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ELECTRICAL PROPERTIES OF SINGLE CRYSTALS OF TUNGSTENITE (WS_2)

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ABSTRACT. The principal electrical conductivities of the naturally occuring single crystals of tungstenite have been studied from room temperature upto about 950°K in vaccum. The study reveals that (*i*) the substance has negative temperature coefficient of resistance ; (*ii*) the conductivities increase permanently after preliminary heat treatment ; (*iii*) the substance is a symmetrical varistor for currents along the basal plane ; (*iv*) for currents perpendicular to the basal plane and at room temperature WS_2 is not only a symmetrical varistor but a thermistor also ; the varistor and thermistor properties becoming less prominent with the rise of temperature ; and (*v*) log σ *vs* $1/T$ curve is straight within the temperature range of 400°K to 950°K, and at lower temperatures (below 400°K) it departs from linearity.

INTRODUCTION

Tungstenite (WS_2) which is isomorphous with molybdenite (MoS_2) (Wyckoff, 1963) occurs in nature as blocks of single crystal but is of rare occurrance than the latter. Like Mo-atoms in molybdenite the *W*-atoms in the tungstenite crystal are arranged in layers parallel to the basal plane and each such layer is sandwiched between two parallel layers of sulpher atoms. The unit cell structure is built up by the repetition of the composite layer, made up of the above three layers. The hexagonal unit cell, which contains two molecules of tungstenite (WS_2). has the following dimensions as compared to molybdenite :

$$WS_2: \quad a = 3.18\text{Å},\ c = 12.50\text{Å},\ c/a = 3.93$$

$$MoS_2: \quad a = 3.1604\text{Å},\ c = 12.295\text{Å},\ c/a = 3.89$$

Compared to crystals of molybdenite which are very soft (hardness varying from 1 to 1.5 Mohs) (Berry *et al*, 1959), those of tungstenite are harder (hardness 2.5 Mohs) (K. C. Li *et al*, 1947). Also, where as molybdenite can be very easily cleaved to flakes of few Angstrom thickness, presumably due to the large distance, 3.66Å, between the basal layers, this is not so easy for tungstenite (interlayer distance 3.13Å) and flakes of thickness varying from 0.1 cm to 0.05 cm can be obtained by grinding with alundum powder or similar other abrasive powders. Most interesting fact is that, while molybdenite is diamagnetic (Dutta, 1944),

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with an approximately inverse temperature dependence of susceptivility (Dutta, 1945), tungstenite shows strong paramagnetism (Dutta and Roy Chowdhury, 1949) with a complicated temperature dependence of susceptibility. MoS_2 crystals are known to be very good semiconducting varistors (Dutta, 1947; Dey 1944) having rectifying properties along c-axis, its electrical conductivities along and perpendicular to the hexagonal axis being of the order 1 and 10^{-4} ohm^{-1} cm^{-1} respectively. But no measurements on the electrical conductivities of single crystals of WS_2 has yet been reported. Only some data on electrical conductivity, Hall effect etc. of powdered WS_2 by Decrue (1956) and Lagrenaudie (1952, 1954) are available. From these it was concluded that WS_2 is a *p*-type semiconductor having an electrical conductivity of the order of 10^{-8} ohm^{-1} cm^{-1} at room temperature and that it is a *p*-type rectifier with almost all metals.

To obtain reliable information regarding the electrical and other allied properties of WS_2 we have therefore carried out measurements with single crystals of WS_2 extended over as wide a range of temperature as possible. We had to use naturally occurring crystals* which often contain impurities, and only a very careful choice of the samples, could give us sufficiently reproducible results. It is needless to point out here that observations with crystals are more reliable than those with powdered samples since, in the latter case the surface effects between the different grains are sure to modify the electrical properties appreciably.

EXPERIMENTAL

Preparation of the working specimens

Small blocks of the specimens were fractured out from a large block of single crystal. These were then ground with alundum powder to rectangular tablets of suitable thicknesses having the flat faces parallel to c-plane. For measuring the electrical conductivity along the basal plane, small regions covering a distance of about 2 to 3 mm from each end along the length of the specimen were electroplated with copper. For measurement along directions perpendicular to the basal plane the two flat surfaces were electroplated. It may be noted tht good copper plating is obtained only if the regions to be plated are first chemically mirrored with silver.

