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Transport evidence for new phase changes in 1T-TaS₂ after intercalation with hydrazine

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Abstract. In this paper, we present evidence, from simultaneous electrical resistivity and thermogravimetric measurements, for a phase transition occurring at ~ 378 K in the charge-density-wave system 1T-TaS₂ when fully intercalated with hydrazine and then heated in a hydrazine environment. We discuss this change in terms of a transition between a commensurate $(\sqrt{7}/8)a^* \times (\sqrt{7}/8)a^*$ superlattice already known to exist at room temperature in the intercalated material, and a weaker incommensurate distortion. We also discuss the effect of hydrazine intercalation on the 282 K transition observed on warming in pure 1T-TaS₂, and give further evidence for the partial inter-layer character of this transition.

1. Introduction

Among the layered transition-metal dichalcogenides, the 1T-polytype of TaS₂ has in particular been the subject of numerous studies, owing essentially to the complexity of the distortions that this charge-density-wave (CDW) system undergoes at various temperatures. The different phases of this compound that have been identified as the temperature is lowered are [1–4] (i) undistorted or normal (N) for temperatures $T > 543$ K, (ii) incommensurate (IC) for $353 \text{ K} < T < 543 \text{ K}$, (iii) nearly- or non-commensurate (NC) for $180 \text{ K} < T < 353 \text{ K}$, and (iv) commensurate (C) for $T < 180 \text{ K}$. Upon warming, the transition from the C phase occurs around 220 K, to a phase different from the NC phase observed on cooling. The first indication for this difference originated from convergent-beam electron-microscopy measurements by Fung *et al* [5], who found that, on heating 1T-TaS₂ from the C phase, the stacking period in the phase following the 220 K transition was $7c_0$ instead of the $3c_0$ periodicity observed in the NC phase. Later on, anomalies in various physical properties were observed at 282 K on warming, such as those in thermal expansion measurements [6], back-scattering yields of He⁺ ions [7], and Young's modulus [8], indicating that only above that temperature (282 K) could the NC phase be recovered. Following these findings, we have reported differential-scanning-calorimetry, electrical-resistivity and Hall-coefficient measurements on this compound [9], where, in addition to providing further strong evidence for this 282 K transition, we have also suggested that the phase obtained above 282 K on warming is still different from the NC phase observed on cooling, since a large hysteresis is obtained, extending up to the 353 K transition to the IC phase. Since then, structural studies by various researchers have focused on the details of this new phase obtained above 220 K on warming: Tanda *et al* [10, 11], after performing x-ray measurements,

found it to be an incommensurate triclinic (T) structure up to ~ 280 K. Scanning tunnelling microscopy (STM) measurements [12–15] have since confirmed the T symmetry of this phase and showed it to be discommensurate, with amplitude and phase modulation as predicted by the theoretical domain model of Nakanishi and Shiba [16]. Recently, however, more precise high-resolution electron-microscopy measurements [17], where observations were made both parallel and perpendicular to the *c*-axis, revealed that, upon warming from the C phase, the obtained (T) phase was constituted of small domains having the C structure, separated by a discommensuration network whose density changes with temperature, and that the stacking order in this phase is intermediate between that of the C phase and the $3c_0$ repeat of the NC phase. At ~ 280 K a sudden change to the $3c_0$ periodicity occurs, the discommensurations persist up to 353 K, whereas no discommensurations at all are observed on cooling from the IC phase, confirming thereby our earlier suggestion [9] that the phase obtained above 282 K on warming is different from the NC phase observed on cooling.

In a compound with such a complex spectrum of distorted phases, intercalation is expected not only to cause interesting changes in the in-plane superlattice wave-vector (because of the charge transfer that accompanies this process), but also to be a useful way to check any partial inter-layer component associated with phase transitions such as the 282 K transition observed in 1T-TaS₂ upon warming.

