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Studies on Explosive Antimony.　II—Its Structure, Electrical Conductivity, and Rate of Crystallization

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[Plates 1 and 2]

1—Introduction

The first paper* of this series dealt with the microscopically visible changes in structure that occur when the presumably amorphous electrolytic deposit of antimony " explodes." It was shown that a rapid (20–40 cm/sec) autogenous crystallization spreads spherically throughout the metal, leaving it with an onion-like structure visible on a polished and etched surface as a sequence of closely spaced (2000–3000 per/cm) concentric lines. The present paper is concerned with the nature of the amorphous deposit as revealed by a microscopic examination of etched surfaces, § 3, and by a study of its electrical resistance, § 4. The rate of crystallization at temperatures below that at which explosion occurs has also been determined, § 5.

It is found that the explosive deposits are characterized by a heterogeneous gel-like structure definitely oriented with respect to the cathode receiving surface. The electrical properties of the deposits are non-metallic in that the conductivity is very small and has a positive exponential temperature coefficient. Ohm's law is obeyed, but Faraday's law does not seem to be involved, although a small polarization is built up at the higher temperatures. At temperatures too low to initiate explosion the deposits crystallize at a rate which is independent of the extent to which they have already crystallized. The rate of crystallization increases exponentially with the temperature.

2—Experimental

The explosive antimony was deposited upon copper cathodes from 10% HCl solutions of commercially pure $SbCl_3$. Solutions containing less than 15% $SbCl_3$ were electrolysed at 0°. The more concentrated solutions (15–75% $SbCl_3$) were electrolysed at room temperature (19–21°). All

* Coffin and Johnston, ' Proc. Roy. Soc.,' A, vol. 146, p. 564 (1934).

depositions were thus well within the range of conditions favourable to the production of the explosive form.*   The anodes of cast commerically pure antimony were carried on heavy platinum wires and were enclosed in linen bags to prevent possible contamination of the cathodes by anode slime.

The specimens required for this work had to be removed from the copper without exploding and were usually desired in the form of long, narrow, and fairly thick bars.   It was necessary also for the deposit to be as uniform as possible, *i.e.*, the temperature, current density, and particularly the $SbCl_3$ concentration at the cathode surface, had to remain constant throughout the deposition.

These requirements were fulfilled in a very satisfactory manner by the combination of cathodes and stirrer shown in fig. 1*a*.   Four flat copper cathodes ($7 \times 1 \times 0 \cdot 14$ cm) were fixed by set screws to a one-eighth inch horizontal brass plate carried by the stirring shaft.   With the object of minimizing the centrifugal displacement of the solution, each cathode was offset so that the leading edge describes a larger circle than the trailing edge, fig. 1*b*.   The whole assembly, with the exception of a $6 \times 0 \cdot 4$ cm area on both sides of each cathode, was heavily painted with melted paraffin wax which, on the cathodes, was built up and roughly stream-lined, as shown in fig. 1*c*.   With this apparatus working in a 600-cc beaker stirring speeds as high as 1000 r.p.m. may be obtained without spilling or splashing.

The electrolyses were run for 20–30 hours at current densities between $0 \cdot 05$ and $0 \cdot 1$ amps/cm². After washing with HCl solution, the cathodes were removed from the stirrer under water in order to prevent any local explosion from setting off the entire deposit.   By carefully bending the copper strips under water, it was usually possible to separate the un-exploded metal from the copper in the form of bars 1 or 2 cm in length. Antimony deposited from solutions containing between 10 and 20% $SbCl_3$ must be cooled in solid CO_2 before it can be safely stripped from the basis metal.   Even at this temperature the greater part of the deposits from solutions of less than 10% $SbCl_3$ are lost.

The small rough bars of the explosive metal were then ground or filed to a rectangular cross-section.   The deposits from solutions of more than 50% $SbCl_3$ may be safely filed under water.   Those made from solutions of more than 20% may be ground by hand with fine emery and plenty of water on plate-glass at room temperature.   Specimens from solutions containing as little as 10% $SbCl_3$ may be ground with emery powder and

† Cohen and Coffin, ' Z. phys. Chem.,' A, vol. 149, p. 417 (1930).

alcohol on a brass plate cooled in solid CO_2. The brass grinding-table shown in fig. 1*d* proved to be very satisfactory.