Methods of Measurement

The holders for measurement of electrical conductivities along and perpendicular to the basal plane were in principle the same as those used by earlier workers of this laboratory (Dutta, 1953; Mukherjee, 1964). The electrical conductivities were measured by the usual potentiometric method using a Pye Precision Potenmeter reading down to 1 micro volt. For measurements at high temperatures the samples were placed in a tubular electric furnace, and the temperatures were measured by a calibrated chromel-alumel thermocouple. All measurements were made by evacuating the furnace tube to 10^{-2} mm of Hg with a two stage rotary oil pump.

RESULTS

In figure 1 are shown the current voltage characteristics at room temperature. From a linear extrapolation of such curves at low currents, the resistances or

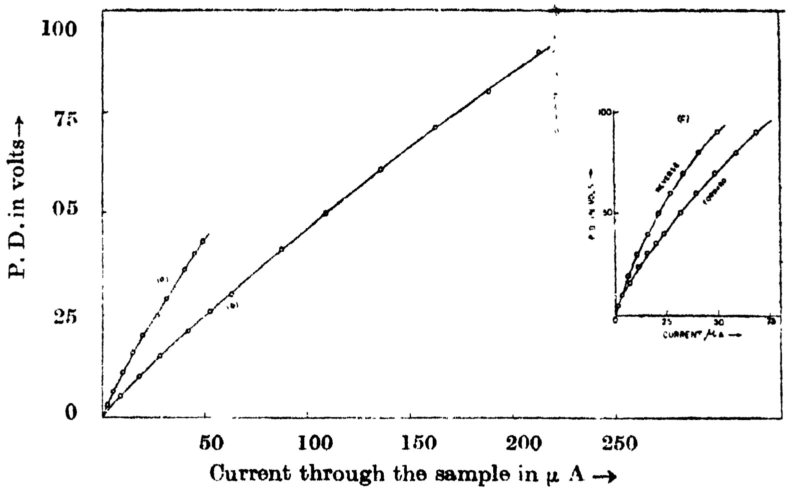

Fig. 1. Current voltage characteristics at 303°K.
(*a*) Current along basal plane with broad contacts.
(*b*) Current ⊥ to basal plane with broad contacts.
(*c*) Current ⊥ to basal plane with one point contact and one broad contact.

conductivities of the crystal are calculated. In table I are shown such conductivities, $\sigma_\perp$ and $\sigma_\parallel$ for currents along and perpendicular to the basal plane respectively for three different fresh samples, which have not undergone any heat treatment.

TABLE 1

Principal electrical conductivities of fresh samples of WS_2 at room temperature

Samples	$\sigma_\perp$ ohm^{-1} cm^{-1}	Mean $\sigma_\perp$ ohm^{-1} cm^{-1}	$\sigma_\parallel$ ohm^{-1} cm^{-1}	Mean $\sigma_\parallel$ ohm^{-1} cm^{-1}
1	3.86×10^{-6}		7.38×10^{-7}	
2	3.31×10^{-6}	3.9×10^{-6}	6.70×10^{-7}	7.3×10^{-7}
3	4.53×10^{-6}		7.82×10^{-7}	

Observation at higher temperatures

When the above mentioned measurements were first carried out at higher temperatures, it was found that the values of conductivity observed at different temperatures including room temperature when the sample was heated up, were not reproduced while it was cooled down (Fig. 2 and Table II).

