Magnetoresistance in molybdenite (MoS₂) crystals

B R. CHAKRABORTY AND A. K. DUTTA

Department of Magnetism,

Indian Association for the Cultivation of Science, Jadavpur, Calcutta 700032

The principal magnetoresistance ratios of molybdenite (MoS₂), the naturally occurring semiconducting crystal have been investigated at magnetic fields ranging from 4.5 KOe to 12.5 KOe and within the temperature range 300°K to 700°K Unlike some previous observations magnetoresistance has been found to be negative Also, for all directions (parallel or perpendicular to the c-axis) of electric current, magnetoresistance (transverse or longitudinal), unlike the usual notion, is maximum when the magnetic field is perpendicular to the c-axis. This has been shown to be a consequence of simultaneous presence of positive and negative magnetoresistance. The variation of magnetoresistance with magnetic field obeys nearly an $H^{0.74}$ law for transverse and $H^{0.8}$ law for longitudinal case in the range of 0 to 12.5 KOe field. With rise of temperature magnetoresistance decreases and reaches a very low value at about 600°K The low value remains temperature independent with further heating or cooling of the sample on the directional characteristics mentioned above. These behaviours are found to be in temperature region in which the conductivity is mainly a contribution from impurities. The results have been suitably analysed and discussed.

1. INTRODUCTION

Magnetoresistance of molybdenite (MoS₂), the well known semiconducting transition metal dichalcogenide, has been very sparingly studied Heaps (1912) first studied magnetoresistance in molybdenite natural crystals with currents along the basal plane only for transverse and presumably also for longitudinal case. Magnetoresistance was found to be negative and practically of the same value for all orientations of the magnetic field and to obey an $H^{0.6}$ (H-magnetic field strength) law of magnetic field variation. Though he obtained electrical contacts by copper-plating and soldering yet he reported no such fluctuations in the observed potential drops. He attributed this to *irregular changes which might be taking place in the specimen* Further he thought that much of the resistance was located at the contacts so that the observed behaviours could hardly be considered to represent the exact behaviour of the substance. But the same author when reporting the results of similar measurements with magnetite (Heaps 1912) utilising the same type of contact did not come across such difficulties. The only other observers of this property of molybdenite are Mansfield

8

& Salam (1953). They worked with a number of natural crystals most of which were not good specimens, their direction of current was along the basal plane and they obtained electrical contacts by smearing the ends of the specimen with aquadag and with simple pressure (obviously not a better method of contact than that adopted by Heaps) and placed the specimen on one of the pole pieces itself by means of wax. They did not report any fluctutations as observed by Heaps (1912) and did not raise the question of contact difficulties. They however found magnetoresistance to be always positive and magnetoconductivity* obeying an H^2 law of field variation. They further observed that magnetoresistance is maximum when the magnetic field is parallel to the c-axis. These authors (Heaps 1912, Mansfield & Salam 1953) have neither extended their observations to different temperatures, nor studied magnetoresistance for currents along the c-axis also. Therefore in view of contradictory nature of the findings and incompleteness of the data it is desirable that the experiments be repeated with some good crystals of molybdenite for all possible relative orientations of current and magnetic field with respect to the crystallographic axes as also at different temperatures. The present communication gives an account of these studies

2. EXPERIMENTAL

Molybdenite samples were obtained from Ceylon through the kindness of Dr. L. J. D. Fernando, Government mineorologist there and of late Dr. D. N Wadia, F.R.S. Experimental specimens were prepared by cleaving from a larger piece of sample and carefully cutting into suitable rectangular shapes. That such operations have not affected the structure in any way has been verified by X-ray methods. For electrical contacts specimens were freshly electroplated (with copper) and held in special holders described earlier (Bhattacharya 1965). Soldering was avoided because, firstly, heating may produce initial damage in the specimen and secondly, soldering by slight and sudden heating may produce imperfect contact.

