PRESSURE EFFECT ON THE METAL-SEMICONDUCTOR TRANSITION IN 1-T TaS_2

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It is found that the metal-semiconductor transition in the 1-T TaS_2 is suppressed linearly by compression up to ~15 kbar with $dT_0/dP = -(3.0 \pm 0.2)$ K/kbar. A two-band model with a small but temperature- and pressure-dependent overlap is proposed.

The transition metal dichalcogenides form two distinct classes of compounds, of which one exhibits a layered structure *. These layered compounds possess different crystal symmetries and diversified electronic properties ranging from metals through semiconductors to insulators. The interest in these dichalcogenides which are two or quasi-two dimensional systems has recently grown immensely [2]. The 1-T phase of TaS_2 is known to be one of the most unusual cases among this system from the standpoint of its crystal structure and its nonmetallic nature at room temperature. However, the unique nature was not unveiled until only recently when Thompson et al. [3] observed three first-order phase transitions at 348, 315 and 180K respectively. The first corresponds to a transition from metal to semiconductor with decreasing temperature T and the last two from semiconductor to semiconductor. The metal-semiconductor transition is the first of this kind observed in layered compounds. The failure [3] to detect any crystallographic change with the metal-semiconductor transition by X-ray and the inadequacy of the empirical band models [1] to account for its semiconductivity are very puzzling. In addition, no magnetic long-range-order near this transition was found by Menth et al. [4]. Hence a pressure study on the metal-semiconductor transition in 1-T TaS_2 is particularly interesting.

We have measured the transition temperature T_0 under pressure P above room temperature.

* For a comprehensive review, see [1]

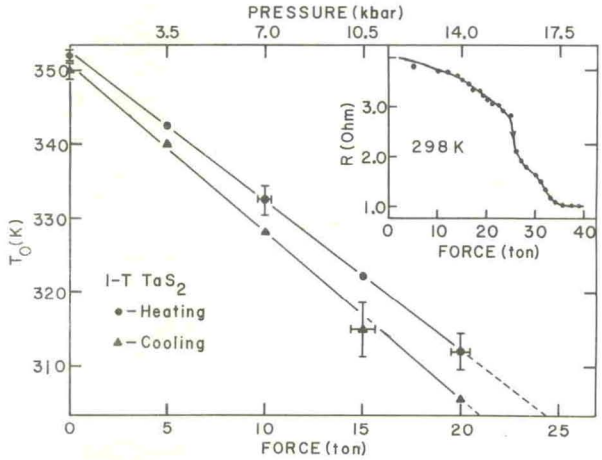

Fig. 1. The variation of T_0 as a function of P. dT_0/dP given in the text was the mean value for both heating and cooling. The insert shows the R-variation with P at 298K. The bars represent the width of the transition and the uncertainty in pressure.

T_0 was found to decrease linearly with $dT_0/dP = -(3.0 \pm 0.2)$ K/kbar throughout the experimental range. The present results combined with those in [2,3] lead us to suggest a two-band model with a small but temperature- and pressure-sensitive overlap in order to explain the metal-semiconductor transition.

The investigation was carried out on single crystals of 1-T TaS_2 which has $T_0 = 350$K at 1 atm slightly higher than that observed by Thompson et al. [3]. The metal-semiconductor

transition was determined by measuring the resistance along the a-axis using a four lead technique. The size of the sample was $4 \times 1 \times 0.2$ mm^3. Pressure was generated between a pair of Bridgeman anvils with AgCl as the pressure medium and was determined by a gauge calibrated against the 25.4 kbar Bi-transition. Constant P was maintained manually both on heating and cooling. The rates of T-change were kept at a minimum to reduce thermal hysteresis which increased from 1 to 6K with P. The transition width also increased with P from 1.5 to 6K. This may be caused by the increase of pressure inhomogeneity.

The results of T_0 versus P are shown in fig.1 for both heating and cooling. The linearity between T_0 and P in the present P-range by no means should be expected at a much higher P if the transition remains first order. However, it does set an upper limit on the critical pressure $\lesssim 118$ kbar to retain the M-phase at 0°K. $P \simeq 18$kbar is sufficient to stabilize the M-phase at 298K. To further demonstrate this, we measured the resistance R as a function of P at 298K and the results are shown in the insert. The small step at slightly higher P following the main transition may be caused by off-stoichiometric effect which also appeared at 1 atm in some of the samples.

The slope of the T_0-P curve dT_0/dP, the volume change ΔV and the entropy change ΔS associated with a first-order transition are related by Clausius-Clapeyron equation: $dT_0/dP = \Delta V/\Delta S$. Using our value $dT_0/dP = -(3.0 \pm 0.2)$ K/kbar and $\Delta S = 0.09$ cal/mole·K given in [3], we obtained $\Delta V = -(3.2 \pm 0.4) \times 10^{-4}$ cm^3/mole. This indicates that only $\sim 3 \times 10^{-2}\%$ volume increase occurs at the metal-semiconductor transition in 1-T TaS_2 which is consistent with the previous failure to observe a volume discontinuity by X-ray [3].

Various models** have been proposed to explain the metal-semiconductor transition in different materials. Mott [6] suggested that the S-phase can arise from the localization of electrons due to Coulomb interaction. However, no local moment was observed in the S-phase of 1-T TaS_2 [4]. We therefore propose a two- (or more) band model to explain the metal-semiconductor transition in 1-T TaS_2. In the M-phase the overlap is small at 1 atm and decreases with decreasing T. The metal-semiconductor transition may be driven by the strong correlation between carriers. At high P the overlap increases and so the M-phase is stable to lower T. The associated volume change deduced from the present study is in agreement with such a proposition. The finding by Thompson et al. [3] that the S-phase has lower entropy and that two-band conduction is involved in this compound are also compatible with the present model. In view of the indication of a superlattice in the electron microscope diffraction pattern [1], the possibility of a long-range-order effect creating an energy gap can not be ruled out. In this alternative model, the small crystal distortion may just be the consequence of the appearance of long-range-order. It is clear that detailed work is needed to elucidate the nature of this transition.

** See the review article by Mott and Zinamon [5].

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