The intercalation of 1T-TaS₂ with hydrazine (N₂H₄) has already been the subject of various studies [18–20]. Upon exposure of 1T-TaS₂ to the room-temperature vapour pressure of hydrazine, a change in stacking sequence from 1T to 3R occurs, and a complex with the composition 3R_{1,1}-TaS₂(N₂H₄)_{4/3} is formed (a stage-2 complex), where the notation I.I indicates the presence of two hydrazine layers in each van der Waals gap separating TaS₂ sandwiches. Heating this complex up to ~ 320 K, or pumping on it to 10^{-2} Torr at room temperature, produces a stage-1 complex, 3R₁-TaS₂(N₂H₄)_{2/3}, where there is only one layer of N₂H₄ between each two host layers. Full de-intercalation is possible by simultaneous heating and pumping. Electron-diffraction studies [18] indicate the presence of a commensurate $(\sqrt{7}/8)a^* \times (\sqrt{7}/8)a^*$ superlattice at room temperature in the 3R_{1,1} complex, while at 80 K a commensurate $(a^*/3) \times (a^*/3)$ superlattice is found, instead of the commensurate $a^*/\sqrt{13}$ superstructure observed in pure 1T-TaS₂ at that temperature. Such an increase in distortion strength is attributed to charge transfer from hydrazine to the host layers, transfer which is also evident from transport measurements [20].

As a consequence of such an increase in distortion strength, the anomalies normally observed in the temperature dependence of the resistivity of pristine 1T-TaS₂, one of which denotes the transition between the commensurate $\sqrt{13}$ superstructure and the discommensurate T phase (or the NC phase on cooling) and the other denoting the transition between the T (NC) phase and the IC phase, could be reasonably expected to be replaced by other anomalies in the intercalated complexes since different superstructures are involved. Indeed, the studies by Sarma *et al* [20] have already revealed that the hysteretic (180–220 K) anomaly associated with the C–NC (T) phase transition in pure 1T-TaS₂ disappears upon hydrazine intercalation, and that it is replaced by an anomaly at ~ 280 K in the 3R_{1,1}-TaS₂(N₂H₄)_{4/3} complex, denoting the transition between the $(\sqrt{7}/8)a^*$ and the $(a^*/3)$ superstructures in this latter compound.

In this paper, we extend the resistivity measurements to higher temperatures and couple them to thermogravimetric measurements, in order to check the effect of hydrazine intercalation on the 353 K anomaly in 1T-TaS₂, and we thus reveal evidence for yet another change in this material. We also reflect upon the discommensurate triclinic (T) phase of 1T-TaS₂.

2. Experimental considerations

Single crystals of 1T-TaS₂ were grown by the vapour transport technique at 900 °C (the hotter end of the tube being at 950 °C) with 1 mg ml⁻¹ excess S and with iodine as a transporting agent. All samples showed typical room-temperature resistivity values of $(9.6 \pm 0.8) \times 10^{-4} \Omega \text{ cm}$, in agreement with the values published in the literature.

The insertion of hydrazine into the samples was performed as described by Sarma *et al* [20]. In addition, however, simultaneous resistivity and thermogravimetric measurements were performed on separate samples having the same size and placed side by side in the intercalation chamber so that the variation of resistivity with weight uptake could be monitored. The intercalation chamber, which consisted of a double-walled glass jacket, provided the possibility of heating the samples, at a desired rate, up to $\sim 420 \text{ K}$, via a temperature-controlled ethylene glycol solution circulating between the walls of the chamber.

For resistivity measurements, the van der Pauw [21] technique was used and the electrical contacts consisted of Au wires attached to the samples via Ag dag. Unlike some of the hydrazine-intercalated group-IV transition-metal dichalcogenides on which we reported earlier [22], the intercalation complexes of TaS₂ are quite stable in a hydrazine environment.

