suitable integral equations, so that all the conditions of the problem should be satisfied. This, in itself, would not amount to more than a formulation of the general problem in different terms and would not advance its practical solution, unless possibly such a form of statement should lead to improved methods of approximation for the equivalent distribution.

The Resistivity of Polycrystalline Wires in Relation to Plastic Deformation, and the Mechanism of Plastic Flow.

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1. *Introduction.*

The subject of metallic conduction of electricity has long been a source of difficulties, which are far from having been overcome by the many admirable and ingenious theories recently put forward.* The peculiarities of the different individual metals, as exemplified, for instance, in the variation of the Wiedemann-Franz ratio from metal to metal seem to fall right outside any scheme so far elaborated. At present it is only possible to treat a metal as if it were a homogeneous crystal, the insufficiency of which assumption may be the source of many of those discrepancies between theory and experiment now attributed to fundamental properties of the electron in metal. Any experimental evidence concerning variations in electrical conductivity which can be produced in one pure metal by mechanical treatment should therefore be of some interest for the general problem. In particular the effect of permanent deformation upon electrical conductivity in metals is full of obscurity,† and seems to offer a field for experiment.

It was decided to investigate the variations of conductivity with certain simple types of deformation which attend the flow of soft metals. The flow of polycrystalline wires under constant stress has been investigated by one of us,‡

* See, *e.g.*, Hume-Rothery, "The Metallic State," (1931), p. 291, *et seq.*

† See, *e.g.*, Hume-Rothery, *loc. cit.*, p. 27.

‡ Andrade, 'Proc. Roy. Soc.,' A, vol. 84, p. 1 (1910), and A, vol. 90, p. 392 (1914).

and the changes of mechanical properties with time examined. The process of flow can be analysed into three phases :—an initial stretch which occurs within a very short time of the application of the stress ; a continuous flow, the rate of which decreases with time, called, from the constant used to express it, the β-flow ; and a flow at constant rate per unit length which occurs simultaneously with the β-flow and continues until the wire breaks. The formula expressing the flow is

$$l = l_0(1 + \beta t^{1/3})\, e^{kt}, \tag{1}$$

where l is the length at time t, and l_0, β and k are constants. Since the formula was first put forward* analogous formulæ, involving $t^{1/3}$, have been found by other workers for different substances. Thus Filon and Jessop found for celluloid† $l = l_0 + at^{1/3} + bt$, and Peirce‡ has expressed the decrease of the couple required to maintain constant torsion in a cotton fibre by a formula $c = c_0 + ae^{-\beta t^{1/3}}$, so that a term in $t^{1/3}$ apparently represents with some generality the observed behaviour of solids during flow. In former publications the general features of the behaviour were expressed in terms of crystal structure,§ but at the time no evidence from other sources could be adduced to support the hypothesis. The object of the present investigation is to measure the specific resistivity of the metal during the plastic extension, and to use the data so obtained to elucidate the changes of structure which take place in a polycrystalline wire when it is extended. One of the chief results has been to show that the β-flow has a real physical significance, and is due to the rotation of the axes of the crystallites which constitute the polycrystalline wire. Experiments have also been carried out on the resistivity of single crystal wires, the results of which will be published in the near future.

To compare the specific resistivity of the wire at any stage of the extension with that of the unstretched wire, it was necessary to measure simultaneously the length and the resistance of the wire flowing under large constant stress. The metal first investigated was cadmium, in the form of wire, of diameter 0·046 cm., which was annealed for 6 hours at 100° before use. It was established by trial that higher temperature or longer time of annealing had no further effect on the properties of the wire that were being investigated. Experiments were also carried out with wires of copper, aluminium and tin,

* Andrade, *loc. cit.* (1910).

† 'Phil. Trans.,' A, vol. 223, p. 89 (1922).

‡ 'Shirley Institute Memoirs,' vol. 2, p. 278 (1923).

§ Andrade, *loc. cit.*

in all of which cases the annealing was performed under the same conditions as for cadmium.

2. *Apparatus for the Application of the Stress.*

An apparatus was designed with the following objects :—

(i) To apply a constant stress to a wire kept at a constant temperature.

(ii) To measure the length of the wire, and

(iii) To measure the resistance of the wire.

One end of the wire, of length 20 cm., was fixed centrally in the bottom of a brass tube and a vertical upward pull was applied to the other end of the wire, by a method to be described later. The brass tube was fixed vertically at its upper end to a horizontal wooden board that carried both the optical and mechanical systems. The tube was immersed in a thermostatic bath below the board, and was pierced with holes to allow the water of the bath to circulate inside it. As the water of the thermostat bath was found to have some action on the wire, causing the resistance to rise, even when no extension was taking place, a glass tube, filled with oil, was placed inside the brass tube, the clamp which held the lower end of the wire passing through a cork in the bottom of the glass tube, so that the whole length of the wire was protected by oil.

In order that the stress acting on the wire may remain constant when the wire is stretched, the force applied to the wire must diminish so as to be at every stage proportional to the cross-section of the wire. Two methods of satisfying this condition were tried. The first method was that of the hyperbolic weight,* in which the stress is applied by a weight having the form of a hyperboloid of revolution. This sinks into a liquid as the wire extends, with consequent automatic reduction of the extending force. The friction at the pulleys, which have to be introduced to apply the force to the wire in an upward direction, was found to be troublesome, and a second method, in which friction was practically eliminated by the use of a knife edge instead of pulleys, was therefore devised for applying the stress, as follows.

An aluminium beam PH, fig. 1, length 40 cm., is supported by a knife edge B, and carries two plates F and C, one at each end. The plate C has a groove along its outer edge HK, the profile of HK being an arc of a circle with centre B. D is a thin steel wire resting in the groove and fixed to the adjusting screw E. The lower end of D is attached to the upper end of the wire to be stretched. F is the second plate, in the groove of which lies a thin steel wire supporting a weight W. The profile of the bottom of the groove PQR is made such that

* Andrade, 'Proc. Roy. Soc.,' A, vol. 84, p. 1 (1910).

the moment of the weight W about the axis through B is inversely proportional to the length of the wire undergoing stretch, which, on the assumption that

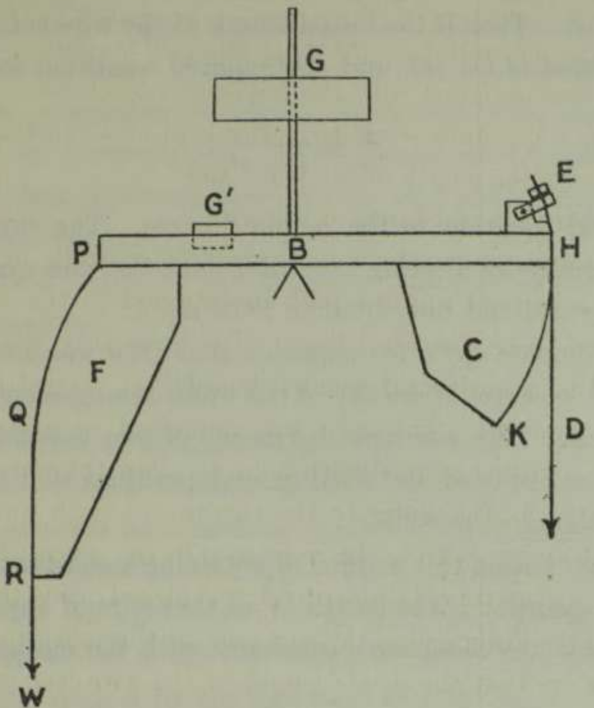

Fig. 1.

any change in density of the metal which may take place during stretch is negligible,* will make the stretching force proportional to the cross-section of the wire. Let p be the length BL of the perpendicular through B on to the vertical LQN through Q (fig. 2), and let this perpendicular make an angle θ

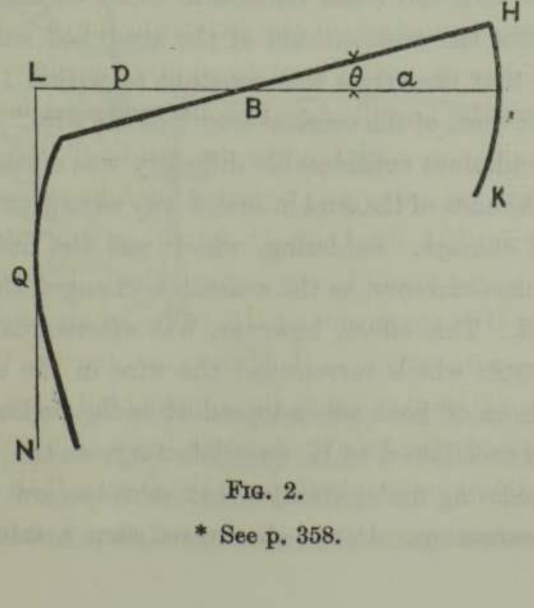

Fig. 2.

