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Enhanced bolometric response of TaS_3 in the non-Ohmic regime

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We report on the infrared bolometric spectrum of orthorhombic TaS_3 between 400 and 1550 cm^{-1} at ~ 100 K, well below the charge-density-wave transition (at 220 K). The bolometric signal is observed to increase dramatically when the voltage across the sample exceeds the threshold for non-Ohmic conductivity. The wavelength and temperature dependence of this unusual bolometric "switch-on" are reported.

Orthorhombic TaS_3, which undergoes a commensurate charge-density-wave (CDW) transition at ~ 220 K,[1,2] has recently been observed to exhibit non-Ohmic conductivity and other unusual electronic properties in the CDW state.[3–6] These properties, which had previously been observed in $NbSe_3$,[7] are considered indicative of CDW motion through the crystal, the so-called "Fröhlich mode." Above ~ 100 K there is a sharp threshold voltage V_T, only above which TaS_3 exhibits these anomalous properties.[4] Below this temperature, the threshold behavior disappears, presumably because crystalline disorder destroys the coherence of the CDW state,[8] with separate domains responding individually to applied fields.

There have been a variety of theories put forth to explain the dc and rf properties of the depinned CDW,[9] but none of these address the question of the CDW response at higher frequencies, where the internal dynamics of the CDW may become important. There has also been little experimental work on the optical properties of $NbSe_3$ and TaS_3 because of the difficulty in preparing samples wide enough for transmission or reflection experiments. We have circumvented this problem in orthorhombic TaS_3 by taking an infrared spectrum (400–1550 cm^{-1}) using the sample as a bolometric detector. We feel that the unusual properties of TaS_3 merited such an investigation, despite the difficulty in interpreting the bolometric signal, V_B, which is, in general, a complicated function of the reflectivity R and absorptivity α.[10] The spectrum is only readily interpreted if the sample thickness $d \gg 1/\alpha(\nu)$, in which case $V_B \sim [1-R(\nu)]$ (Ref. 10); however, it is impossible to estimate $\alpha(\nu)$ for TaS_3 at present.

In the course of our investigation, we have discovered that as the dc voltage across the sample is increased above the non-Ohmic threshold the bolometric signal increases extremely rapidly. We have studied this very novel effect as a function of wavelength and temperature. To assure ourselves that we were not being misled by instrumental effects, we also measured the bolometric response of semiconducting NbS_3,[11] which has a similar morphology to TaS_3; no unusual behavior was observed for NbS_3. In this Communication, we report on the results of this study.

Fibers of orthorhombic TaS_3 and NbS_3 were prepared by heating stoichiometric amounts of the metal and sulfur at $\sim 600\,^{\circ}C$ in evacuated quartz tubes for several weeks. Below 200 K, the conductivity of TaS_3 is activated, with an activation energy $\Delta = 585$ cm^{-1}, in agreement with the results of Sambongi *et al.*[1] Our NbS_3 samples are semiconducting at room temperature, with a low conductivity of $\sigma \sim 2 \times 10^{-2}$ $\Omega^{-1}cm^{-1}$ and activation energy $\Delta = 736$ cm^{-1}.

Samples, typically ribbons 3 mm × 30 μm × 3 μm in size, were mounted by heat sinking their ends into indium pedestals soldered onto a sapphire substrate. The sample was placed at the image of the exit slit of the monochromator of a Perkin-Elmer model 301 spectrophotometer. A mirror could be switched in place to deflect the monochromatic beam onto a blackened pyroelectric detector with a flat spectal response. In the present experiments, the light was not polarized and was incident on the sample from a large solid angle ($\Delta\theta \sim 90°$).

The sample was cooled by using a miniature nitrogen gas refrigerator[12] equipped with a KRS5 window. Temperature was stabilized to ±30 mK by using a diode thermometer and resistive heater. [In comparing TaS_3 data from separate runs, the sample, whose resistance and activation field (see below) were monitored, was used as a self-consistent thermometer. Absolute temperatures cited are correct to ~ 5 K, temperature differences to ~ 0.5 K (Ref. 13)]. The bolometric data were taken with a constant dc current passed through the sample, and the alternating voltage V_B across the sample at the chopping frequency, 14 Hz, was measured with a lock-in amplifier. TaS_3 data were taken up to 112 K; at higher temperatures, the sample resistance and V_B became excessively small, and data have not yet been taken. The resistance of the NbS_3 sample was sufficiently large (14.5 MΩ) that data on it were taken at room temperature.

Typical results of V_B/V_{dc} vs V_{dc} for TaS_3 and NbS_3

are shown in Fig. 1. The bolometric signal is given by

$$\frac{V_B}{V_{dc}} = \Delta T \left| \left(\frac{\partial \ln V_{dc}}{\partial T} \right)_I \right| = \Delta P/(\kappa + i\omega c) \left| \left(\frac{\partial \ln V_{dc}}{\partial T} \right)_I \right| , \tag{1}$$

where ΔP and ΔT are the absorbed power and the average temperature modulation of the sample (at the chopping frequency ω), and κ and c are the effective thermal conductance and heat capacity. [In general, V_B may be enhanced by a photoconductive signal,[10] but our measured signals were in quadrature with the chopping signal ($\omega c \sim 10\kappa$), indicating that photoconductive contributions were small.] For an Ohmic resistor, such as NbS_3, the logarithmic derivative is independent of current, and therefore V_B/V_{dc} is expected to be independent of V_{dc}, as we observed [Fig. 1(a)].