3. Results and discussion

In figure 1 we report the variation of the resistivity as a function of hydrazine content, x , in the complex TaS₂(N₂H₄) _{x} ; the data are taken during de-intercalation. The resistivity at a particular stage of intercalation, $\rho(x)$, is normalized to the resistivity $\rho(0)$ of the pristine sample, and the ratio is plotted as a function of x . Since heating is required in order to de-intercalate the sample, the $\rho(x)$ values are taken at different temperatures and, therefore, in the ratio $\rho(x)/\rho(0)$, the $\rho(0)$ value considered is that taken at the same temperature as the corresponding $\rho(x)$ value. It may be seen that the resistivity upon full intercalation of the sample is about 60 times that of pure 1T-TaS₂, and that it decreases gradually with hydrazine content upon de-intercalation, to regain its original pristine-sample value when all the hydrazine has left the sample. The increase in resistivity upon intercalation is in agreement with the results of Sarma *et al* [20], and is in line with the formation of a stronger CDW distortion [18].

The temperature dependence of the resistivity, from room temperature up to $\sim 400 \text{ K}$ (between 20 °C and 120 °C) is shown in figure 2 for 1T-TaS₂ and some of its hydrazine intercalation complexes. Because the hydrazine content, x , is very much temperature dependent at these high temperatures [20], the curves shown in figure 2 for the intercalated compounds do not correspond to a fixed value of x but rather to a continuously varying x value. The numbers on the diagram represent some of the x values corresponding to different experimental data points.

As mentioned in section 1, Sarma *et al* [20] report that heating the 3R_{LI} complex while in a hydrazine environment causes partial de-intercalation starting at $\sim 308 \text{ K}$ (35 °C) and leading to the 3R_I complex around 323 K (50 °C), and that this behaviour is reversible on cooling. We find that under these conditions (i.e. heating in a hydrazine environment), the 3R_I state persists to even higher temperatures, up to $\sim 388 \text{ K}$ ($\sim 115 \text{ °C}$), after which further de-intercalation takes place, the phenomenon still being reversible on cooling. The stability of the 3R_I complex between 323 K and 388 K allows, therefore, the study of the effect of the presence of hydrazine in this complex on the phase transition normally observed at 353 K (80 °C) in un-intercalated 1T-TaS₂.

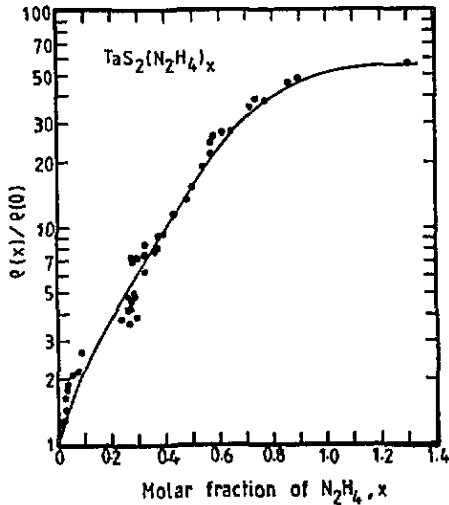


Figure 1. The variation with x of the resistivity $\rho(x)$ of the complex $\text{TaS}_2(\text{N}_2\text{H}_4)_x$ normalized to the resistivity $\rho(0)$ of un-intercalated 1T-TaS₂, both resistivities being taken at the same temperature. The data shown here are obtained during a de-intercalation run.