* See p. 358.

with a line, fixed in the beam, which is horizontal at the beginning of the experiment, when the wire is unstretched. Let a be the radius of the circular arc HK, centre B. Then if the initial length of the wire is l, its length at the moment considered is $l + a\theta$, and the required condition for the moment is

$$\frac{p}{a} = \frac{l}{l + a\theta},$$

which is a pedal equation to the required curve. The curve can easily be obtained graphically by drawing tangents, since the wire carrying the weight W is always vertical and tangential to PQR fig. 1.

In order to eliminate any other moments about B it was necessary to arrange the position of the centre of gravity of the whole arrangement to coincide with the knife edge B. This was done by means of two movable weights G, G′, fig. 1, which were adjusted and fixed in such positions that the time of swing about B was as long as possible.

An advantage of using this method of obtaining a constant stress is that the only specified quantity is the length l; so that wire of any cross-section can be used with any stretching force consistent with the mechanical strength of the beam.

To prove the efficiency of the apparatus, and to ascertain how nearly the stress remained constant, the following test was made. A constant weight was supported by the wire D, fig. 1, and the angles at which the beam was in equilibrium when various larger weights were fixed to W were measured. From these data the ratio of the force acting on the wire with the beam at any angle to the force with the beam horizontal could be calculated. The angle of the beam enables the cross-section of the stretched wire to be calculated, and it was found that the stress was constant to within 1 per cent. up to an extension of 30 per cent. of the original length of the wire.

In the case of cadmium considerable difficulty was encountered in finding a method of fixing the ends of the wire in such a way as to give consistent mechanical and electrical contact. Soldering, which was the first method adopted, appeared to be unsatisfactory, as the resistance changed slowly even when no stress was applied. This effect, however, was afterwards found to be attributable to the water which surrounded the wire in the earlier experiments. As already stated, an oil bath was adopted after the preliminary experiments, but soldering was still found to be unsatisfactory, as the wire fractured near to the point of soldering under stresses that were too low to give satisfactory readings for the extension. It was discovered that a satisfactory method of fixing the ends of the wire was to fuse them into spheres whose radius was two or three times that of the wire, and to grip these spheres in small four-jaw chucks. The ends were fused by heating in a small gas flame with a small quantity of soldering flux. Unless flux was used, the metal would not fuse satisfactorily, but retained its cylindrical shape, even when raised to a temperature well above its melting point. It was found after most of the readings had been taken that wires prepared in this way and subsequently soldered, gave quite satisfactory results.

With both tin and copper, no special precautions were necessary and ordinary soldering was employed.

3. *Measurement of Length.*

To obtain simultaneous values of the change in length and resistance of the wire a continuous record of the extension was made automatically; the resistance measurements were made at regular intervals which were marked on the record by the depression of a key. The recording of the extension was effected as follows. A light brass frame carrying a transparent scale was attached to the upper end of the wire whose extension was to be measured, the upward pull being applied by the fine steel wire D, fig. 1. The brass frame was constrained to move in a vertical plane by means of guiding grooves; the friction introduced by these was measured and found to be negligible. By means of a pointolite lamp P and lenses L_1, L_2, fig. 3, an image of the scale, T,

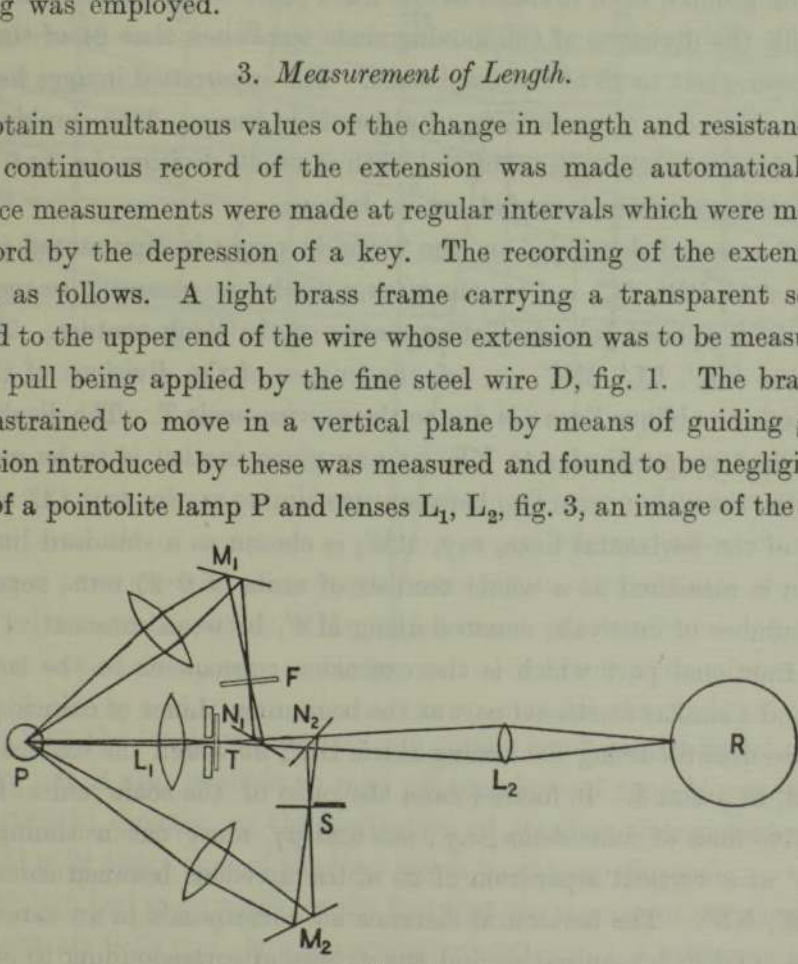

FIG. 3.

limited in breadth by an opaque vertical slit, was thrown on to a sheet of sensitive bromide paper wrapped tightly round a clock-work drum R. As the drum rotated the images of the scale divisions traced out a series of parallel lines, inclined to the horizontal more or less according as the wire was stretching faster or slower. To facilitate the measurement of the extension an image of a fixed scale F was simultaneously recorded on the drum by means of a mirror M_1 and a half-silvered mirror N_1, while for the time measurements an image of the slit S was similarly thrown on the drum by means of the mirror M_2 and the half-silvered mirror N_2. This slit was obscured by a shutter which was opened once every minute by the agency of a clock actuating a mercury contact. The optical paths of the rays forming the images of the two scales and of the slit were carefully adjusted to equality.

Both scales were prepared photographically to show transparent markings on a black ground, each division of the fixed scale being approximately 0·25 mm., while the divisions of the moving scale were such that 24 of them were exactly equivalent to 25 of the fixed scale. The superposed images formed on the drum showed a magnification of about four times. This combination of scales enabled readings to be taken to 1/25th of a scale division, *i.e.*, to 0·01 mm. by a coincidence method carried out as follows.

Part of a record developed on the bromide paper is represented in fig. 4. The lines AA′, BB′, CC′, ..., are the timing marks, representing images of the vertical slit S opened periodically by means of the clock contact. The horizontal lines KK′, LL′, MM′, ..., are the images of the divisions of the fixed scale F and the oblique lines are due to the moving scale T. The displacement of these lines perpendicular to KK′ at any given instant is to be measured. To read the extension occurring between two timing marks, say, CC′ and DD′, any one of the horizontal lines, say, MM′, is chosen as a standard line. The extension is measured as a whole number of units of 0·25 mm., represented by the number of intervals, counted along MM′, between consecutive oblique lines, a fractional part which is the extension subsequent to the last intersection and a similar fractional part at the beginning. Lines of coincidence *mn* and *pq* are drawn cutting the timing mark DD′, at which the extension is to be found, in *g* and *h*. It follows from the ratio of the scale units that two consecutive lines of coincidence, *e.g.*, *mn* and *pq*, must cut a timing mark, *e.g.*, DD′ at a vertical separation of 25 of the divisions between consecutive lines MM′, NN′. The horizontal distance *ad* corresponds to an extension of 0·25 mm., and it is required to find the extension corresponding to *ab*.