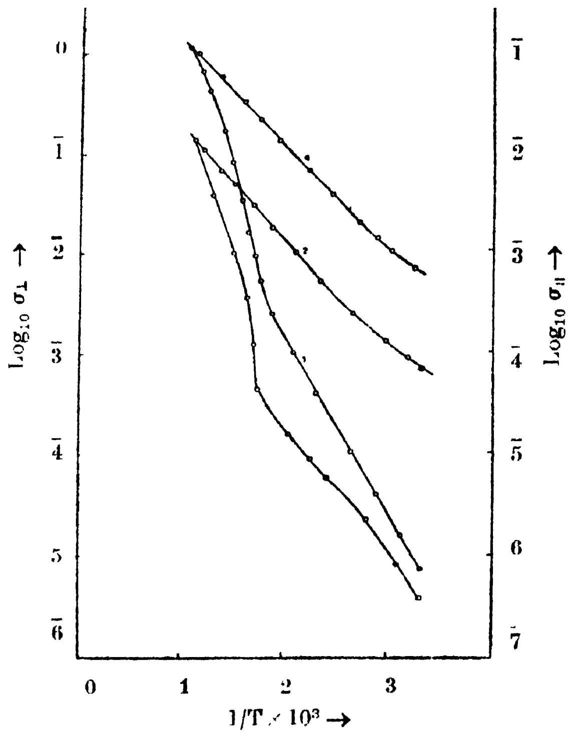

Fig. 2. Temperature variation of $\sigma_\parallel$ and $\sigma_\perp$, conductivities $\parallel$ and $\perp$ to the c-axis respectively.
Curves 1 and 3 for initial heatings of samples.
Curves 2 and 4 after attainment of steady state.

TABLE II

Principal conductivities at room temperature of the samples of Table I after attaining steady state

Samples	$\sigma_\perp$ ohm^{-1} cm^{-1}	Mean $\sigma_\perp$ ohm^{-1} cm^{-1}	$\sigma_\parallel$ ohm^{-1} cm^{-1}	Mean $\sigma_\parallel$ ohm^{-1} cm^{-1}
1	3.78×10^{-4}		5.13×10^{-4}	
2	4.82×10^{-4}	5.05×10^{-4}	5.75×10^{-4}	5.85×10^{-4}
3	6.56×10^{-4}		6.67×10^{-4}	

However, after one or two heating and cooling cycles in vacuum the values become perfectly reproducible. Such a behaviour is not uncommon with semiconductors under similar conditions and possibly arises from absorbed gases and internal stresses. In figure 2 are also shown the temperature variation of the principal conductivities of a typical sample of WS_2 after the attainment of the steady state.

In figures 3 and 4 are represented the current-voltage characteristics at different temperatures of samples which have attained the steady state.

In order to study the phenomena which might be taking place during the process of attaining the steady state, an experiment was performed in which the sample is successively heated to different high temperatues, allowed to remain at those temperatures for sufficient time to attain steady temperatures, cooled to the room temperature and the change in resistance which has taken place at the room

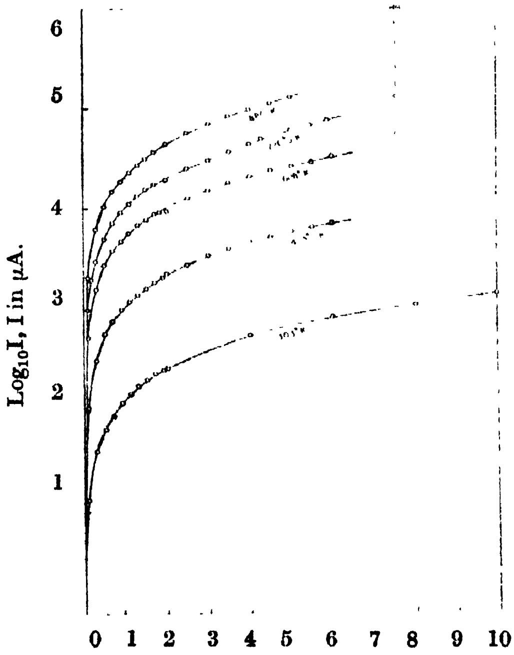

Fig. 3. Current voltage characteristics at different temperatures for currents along the basal plane with broad contacts. Curves are symmetrical for currents in reverse direction.

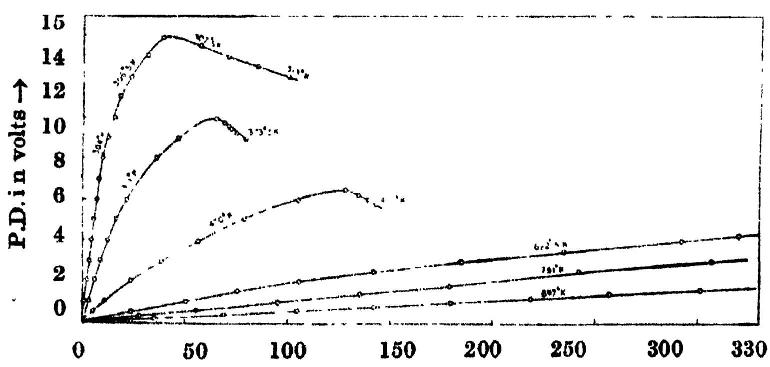

Fig. 4. Current voltage characteristics at different temperatures for current perpendicular to basal plane with broad contacts. Curves symmetrical for reverse current.

temperature is observed. The results of these observations are represented in figure 5.