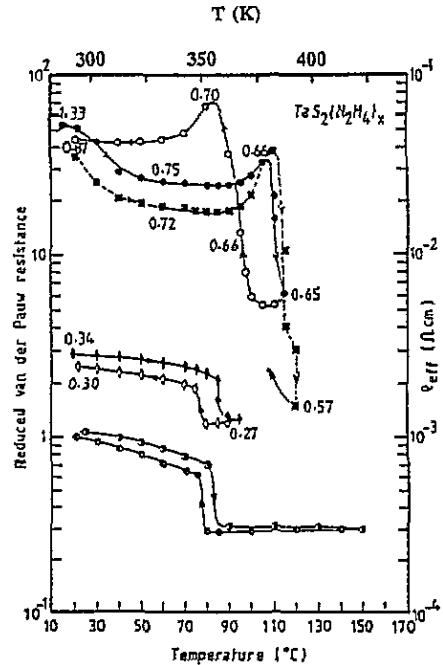


Figure 2. The temperature dependence of the resistivity of 1T-TaS₂ and its hydrazine intercalation complexes for temperatures between 300 K and 390 K: ○, heating of pure 1T-TaS₂; ●, cooling of pure 1T-TaS₂; ◆, ●, ■, heating of $\text{TaS}_2(\text{N}_2\text{H}_4)_x$; ◇, ○, cooling of $\text{TaS}_2(\text{N}_2\text{H}_4)_x$. The numbers by the curves represent various x values. The arrow at the end of the dashed curve indicates that the cooling run reproduces the same behaviour as represented by the continuous curve.

The results of figure 2 show that, for a hydrazine content smaller than $\frac{2}{3}$ (i.e. $0.27 \leq x \leq 0.34$), the transition remains around 80 °C although with a somewhat larger hysteresis than in the case of the pristine material. For $x > \frac{2}{3}$, however, no resistivity anomaly is seen at 80 °C. Instead, a huge anomaly is seen at ~ 105 °C (378 K) with a hysteresis of ~ 15 °C. The temperature of this compound was not raised any higher than 115 °C as de-intercalation starts occurring above that temperature.

One may argue that the sudden decrease of resistivity at ~ 105 °C could be interpreted as signalling the onset of de-intercalation. We believe that this is extremely unlikely, since x changes from 0.66 to only 0.65 while the resistivity shows a drop by a factor of ~ 10 (a much smaller change of resistivity would be expected for such a small change in x (as is clear from figure 1) if the decrease in resistivity were only due to de-intercalation). Furthermore, cooling the sample back to room temperature and then heating it again up to 115 °C reproduces a similar behaviour as in the first heating run.

We believe that the resistivity anomaly observed around 105 °C in the 3R_I complex most probably denotes a transition between two different CDW phases in this compound.

Tatlock and Acrivos [18] had in fact noted in their electron diffraction measurements that, upon heating the 3R_I complex up to 360 K, the $(\sqrt{7}/8)a^*$ superstructure gave way to an incommensurate distortion with wave-vector $q = 0.288a^*$, and that on returning to room temperature, the $(\sqrt{7}/8)a^*$ superlattice was replaced by two $\sqrt{13}$ superlattices, as

would be expected if de-intercalation had occurred. It should be noted, however, that the electron-diffraction data [18] were acquired before the thermogravimetric measurements by Sarma *et al* [20] were published, and that it is now well known that heating the 3R_{1,1} complex to 360 K causes partial de-intercalation of the sample, and that the cooling back to room temperature cannot reproduce the same original result unless this is performed in a hydrazine environment, which, in the experiment of Tatlock and Acrivos [18], may not have been the case, yielding thereby two $\sqrt{13}$ superstructures instead of reproducing the $\sqrt{7}/8$ superlattice upon cooling back to room temperature.

We therefore believe that the resistivity anomaly we observe around 105 °C (figure 2) is most probably the manifestation of the transition between the commensurate $(\sqrt{7}/8)a^*$ superstructure and an incommensurate superlattice whose wave-vector would be determined by the amount of charge transferred from hydrazine to the host TaS₂ layers, and would therefore depend in part on the amount of hydrazine present in the sample. The interdependence between the degree of d-band filling, n , and the wave-vector q of the distortion in the TaS₂ layers has been studied by DiSalvo *et al* [23], where the band filling was decreased by partially substituting Ti for Ta in 1T-TaS₂. In those studies, n was found to be proportional to q^2 . An extrapolation of this relationship to the case of the 3R_{1,1}-hydrazine intercalated complex, where a 30% electron increase per TaS₂ formula unit is estimated [20], yields a value of $0.332a^*$ for the corresponding wave-vector, a value which is in excellent agreement with that of the $(\sqrt{7}/8)a^*$ commensurate superlattice observed in this complex at room temperature.