Now

$$ab/ad = gb/gh,$$

but *gh* is 25 scale divisions, so that if *gb* is expressed as a number of scale divisions, then

$$ab = gb \times \frac{ad}{25}.$$

The distance ad corresponds to 0·25 mm. and hence gb, measured in terms of the unit separation of the horizontal lines, represents the extension in hundredths of a millimetre.

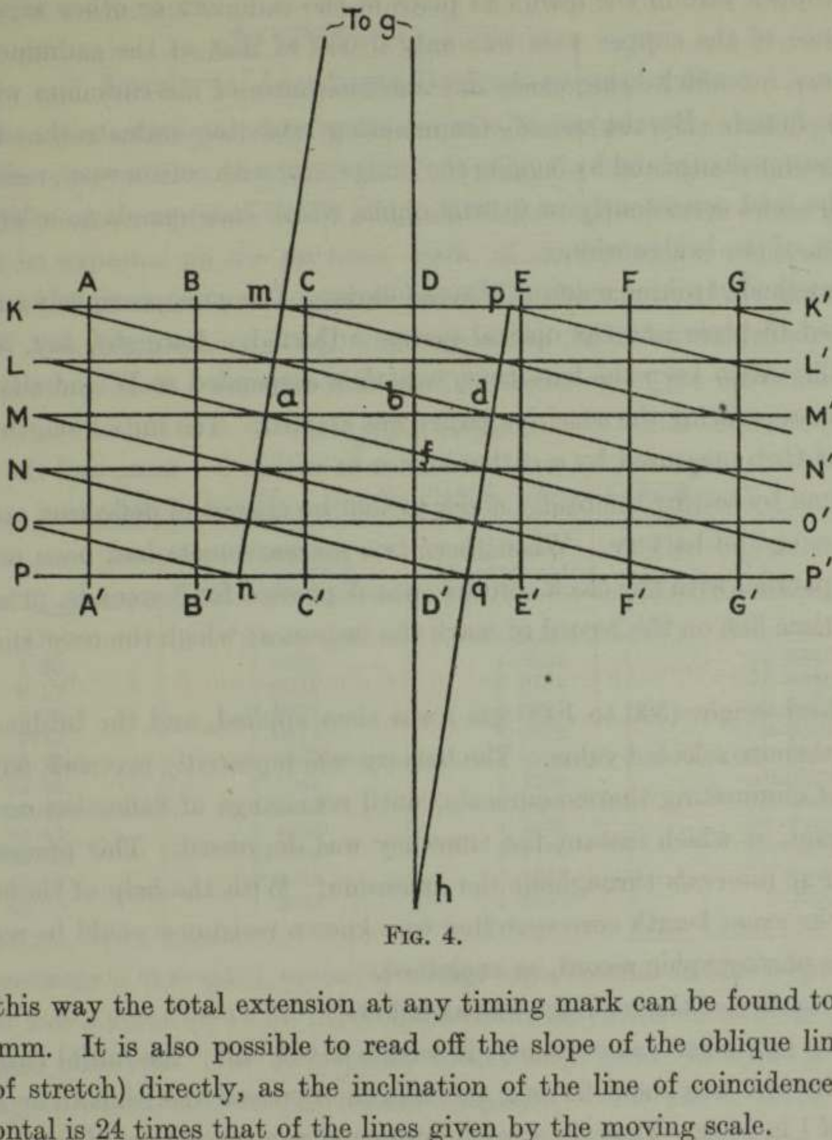

FIG. 4.

In this way the total extension at any timing mark can be found to within 0·01 mm. It is also possible to read off the slope of the oblique lines (*i.e.*, rate of stretch) directly, as the inclination of the line of coincidence to the horizontal is 24 times that of the lines given by the moving scale.

A correction had to be made for the fact that the spacing of the moving scale was not exactly 0·25 mm., but was actually 0·261 mm. A table was prepared to facilitate the reduction of readings.

4. *Resistance Measurements.*

The resistance of the wire was measured with a Callendar-Griffiths bridge of high accuracy used by Mr. N. Eumorfopoulos in his standard determinations of the boiling point of sulphur, and kindly lent to us by him. The clamps holding the wire were used as leads, and their resistances, together with those of the leads to the bridge, were found by taking a reading on the bridge with a thick copper wire in the clamp in place of the cadmium or other wire. The resistance of the copper wire was only 0·006 of that of the cadmium wire, allowance for which being made the true resistance of the cadmium wire was at once found. By the use of compensating leads to eliminate the effect of temperature change and by lagging the bridge wire with cotton wool, resistances could be read consistently to 0·0002 ohms, which corresponds to a length of 0·1 mm. of the bridge wire.

The method of taking readings was as follows. The wire, previously annealed was fixed in place and the optical system adjusted. A weight, say, 50 gm., just sufficient to keep the wire taut, was then suspended at W and the clockwork drum carrying the sensitive paper was started. The initial length of the wire was then measured by a cathetometer to within 0·1 mm., and the resistance found by setting the bridge slider so that no change of deflection occurred on reversing the battery. When these two measurements had been made, a key, in parallel with the clock contact, was depressed for 3 seconds, producing a thick time line on the record to mark the instant at which the resistance was known.

The final weight (300 to 1000 gm.) was then applied, and the bridge slider set to a definite selected value. The battery was repeatedly reversed, with the object of eliminating thermo-currents, until no change of deflection occurred on reversal, at which instant the time key was depressed. This process was repeated at intervals throughout the extension. With the help of these time marks, the exact length corresponding to a known resistance could be read off from the photographic record, as explained.

The accuracy of the readings was as follows :—

(*a*) The extension was measured to within 0·001 cm. ; the initial length of the wire was about 20 cm., and was itself measured within an accuracy of 1 in 2000. Thus the stretch, measured as a percentage of the original length, could be measured to 1 in 2000, while on a total stretch of, say, 20 per cent. of the original length, the stretch at any moment could be measured to within 1 in 4000 of the total stretch.

(*b*) The limit of accuracy in the resistance measurements was about 1 in 5000, the total resistance being of the order of 0·1 ohm. With the rates of stretch obtained a change of resistance of the magnitude of the possible error took place in about 2 seconds. The estimated error in recording the time at which the resistance was measured was about 3 seconds, so that the resistance corresponding to a given length registered on the record was probably obtained correctly to 1 in 3000.

Experimental Results.

5. *Variation of Length with Time under Constant Stress.*

The variation of length with time of annealed cadmium wires under constant stress for temperatures ranging from 0° to 100° C., and for stresses varying from 180 kilogram wt./cm.^{2} to 600 kilogram wt./cm.^{2} gave curves of the general type to be expected on the previous work of Andrade (*loc. cit.*), on other metals. A typical example obtained at 66° C. with a load of 500 gm., *i.e.*, a stress of 301 kilogram wt./cm.^{2}, is given in the following table, where the observed extension is compared with that calculated from the formula

$$l = l_0 (1 + t^{1/3}) e^{kt}. \qquad (1)$$

$\beta = 0{\cdot}0288. \quad k = 0{\cdot}001895. \quad l_0 = 1{\cdot}0053.$

t.	Length (experimental).	Length (calculated).	E. − C.
0	1·000	1·000	0
1·20	1·0357	1·0384	−0·0027
2·17	1·0451	1·0471	−0·0020
4·75	1·0631	1·0635	−0·0004
8·48	1·0814	1·0816	−0·0002
12·72	1·0992	1·0991	+0·0001
19·98	1·1261	1·1258	+0·0003
25·20	1·1438	1·1435	+0·0003
30·45	1·1604	1·1609	−0·0005
35·60	1·1778	1·1774	+0·0004
43·33	1·2018	1·2018	0·0000
45·70	1·2092	1·2092	0·0000