On the other hand, for TaS_3, V_B/V_{dc} increases dramatically at very small voltages, as seen in Figs. 1(b) and 1(c). Also plotted in Fig. 1(b) is the resistance V_{dc}/I. The bolometric increase occurs just as the non-Ohmicity becomes apparent, although we did not determine if there was a sharp non-Ohmic threshold for our samples at these temperatures. [Some of the resistance variation observed is due to Joule heating, but at the largest currents used, this accounted for only a 1% decrease in resistance (i.e., $\Delta T \sim 0.3$ K).] It should be noted that the bolometric increase is not due to an increase in the sensitivity, $|\partial \ln V_{dc}/\partial T|$, which decreases as the material goes non-Ohmic [see Fig. 1(c)]. Behavior qualitatively similar to that shown in Fig. 1 was observed in all five TaS_3 samples checked, although the size of the effect [a/b in Fig. 1(b)] varied from 2–9. All data reported on here were from a single sample.

As seen in Fig. 1, after reaching a maximum, V_B/V_{dc} starts decreasing with increasing voltage; at the higher temperatures measured, this peak appears as a plateau. We have not yet investigated this "high-field" behavior, but have characterized the "low-field" rapid increase of V_B/V_{dc}. For further discussion, we refer to this increase as the "switch-on" effect. We have defined three quantities that characterize the effect [see Fig. 1(b)]: the ratio a/b, where a is the peak (or plateau) height and b the low-field value of V_B/V_{dc}, the width W (10%–90%) of the switch region, and the "switch-on voltage" V_1 at which V_B/V_{dc} has changed by 50%. These parameters are plotted in Fig. 2. Also shown in Fig. 2(a) is the non-Ohmic activation field V_0, defined by fitting the high-field resistance to[7]

$$R^{-1} = R_a^{-1} + R_b^{-1} \exp(-V_0/V) , \tag{2}$$

where R_a is the measured low-field resistance. This expression neglects the effect of a threshold voltage V_T, but is expected to hold for voltages $V >> V_T$,[4] and it provides a convenient parameter to characterize the non-Ohmicity. The switch-on voltage V_1 is a factor of 10 smaller than V_0; in comparison, Zettl and Grüner[5] found (at 170 K) that $V_T = \frac{1}{5} V_0$. For each wavelength, the temperature dependence of V_1 and W *roughly* follow that of V_0, i.e., they are independent of temperature above 95 K, and increase below this. These observations, and the lack of any switch-on effect in NbS_3, suggest that the effect is indeed due to the depinning of the CDW.

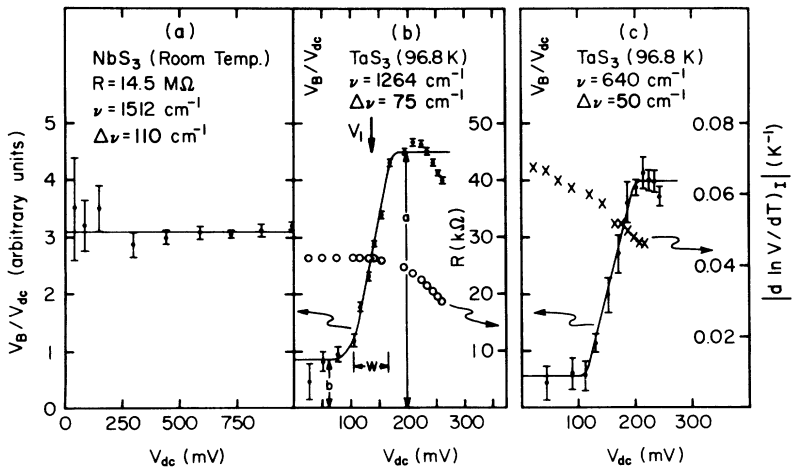

FIG. 1. Bolometric signal divided by the dc voltage, V_B/V_{dc}, vs V_{dc} of NbS_3 and TaS_3 at different wavelengths and temperatures is shown. The vertical scales for (a)–(c) are arbitrary and not related. Lines are drawn as a guide to the eye. Also shown in (b) are the resistance of the TaS_3 crystal at 96.8 K vs V_{dc} and the parameters V_1, W, a, and b, discussed in the text. Shown in (c) is the measured bolometric sensitivity $|(\partial \ln V/\partial T)_I|$ at 96.8 K; it decreases when V_{dc} exceeds threshold.

