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# Bolometric measurement of the charge-density-wave gap in $TaS_3$

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Polarized bolometric spectra were measured on orthorhombic $TaS_3$ between 20 and 100 K. At the lowest temperature, the spectra are clearly absorption spectra, indicating that $o$-$TaS_3$ has a semiconducting Peierls gap of $E_g = 1240\ \text{cm}^{-1} = 8.1 k_B T_c$. No sharp lines indicative of midgap soliton states are observed, although a long tail may be due to weakly pinning impurity states. The spectra become more complex at higher temperatures, but indicate that the gap decreases to 1025 $\text{cm}^{-1}$ at 95 K. The gap energy is close to twice the activation energy observed in transport measurements.

Orthorhombic $TaS_3$ ($o$-$TaS_3$) is a quasi-one-dimensional conductor which undergoes a charge-density-wave (CDW) transition at $T_c \sim 220$ K.[1] In the CDW state it exhibits a number of unusual electronic properties, caused by the depinning of the CDW from the lattice by small electric fields; these properties have been the subjects of extensive theoretical and experimental studies.[2] On the other hand, the static properties of the CDW state in $o$-$TaS_3$ are not well known, principally due to the small size (typically 5 mm $\times$ 20 $\mu$m $\times$ 3 $\mu$m) of available crystals. In particular, the magnitude of the CDW energy gap has not been unambiguously measured, although various estimates have been inferred from other experiments.[1,3-5] In this paper, we report on polarized infrared spectra of $o$-$TaS_3$ at temperatures between 20 and 100 K, taken using a bolometric technique;[6] these are the first such measurements reported for a quasi-one-dimensional transition-metal chalcogenide. The 20 K spectra clearly show that $o$-$TaS_3$ is a semiconductor with an energy gap of $E_g = 1240 \pm 10$ $\text{cm}^{-1}$. However, the gap is strongly temperature dependent, falling to $\sim 1025$ $\text{cm}^{-1}$ at 95 K, deviating strongly from simple BCS-like behavior.

We first briefly review previous discussions of the semiconducting behavior of $o$-$TaS_3$ and estimates of its CDW energy gap. Tsang, Hermann, and Shafer,[3] on the basis of line broadening in the Raman spectra, inferred that $E_g(T=0\ \text{K}) = 530$ $\text{cm}^{-1}$; since the activation energy of the conductivity (above 110 K)[1] is $\Delta \sim 600$ $\text{cm}^{-1}$, they suggested that the Fermi surface is pinned to the CDW gap edge by impurities. A detailed fit of the conductivity assuming a temperature-dependent activation energy[4] found a somewhat smaller $\Delta(100\ \text{K}) \sim 400$ $\text{cm}^{-1}$. Higgs and Gill[7] suggested that $o$-$TaS_3$ remains a semimetal below $T_c$, with a temperature-dependent CDW wave vector resulting in vanishing pockets of electrons and holes with decreasing $T$. However, Latyshev, Savitskaya, and Frolov[5] showed that the Hall constant was positive and activated, with a temperature-independent activation energy (above 100 K) of $\Delta_H \sim 700$ $\text{cm}^{-1}$, suggesting that, below $T_c$, $o$-$TaS_3$ is a semiconductor with a *single,* condensed (hole) band, temperature-independent gap, and strongly temperature-dependent mobility. The temperature independence of $\Delta_H$ is in contrast to the x-ray diffraction results of Tsutsumi, Sambongi, Kagoshima, and Ishiguro,[8] who observed that the intensity of superlattice spots, and hence CDW distortion amplitude and gap, were strongly dependent on temperature. Finally, from an analysis of the magnetic susceptibility above $T_c$, Johnston[9] concluded that the mean-field transition temperature $T_{MF} = 2.5 T_c$. Since $E_g(T=0\ \text{K}) = 3.5 k_B T_{MF}$,[10] this suggests that $E_g(T=0\ \text{K}) = 1340$ $\text{cm}^{-1}$.