Magnetoresistance was measured by the usual D.C. potentiometric methods with currents along and perpendicular to the basal plane for both transverse and longitudinal cases as also for directions of magnetic field making other angles with current direction and the c-axes. Observations were also recorded for different values of magnetic field ranging from 4.5 KOo to 12.5 KOo and at different temperatures ranging from 300°K to 800°K. All observations were made in dark and in vacuum. Magnetoresistance of a particular sample for current along the basal plane and magnetic field perpendicular to the c-axis has been recorded at room temperatures after the sample has been successively

---

* The definition is the ratio of change of conductivity $\Delta\sigma$ in σ (conductivity without field) to σ_H, conductivity in magnetic field. In the said paper there is an obvious printing error in writing σ for σ_H.

heated to different high temperatures and then cooled again to the room temperature.

Since magnetoresistance falls to negligible low permanent values after the samples are once heated to about 700°K, detailed X-ray observations were also made before and after such heat treatment.

3. RESULTS

Results of measurements are diagrametically represented in figures 1 to 4. It is observed from these figures that magnetoresistance is negative in all cases. It is also observed that whatever be the direction of current with respect to the c-axis, magnetoresistance (transverse or longitudinal) is maximum whenever the c-axis is perpendicular to the magnetic field. Further, with rise of temperature negative magnetoresistance in all the different cases decrease and attain extremely low value (also negative) at about 600°K and this value remain practically steady with further heating or cooling of the sample. This low value possesses all the directional characteristics stated above. Due to experimental
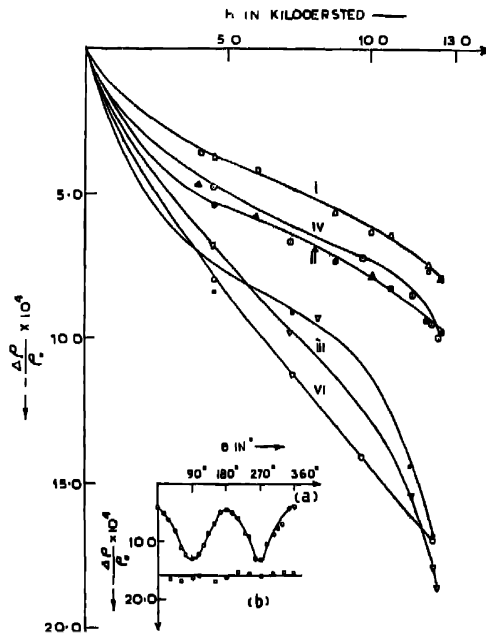

Fig 1. Magnetoresistance $(\Delta\rho/\rho_0)$ vs. magnetic field (H) : current (i) in the basal plane : H horizontal direction, i and c-axis is vertical or horizontal.

(1) $i_{vert} \perp H \parallel c_{hor}$; (2) $i_{vert} \perp H \perp c_{hor}$; $\triangle$–● observed values—▲ ○ calculated values; (3) $i_{hor} \parallel H \perp C_{hor}$; (4) $i_{hor} \perp H \parallel C_{hor}$; (5) $i_{hor} \parallel H \perp C_{vert}$; (6) $i_{hor} \perp H \perp C_{vert}$;

(a) $\Delta\rho/\rho_0$ vs. $\theta \to \overset{\wedge}{H\ C_{hor}}$; (b) $\Delta\rho/\rho_0$ vs $\theta \to \overset{\frown}{i_{hor}\ H}(C_{vert})$.

difficulties we could not make observations above 700°K except in one case where we could go up to about 780°K when negative magnetoresistance became practically unobservable. We could not however go deep into the intrinsic region which starts after 800°K (Guha Thakurta 1969).
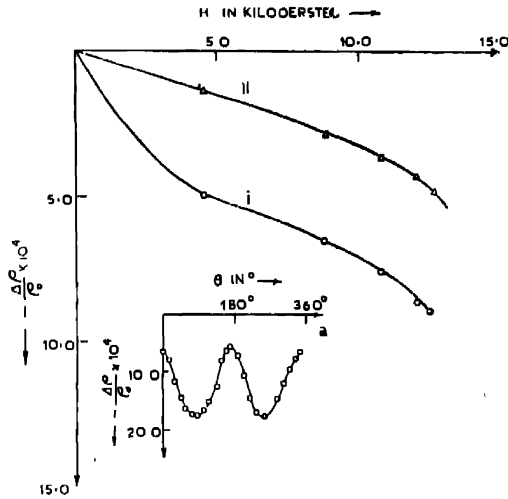
Fig. 2. $\Delta\rho/\rho_0$ vs H for i along c-axis : H horizontal.

