CHAPTER 9

MEASUREMENTS OF ELECTRICAL PROPERTIES OF 1T-TaS_2 SINGLE CRYSTALS

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9.1 Introduction

1T-TaS_2, 1T-$TaSe_2$ and the alloy systems based on them, stand out as a group of materials, whose electric and magnetic properties[1-3] are fairly difficult to interpret in a coherent fashion. Their structural transitions are thought to be reasonably well understood[4] like those of other transition metal dichalcogenides in terms of Fermi surface[5] (FS) driven charge density wave (CDW) instabilities, and their eventual lock-in with the underlying lattice.

The difficulty with the above mentioned group of materials is that, over wide ranges

of temperature and composition they conduct too well to be called ordinary semiconductors but too poorly to be called semimetals. The most conspicuous feature is the low temperature resistivity anomaly (at $T \leq 60^{\circ}K$) in pure 1T-TaS_2 which has been ascribed to a variety of causes : complete gapping[3], Anderson localization[5] and Mott localization[6-7].

Though considerable research has been conducted on these compounds, but in general all the workers, for their investigations, have employed the crystals, grown either by bromine or iodine transport method or the crystals either doped or intercalated. The probable incorporation of bromine or iodine in the crystals grown by such method will naturally have some adverse effects on electrical properties measurements carried out so far. Hence, it was found necessary to study the electrical properties of crystals grown in the present work without using any transporting agent.

Studies thus carried out in this way have been discussed in the present chapter.

9.2 Experimental

9.2.1 Electrical contacts

In order to study the electrical properties

the important point that one has to bear in mind is about the ideal contacts. For the ideal contact to a crystal, the following conditions must be fulfilled:

1. No resistance to the flow of the current is induced.
2. It does not react chemically with the material of the crystal.
3. Contact properties are not affected by variation of illumination temperature, electrical field or any other ambient conditions, and
4. The material of the crystal with contacts applied should satisfy Ohm's law.

The existence of a barrier is usually observed when a contact is made between the crystal material and the contacting material because of either improper matching of the work functions between these two materials, or the presence of surface states on the sample crystal or the presence of thin layer of oxide. A contact between a contacting material and the material of the crystal will be proper when no such barrier exists, such contact is generally known as "Ohmic contact".

9.2.2 Measurement of specific resistivity

As our as-grown crystals were in the form of flat samples of arbitrary shape, the measurement of the specific resistivity was carried out by Van der Pauw[8] technique. For such samples the specific resistivity can be measured without knowing the current pattern if the following conditions are fulfilled.

1. The contacts are at the circumference of the sample.
2. The contacts are sufficiently small.
3. The sample is homogeneous in thickness.
4. The surface of the sample is singly connected, i.e. the sample does not have isolated holes.

Let as shown in Fig. 9.1, A, B, C and D be the successive contacts fixed on arbitrary places along the circumference, of a flat TaS_2 single crystal of arbitrary shape, such that all the above mentioned conditions (1) to (4) are fulfilled. We define resistance R_1 as the potential difference $V_D - V_C$ between the contacts D and C per unit current through the contacts A and B. The current enters the sample through the contact A and leaves it

through the contact B. Similarly we define the resistance R_2 as the potential difference $V_B - V_A$ between the contacts B and A per unit current through the contacts C and D, the current entering the sample through the contact C and leaving it through the contact D. It can be shown that the following relation holds :

$$\exp(-\pi R_1 d/\rho) + \exp(-\pi R_2 d/\rho) = 1 \qquad .. (9.1)$$

Equation 9.1 determines uniquely the value of specific resistivity ρ as a function of R_1, R_2 and d, where d is the thickness of the sample. In order to facilitate the solution of ρ from equation 9.1, we write it in the form

$$\rho = \frac{\pi d}{\ln 2} \left(\frac{R_1 + R_2}{2} \right) f \left(\frac{R_2}{R_1} \right) \qquad .. \qquad (9.2)$$

where f is a function of the ratio $\frac{R_1}{R_2}$ only and satisfies the relation

$$\frac{R_1 - R_2}{R_1 + R_2} = \frac{f}{\ln 2} \operatorname{arc\,cosh} \left\{ \frac{\exp (\ln 2/f)}{2} \right\}$$

The value of $f\left(\frac{R_2}{R_1}\right)$ can be found out from the graphical presentation of Van der Pauw's article[8] (the function f used for determining the specific resistivity of the sample, plotted as a function of $\frac{R_1}{R_2}$).