The agreement is very good, probably within experimental error, except during the first 2 or 3 minutes, where the formula shows an extension a little greater than that observed. The discrepancy is not very great, as appears clearly from fig. 5, which exhibits the results embodied in the above table, and is

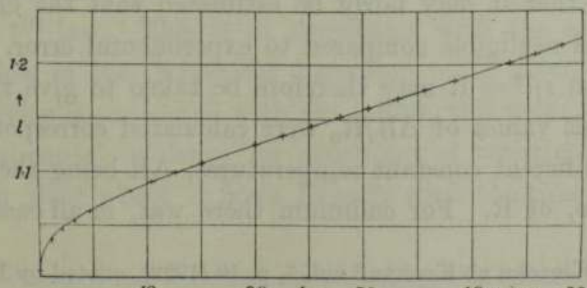

Fig. 5.

given to illustrate the general form of the curve. The continuous line represents the formula, the crosses being the observed points. While the extension at this early stage may possibly be slightly affected by irregularities in the first application of the stress, the weight being lowered into position by hand, other results seem to establish the fact that the formula does not represent the extension for cadmium quite exactly during the first minute or two. For high temperature and large stresses, in particular, while a good fit can be obtained it is necessary to take for this a value of l_0 which is *less* than the initial length of the wire. In this paper the formula is used to separate out that part of the flow which diminishes steadily with time, and there is no doubt that, apart from the first minute or two, it does represent the facts exceedingly closely. In place of $t^{1/3}$ is probably required a function, possibly an exceedingly complicated one depending on temperature and stress, which is distinctly less than $t^{1/3}$ for very small values of t, but which agrees closely with $t^{1/3}$ over a large range.

The total β-stretch in the above case is about 10 per cent. of the original length. Occasionally somewhat greater values were obtained. The maximum *total* extension was of the order of 30 per cent. of the original length.

6. *Specific Resistance.*

The specific resistance is, of course, obtained from the measured resistance r by dividing by the length l of the specimen, and multiplying by the cross-section s. If the density of the metal may be taken as constant throughout the flow, then the product ls is constant, and a quantity proportional to the specific resistance is obtained by dividing r by l^2. It is known that the density of a single crystal is not the same as that of the polycrystalline metal, so that it is probable that the stretching of an annealed polycrystalline wire has some effect on the density. For the complete change from single crystal to polycrystal the effect is, however, of the order of 1 in 3000 for, *e.g.*, iron, nickel and aluminium,* so that it may fairly be estimated that the change in density during stretch is negligible compared to experimental error.

The expression $r/l^2 = \text{R}$ may therefore be taken to give the resistivity R, and on this basis values of $\Delta\text{R}/\text{R}_0$ were calculated corresponding to various values of l at different constant temperatures, ΔR being the change, and R_0 the initial value, of R. For cadmium there was, in all cases, a decrease of

* Seiji Kaya, 'Kinzoku no Kenkyu,' vol. 5, p. 10 (1928), quoted by H. C. H. Carpenter, 'Not. Proc. Roy. Inst.,' vol. 26, p. 267 (1930).

resistivity, so that ΔR is negative. Fig. 6 shows $-(\Delta R/R_0)$ plotted against l for various temperatures and loads, the initial cross-sectional area of the wire being 0·166 sq. mm. in all cases. The curves show clearly certain general features. During the immediate extension there is no change of resistivity, although in the case of the experiment at 0° this immediate extension amounted to 8 per cent. of the original length, and in the smallest case shown nearly 2 per cent. During the intermediate extension the resistivity *decreases* markedly, but during the last phase of the extension, when the flow is tending towards the constant rate expressed by k, the resistivity is tending to a constant value. It would appear, then, that to the three phases into which the flow

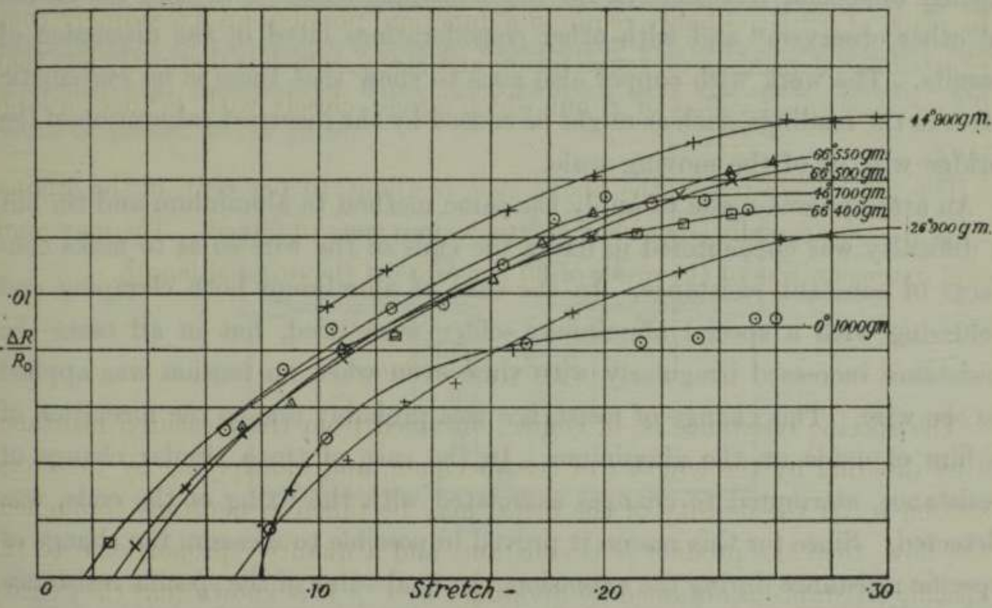

FIG. 6.

has been analysed correspond three distinct types of behaviour of the resistivity, but that, as appears from comparison of fig. 5 with the corresponding curve of fig. 6, the immediate extension is greater than is given by the formula, that is, by the $t^{1/3}$ law. This is in agreement with the argument already adduced. In view of the theoretical discussion to be given later, where the change of resistivity is connected with the β-flow, this point is of importance. The clear experimental evidence for constancy of resistivity when the wire has reached the state where it flows linearly with the time should also be noted.

The detailed course of the different curves of fig. 6 is somewhat complicated. For instance, the three curves for 66° cross one another. These points are not discussed here since it will be argued later that the significance of the experimental results is better revealed by a different method of treatment.

The experiments were also carried out with copper and tin. In the case of copper, a load of 400 gm. applied to annealed copper wire, S.W.G. 36 (stress 1368 kilogram wt./cm.^{2} at 100° C.) gave a stretch curve of the same form as that found for cadmium, the final extension being 7·5 per cent. of the initial length. The value found for the specific resistance was constant to within 0·1 per cent., the variations, of less than this amount, being quite irregular. Hence if any change of specific resistance does occur it is certainly less than one-tenth of the smallest change found for cadmium. The conclusion that there is no change of specific resistance in the case of copper agrees both with the results of other observers* and with other considerations cited in the discussion of results. The work with copper also goes to show that there is no systematic error in the readings, such as might be caused by the incorrect calibration of the bridge wire or of the moving scale.

An attempt was made to apply the same method to aluminium and tin but a difficulty was encountered in fixing the ends of the wire so as to make contacts of constant resistance. In the case of aluminium both clamping and soldering with a special aluminium solder were tried, but in all cases the resistance increased irregularly with time even when no tension was applied to the wire. This change of resistance was probably due to the formation of a film of oxide on the aluminium. In the case of tin a similar change of resistance, attributed to changes associated with the fixing of the ends, was detected. Since for this reason it proved impossible to measure the change of specific resistance during the extension, the final value of the specific resistance after stretching was compared to the initial value in order to determine whether any change had taken place.