Although temperature-dependent reflectivity spectra for frequencies greater than 4000 $\text{cm}^{-1}$ have been reported,[11] the small sample size has prevented extension of these measurements to lower energies comparable to the expected gap. On the other hand, unpolarized bolometric spectra for $T > 80$ K have been reported by ourselves[12] and Itkis and Nad' (IN).[13] In bolometric spectra, changes in the sample's electrical conductance due to heating from the absorbed radiation are measured as a function of wavelength. For light chopped at a frequency $\omega$, the change in conductance $\Delta G$ is given by

$$\Delta G = [P_{\text{in}}/K(1+i\omega\tau)]F(n,k,d)\partial G/\partial T \ ,$$

where $P_{\text{in}}$ is the incident power, $K$ the thermal conductance, $\tau$ the thermal time constant, and $F$ gives the fraction of incident light absorbed. As discussed extensively by Bates, Eldridge, and Bryce,[6] $F$ is, in general, a complicated function of the optical constants and thickness $d$ of the sample, but for optically thin ($\alpha d \ll 1$) crystals, $F = \alpha d$, while for optically thick ($\alpha d \gg 1$), $F = 1 - R$, where $\alpha$ is the absorptivity and $R$ the reflectivity. While similar unpolarized bolometric spectra were reported by IN[13] and ourselves,[12] IN assumed they were in the former limit and interpreted a strong plateau in the spectrum for $E > 1000$ $\text{cm}^{-1}$ as due to absorption across the CDW gap and a strong peak at 500 $\text{cm}^{-1}$ as absorption from a midgap soliton state.[13,14] In contrast, we assumed that we were in the optically thick limit and made no such identifications.[12] To help identify the nature of the spectra, we undertook the present study, extending our measurements to lower temperatures and separately measuring spectra for radiation polarized along the conducting chains ($\epsilon \parallel \hat{c}$), and transversely ($\epsilon \parallel \hat{b}$).

Lower limits on the absorptivity can be found by considering the dc conductivity due to thermally excited electrons. At 100 K, $\sigma_c \sim 150\sigma_b \sim 1.5 \times 10^{13}$ $\text{sec}^{-1} < 2\pi\nu$.[15] Using the standard low-conductivity limit to estimate the absorptivity, $\alpha_j \sim 4\pi\sigma_j/c\sqrt{\epsilon}$, and assuming an isotropic dielectric constant $\epsilon \sim 5$,[11] we find that $\alpha_c d \sim 1$, $\alpha_b d \sim 10^{-2}$; consequently, the optically thin limit may be appropriate for the transverse polarization if the optical anisotropy is as large as the dc anisotropy, which is unlikely. On the other hand, at 20 K, $\sigma_c \sim 10^9$ $\text{sec}^{-1}$,[7] and we are almost certainly in the optically thin limit for both polarizations.

The bolometric spectra were taken on samples whose

 

ends were heat sunk into indium pedestals soldered onto sapphire slides, which were attached to the cold finger of either a liquid-helium cryostat or a miniature nitrogen-gas refrigerator. The sample, in vacuum, was placed at the image of the exit slit of the monochromator of a Perkin-Elmer model No. 301 spectrophotometer. The radiation was incident normally ($\pm 45°$) on the *bc* face of the crystal. A wire-grid polarizer on a KRS5 (thallium bromide iodide) substrate also served as the room-temperature window on the cryostat. Space limitations due to the short focal length ($\sim 1$ cm) of the focusing mirror did not permit the use of cold filter between the sample and polarizer, resulting in considerable sample heating ($\lesssim 15$ K). The *average* temperature of the sample was found by comparing its resistance to that previously measured in an exchange gas cryostat.

At low temperatures ($< 50$ K), the change in sample conductance at the chopping frequency (13 Hz) was found by measuring changes in the current when the sample was held at a constant voltage (below the threshold for CDW depinning[2]); at higher temperatures, constant currents (below threshold) were used and the voltage measured. At all temperatures, considerable $1/f$ noise was observed; therefore, 1 kHz excitation currents (voltages) were used rather than dc. Phase-sensitive measurements of the modulating signal at 13 Hz were made using a low-noise heterodyning preamplifier. Even so, the measured noise was one order of magnitude larger than the theoretical (Nyquist plus shot) noise limit. At each wavelength, the incident power was measured using a blackened pyroelectric detector. Typical resolution was $\Delta\nu = \pm 8$ cm$^{-1}$.