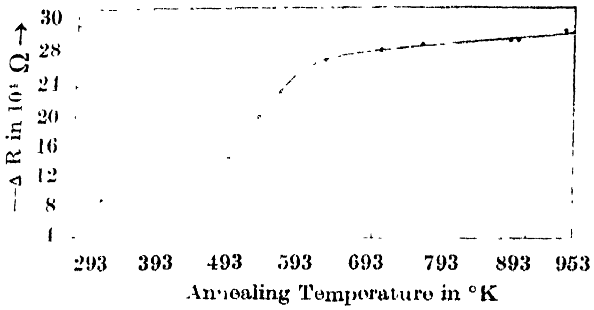

Fig. 5. Annealing effect of temperature on resistance of fresh samples.

DISCUSSIONS

1) *Chemical binding and conductivity in WS_2*

From a consideration of the paramagnetic properties of WS_2 it has been suggested (Dutta and Roy Chowdhury, 1949) that the bindings in it are of the type which are present in the salts of the iron group of elements. These are distinctly different from bindings in MoS_2 where there are strong covalent bonds between disimilar atoms and a partial metallic type of planar bonds between similar atoms (Dutta, 1944). As a consequence MoS_2 possesses high diamagnetic anisotropy combined with fairly high electrical conductivity in the basal plane (Dutta, 1945). It is therefore evident that owing to the distinct ionic nature of bond in WS_2, it should have much poorer electrical conductivity than MoS_2. This is exactly what has actually been observed (Table III).

TABLE III

Magnetic susceptibilities $\chi_{\parallel}$ and $\chi_{\perp}$ along and perpendicular to the c-axis, $\Delta\chi = \chi_{\perp} - \chi_{\parallel}$ and $\sigma_{\parallel}$ and $\sigma_{\perp}$ corresponding electrical conductivities of MoS_2 and crystals of WS_2 before heat treatment

Specimen	Electrical properties		Magnetic properties			
	$\sigma_{\parallel}$ Ω^{-1} cm^{-1}	$\sigma_{\perp}$ Ω^{-1} cm^{-1}	$\Delta\chi.10^6$/gmmol c.g.s.e.m.u.	$\chi_{\parallel}10^6$/gmmol c.g.s.e.m.u.	$\chi_{\perp}10^6$/gmmol c.g.s.e.m.u.	Anisotropy
WS_2	7.3×10^{-7}	3.9×10^{-6}	1397.4	4916.8	6314.2	24%
MoS_2	3.1×10^{-1}	1.2	−42.8	−87.1	−44.3	72%

(2) *Origin and nature of conductivity in WS_2*

In view of the type of bindings proposed for WS_2 its conductivities should have, evidently, been much lower than what has been experimentally obtained. Therefore to explain this appreciable conductivity, the obvious suggestion is that impurities are contributing to electrical conduction. This suggestion is further corroborated by the following considerations.

The small electrical anisotropy of $WS_2\left(\frac{\sigma_\perp}{\sigma_\parallel} \approx 5.3\right)$ observed on a fresh sample at room temperature disappears permanently when the sample is heated to higher temperature (figure 2) and considerable permanent increments take place in the actual values of conductivities also ($\sigma_\perp = \sigma_\parallel \simeq 10^{-4}$ ohm^{-1} cm^{-1}) by these treatments. But the magnetic anisotropy only changes from 24% to about 18% (Dutta, 1949) in course of such treatments. The obvious conclusion is that electrical conduction phenomena in WS_2 is not a regular contribution from the crystal lattice but from sources in the crystal external to regular lattice positions. In other words WS_2 is an extrinsic semiconductor. From resuts of our preliminary measurements of Hall effect of single crystals, as also from those of earlier measurements with powders of WS_2, we find that WS_2 is a p-type semiconductor.

