THE ELECTRICAL CONDUCTIVITY OF MOLYBDENITE

By A. T. Waterman

Abstract

Electrical conductivity of molybdenite (MoS_2) as a function of voltage and temperature.—Measurements of the currents through narrow flat strips cut perpendicular to the crystallographic *c*-axis gave results for the range from 0° to about 200° C, in agreement with the equation: $i = KV^be^{-k/T}$, where, for the mineral in the ordinary state, k is about 3,000 and b generally about 1.6. When the voltage is increased to a critical value, breakdown occurs, due to the electric heating. An expression is derived for the breakdown temperature, which is shown to increase as k diminishes. Above 200° irregularities appear; and after heating to 400° and higher or after current heating beyond the breakdown point, the conductivity at ordinary temperatures is usually permanently improved, and k is decreased. In fact, by the use of proper current cycles, a strip may be transformed by stages from a very poor conductor (resistance several megohms) into a reasonably good conductor (resistance only a few ohms), obeying Ohm's law ($b = 1$). At the same time, k diminishes and the breakdown temperature rises until the break disappears at the limiting value of k predicted by the equation; also the *photoelectric sensitivity and dielectric polarization* disappear. A high potential discharge likewise increases the conductivity. This remarkable *permanent change of conducting state* may indicate a corresponding change of structure from an α to a β form, as suggested for selenium. If the constant k is interpreted as being equal to φ/R, where φ is the energy required to change a bound to a free electron and R is the gas constant, then φ is computed to vary from 0.26 volt for MoS_2 in its normal state to 0.13 for the conducting state. This may be of interest in connection with the electron theory of conductivity.

THE mineral molybdenite (MoS_2) is one of an interesting class of substances, the poor conductors of electricity, and has been the subject of considerable research, chiefly in regard to its optical properties and its photoelectric sensitivity.[1] The writer was led to the present investigation by peculiarities noted in its conductivity when examining its thermionic emission.[2] The general behavior of a fresh sample of molybdenite when heated by an electric current resembles that of any material having a large negative coefficient of resistance, including breakdown, and is shown graphically in the above-mentioned paper by the author.

Inasmuch as Ohm's law is not obeyed by molybdenite (like many other

---

[1] Koenigsberger and Schilling, Centralblatt f. Mineralogie, p. 454, 1905; Coblenz, Bureau of Standards, Scientific Papers **15**, 121, 1919; **16**, 595, 1920.

[2] Waterman, Phil. Mag. **33**, 225, 1917.

substances of this class), it has seemed best in this investigation to examine the effects of temperature and applied e.m.f. on the current transmitted rather than on the resistance as ordinarily done. In all experiments the material was used in the form of narrow flat strips of length generally between 1 and 2 cm. The current was passed lengthwise through the strip, at right angles to the crystallographic *c*-axis. The strips were mounted in a number of ways (soldering, copper-plating and soldering, and clamping between leads of different materials), but the method of mounting did not appear to change the essential behavior when due account had been taken of the effect of the mounting process (*e.g.*, heating) on the state of the strip.

Electrical conduction at ordinary temperatures.—By observations on the variation of current with temperature under constant applied potential difference, and on the variation of current with applied e.m.f. at constant temperature, the following formula for the conductivity of molybdenite in its ordinary state was found to hold to a fair degree of approximation:

$$i = KV^b e^{-k/T}, \tag{1}$$

where i is the current, V the applied e.m.f., T the temperature absolute, and b, k and K are constants. The value of b is generally about 1.6, although for one strip a value of 2.8 was found. k is nearly always approximately 3,000 degrees. K is a function of the dimensions of the strip, pressure applied at contact, etc. The graphs in Fig. 1,