The potential method was used, which was also employed for the measurement of specific resistance of single crystal wires (described in a paper to be published shortly). The wires whose resistances w_1 and w_2 are to be compared are arranged in series, being soldered to massive copper leads L, M, N, fig. 7. Each pair of potential contacts A, B and C, D consists of two safety razor blades of the three-hole type, fixed parallel and at about 8 cm. apart by glass rods passing through the holes and cemented. The contacts were held gently to the wires by rubber bands. Leads soldered to the blades pass to four mercury cups E, F, G, H, any one of which could be connected through a

* Cited by H. C. H. Carpenter in an unpublished lecture.

sensitive galvanometer to a sliding contact moving on a potentiometer wire ST. The potential drops p_1 and p_2 over AB and CD were measured on this wire in the usual way. The wires, whose resistances were being compared, were then cut off between the potential contacts by pressure on the razor blades and weighed, their masses being m_1 and m_2. The ratio of the two resistances is then given by $w_1/w_2 = p_1/p_2$ and since

$$\sigma a l = m,$$

where σ is the density

$$R_1/R_2 = p_1 m_1 l_2^2 / p_2 m_2 l_1^2,$$

where R_1 and R_2 are the specific resistances. The lengths l_1 and l_2 were very nearly the same. To eliminate the effect of any possible inaccuracy in the measurement of the length a second experiment was always carried out with stretched and unstretched wires interchanged, and the mean taken. This mean is quoted as the ratio.

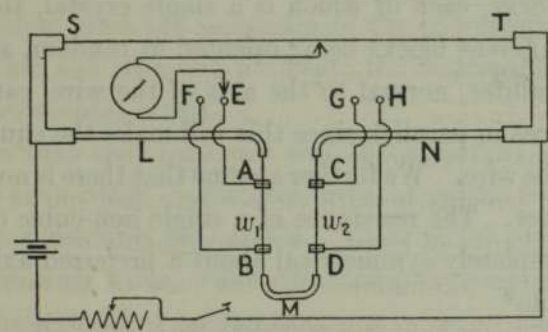

FIG. 7.

With a total extension of 5 per cent. the ratio stretched to unstretched for the resistivity was 0·999 for a particular stretched wire, and for a different stretched wire 0·998, giving a mean value of 0·9985. The estimated accuracy was $\pm$ 0·002, so that, within experimental error, there is no change of resistivity for aluminium.

In the case of tin it was found that the change of specific resistance was in the opposite sense to that of cadmium, *i.e.*, the specific resistance *increased* during the second phase of the extension. As an example of the magnitude of the change, the case of an 18 S.W.G. wire at 100° C. may be cited, with initial load 1200 gm., which gives a stress of 1028 kilogram wt./cm.^{2}. The total extension during the second phase amounted to about 17 per cent. of the original length, during which the specific resistance increased by 2·3 per cent. During the first and during the third phase of the extension the specific resistance remained unaltered as with cadmium. In a second experiment at the same temperature a total extension of 15 per cent. led to an increase of 2·4 per cent. in specific resistance.

Discussion of Results.

7. *Resistance of Polycrystalline Wires in terms of Single Crystal Resistances.*

A general explanation of the results obtained with polycrystalline wires is to be sought in terms of the resistances of the crystallites of which they are made up. It is clear that this will be easier to find if, in the case of the soft metals in question, the crystallites alone need be considered, special effects at the interfaces being either non-existent or negligible. Information as to the magnitude of these possible effects can be obtained by considering the resistance of an unstrained polycrystalline wire in terms of its components.

For this purpose we suppose that the wire can be treated as an assemblage of small cubical blocks, each of which is a single crystal, the axes of crystal symmetry in the different blocks being oriented at random, and further that a layer of such crystallites, normal to the axis of the wire, can be treated as a number of resistances in parallel, since this will make the equipotential surface a plane normal to the wire. We further assume that there is no special resistance at crystal boundaries. The resistance of a single non-cubic crystal of a metal with properties completely symmetrical about a preferred axis of symmetry is given by the formula*

$$\begin{aligned} R &= R_{\parallel} \cos^2 \phi + R_{\perp} \sin^2 \phi \\ &= R_{\perp} + (R_{\parallel} - R_{\perp}) \cos^2 \phi, \end{aligned} \qquad (2)$$

where ϕ is the angle which the axis of symmetry makes with the direction of the current and $R_{\parallel}$ and $R_{\perp}$ are the resistances along the unique axis of symmetry and normal to it respectively. The fraction of the crystallites for which the axis makes an angle between ϕ and $\phi + d\phi$ with the axis of the wire is, on the assumption of random distribution, $\sin \phi \, d\phi$, and therefore the resistance R_0 of the polycrystalline wire is given by

$$\begin{aligned} \frac{1}{R_0} &= \int_0^{\pi/2} \frac{\sin \phi \, d\phi}{R_{\perp} + (R_{\parallel} - R_{\perp}) \cos^2 \phi} \\ &= \frac{1}{\sqrt{R_{\perp}(R_{\parallel} - R_{\perp})}} \tan^{-1} \sqrt{\frac{R_{\parallel} - R_{\perp}}{R_{\perp}}}, \end{aligned}$$

* Voigt, "Lehrbuch der Krystallphysik" (1910). See Hume-Rothery, "The Metallic State," p. 7 (1931).

or

$$R_0 = \sqrt{R_\perp (R_\parallel - R_\perp)} \Big/ \tan^{-1} \sqrt{\frac{R_\parallel - R_\perp}{R_\perp}},$$

and

$$\frac{R_0}{R_\perp} = p/\tan^{-1} p,$$

where

$$p^2 = \frac{R_\parallel - R_\perp}{R_\perp}.$$

Bridgman gives for cadmium the values $R_\parallel = 8 \cdot 30$, and $R_\perp = 6 \cdot 8$, while Grüneisen and Goens* give $R_\parallel = 7 \cdot 79$ and $R_\perp = 6 \cdot 54$. With Bridgman's values the above equation gives $R_0 = 7 \cdot 27$, while with Grüneisen and Goen's values $R_0 = 6 \cdot 94$. In the course of some later work, shortly to be published, we found $R_\perp = 993$ in terms of $R_0 = 1000$. Taking Bridgman's value of $R_\perp$ this gives $R_0 = 7 \cdot 24$ as against the calculated $7 \cdot 27$, while with Grüneisen and Goen's value of $R_\perp$ we have $R_0 = 6 \cdot 96$ as against the calculated $6 \cdot 94$. The formula therefore gives the resistance of the polycrystalline wire in terms of $R_\parallel$ and $R_\perp$ within less than $0 \cdot 5$ per cent., the discrepancy being within the limits of the experimental errors.

The hypothesis that the resistance can be considered as made up of the resistances of the elementary crystallites, without special interfacial resistance, may therefore be considered reasonable. There is, of course, the possibility that the polycrystalline wires, while containing crystallites set at all angles, have, owing to the method of preparation, one or more preferred directions in which more crystallites are oriented than would be given by a purely random distribution. This is a point that can only be settled by X-ray examination, and Dr. R. E. Gibbs now has this and other points under examination.

8. *Quantitative Explanation of Change of Resistance during Extension.*

As a preliminary to the consideration of the change of resistance during extension in terms of the behaviour of the crystallites, certain properties of metal single crystals may be recalled. When a single crystal wire is extended, glide takes place along a certain set of parallel crystal planes ; if, as with certain classes of crystals, this set is one of a group of planes which are crystallographically equivalent, then, of course, slipping takes place along that set of the group which is, mechanically, the most favourably disposed. In addition, glide takes place in a certain direction in this plane, or in one of a certain group of equivalent directions. Thus, to take an example, with cadmium, which crystallises

* 'Z. Physik,' vol. 26, p. 250 (1924).

in the hexagonal form, the glide takes place in the basal, or (0001) plane, and in the direction of a digonal axis from the centre to one of the vertices of the hexagon. The direction actually chosen by the glide will be the one among the preferred axes which makes the smallest angle with the direction of the applied force; since the digonal axes make an angle of 60° with one another the direction of glide cannot be more than 30° from the line in the glide plane which makes a minimum angle with the direction of the force.*

Thus consider a single crystal wire of cadmium, in which the axis of crystal symmetry makes initially an angle ϕ_0 with the axis of the wire, while the glide planes make an angle θ_0 with the axis of the wire; here θ_0 and ϕ_0 are complementary. When the wire is stretched by a force applied in the direction of the axis the planes glide parallel to themselves, but the axis of the wire in which glide has taken place is constrained by the force to remain in the original direction of the axis. The result is that ϕ_0 and θ_0 take new values ϕ and θ which are still complementary. It can easily be shown† that

$$l/l_0 = \frac{\sin \theta_0}{\sin \theta} = \frac{\cos \phi_0}{\cos \phi}, \tag{3}$$

where l, l_0 are the final and original lengths of the wire. Extension by glide in the single crystal of cadmium therefore leads to a rotation of the unique set of glide planes.