(1) $i_{hor} \parallel c_{hor} \perp H$,   (2) $i_{hor} \parallel c_{hor} \parallel H$

(a) $\Delta\rho/\rho_0$ vs $\theta \to H \hat{C}_{hor}$.
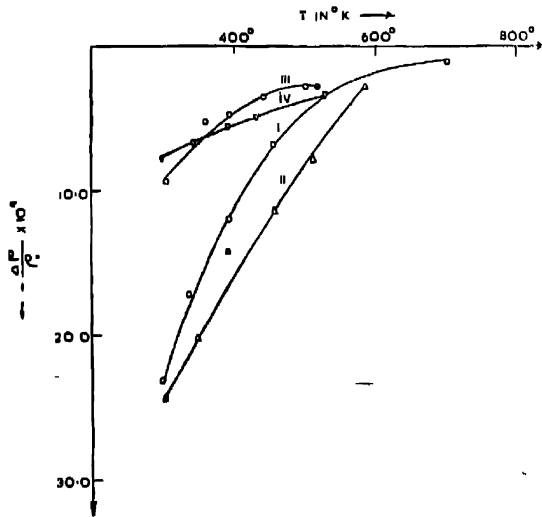

Fig. 3. $\Delta\rho/\rho_0$ vs T (temperature) °K : H horizontal

(1) $i_{vert} \perp C_{hor} \perp H$;   (2) $i_{hor} \parallel C_{hor} \perp H$;   (3) $i_{hor} \parallel C_{hor} \parallel H$;   (4) $i_{hor} \parallel H \perp C_{vert}$.

Fig. 4.   Effect of annealing on magnetoresistance.

1) Room temp. ($\Delta\rho/\rho_0$) for $i_{vrt} \perp H \perp C$ after annealing at different temperatures.

2) Unannealed fraction of impurities and defects at room temperature at different annealing temperatures.

3) Log of (2) vs temperature of annealing

From a scrutiny of the figures 1 and 2 it is observed that with the change of magnetic field the magnetoresistance ratio obeys the following laws of magnetic field variation for different cases, (i) an $H^{0.74}$ law for transverse, and (ii) an $H^{0.8}$ law for longitudinal case for 0 KOe to 12.5 KOe at room temperature.

The curves representing the temperature variation of magnetoresistance (figure 3) for the different cases have been found to obey a law of the type $A \exp(-\alpha t)$, α varying from 1.3×10^{-3} to 3.5×10^{-3} for different cases.

It may be mentioned here that in course of study of the temperature variation of electrical conductivity or magnetoresistance with fresh samples a fluctuation of the type reported by Heaps (1912) has also been observed by us. Once the samples are heated to the highest temperature all such fluctuations disappear— magnetoresistance, however, then becoming negligibly small. All our earlier observations on electrical conductivity, Hall effect and thermoelectric power (Guha Thakurata 1969) have been with samples once heat treated. Mansfield & Salam (1953), however, did not mention whether their samples were once heat treated or not. It may be mentioned here that our samples were of p-type

changing to n-type at $\sim 750°K$ while those of Mansfield and Salam were of n-type.

From the X-ray powder photographs obtained with molybdenite samples before and after heat treatment we find that no observable change in the powder pattern takes place by such treatment.

4. DISCUSSION

i) *Crystal structure and anisotropy in magnetoresistance*

The crystals used for this investigation were of natural origin and belong to the hexagonal layer lattice class having a space group D_{6h}^4 ($C6/mmc$) and polytype 2H. The lattice spacings and the different interatomic distances may be stated as follows :

$$a_0 = 3.1604\text{Å}, \quad c_0 = 12.295 \text{ Å}.$$

Layer distance = 3.66 Å (S–S distance between double layers),
Mo—S separation = 2.35 Å.