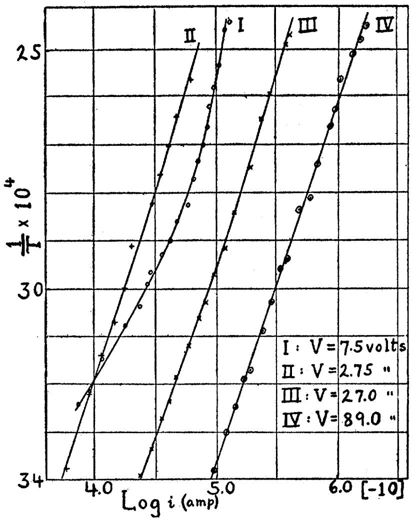

Fig. 1

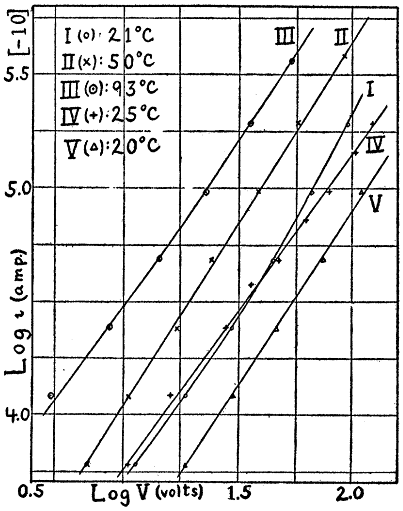

Fig. 2

where the logarithm of the current is plotted against the reciprocal of the absolute temperature, show the degree of verification of the constant e.m.f. relation for four values of the latter, from 2.75 to 89.0 volts. Graph I. shows a slight fatigue effect common to fresh strips, which causes a departure from the linear relation. The temperature range employed was from 0° C to 150° C, obtained in an oil bath. Attempts to secure greater range by means of an electric oven led to inconsistent and uncertain readings above about 200° C, due apparently to partial breakdown which is facilitated by rise in temperature of the surroundings. The graphs in Fig. 2, where the current is plotted logarithmically against the applied e.m.f., show the results of the observations at constant temperature, maintained by an oil bath.

Change in conductivity after treatment at higher temperatures.—Assuming the validity of the Eq. (1), a linear relation should be found between log V and $1/T$ at constant current. The extent of the agreement is shown in Fig. 3 where a number of curves are given for successively

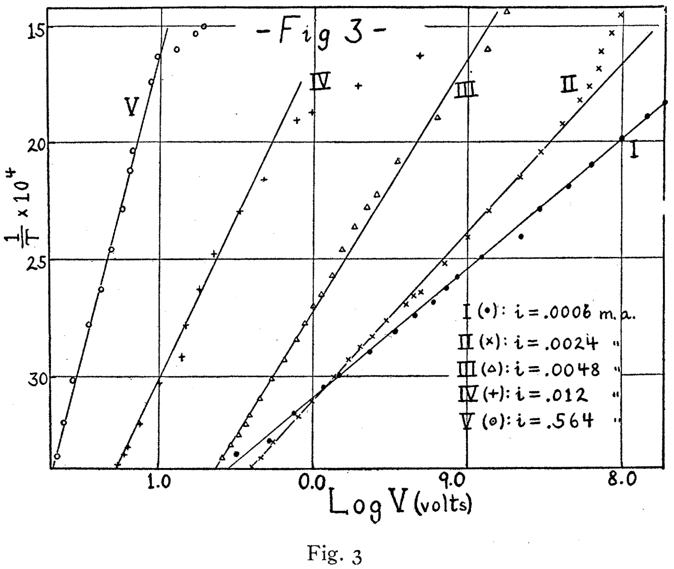

Fig. 3

larger values of the (constant) current, from observations made in the oven from room temperature up to 400° C and higher. The oven method of heating proved here more satisfactory due to the decrease in the applied e.m.f. as the temperature was raised. Heating in the oil bath gave results consistent with the formula for $k = 3{,}000$ and $b = 1.5$ to 1.6. From Fig. 3 it appears that the type of formula found above is satisfied for temperatures at least below 200° C. At some point above this temperature each curve departs from the linear relation, in many cases showing irregularities of which some were traced to contact variations. But the outstanding feature of these results is that the slope of the curve, which is proportional to b/k, increases with each series of observations. The ratio b/k is not however a function of the current, since, when the heating is carried to high temperatures, the cooling curve (not shown) for any particular value of the current has a greater slope than the heating curve but the same slope as the heating curve for any other current to which the strip is then subjected. Thus the passage of the current through the strip at temperatures over 200° C seems to result in a permanent increase in the ratio b/k, while for temperatures below this point b/k remains substantially constant. The value of b was found to be a maximum for new strips, consequently this permanent increase in b/k must be attributed to a marked decrease in the value of k. The constant K also undergoes considerable change but as it is quite sensitive to contact variations little may be concluded from these changes.