The results of which an explanation is sought are that there is no change of specific resistance with copper or aluminium at any stage of the extension, nor during the immediate extension or the final flow at constant rate with any of the metals. With cadmium and tin, however, there is a definite change of specific resistance when wires are extended at atmospheric or higher temperatures, the change (which is a decrease for cadmium but an increase for tin) being closely associated with the β-flow.

A polycrystalline wire can be considered as an assemblage of crystallites in which the axes of crystal symmetry are oriented at random. When the wire is stretched three possible mechanisms can be imagined: (*a*) that the crystallites break up into smaller fragments, which move without rotation so as to

* See, *e.g.*, Taylor and Elam, 'Proc. Roy. Soc.,' A, vol. 108, p. 28 (1925); Mark, Polanyi and Schmid, 'Z. Physik,' vol. 12, p. 58 (1922); Georgieff and Schmid, 'Z. Physik,' vol. 36, p. 759 (1926); and Boas and Schmid, 'Z. Physik,' vol. 54, p. 16 (1929). For collected accounts see Wien-Harms, Handbuch der Experimentalphysik, vol. 5 (Plastische Verformung, by G. Sachs) (1930), and Masing and Polanyi, 'Ergebn. exakt. Naturwiss.,' vol. 2, p. 177 (1923).

† *E.g.*, Ewald, Pöschl and Prandtl, "The Physics of Solids and Fluids," p. 120 (1930).

accommodate their positions to the bulk deformation of the wire. The necessary accommodations may lead to slight deformations, of the cylindrical form, and, in fact, the surface of a stretched polycrystalline wire generally appears somewhat rough; (*b*) that twinning takes place; (*c*) that the individual crystallites become extended in the direction of the axis of the wire, not necessarily all by the same amount. In this case, if the glide takes place entirely upon a unique set of glide planes, as it undoubtedly does in single crystals of cadmium, or even if it is mainly upon such a set of glide planes, there must be a change in the angle ϕ, determined by the extension, that is, a rotation of the crystalline axis of the crystallite.

In the first case no change of resistance is to be expected, as far as the crystallites are concerned, and it has already been shown that with cadmium, at any rate, the resistance can be wholly accounted for by the crystallites, without interfacial considerations.

Consideration of the second case will be postponed, since examination of polycrystalline wires, stretched at atmospheric or higher temperature, has failed to reveal twinning. The examination was carried out by polishing the surface of the wire, and etching with dilute nitric acid, which shows up the crystal boundaries, but not slip planes. That this process will also reveal twinning if it has taken place is evidenced by cadmium wires stretched at low temperatures of $-180°$ C. which show extensive twinning, as recorded in the last section of this paper.

In the third case we must expect a change of resistance for all metals in which there is a unique axis of crystal symmetry, for in such metals the electrical resistance depends upon the inclination of the axis to the direction of flow of the current. The results of the experiments here described lead to the conclusion that, during the β-flow, the extension takes place mainly, if not wholly, by extension of the crystallites, accompanied by rotation of the axes. It may be mentioned that an early study of the mechanical aspect of the flow in soft metals led to the conclusion that the β-flow was due to crystalline rotation.*

A strong quantitative confirmation of this view is furnished by the comparative behaviour of cadmium, tin, copper and aluminium. In the hexagonal crystals of cadmium the glide planes are normal to the unique axis of symmetry; in the tetragonal crystals of tin they are parallel to the unique axis.† In the case of both metals the resistance in the direction parallel to the unique axis

* Andrade, 'Proc. Roy. Soc.,' A, vol. 84, p. 1 (1910).

† Polanyi, 'Naturwiss.,' vol. 16, p. 209 (1928).

is greater than in the normal direction.* The effect of stretch of a crystal or crystallite of either metal is to tend to set the glide planes parallel to the direction of stretch, which means, in the case of cadmium, setting the unique axis normal to the direction of stretch, in the case of tin, bringing the unique axis parallel to the direction of stretch. Hence in the case of cadmium there would be a decrease of specific resistance accompanying β-stretch, in the case of tin an increase, which is what is observed. In the case of a cubic crystal, like copper, the resistance is independent of the direction, so that there should be no change of resistance.

There is, then, good experimental evidence for believing that, in the case of soft metals, at any rate, the first immediate stretch takes place by break-up of the crystallites and movement of the fragments without distortion, by slipping at the boundaries; that in the slow stretch which follows, rotation of the crystallites takes place, with consequent change of specific resistance, and that in the final stage of steady flow the rotation is complete, and that slipping without rotation occurs. It may be objected that there is a difficulty, of a geometrical nature, in imagining exactly how the adaptation at the boundary between individual crystallites takes place so that the metal may remain continuous. At present so little is known of the behaviour of a mass of plastic crystallites that a precise handling of the problem is not in question, but attention may be directed to certain arguments that seem to justify the assumption of rotation. In the first place, it is well known that in the case of wire drawing of many metals, *e.g.*, copper and aluminium, a preferential orientation of certain crystal planes takes place, although no experimental results on wire drawing with cadmium are known to us. Mark has shown by the X-ray method a strong preferential orientation in a drawn tin wire.† Rolling is also known to produce a regular texture and, for instance, in the case of zinc and cadmium about 70 per cent. of the crystals lie, after rolling, with their hexagonal axes making an angle between 50° and 70° with the normal to the sheet.‡ Although the deformation in our case is not nearly as severe as that produced by rolling or wire drawing, work on these methods shows clearly that mechanical deformation, can lead to orientation with the necessary adaptations.

Again, in soft metals of the kind in question the crystal planes can bend so as to adapt themselves to geometrical constraints, as evidenced, for example, by a cadmium single crystal wire gripped at one end, and extended by a load.

* See, *e.g.*, Bridgman, *loc. cit.*

† Wien-Harms, "Handbuch der Physik," vol. 7, p. 311 (1928).

‡ Mark, 'Z. Kristallog.,' vol. 61, p. 75 (1925).

In the part where the wire is gripped the planes retain their original inclination; at some little distance from this part the inclination of the planes has a different value, and in the intermediate region the adaptation between the two inclinations is effected by a bending of the crystal planes. Again, the picture put forward does not exclude the possibility that the general movement of the undistorted crystallites may be accompanied by a slipping and rotation in a relatively small fraction of the total number, nor that general slipping and rotation may be accompanied by a breaking-up of a few crystallites. The variation of the specific resistance with extension cannot be calculated without special hypotheses as to the way in which glide is initiated, continues and ceases in the individual crystallites of the polycrystalline wire. While on the basis of such special hypotheses we have obtained fairly close agreement with experiment, it is well, perhaps, to reserve such calculations until the hypotheses have further experimental support, which is now being sought.

Meanwhile the experimental results can be expressed in terms of a mean angle $\bar{\phi}$, chosen so that, if in all the crystallites the angle made by the crystal axis with the axis of the wire had the same value $\bar{\phi}$, then the resistance would be the same as it is in the actual polycrystalline wire. Any preferential orientation in the polycrystalline wire modifies the value of $\bar{\phi}$ so defined.

By definition,

$$R = R_{\perp} + (R_{\parallel} - R_{\perp}) \cos^2 \bar{\phi} = R_{\perp} (1 + p^2 \cos^2 \bar{\phi}). \tag{4}$$

For an unstretched polycrystalline wire, with random orientation,

$$\frac{R_0}{R_{\perp}} = p/\tan^{-1} p = 1 + p^2 \cos^2 \bar{\phi}_0$$

or

$$\cos \bar{\phi}_0 = \frac{1}{p} \sqrt{p/\tan^{-1} p - 1}$$

$$= 0{\cdot}5617 \text{ with Bridgman's value of } p.$$

$$\bar{\phi}_0 = 55^\circ\, 50'.$$

For any given stretched polycrystalline wire $\bar{\phi}$ is obtained from the experimental value by substituting the value of R in equation (4).