Prior to the resistivity measurements, the ohmicity of the contacts was checked from the I.V. characteristics. The dc electric field was generated by Aplab electronically regulated power supply. The voltage and the corresponding current passing through the specimen were measured independently. Resistivity measurements at different temperatures were carried out by keeping the specimen sample in the vacuum chamber in which specimen can be heated up to a maximum of 200° C. All the measurements were carried out at a pressure of 10^{-5} torr. Test temperatures ranged from 298 to 475° K and were accurate to about ± 1° K. The temperature measurements were taken by a calibrated Pt/Pt-Rh thermocouple.

9.2.3 Thermoelectric power measurements

The Seebeck coefficient α is defined as the ratio of the gradient in voltage to the gradient in temperature, as the latter tends to zero, i.e.

$$\alpha = \left(\frac{\Delta V}{\Delta T}\right)_{\Delta T \to 0}$$

For the determination of α there are two basic methods.

(1) **Integral method**

In this method one end of the sample is held at a fixed temperature T_1 and the other end is heated to a temperature T_2. Then a thermoelectric potential difference is produced along the sample and the thermoelectric voltage is given by

$$V(T_2) = \int_{T_1}^{T_2} \left[\alpha_s(T_2) - \alpha_m(T_2)\right] dT$$

where α_s is Seebeck coefficient of the sample, and α_m is that of lead wires. The voltage drop across the sample is measured on a null basis across the contact junctions of the sample. The

sign of the majority charge carriers can be deduced from the sign of the cold end.

(2) Differential method

In this method at a desired mean equilibrium temperature, the thermoelectric voltage ΔV is measured as a function of the imposed temperature gradient, T, obtained by a heat pulse

$$\left(\alpha_s - \alpha_m\right) \frac{\Delta V}{\Delta T}.$$

Seebeck coefficient was measured by employing the differential method. The Seebeck coefficient specimen holder used is shown in Fig. 9.3. The measurements were carried out from room temperature to 200° C, using a technique described by Revolinsky and Beerntsen[9]. Thermal E.M.F. was generated by butting the bars between two copper blocks, turned from the same piece of stock, both heated by means of Nichrome wire heating coils wound on the copper rods. The heat sink is connected to the other end of the rod, in order to maintain the required temperature gradient. The temperature gradient was measured by means of two Chromel-Alumel (40 SWG)

thermocouples located in holes drilled to the centre of the screw immediately behind the contact faces of the sample crystals of thickness 0.04 mm and having the shapes of rectangle of 10 mm and 4 mm sides. The crystal was rested on a mica base plate. The variation in temperature of one end of the specimen was obtained by controlling current with the help of dimmerstat. The entire system was mounted in an evacuated glass chamber evacuated to the order of 10^{-5} torr to avoid the oxidation of the samples. During the measurement, the specimen was equilibrated at each temperature for about 20-30 minutes. The thermoelectric voltage developed across the specimen and the temperature between the two ends of the specimen were measured on Philips D.C. microvoltmeter.

9.3 Results and Discussion

9.3.1 Resistivity measurements

In order to determine the variation of resistivity with temperature, measurements of resistivity of TaS_2 samples were made at different temperatures. All these observations are given in Table 9.1.

Table 9.1

Temperature ^{o}K	Resistivity $\times 10^{-4}$ Ω cm
298	13.95
303	14.59
313	12.68
323	12.25
333	12.05
343	11.42
353	11.40
363	11.60
373	11.75
383	12.06
393	12.90
403	14.30
413	16.04
423	20.30
433	25.00
443	31.52
453	36.16
463	43.13

A graph showing the variation of resistivity versus temperature is shown in Fig. 9.2. From the graph it is observed that the resistivity ρ decreases with temperature, up to the temperature of 350° K, after that it shows a gradual increase with the further increase in temperature. This discontinuity is because of the fact that the crystal under investigation undergoes a phase transition from semiconductor to metal.