The phenomenon of breakdown.—The break is encountered only when the strip is heated by means of the current. Unless suitable resistance is provided in series, there is a large discontinuity in both current and voltage at the break, the current rising to many times its former value with a corresponding drop in the voltage. With proper precautions however the break may be made to take place slowly and continuously and the current and voltage are comparatively stable. As the current is made to increase continuously, the potential difference across the strip at first increases, reaching a definite critical maximum (the break), and then decreases steadily. This phenomenon has been explained by Lyle [1] in the case of boron. The explanation is based upon the fact that the condition for stability for any reading is that of equilibrium between the rate of heating by the electrical power and the rate of cooling by radiation, conduction, etc. If the material has a large enough negative coefficient of resistance, the heating effect may automatically increase more rapidly than the cooling effect. Thus there comes a point where there can be no equilibrium between the two unless either the temperature rises to a high value or the rate of increase in electric power is limited by external resistance. Since the rate of heating may be taken to be the product of the current and the voltage and the rate of cooling for a given set-up equal to $c(T - T_0)^x$, where $T - T_0$ is the difference in temperature between the strip and its surroundings and c and x are constants, the conditions under which breakdown occurs may then be readily derived from Eq. (1).

---

[1] Phys. Rev. (2), 11, 253, 1918.

Differentiating (1) logarithmically with respect to i

$$\frac{1}{i} = \frac{b}{V}\frac{dV}{di} + \frac{k}{T^2}\frac{dT}{di}$$

for the range over which k is constant. The condition for the break is $dV/di = 0$. Hence

$$\frac{1}{i} = \frac{k}{T^2}\frac{dT}{di}.$$

But

$$\frac{dT}{di} = \frac{dT}{dP}\cdot\frac{dP}{di},$$

where P is the power supplied, and since V is constant at the break, $dP/di = V$, while dT/dP may be found from the condition for equilibrium $P = c(T - T_0)^x$, *i.e.*, $dT/dP = (T - T_0)/Px$. Hence,

$$\frac{k}{x} = \frac{T^2}{T - T_0}, \tag{2}$$

which gives the temperature of the break for particular values of x, k and T_0.

For a given arrangement of the apparatus it is seen that the temperature required for the break will be higher as k becomes smaller, and consequently more electrical power must be supplied to bring this about. Furthermore, there is a limiting value of k for given value of T_0, the temperature of the surroundings, below which no break will be obtained. In other words, as the value of k diminishes it becomes increasingly difficult to effect a breakdown. The effect of increasing T_0 is to facilitate the break, although it then takes place at higher temperature.

Progressive change in conductivity under current heating.—This behavior is illustrated in Fig. 4, where current-e.m.f. curves are shown for successive current heatings of a single strip in a vacuum. The scale used varies from curve to curve as indicated. A distinct hysteresis effect is apparent, together with permanent increase in conductivity, occurring chiefly when the heating is carried beyond the break. After any single cycle the current-voltage curve is quite reversible for voltages below breakdown.

A fresh strip has a very low conductivity, but after such treatment it appears to possess metallic conductivity at ordinary temperatures since Ohm's law is obeyed, the temperature coefficient of resistance vanishes or even becomes slightly positive, and the specific resistance approaches that of metals. With sufficient heating, however, the hysteresis effect again appears. The resistance of the specimen illustrated was changed by this process from about 20 megohms for 1 volt at room temperature to 4 ohms. This strip was never brought to a visible red heat and remained unchanged in general appearance.