9. *Analysis of Experimental Results.*

There is, it appears, good reason to associate the change of resistance in metals of non-cubic structure with the β-flow. By fitting to the length-time curves the equation $l = l_0 (1 + \beta t^{1/3}) e^{kt}$ the appropriate value of β can be found for each (constant) stress and temperature, and so for each observed value of the specific resistance, taken at a time t during the flow, the corresponding value $\beta t^{1/3}$ of the β-stretch can be found. In this way figures were obtained from which the curves of figs. 8 and 9, exhibiting $-\Delta R/R_0$ for cadmium as

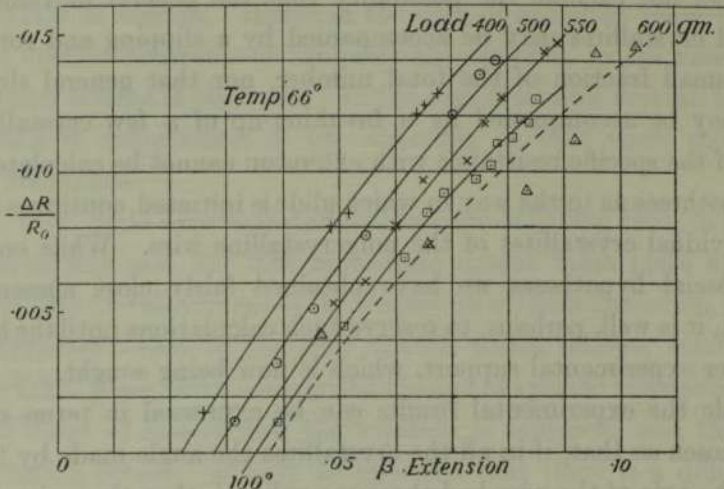

FIG. 8.

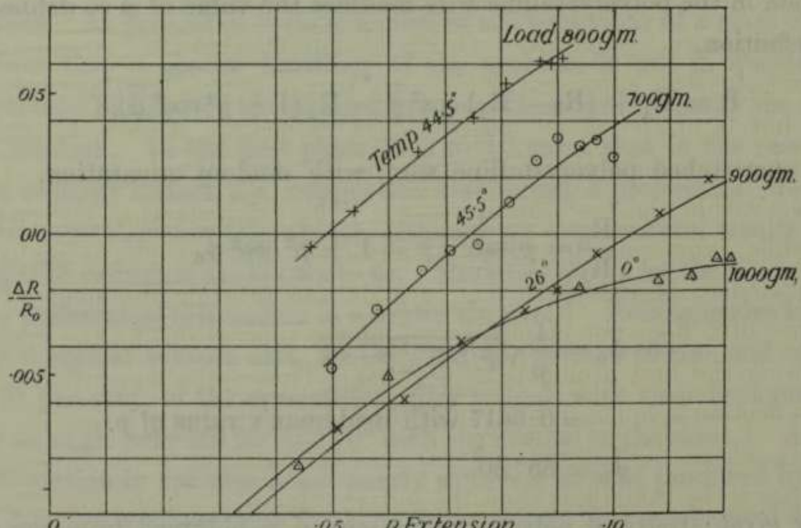

FIG. 9.

ordinate against β-stretch as abscissa were plotted. Each curve refers to a wire extended at fixed temperature and constant stress. The curves of fig. 8 were all obtained at temperature 66° C., with the exception of the curve marked 100°, obtained at that temperature, the initial load being indicated on each curve. The initial cross-sectional area of the wire being 0·166 sq. mm. the constant stresses corresponding to 400, 500, 550 and 600 gm. weight are 2·41, 3·01, 3·31, 3·61 × 10^5 gm. wt./sq. cm. The points obtained with the 600 gm. load are very irregular; the flow in this case was the most rapid observed in the course of this investigation, the wire stretching from an initial length of 20 cm. to a final length of about 25 cm. in 13 minutes. On account of its uncertainty the curve is indicated by a broken line. It is difficult to fix β closely for the rapid flow at 100°, and therefore the slope (but not the form) of this curve is not so certain as that of the other curves. Two of the curves of fig. 9 were obtained at about 45°, one at 26° and one at 0° C.

The nearly straight nature of the curves, and the parallel course of curves obtained for different stresses at the same temperature, is in striking contrast to the unsystematic character of the group of curves of fig. 6, where the same ordinate is plotted against the total stretch, and at once suggests that there is a real physical significance in the analysis of the flow into immediate stretch, β-flow, and final flow at constant rate, or viscous flow, and that it is, in fact, the β-flow which is closely bound up with the change of resistance. The curves of figs. 8 and 9 do not, in general, pass through the origin, that is, when the flow is analysed into immediate stretch and β-flow by the help of the $t^{1/3}$ formula there is, included in the β-flow, an immediate extension which produces no change of resistance. This may be taken to indicate that the extension during the first minute or so, expressed as the early part of $\beta t^{1/3}$, is not due to glide and rotation, but is of the same nature as the immediate stretch, for the first resistance measurements shown on, *e.g.*, the 400 and 500 gm. curves of fig. 8 were taken within the first minute or so. This suggests that the empirical $t^{1/3}$ law, while expressing accurately a physically distinct process, which we have indicated to be extension due to glide and rotation, for moderate and large values of t, does not closely represent the process during the minute or two following the first application of stress. This is the conclusion already reached in Section 5, in the discussion of the fitting of the length-time curves by formula (1), where it is pointed out that, in some cases, to fit the experimental results l_0 has to be taken less than the initial value of l, which shows that $\beta t^{1/3}$ is initially too large to represent the physical process in the first minute or two.

Accordingly, we proceed on the assumption that the immediate stretch, indicated in figs. 8 and 9, which takes place without change of resistance is due to a displacement of the crystallites without glide or rotation, and proceed to consider the rate at which resistance decreases with increase of β-extension, supposed due to glide and rotation. It is clear that the curves obtained at one temperature, *i.e.*,the 400, 500 and 600 gm. curves at 66°, or the 800 and 700 gm.

curves obtained at 45°, differ only in their intercept on the horizontal axis, so that a given extension due to glide and rotation is, at a given temperature, connected with a given change of specific resistance. From the change of specific resistance we can calculate $\bar{\phi}$. In this way the curves of fig. 10 have

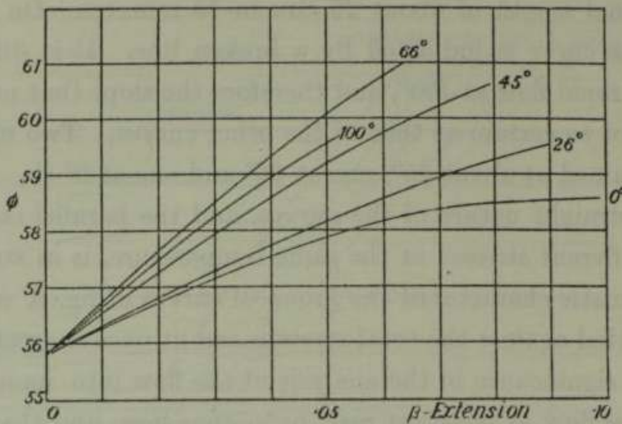

Fig. 10.

been obtained, which show $\bar{\phi}$ as a function of the extension, measured from the intercept on the horizontal axis in figs. 8 and 9, which, on our assumption, is due to rotation.

The curve for 100° represents only one experiment; it has been already pointed out that, on account of the very rapid flow, it is not possible to fix the β-extension accurately in this case. No great significance can be attached to the fact that the slope of this curve is less than that of the 66° curve. Leaving it out of account we see that, as the temperature falls, the change of $\bar{\phi}$ for a given extension diminishes, although for the 26° which separates the lower two runs the change is less marked than for the 20° intervals which separate the other curves. This can be simply interpreted if it is remembered that for crystallites for which ϕ_0 is large, *i.e.*, whose glide planes make small angles with the wire axis, a small change of angle corresponds to a large increase in length, while for those for which ϕ_0 is small a large change in angle is needed to give a small change in length. If for crystallites of small ϕ_0 glide takes place more readily at high temperatures than it does at low our results are explained.