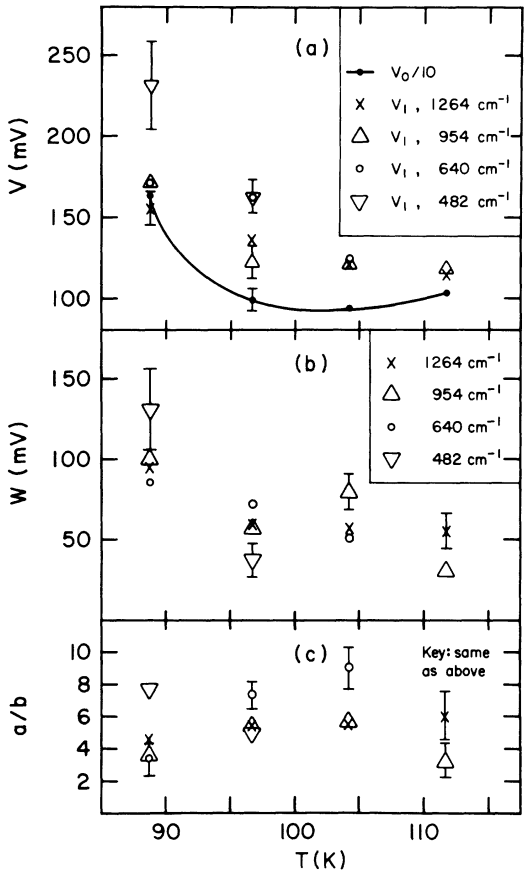

FIG. 2. Parameters V_1, W, and a/b, described in the text, are plotted as a function of temperature for different infrared frequencies, with representative error bars. Also shown in (a) is the non-Ohmic activation voltage V_0. W and V_1 roughly track V_0 with temperature (the line is a guide to the eye), indicating the correlation of the switch-on to the CDW depinning. However, there is no strong temperature or frequency dependence of a/b.

There does not appear to be any well-defined wavelength dependence to V_1, W, or a/b. This is reflected in the two spectra taken at 4 and 10 μA (i.e., below and above the switch-on) at 96.8 K, shown in Fig. 3. To improve the signal-to-noise ratio of the 4-μA data, we excited the sample with an ac current (at 1 kHz) rather than dc, and used a heterodyning circuit to do a phase-sensitive measurement of the modulating signal at the chopping frequency. The two spectra are remarkably similar, the only significant difference being that the shoulder at 625 cm^{-1} and broad peak at 825 cm^{-1} are relatively larger in the 10-μA spectrum. Specific features of the spectrum will be discussed in a later publication.

If the switch-on effect were due to a specific optical mode turning on, one would not expect to see the entire spectrum enhanced at 10 μA. On the other hand, if the enhancement were due to a broad "white" process, one would expect to see the various phonon features washed out at 10 μA. That the switch-on effect amplifies the entire spectrum, roughly independent of frequency, suggests that it is thermal in origin. However, neither the specific heat nor thermal conductivity is expected to be effected by the CDW depinning, certainly not as abruptly or strongly as the bolometric signal; in fact, no field dependence of the thermal conductivity was observed in $NbSe_3$,[14] and a thermal origin to the switch-on effect seems unlikely.

Therefore, in spite of its weak wavelength dependence (which may be partially due to the large range of incident angles), we feel that the bolometric switch-on is optical in nature. The bolometric signal remains in quadrature with the chopping signal at high currents, so the switch-on is not due to photocarriers with a field dependent mobility, e.g., the CDW excited across a pinning gap ($\sim 10^{-3}$ cm^{-1}).[5,15] Changes in the optical activity may be induced by drastic changes in the domain configuration with electric field. At 100 K, the CDW is thought to be in a disordered state with small commensurate domains. As the voltage is increased past V_T, the CDW becomes depinned incoherently in individual domains[8]; at larger voltages, the CDW response becomes coherent. Therefore, for $V \sim V_T$, there may be a realignment (and growth) of domains.

In conclusion, we have observed that at ~ 100 K orthorhombic TaS_3 shows a sharp switching-on of bolometric signal in the infrared when an electric field comparable to the non-Ohmic threshold field is exceeded. The switch-on is only weakly wavelength dependent in the spectral region investigated, making its interpretation at present very difficult.

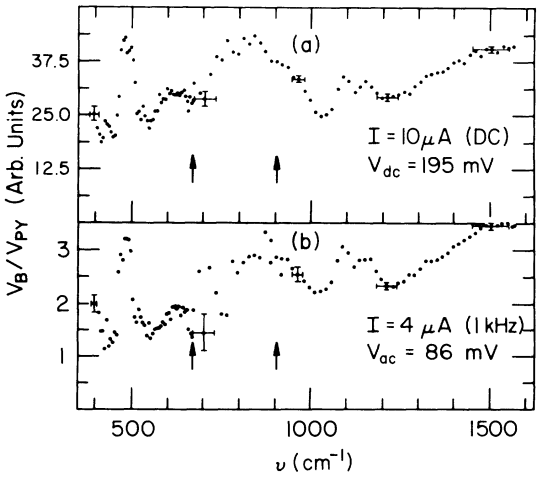

FIG. 3. Bolometric signal V_B of TaS_3 at 96.8 K, normalized to the pyroelectric signal V_{py}, is plotted as a function of infrared frequency. Spectra are shown for two different excitation currents. The arrows denote frequencies at which optical filters and/or gratings were changed and spectra renormalized.

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