Polarized spectra at 21 K are shown in Fig. 1. Very similar spectra were measured for a second sample, but the strength of the dips at 3000 and 3400 cm$^{-1}$ varied in different runs, and these features may be due to surface contamination. The spectra are striking for their typical semiconducting behavior, with strong absorption edges at $E_g = 1240 \pm 10$ cm$^{-1}$ seen for both polarizations; these edges we associate with excitation across the CDW gap. Our measured $E_g$ is twice the activation energy obtained from a simple, two-parameter fit of the conductivity above 110 K,[1] but this agreement is coincidental because, as shown below, the gap remains temperature dependent below

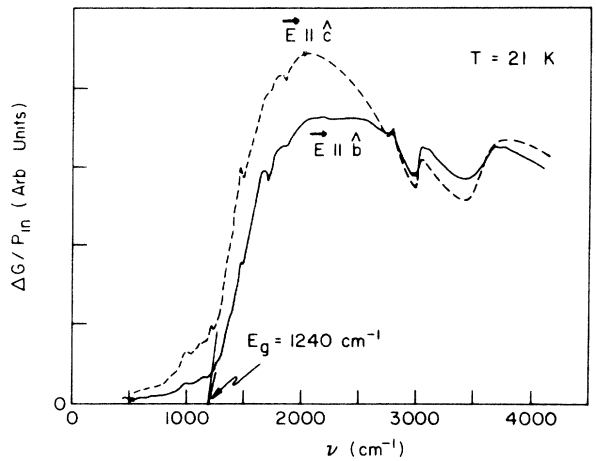


FIG. 1. Bolometric spectra for sample No. 1 at 21 K. The scales for both polarizations are the same.

100 K. In view of the anisotropy in the transport properties, the near isotropy of the absorption is very striking, implying that the conduction-band states have a large transverse dipole moment, e.g., due to strong hybridization of the Ta *d* orbitals and the *p* orbitals of the sulfur ions in the surrounding distorted trigonal prisms.[2]

No sharp absorption lines are observed in the gap for either polarization; such have been proposed for solitonlike states due to discommensurations in a nearly commensurate CDW.[14] On the other hand, there is a long tail, suggestive of an indirect gap of $\sim 800$ cm$^{-1}$; however, the Peierls distortion itself opens up direct gaps at $\pm 2k_F$,[2] so an indirect gap implies the existence of a local energy extremum very near the Fermi level. Alternatively, the tail may be due to impurity states; Tüttö and Zawadowski[16] have shown that for impurities which weakly pin the CDW, there will be a continuum of states near the gap edges, resulting in an indirect gap $E_g' \sim E_g(1-t^2)^{1/2}$, where $t \sim T/v_F$ and $T$ is the impurity backscattering amplitude. In the present case, $E_g' \sim 0.7E_g$ and $|T/v_F| \sim 0.7$, consistent with weak CDW pinning.[16]

Spectra at 96 K are shown in Fig. 2. (Similar spectra were obtained for several samples, except that the large peaks at