If we can apply results obtained with single crystals to the crystallites in the wire, then glide takes place most easily in those for which the glide planes, and hence the crystal axes, make an angle of 45° with the wire axis. If we assume that glide takes place only in crystallites, for which the angle is in the neighbourhood of 45°, we can obtain an estimate of the change in resistance to be expected in association with a given change in length. No doubt this is only a rough approximation, except in the early stages, but it affords a check as to whether changes of resistance of the magnitude observed by us are reasonably explained on the hypothesis of glide. Various more complicated assumptions give, as a matter of fact, not very different numerical results.

Suppose then, that on extension the axes of a fraction f of the crystallites, which initially made angles in the neighbourhood of 45° with the wire axis, change their directions by $d\phi$. We then have

$$\frac{\Delta l}{l} = f \, . \, d\phi,$$

from

$$\frac{l}{l_0} = \frac{\cos\phi_0}{\cos\phi},$$

while, as an approximation,

$$\frac{\Delta \mathrm{R}}{\mathrm{R}_0} = \frac{p^2 f \, . \, d\phi}{p/\tan^{-1} p} = p \tan^{-1} p \, \frac{\Delta l}{l}.$$

The numerical values being $p = 0 \cdot 489$, $\tan^{-1} p = 0 \cdot 439$

$$\frac{\Delta \mathrm{R}}{\mathrm{R}_0} = 0 \cdot 206 \, \frac{\Delta l}{l}.$$

If

$$\frac{\Delta l}{l} = 0 \cdot 01 \quad \frac{\Delta \mathrm{R}}{\mathrm{R}} = 0 \cdot 00206 \quad \text{and} \quad \bar{\phi} = 56^\circ \, 25',$$

while if

$$\frac{\Delta l}{l} = 0 \cdot 05 \quad \frac{\Delta \mathrm{R}}{\mathrm{R}} = 0 \cdot 0103 \quad \text{and} \quad \bar{\phi} = 58^\circ \, 57'.$$

These are very slightly less than the experimentally found values for 45° C., as can be seen by consulting the curves of fig. 10. The changes of resistance are therefore of the right magnitude. A glide in the crystals for which the slip planes make smaller angles than 45° will tend to make the change of resistance less, in those for which the slip planes make larger angles will tend to make the change of resistance greater, for a given change in length.

10. *Results at Low Temperatures.*

The extension by glide and rotation, for which evidence is offered in this paper, is associated with the slow β-flow, and so apparently requires time for the necessary adjustments to take place. It will, therefore, characterise soft metals, or, speaking more correctly, metals at a temperature such that they are soft, and it is not contended that it will be found to accompany the extension of harder metals. As the distinction drawn between the mechanism of flow in hard and soft metals has been criticised it seemed to us advisable to seek further experimental evidence on this point. If the contention is correct, then a cadmium wire at very low temperature, where the β-flow cannot take place, should behave differently, in respect of its changes of resistivity, from one at a temperature in the neighbourhood of atmospheric. Early experiments in which we attempted to produce extension at liquid air temperature failed because of difficulties found in gripping the end of the wire. Since the main work was completed it has, however, been found possible to hold the ends of the wire adequately, and a cadmium wire has been extended by 3 per cent. and more at both —180° C. and —78° C.

The results of these low temperature experiments were that while at —78° an extension of 3 per cent. produced a decrease of resistivity amounting to 0·7 per cent. (mean of two experiments), at —180° a stretch of 3 per cent. produced an *increase* of resistivity of 1·3 per cent., which seems at first astonishing. Examination of the wires after etching showed, however, that in the case of the wire stretched at —180° very extensive twinning had taken place. The bands of twinning in most of the crystallites made angles with the axis of the wire which were not far from 45°; no bands either parallel to or perpendicular to the axis were observed. The increase of specific resistance can be explained in terms of these observations.

In the first place, working with single crystal wires of cadmium we have found that after primary stretch, which brings the hexagonal axis to a position nearly perpendicular to the force, is completed, a secondary stretch takes place if the stress is increased. This secondary extension is accompanied by twinning, and by a rise of resistivity. Cadmium twins on a $(01\bar{1}2)$ plane, when the shearing stress in the plane exceeds a certain limiting value. The twinning plane makes an angle of not far from 45° with the original basal plane, so that after twinning the basal plane of half the twin stands nearly at right angles with the original basal plane, that is, nearly perpendicular to the axes of the single crystal wire. As the resistance parallel to the hexagonal axis is the larger one it is clear that twinning in such a stretched single crystal wire should increase the resistivity, as observed.

Turning now to the polycrystalline wire, where the directions of the axes are distributed at random, it might at first be supposed that twinning, which brings the axes nearly normal to their original positions, should not affect the resistivity. If, however, the twinning planes are mainly in the neighbourhood of 45° to the wire axis, as would be expected, and as is confirmed by examinations of the twinned wire, then the crystals affected are mainly those in which the axis is either nearly parallel to or nearly normal to the wire axis. The latter class is clearly the more numerous in the case of random orientation. Since twinning in the former class leads to decrease of resistance, in the latter class to increase, it is clear that, on the whole, the effect of twinning should be to increase the resistivity, as is, in fact, observed.

The mechanism of yield is, then, essentially different for the tough wire at -180° and for the softer wire at atmospheric temperatures. The wire at -80° represents an intermediate case. The stretch at low temperatures has not been studied in detail, but it may be mentioned that a particular wire, extended at -180° by a very large load, under which it broke, showed a much greater increase of resistivity for unit extension than that quoted above.

We are much indebted to Dr. R. E. Gibbs for helpful discussion during the work. One of us (E. N. da C. A.) enjoys a grant for apparatus from the Imperial Chemical Industries Company, expenditure from which has been made in connection with this research, while the other (B. C.) has been in receipt of a grant from the Department of Scientific and Industrial Research. To both these bodies our best thanks are due.

11. *Summary of Results.*

(1) The specific resistance of certain typical metals has been determined at various stages of the plastic flow under large stresses.

(2) The specific resistance of metals which crystallise in the cubic system is unaffected by the flow.

(3) The specific resistance of metals which crystallise with a unique axis of symmetry does not change during two of the three stages into which the flow can be analysed, namely, during the immediate extension, and the final flow at constant rate. During the intermediate stage of flow at diminishing rate, called the β-flow, it changes by an amount of the order of 2 per cent. in extreme cases.

(4) The facts can be explained on the assumption that the crystallites slip, with consequent rotation of the unique axis, during the β-flow. In particular it follows at once on this hypothesis that with metals whose crystals have the slip planes parallel to the unique axis an increase of specific resistance with extension should be expected, while with crystallites which have the slip planes normal to the unique axis there should be a decrease, supposing that, as in the cases treated in this paper, the resistance is greatest along the unique

axis. This is what is found experimentally with tin and cadmium, which respectively represent the two classes of crystallite.

(5) The magnitude of the change of resistance during β-flow is in good accord with this hypothesis that β-flow is due to rotation of crystallites.

(6) Further evidence for the views put forward is afforded by experiments at low temperature, where there is marked immediate stretch, but no β-stretch. It has been found that, under these conditions, an increase of resistivity of cadmium is obtained as against the decrease at ordinary temperatures. This is caused by the extensive twinning which accompanies the stretch under these conditions.

(7) The results suggest that in all cases where flow is observed in solids the mechanism of the immediate stretch is essentially different from that of the β-flow, which is connected with a rotation of crystallites to a final position.

The Photochemistry of Phosphine.

By H. W. Melville.

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Within recent years the spectroscopy and the photochemistry of the hydrides of the non-metallic elements has been the subject of much study and the results explained with considerable success on the basis of the newer theories of photochemical reactions. In spite of the fact that the photochemistry of ammonia has attracted some attention, yet the investigation of the equally simple molecule of phosphine seems to have been entirely neglected. It is with the object of filling this gap in photochemistry that the present experiments have been undertaken.

The investigation naturally falls into three parts : (*a*) the absorption spectrum of phosphine, (*b*) the direct photochemical decomposition, (*c*) the photosensitised decomposition. Experimental data on the photo-oxidation are also of importance in view of the fact that the thermal oxidation of phosphine is a chain reaction.

In the present communication attention will be devoted to the photosensitised reactions, while the absorption spectrum and direct photo-reactions will, it is hoped, be dealt with in another paper.