9.3.2 Measurements of Seebeck coefficient

Seebeck coefficients were measured at different temperatures and the observations thus recorded are given in Table 9.2. A graph of Seebeck coefficient versus temperature is shown in Fig. 9.4. From the figure it is seen that the Seebeck coefficient changes sign from negative to positive on warming through 350° K transition. This is clearly in agreement with the results of Benda[2].

The small value of Seebeck coefficient observed in TaS_2 sample crystals, supports the conjecture that above 350° K TaS_2 possesses a metallic character.

It will be seen in the electron microscopic studies described in Chapter 14 that at

Table 9.2

Variation of Seebeck coefficient with temperature

Temperature ^{o}C	μ V/^{o}C
35	- 7.00
40	- 6.10
45	- 5.20
55	- 3.52
63	- 1.73
70	- 0.65
75	- 0.10
85	1.60
95	3.44
105	5.00
115	6.00
125	6.10
135	5.93
145	5.90
155	5.80
165	5.50
175	5.22
185	5.10
195	5.10
205	4.70
215	4.60
225	4.52

this transition temperature of 350° K there is also a phase change from $1T_{\alpha}$ to $1T_{\beta}$ i.e. from semi-conductor to metallic.

9.4 Conclusions

The measurements of physical properties e.g. resistivity and Seebeck coefficient suggest a phase transformation at a temperature of 350° K. This is completely in agreement with the results of earlier workers. A further support to the existence of phase transformation is provided from the electron microscopic studies to be discussed in detail in Chapter 14.

9.5 References

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Captions of the figures

Fig. 9.1 Four probe method of Van der Pauw for irregular geometry of crystals.

Fig. 9.2 Variation of resistivity ρ as a function of temperature.

Fig. 9.3 Sample holder assembly for

TEP measurements
H , H - Heaters
Th - Thermocouple positions
E , E - Electrodes
S - Specimen
M - Mica sheet
SH - Shield

Fig. 9.4 Seebeck coefficient as a function of temperature.

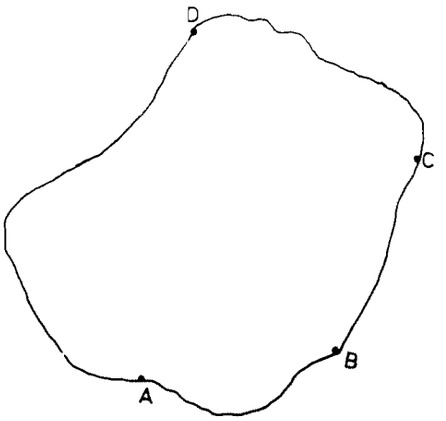

Fig. 9.1

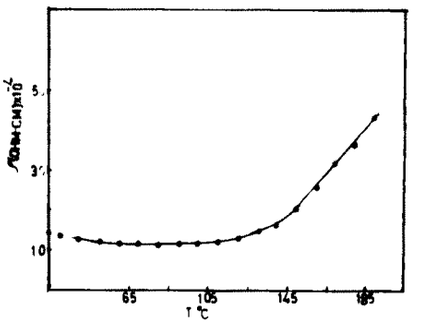

Fig. 9.2

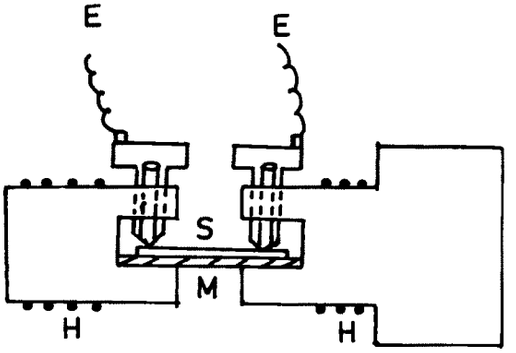

Fig. 9.3

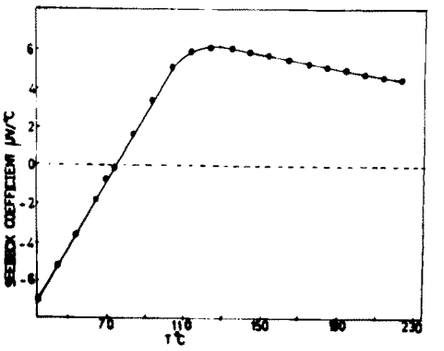

Fig. 9.4