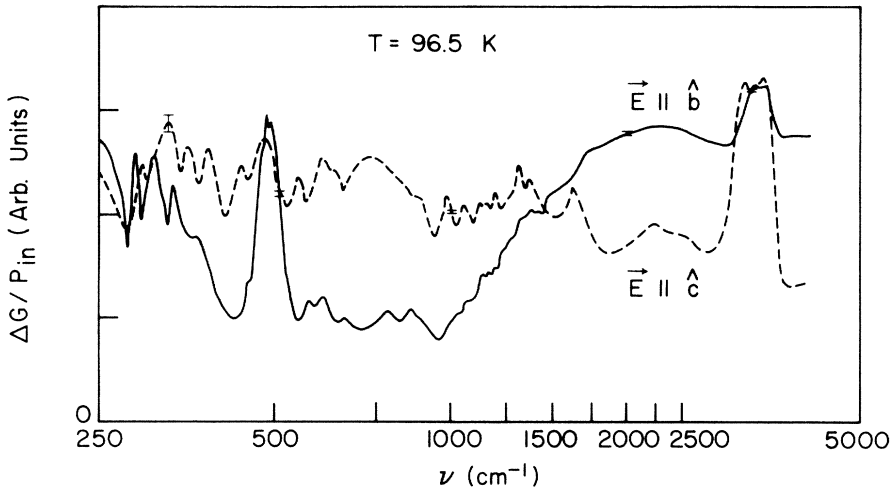


FIG. 2. Bolometric spectra for sample No. 2 at 96.5 K. The scales for both polarizations are the same.

3400 $cm^{-1}$ do not always appear, and again may be due to contamination. The relative amplitudes of other features are also sample dependent.) Here the spectra for the two polarizations are very different; for polarization along the chains, there is no indication of an absorption edge, and we are presumably in the optically thick, $F_c \sim (1-R_c) \sim 0.3$ limit.[11] On the other hand, the absorptionlike edge at 1000 $cm^{-1}$ and strong peak at 500 $cm^{-1}$ previously measured in unpolarized spectra[12,13] dominate the transversely polarized spectrum; as discussed above, it appears as if $F_b \sim \alpha_b d$. However, the fact that the absorption edge is 25% larger at 20 K while *all* the structure below the edge disappears suggests that perhaps $F_b$ also changes nature between 20 and 95 K. To check this possibility, low-resolution ($\Delta\nu \sim \pm 15$ $cm^{-1}$), $\epsilon \| \hat{b}$ spectra were taken at several intermediate temperatures. The results are shown in Fig. 3. It is seen that the absorption edge *gradually* decreases and broadens with increasing temperature. We suggest that at 95 K, $\alpha_b d \sim 1$, so that $F_b$ contains both absorption and reflection features, and the 500 $cm^{-1}$ peak is, in fact, a dip in reflectivity due to, e.g., a phonon mode and not an electronic absorption. (Note that there is a strong, mostly transversely polarized, Raman-active mode at this frequency.[17]) This hypothesis could also explain the sample dependence of the relative intensities of different features.[13] At lower temperatures, the spectrum becomes increasingly an absorption spectrum. [An alternative possible explanation for the disappearance of the low-energy features in $F_b$ is that, as mentioned below, the CDW becomes commensurate at low temperatures so that features due to soliton states (i.e., discommensurations) disappear.]

It might be argued that the relative increase of the absorption above 1000 $cm^{-1}$, with respect to other features with decreasing temperature, is due to a photoconductive enhancement of the bolometric signal at low temperatures.[6,18] (The measured signal below 50 K is in phase with the chopping signal due to the small heat capacity, so bolometric and photoconductive effects cannot be separated by their relative phase shifts.[18]) The spectra shown in Fig. 3 are arbitrarily normalized; the absolute ($\Delta G$) and relative ($\Delta G/G$) signals at 1000 and 2000 $cm^{-1}$ are listed in Table I. As seen, $\Delta G$ at 2000 $cm^{-1}$ actually decreases with decreasing temperature, implying that there is no significant photoconductive contribution to the signal. The approximate isotropy of the low-temperature absorption also suggests that photoconductive effects are not large. Nonetheless, the temperature dependence of the bolometric signal is anomalous at the lowest temperatures, i.e., $\Delta G/G$ is roughly independent of temperature above 40 K, but increases by two orders of magnitude below this temperature, while $|d \ln G/dT|$ only increases by a factor of 4. It is unlikely that the thermal conductivity decreases by an order of magnitude; much of the increase in relative bolometric signal may be due to the decrease in thermal hysteresis at low temperatures.[7,12]

