown in Fig. 3 at 20 K as such a gap.¹² Figure 4 shows the gap structure obtained by interpolating the reflectivity through the gap region to simulate the non-CDW structure. The integrated strength of the absorption peak at 20 K is very weak. In Cr metal the SDW causes gaps which remove about 30% of the Fermi surface.⁴ Making similar types of estimates here^{4,5} we must conclude that the CDW gap removes only about 1% of the Fermi surface at 20 K. This small change would be difficult to measure and would explain the lack of a sharp step or cusp in the dc conductivity.

The 80-K spectrum shown in Fig. 4 also yields

a "gap" feature. At this higher temperature the peak is broader, similar to the behavior observed in Cr. In the latter material thermally excited phonons were shown to be the likely cause of the increased width. The data analysis used to produce the net absorption spectrum shown at the bottom of Fig. 4 contains large enough uncertainties that no reliance can be placed on the temperature dependence of the integrated absorption. Within a factor of 2, the 80-K peak also corresponds to removal of about 1% of the Fermi surface. An additional spectrum taken at 100 K, just above the 90-K commensurate lock-in temperature, shows a very weak feature in reflectivity still centered near 0.3 eV. The corresponding absorption is at least a factor of 2 weaker than the 80-K absorption.

There is one other feature of the $2H$ -TaSe₂ data which deserves comment. Unlike the $1T$ -TaS₂ the conductivity shown in Fig. 3 does not extrapolate towards the measured dc value. At 300 K the inferred infrared value is about 4 times lower than the dc conductivity. However, at 20 K it is nearly 30 times lower than the dc value. If a Drude model is adopted for the low-energy conductivity spectrum this result suggests that the relaxation energy is anomalously low (well below 0.02 eV) and very temperature dependent.

Recently, Rice and Scott have proposed that the CDW instability in the $2H$ compounds arises from the occurrence of saddle points in the energy bands.¹³ Their model can predict a transition with very little Fermi-surface truncation. The energy-gap relation they obtain is $\hbar\omega_g \geq 4.4kT_c$. Prefactor values larger than 4.4 are obtained for increasingly asymmetric saddle points. Our results on $2H$ -TaSe₂ of a small area absorption peak and a large energy gap (0.25 eV) are in accord with this model. Our energy gap suggests that their asymmetry parameter θ is about 4 degs. Such large asymmetry is very unlikely, however, considering the APW band calculation, and a more definitive comparison must await the extension of their model to include the coupling of three bands.

V. CONCLUSIONS

The $1T$ form of TaS₂ exhibits an infrared reflectivity with some metallic characteristics in its high-temperature phase. The optical conductivity does not have a simple Drude form, however. At 380 K there appears to be weak structure, which suggests that there are gaps present near 0.1 eV. Cooling into the lower-temperature phases produces drops in conductivity but a spectrum typical of a semiconductor does not result. Rather there is a considerable decrease in transition strength at energies ranging from less than 0.04 to about 0.5 eV together with an absence of a distinct single energy-gap absorption. These spectra suggest that unlike the transition in Cr and α -NiS a unique gap does not open in TaS₂, but rather a distribution of gaps exists in the low-temperature phases, which on cooling, progressively remove carriers from the optical conductivity, and spreads the lost sum-rule strength over a broad range of energies.

In $2H$ -TaSe₂ a very weak gap structure is observed with a threshold near 0.25 eV. This energy is much higher (by about 5 times) than a simple nesting-Fermi-surface model would predict. This result is reminiscent of the high gap energies observed in Cr alloys which had commensurate SDW locked to the lattice periodicity.³ However, in the present case this value obtains both above and below the commensurate lock-in temperature. The saddle-point model of Rice and Scott may explain this result. From the strength of the optical peak it is clear that $2H$ -TaSe₂ retains most of its metallic bands, with gaps opening over rather restricted regions of \vec{q} space.

The interesting possibility exists in both compounds studied here that some of the sum-rule strength in the CDW state may go into a very-low-energy sliding-charge-density mode¹⁴ such as has been suggested for some one-dimensional metallic solids. Such a mode would probably lie below 0.01 eV.

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