The results of DiSalvo *et al* [23] also show that the lock-in temperature for the distortion to be commensurate increases with the distortion wave-vector. It is not surprising, therefore, that the temperature of 105 °C (378 K) around which we observe the anomaly in the resistivity data is indeed higher than the temperature of 353 K of the transition between the incommensurate and the nearly commensurate $\sqrt{13}$ superstructure of pure 1T-TaS₂.

The same argument also explains the temperature of 360 K at which Tatlock and Acrivos [18] observe the incommensurate $0.288a^*$ superlattice, since such a wave-vector would correspond to a 3% electron increase per TaS₂ formula unit, showing at the same time that their sample must have de-intercalated to a large extent, as suggested earlier.

Finally, in order to study the effect of hydrazine intercalation on the 282 K transition observed on warming in pure 1T-TaS₂, we have performed low-temperature resistivity measurements on the partially intercalated TaS₂(N₂H₄)_{*x*} sample (with $x < \frac{2}{3}$), the high-temperature resistivity of which is shown here as the intermediate curve in figure 2. The low-temperature measurements (not shown here) were performed before heating the sample above room temperature (so that $x = 0.34$ throughout the low-temperature run). These measurements reveal that the hysteretic anomaly observed around 200 K in pure 1T-TaS₂ is still present in the partially intercalated sample although with a larger hysteresis, and so is the discrepancy between cooling and warming curves characteristic of the discommensurate triclinic (T) phase. However, no anomaly is noted at or near 282 K, but instead the discrepancy between warming and cooling curves persists up to 353 K, as is shown in the intermediate curve of figure 2. This could mean that for low hydrazine concentrations (i.e. before the $(\sqrt{7}/8)a^*$ superlattice is set up), the discommensurate T phase persists up to the transition to the IC phase, with no rearrangement in the stacking sequence such as that which occurs at 282 K on warming in pure 1T-TaS₂. This provides further evidence for the partial inter-layer character of the 282 K transition in 1T-TaS₂, and is in line with the data of Guy *et al* [24], where this same transition occurs at a lower temperature (260 K) when 1T-TaS₂ is under a pressure of 5.4 kbar, since intercalation is expected to have the opposite effect to that of pressure.

4. Conclusion

In addition to the previously documented changes that were reported to occur below room temperature in 1T-TaS₂ upon intercalation with hydrazine [18, 20], this paper gives transport evidence for two further changes in hydrazine-intercalated 1T-TaS₂, namely those affecting the 282 K and the 353 K phase transitions normally observed in the pristine material.

We find that the 282 K anomaly in the resistivity data disappears after the insertion of only a small amount of hydrazine ($x < \frac{2}{3}$) between the layers, but that the signature of a discommensurate triclinic phase is still present upon warming from the C phase, and persists up to 353 K, where the transition to the IC phase continues to occur around this same temperature for these low hydrazine concentrations. For higher hydrazine contents, however, i.e. for the samples where a $(\sqrt{7}/8)a^*$ superstructure is present at room temperature, no anomaly is observed at 353 K in the resistivity data, but, instead, a huge anomaly is noted around 378 K. We attribute this anomaly to a phase transition from the commensurate $(\sqrt{7}/8)a^*$ superlattice to an incommensurate superstructure.

Detailed structural characterization is now needed to provide further evidence for the two changes mentioned above, and to clearly define the periodicity of the IC superlattice that, we believe, exists above 378 K in the $3R_1$ -TaS₂(N₂H₄)_{2/3} complex.

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