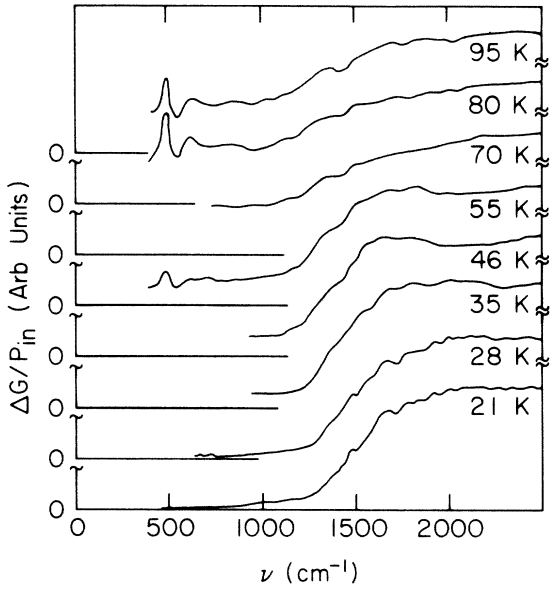


FIG. 3. Transversely polarized ($\epsilon \| \hat{b}$) spectra for sample No. 1 at several temperatures. The scales for the different temperatures are arbitrary and different; the zeros are offset as shown.

The strong temperature dependence of the gap is unusual; the absorption edge moves and broadens by an energy $\sim 3k_BT$, so that these cannot be simple thermal effects. The change in gap is also an order of magnitude larger than would be expected for BCS behavior for a transition at 220 K. (The variation of the gap between 20 and 100 K is comparable to that in the x-ray superlattice spot intensity measured by Tsutsumi *et al.*[8]) If, however, as suggested by the Hall-effect results,[5] the gap is constant at higher temperatures, the increase in gap below 100 K may be due to a

TABLE I. Conductance, energy gap, $\Delta G/P_{in}$, and $(\Delta G/G)/P_{in}$ for sample No. 1 measured with $\epsilon \| \hat{b}$ at 2000 and 1000 $cm^{-1}$ at different temperatures.

| $T$ | $G$ | $\Delta G/P_{in}$ ($\mu$mho/$\mu$W) | | $\frac{\Delta G/G}{P_{in}}$ ($\mu W)^{-1}$ | | $E_g$ |
|---|---|---|---|---|---|---|
| (K) | ($\mu$mho) | 2000 $cm^{-1}$ | 1000 $cm^{-1}$ | 2000 $cm^{-1}$ | 1000 $cm^{-1}$ | ($cm^{-1}$) |
| 21 | 0.02 | 0.34 | 0.022 | 17 | 1.1 | 1240 ± 10 |
| 28 | 0.10 | 0.45 | 0.025 | 4.5 | 0.25 | 1220 ± 15 |
| 35 | 0.67 | 0.44 | 0.048 | 0.66 | 0.071 | 1200 ± 15 |
| 46 | 5.0 | 1.24 | 0.25 | 0.25 | 0.048 | 1165 ± 15 |
| 55 | 7.7 | 1.22 | 0.32 | 0.16 | 0.041 | 1120 ± 15 |
| 70 | 25 | 4.10 | 1.78 | 0.16 | 0.071 | 1090 ± 20 |
| 80 | 71 | 14.7 | 7.2 | 0.21 | 0.101 | 1085 ± 20 |
| 95 | 200 | 27.3 | 13.2 | 0.14 | 0.066 | 1025 ± 20 |

gradual incommensurate-commensurate transition; the presence of such a lock-in transition near 50 K was suggested in Ref. 7.

In summary, $o$-$TaS_3$ is clearly a semiconductor at low temperatures; the measured gap is roughly twice the activation energy obtained in the various transport measurements,[1,4,5] indicating that while the Fermi level is affected by impurity states, it is not pinned to the gap edge by them. The mean-field transition temperature $T_{MF} = E_g(T=0\text{ K})/3.5k_B = 504$ K is close to that obtained by Johnston (550 K). For a strictly one-dimensional band, the CDW transition is expected to be suppressed by fluctuations to $T_c \sim T_{MF}/4$;[10] our result indicates that while fluctuations suppress $T_c$, they are somewhat inhibited by interchain coupling and/or commensurability effects.[4] A tail in the low-temperature absorption is interpreted as being due to impurity states in an incommensurate potential;[16] alternatively, the strong ($\sim 25\%$) temperature dependence of the low-temperature gap may be due to a commensurate lock-in transition.

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