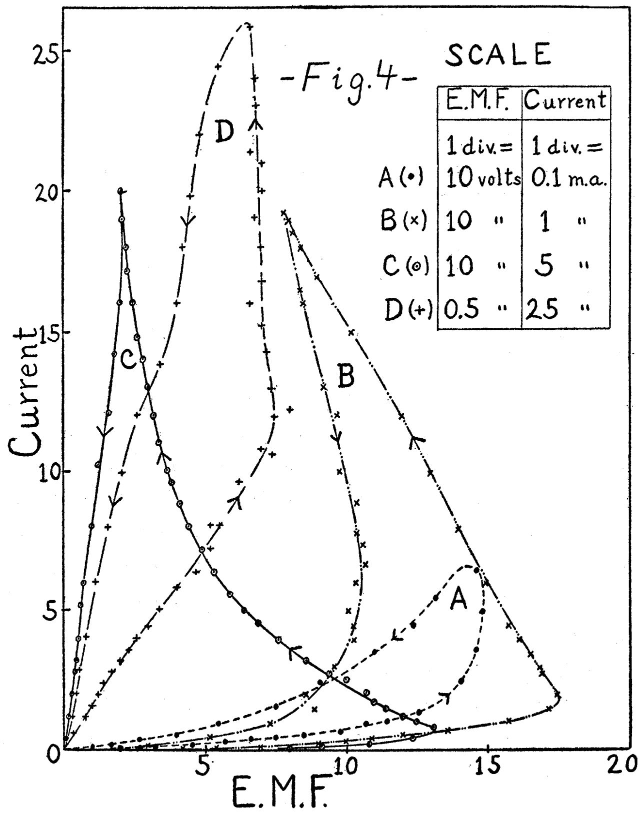

Fig. 4

In two instances a strip in the intermediate state, when brought just to the break, went through a reverse cycle, resulting in permanent *decrease* in conductivity.

Successive breakdown temperatures and values of constants.—Under this treatment the exponent b of the formula decreases to unity (Ohm's law). Its successive values are listed in Table I.

Since the value of k is known at the outset (Graph A), the temperature of the break as calculated from Eq. (1) is 69 ± 3° C. As computed from Eq. (2) the break should occur at $T' = 69 \pm 5°$ C. For the remaining graphs B, C and D the values of k and of T', the temperature of break, may be calculated from the experimental data and Eqs. (1) and (2). These values are shown in Table I., and were checked by calculation based on the power necessary for breakdown, with the exception of Graph *A* where the applied e.m.f. seems to be the chief factor in the change of state in a manner similar to the initial fatigue effect first mentioned. It will be noted that the value of k decreases from graph to graph as found before, and the temperature of breakdown increases.

TABLE I

Graph	b*	k*	T'	ϕ (equivalent volts)
A	1.65	3,000	69° C	0.26
B	1.65	2,500	82	0.215
C	1.14	2,000	109	0.17
(not shown)	1.0	1,760	138	0.15
D	1.0	1,520	205	0.13

* From heating curve.

As k decreases it is observed that the slope of each successive graph beyond the break increases. From examination of the graphs one might expect to find no voltage maximum for values of k below some limiting value not far below its value 1,520 for Graph *D*. This prediction was verified. Now from Eq. (2) it is seen that under the conditions of this experiment there is no real value of T', *i.e.*, no voltage maximum, when k is less than about 1,450. This fact strengthens the validity of the foregoing discussion.

Interpretation of k.—The relation $i = K_v e^{-k/T}$ is consistent with the expression found by Koenigsberger and Schilling[1] for the temperature variation of specific resistance for a number of poor conductors. In the theory underlying this relation kR is the latent heat (at constant volume per gram electron) of a hypothetical chemical reaction giving rise to free electrons, R being the gas constant. If this significance is attached to k in the present case, the mean energy ϕ thus required to produce a free electron is computed to be 0.26 equivalent volts for molybdenite in its normal state. This does not appear to be an impossible value, being considerably less than the corresponding quantity for thermionic electron emission (or, more briefly, "thermelectron" emission), for photoelectrons, and for electrons produced in ionization of gases. Furthermore, ϕ decreases as metallic conduction is approached, as might be expected, its values being listed in Table I. for the specimen there considered. This interpretation then yields results which are so far consistent with the ordinary electron theory conception of conduction and insulation. Thus a large value of k would be indicative of an insulator for which a corre-

---

[1] Koenigsberger and Schilling, Ann. der Phys. 32, 179, 1910.

spondingly large e.m.f. would be required to effect breakdown, though this would be expected to occur under less electrical power and with very slight rise in temperature above the surroundings. A small value of ϕ, on the other hand, would mean metallic conduction and absence of breakdown. An equilibrium theory of electrical conduction has been developed by the writer along these lines, and will shortly be published.

Miscellaneous observations.—(1) The light sensitivity in conduction of a fresh strip of molybdenite becomes inappreciable as metallic conduction is approached.

(2) The unipolarity of a fresh sample is in general slight.[1] However, a moderate e.m.f. applied in one direction may cause a temporary decrease in resistance (to $\frac{3}{4}$ or $\frac{1}{2}$ its original value) to a small current passed in the opposite direction, but the effect soon disappears. The effect was not cumulative either in magnitude or duration; hence some variety of electrolysis seems out of the question, and a Peltier effect inadequate. This effect disappears as metallic conduction is brought about.

(3) Heating to redness in a Bunsen flame for several minutes reduced the resistance to $\frac{1}{2}$ or $\frac{1}{4}$ its value, but further heating produced practically no further effect.