(3) *Permanent changes in conductivities by heat treatments*

The observed permanent changes in conductivities (fig. 2), as stated above, may be explained if it is assumed that initially there had been a number of scattering or trapping or both kinds of centres in the crystal, which go to add to its resistance and that these centres are annealed out at higher temperatures. Existance of such an annealing effect in respect to these centres which may be foreign atoms, dislocations, or interstitials, vacancies etc. and possible combinations of some of these, is evident from figure 5+. It is to be noted, however, that similar annealing effects might also be caused by structural or chemical changes. But since no such effects are observed with magnetic properties, these (structural or chemical) may be ruled out. It may also be mentioned here that these centres which affect the transport properties considerably are evidently so low in number that their magnetic contributions would b e very feeble, and hence these can not in any way appreciably affect the high paramagnetic contribution of the host crystal. Therefore their removal, by heat treatment, will not affect the magnetic properties.

(4) *Activation energies*

From fig. 2 where $\log \sigma$ has been plotted against $1/T$ where T is the absolute temperature, we find that the plots are straight lines within the temperature range 400°K to 950°K (below 400°K there being a slight departure from linearity) indicating that a single type of carrier is effective in this temperature range (400°K

+From a study of such curves one can obtained information regarding the nature and kinetics of such scattering centres, a line of investigation which we propose to undertake in future.

to 950°K). Within this range the variation of σ with T can therefore be expressed by a relation of the type

$$\sigma = \sigma_0 e^{-\frac{\Delta E}{2KT}}$$

where σ is the observed electrical conductivity, σ_0, a constant, and ΔE the activation energy and the rest of the symbols have their usual significances. The values of ΔE (Table IV) obtained from the figure 2 represent the energy gap between the valence and the acceptor level in the forbidden region—the current being mainly carried by the holes in the valence band as already indicated. The values of ΔE obtained by other workers are also included in the table IV and are found to be lower than those obtained by us. The reason for this may be (i) the samples were in the form of powders and (ii) the temperature ranges were much lower, to cause proper annealing so that carriers of lower excitation energies might be effective in producing conduction. The trend of our curves (figure 2) at lower temperatures (below 400°K) also indicates the existence of such low energy carriers.

Table IV

Activation energy, ΔE of WS_2. $\Delta E_{\parallel}$ and $\Delta E_{\perp}$ refer to current directions parallel and perpendicular to c-axis respectively

<table>
<tr><th>Author</th><th>Nature of the specimen</th><th>Temperature range</th><th colspan="2">$\Delta E_{\perp}$ in e. volts</th><th>$\Delta E_{\parallel}$ in e. volts</th></tr>
<tr><td>Present author</td><td>Single crystal (Natural)</td><td>400°K – 950°K</td><td colspan="2">0.45</td><td>0.45</td></tr>
<tr><td></td><td></td><td></td><td colspan="3">ΔE in e. volts</td></tr>
<tr><td>Lagrenaudie (1954)</td><td>Powder (artificial)</td><td>77°K – 293°K</td><td>0.04,</td><td>0.11,</td><td>0.18</td></tr>
<tr><td>Decrue (1956)</td><td>Powder (artificial)</td><td>297°K – 373°K</td><td colspan="3">0.17</td></tr>
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(5) *Current—voltage characteristics*

Current voltage characteristics after the specimen had attained steady state through preliminary heat treatments are represented in fiures 3 and 4.

From these curves, it is observed that at room temperature and for currents along the basal plane WS_2 behaves like a symmetrical varistor i.e. curves remain symmetrical for both direct and reverse currents. At higher temperatures also this behaviour persists. For currents perpendicular to the basal plane, the said characteristics are shown in figure 4, wherein it is observed that at room temperature WS_2 is not only a symmetrical varistor but its resistance also decreases due to self heating by the passage of current through it i.e. it behaves as a thermistor also. Both these properties, however, become gradually less prominent as the temperature is raised. These interesting observations are being theoretically analysed and the results will be published in a subsequent communication.

Under proper conditions i.e. with one broad contact and one point contact rectification in single crystals of WS_2 has been observed at room temperature for currents perpendicular to the basal plane only. From fig. 1 where the current-voltage characteristics for both forward and reverse currents along the *c*-axis of a fresh sample of WS_2 are represented, one finds that the rectification ratio, is rather poor suggesting that '*spreading resistance*' due to radial distribution of current in this case is very small (Lagrenaudie 1952)

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