Thus a layer of Mo atoms is sandwitched between two parallel layers of S atoms and S atoms are at the corners of right equilateral trigonal prisms.

In keeping with this structure the diamagnetic susceptibility as well as electrical conductivity show remarkable anisotropies, susceptibility with magnetic field along the c-axis is much larger than that in a perpendicular direction, anisotropy ($\Delta\chi/\chi$) being $\sim 72\%$ and electrical conductivity in the basal plane is much larger (10^3 times) than that in a perpendicular direction. Thermoelectric power, however, does not show any anisotropy (Guha Thakurta 1969), the origin of which is of course different.

Now coming to the case of negative magnetoresistance (at room temperature) as observed by us, we arrive at an altogether different situation. No anisotropy of magnetoresistance is observed with respect to the direction (along or perpendicular to c-axis) of electrical current, whereas, appreciable anisotropy is observed with respect to the direction of magnetic field. But contrary to usual notion regarding this type of crystals, magnetoresistance here is maximum when magnetic field is perpendicular to the c-axis. The reason for this anomalous behaviour becomes obvious from the following considerations.

It is now well known that appearance of negative magnetoresistance is to be attributed to the presence of impurities and defects in the specimen. In the case of molybdenite we know (Guha Thakurta, thesis, unpublished), that it contains impurities which are mainly responsible for the low temperature behaviours (including the unstable behaviours during initial heating) of many of its electrical and thermoelectric transport properties It is reasonable to presume here that

all these impurities are not equally bound to the lattice, some may be rather loosely bound. However, negative magnetoresistance may be considered to be due to all such impurities. But in addition to this negative magnetoresistance it is natural to expect that molybdenite should also show the usual type of positive magnetoresistance. The observed magnetoresistance (negative) should therefore be considered as the resultant of those two effects, the negative effect always masking the positive. The actual numerical values of these effects should be such that this resultant is always the greatest when the magnetic field is perpendicular to the c-axis. The origin of observed anomalous anisotropy of magnetoresistance becomes then quite obvious. But these explanations should be confirmed by other considerations before final acceptance.

ii) *Magnetic field variation of negative magnetoresistance*

From what has been stated above it is obvious that the observed magnetic field variation is a combined effect of the field variation of both positive and negative magnetoresistance. The observed resultant negative magnetoresistance will therefore be related (assuming both positive and negative types of magnetoresistance to vary with some powers of H, the powers being different for the two cases) to magnetic field in a rather complicated way and may be represented as,

$$m_{obs} = Bf(H)H^\beta,$$

where m_{obs} is the observed transverse magnetoresistance; and $f(H)$, some function of H $\left(= 1 - \dfrac{A}{B}H^{\alpha-\beta}; A, B \text{ and } \alpha, \beta \text{ are constant}; A \text{ and } \alpha \text{ representing the positive} \right.$ case and B and β the negative). Here instead of taking an H^2 law for field variation (Mansfield & Salam), we have assumed an H^β and H^α type of field variation for negative and positive magnetoresistance, respectively.

In view of this relation, in order to verify some of the observations and assumptions of the preceding section and to calculate the different parameters arising in the relation, we need to consider only the particular case where the transverse condition is always maintained for all orientations of the magnetic field with respect to the c-axis i.e., when the electric current is along the basal plane flowing in a vertical direction and the magnetic field is horizontal. From the observed magnetic field variation for this particular case the different parameters have been calculated for a typical specimen studied. The values of parameters for two different dispositions i.e., when the c-axis is parallel and perpendicular to H respectively are given in the table 1, in which the calculated values of positive and negative parts of the total magnetoresistance are also shown.