(4) The resistance was diminished to about half value by the momentary passage of a high voltage discharge, as from a small induction coil, but repetition caused no further decrease.

(5) The resistance is not affected by strong magnetic fields.

(6) Slow oxidation occurs on heating in air, the products being given as SO_2 and MoO_3, the latter forming in crystals on the surface of the strip. This does not seem to affect the general behavior of the substance otherwise than would be expected. Under a low power microscope oxidation is seen to be preceded by local eruptions of a dark blue liquid, mentioned by Coblenz[2] and presumably due to a lower oxide of molybdenum.

Discussion of conduction in ordinary state.—In accounting for the initial relation between current and e.m.f. at constant temperature, if the number of conducting electrons is assumed independent of the e.m.f. applied, we have as possibilities:

(1) Variation in contact conditions. This seems unlikely, since the current-voltage function does not appear to be affected by changes in nature or pressure of contact.

(2) Action resembling space charge effect. The form of the function $i \alpha V^{1.6}$ recalls Child's law for thermionic emission, but such an explanation does not seem compatible with the temperature variation. More-

---

[1] Cf. Coblenz, Bureau of Standards, Scientific Papers **16**, 595, 1920.

[2] Coblenz, Bureau of Standards, Scientific Papers **15**, 155, 1919.

over, the same law should then hold even more for greater concentrations of the free electrons, where Ohm's law holds instead.

(3) E.m.f. of polarization varying in such a way that the resultant electric intensity would produce the observed function. Thus the temporary polarization produced by an applied e.m.f. may be the fatigue effect of a stronger instantaneous polarization.

(4) Orientation of elementary crystals under action of the electric field, thus increasing the mean free path of the conducting electrons. This explanation, commonly reached for similar phenomena by the process of elimination, is hardly open to direct argument at present.

If it be assumed that the number of free electrons is a function of the applied e.m.f., we may imagine a gradual breakdown of the material as a dielectric or possibly ionization by collision if the mean free path is as long as the recent experiments of Bridgman indicate for metals, since an electronic kinetic energy approaching 0.26 equivalent volt might not then seem impossible. As evidence may be mentioned the effect of a high potential discharge on the state of a fresh specimen and the similar change illustrated in Graph *A*, Fig. 4, where the heating was slight.

Discussion of permanent change in conductivity.[1]—The remarkable permanent or semi-permanent change in conductivity may be closely bound up with the nature of the temporary change produced by temperature and electric field, in that the latter when carried far enough bring about a different condition for equilibrium within the material. The only evident change in physical properties is an increase in hardness. No chemical or x-ray analyses were made of the substance in its state of metallic conduction. The purity of the mineral renders unlikely any extensive reaction with impurities contained. The most reasonable supposition is suggested by the prevalent view in regard to the constitution of Se, that molybdenum sulphide may exist in two forms, α of high resistance and β of low resistance. By means of various agencies (heat, electric field and light) the ordinary form α may be transformed into the β variety. α would be characterized by a large value of k and β by a small value. It would be further necessary to credit the form β with metallic conductivity, which is possibly an objection to this hypothesis although it may be that a very small value of k in itself necessitates metallic conduction.

One other compound of molybdenum with sulphur is known, namely, MoS_3, and if a chemical change occurs it may be the formation of metallic molybdenum within the substance according to the reaction: $3MoS_2$

---

[1] At present writing it appears that the condition of improved conductivity is not stable but that the substance tends slowly to revert of itself to its original state.

$\rightarrow 2MoS_3 + Mo$. This might be expected to cause a decrease in the mean value of k, followed by increasing evidence of metallic conduction. A fact of uncertain significance in this connection is the author's discovery [1] of an emission of Mo^{++} ions from molybdenite at temperatures near the change of state.

In explanation of the light sensitivity of molybdenite in its conduction it is suggested that the absorption of radiation would decrease the mean energy necessary to free an electron and thus the resulting decrease in k would show in an increase in current. In connection with the curious light negative response found by Coblenz,[2] the permanent decrease in conductivity found under special conditions is interesting. For the explanation of this effect the hypothesis of the existence of two forms of the crystal appears to be the most illuminating.

This paper comprises the results of experimental investigations begun at the University of Cincinnati and completed at Yale University.

SLOANE PHYSICAL LABORATORY,
YALE UNIVERSITY,
August 25, 1922

---

[1] Waterman, loc. cit.

[2] Coblenz, Bureau of Standards, Scientific Papers 16, 595 (1920).