From the above table we find that both the positive and the negative portions of the total magnetoresistance show the type of anisotropy as is relevant for this class of crystals, their individual numerical values being such that the total

Table 1

Relative disposition of current (i), magnetic field (H) and the c-axis	A	B	α	β	$M-$ (positive magneto-resistance at $H = 10$ KOe)	$M-$ (negative magneto-resistance at $H = 10$ KOe)	Total magnetoresistance at $H = 10$ KOe	
							Calculated	Observed
$i_{vert} \perp H \perp C_{hor}$	1.81×10^{-8}	6.6×10^{-7}	1.17	0 85	8.66×10^{-4}	$16\ 56 \times 10^{-4}$	$7\ 89 \times 10^{-4}$	7.95×10^{-4}
$i_{vert} \parallel H \parallel C_{hor}$	$3\ 38 \times 10^{-9}$	1.2×10^{-7}	1.39	1 05	$12\ 27 \times 10^{-4}$	$19\ 49 \times 10^{-4}$	6.75×10^{-4}	6.30×10^{-4}

magnetoresistance also show the anomalous anisotropy referred to in the preceeding section. Indeed the calculated values of total magnetoresistance at different fields are in fair agreement with the observed ones (figure 1(i) & 1(ii)). Thus the assumptions made in the preceding section appear to be justified so far as the room temperature behaviours are concerned.

iii) *Temperature variation of magnetoresistance*

According to the above assumptions it may naturally be thought that the rather loosely bound impurities might be permanently and progressively removed by heat treatment as well as the defects might be similarly annealed. So the carriers, which are available at any particular temperature due to such impurities and defects, might not be all available at some higher temperature. The observed sharp rate of decrease of magnetoresistance with rise of temperature may therefore be mainly associated with this progressive permanent decrease of carriers Effect of usual temperature variation of magnetoresistance due to temperature variation of the relevant characteristics of the carriers are usually not very large and significant. Heat treatment to the highest possible temperature removes most of the loosely bound impurities and defects so that the instabilities initially observed in magnetoresistance and conductivity measurements are removed. The small nearly constant magnetoresistance observed after the final heat treatment no doubt arise from the strongly bound impurities and defects which are not so removed.

Under these assumptions the thermal rate of decrease of magnetoresistance should nearly be the same as that of removal of impurities and defects. As shown in a previous section the decrease of magnetoresistance with temperature follow a law of the type $A \exp(-\alpha T)$, where α varies from 1.3×10^{-3} to 3.5×10^{-3} from sample to sample. Now utilising figure 4(1) where the effect of isochronal annealing on magnetoresistance has been shown against the temperatures we can find, under the above assumptions, the fraction of unannealed impurities and defects at different temperatures (figure 4(2)). The thermal variation of this fraction has been found (figure 4(3)) also to obey a law of the type $A' \exp(-\alpha' T)$, where $\alpha' = +.61$. Thus our above expectation appears to be more or less justified.

The negative value of the small, residual and temperature independent magnetoresistance observed after initial heat treatment may be explained to be due to the fact that the retained impurities contribute to negative mangnetoresistance whose numerical value is still slightly larger than that of the positive magnetoresistance.

iv) *Origin of negative magnetoresistance in molybdenite*

Magnetoresistance arises from the fact that the mobility of the charge carriers is affected by the imposition of the magnetic field. Generally, the effect of magnetic field is to decrease the average mobility of the carriers so that resistance

increases and the magnetoresistance is then said to be positive. A negative magnetoresistance i.e., a decrease in resistance due to the imposition of the magnetic field can sometimes arise in nonferromagnets due to the following reasons. One of these (Ziman 1962) postulates the existence of carriers with free spins (due to defects and impurities) which align on the application of magnetic field and hence there is a decrement of resistance. According to the other suggestion (Sasaki et al 1960) the carriers in specimens showing negative magnetoresistance may be supposed to be lying in two impurity bands, one of higher mobility and the other of lower mobility. Effect of magnetic field is to cause different energy shifts in these two bands which increase the population of the former band so that the average mobility of the carriers increases and negative magnetoresistance is observed.

The idea of existence of such bands has however been obtained from the suggestion of Toyozawa (1960) that there are two kinds of impurity levels. This latter suggestion regarding magnetoresistance could very easily explain the phenomena at extreme low temperatures and high magnetic fields but are not evidently so easily applicable at ordinary temperatures and moderate magnetic fields. These suggestions inspite of their limitations indicate that appearance of negative magnetoresistance is associated with the existence of defects and impurities in the specimen. Experimental evidences also support this view In fact, negative magnetoresistance is found to exist in those cases where electrical conductivity is mainly due to impurities, the value of the effect being dependent on the concentration of impurities etc. Now coming to the case of molybdenite no existence of free spins could be detected from our magnetic studies, the specimens being totally diamagnetic (Dutta 1945, Das 1963). Existence of impurities which could be easily removed by heat treatment (loosely bound impurities) as well as of those which could not be so removed have already been indicated from conductivity measurments (Guha Thakurta, thesis, unpublished). Thus the observed magnetoresistance in molybdenite as earlier surmised is to be associated to these impurities—initial magnetoresistance being due to both the loosely bound impurities and the strongly bound ones and the residual small magnetoresistance observed after heat treatment being due to the strongly bound impurities. When these latter impurities completely ionise at higher temperatures (above 750°K), when intrinsic conduction is about to start and the type of conduction about to change from p-type to n-type negative magnetoresistance is not observable. Observations at still higher temperatures would have yielded interesting results, but unfortunately we could not, as stated earlier extend our observations to such high temperatures.

5. CONCLUDING REMARKS

Since our observations on magnetoresistance are at variance with those of Mansfield & Salam (1953) it would be useful to review here some features of

their work also. They had 23 specimens at their disposal of which five (Specimen 14, 15, 5, 21, 22) were used for detailed studies. Of those only two, namely specimens 5 and 21 were good single crystals. Though homogenity tests were performed on all the five specimens yet results on only three specimens (5, 21 and 22) were given where from samples 5 and 21 were found to be also the best ones. Results of conductivity and Hall effect measurements were given for all these five specimens, and those of thermoelectric power for three specimens (5, 21 and 22), but a different specimen not included in the above list of five, namely specimens 7 was used for magnetoresistance measurements—nothing being reported regarding its type, perfection and homogeneity. Though there was a sample to sample qualitative variation of the different properties (except magnetoresistance) studied by them yet within their range of temperature the general nature of their results were the same as those of ours (Guha Thakurata 1969) Therefore in the absence of measurements of other transport properties with sample 7 nothing can be said conclusively from their observations

Inspite of its limitations if we, for the present case, take into consideration the second suggestion regarding the origin of negative magnetoresistance according to which the carriers are supposed to exist in two impurity bands differing in mobilities and that due to the imposition of magnetic field there is an increase in the population of the higher mobility band, it is natural that the mobilities themselves will undergo change in the usual manner by the magnetic field leading to positive magnetoresistance effect Therefore our earlier assumptions of simultaneous existence of positive magnetoresistance appears justified.

The loosely bound impurities, which has been referred to in some previous section and to which the appearance of a portion of negative magnetoresistance has been ascribed, may either be trapped centres or/and absorbed gases But in the latter case decrease of negative magnetoresistance due to desorption by heating would have been partially restored due to readsorption after cooling. No such phenomenon being observed, trapped centres seem to be the cause of the observed unstable magnetoresistance phenomena of molybdenite. It may be mentioned here that there is no such observation in case of magnetic studies— room temperature magnetic susceptibility as well as its temperature variation remaining the same after initial and subsequent heat treatment The reason for this may be that the number of trapped centres is such that it cannot appreciably affect the bulk magnetic susceptibility but can affect the transport properties by creating sufficient charge carriers

REFERENCES

Bhattacharya R. 1965 *Ind. J. Phys.* **39**, 53.

Das D. 1963 *Ind. J. Phys.* **37**, 582.

Dutta A. K. 1945 *Ind. J. Phys* **18**, 249.

Guha Thakurta S. R. 1969 *Ind. J. Phys.* **43**, 169.

Heaps C. W. 1912 *Phil. Mag.* **24**, 813.

Mansfield M. & Salam S. A. 1953 *Proc. Phys. Soc. (Lond.)* **66B**, 377.

Sasaki W., Yamonouchi C. & Hatoyama G. M. 1969 *Proc. Intern. Conf. Semicond. Phys.* Prague, p. 159.

Toyozawa Y. 1960 *Proc. Intern. Conf. Semibond. Phys.* Prague, p. 216.

Ziman J. M. 1962 *Electrons & Phonons*, Oxford Univ. Press, p. 348.