The surfaces to be etched were polished with fine rouge on wet chamois leather. Etching was done by making the polished specimen an anode in aqueous HCl or by immersing for 5–15 minutes in strong ammonium sulphide solution. Both methods give identical etch figures. The latter is the easier to control and was used in preparing the subjects of the accompanying photomicrographs.
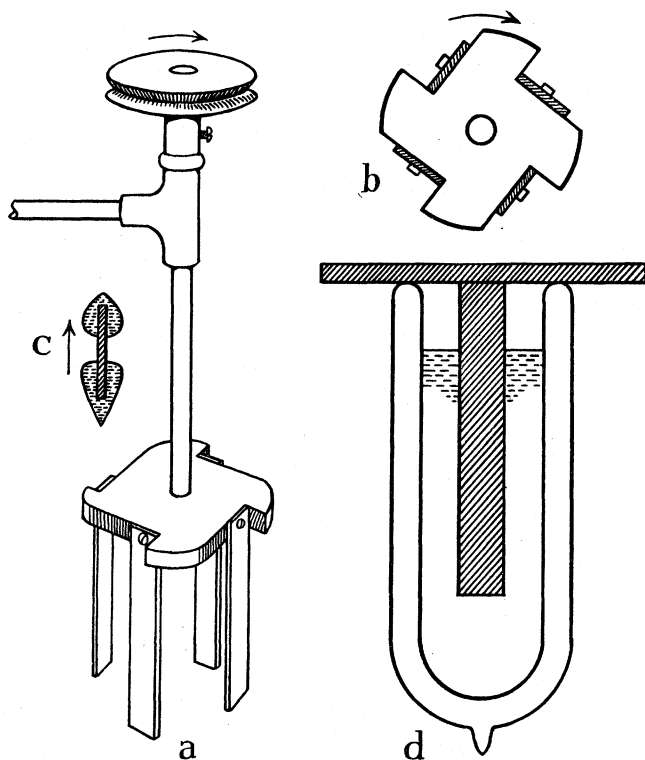
FIG. 1—*a, b,* and *c,* cathode stirrer; *d,* low-temperature grinding-table.

The small bars to be used for the resistance measurements were painted, except for a short distance from either end, with a quickly drying lacquer. Leads of No. 28 copper wire were wrapped several times about the bare ends of the specimen, which was then made a cathode in a silver-plating bath until a firm connexion of negligible resistance was established between the copper and the antimony. In cases where it was desired to determine the specific resistance of the specimen the dimensions of the painted (*i.e.,* not silver-plated) section were measured (before painting) with micrometer calipers. The specimens were then mounted as

" resistance thermometers " in thin 5 mm glass tubes sealed off at one end and closed at the other with sealing-wax through which the leads passed. To determine the specific resistance of the deposits in the direction at right angles to their length (*i.e.*, parallel to the lines of the depositing current), small pieces were ground to rough cubes which were lightly silver plated. The silver was then ground off all but two opposite faces of each cube, which was measured up and fixed firmly in the amalgamated and insulated brass jaws of a small vice which could be slipped into a glass tube for temperature control.

Resistances were measured with a calibrated Wheatstone bridge.

3—THE MICROSTRUCTURE OF EXPLOSIVE DEPOSITS

The appearance of a polished and etched surface of explosive antimony is dependent upon whether the surface in question is parallel or perpendicular to the electrode face. If parallel to the cathode length, *i.e.*, normal to the stream lines of the depositing current, the etched surface is covered with a network of random markings somewhat like the crackle of pottery glaze, figs. 4, 5, and 8, Plate 1. If a surface perpendicular to the cathode face, *i.e.*, parallel to the current lines, is polished and etched a totally different type of marking is visible, figs. 6, 7, and 9, Plate 1, and figs. 10 and 11, Plate 2. In this case the etch figures are very definitely oriented in a direction parallel to the current lines. In the following the two types of etch figures will be called respectively " random " and " radial " markings.

It is at once apparent that the term " amorphous " should not be used in connexion with a material so definitely anisotropic as explosive antimony. The obvious contradiction loses a great deal of its significance, however, when it is remembered that the explosive deposits contain from 2 to 10% of $SbCl_3$* possibly in a crystalline condition.† Any anisotropism of the system as a whole may then be due to some preferred orientation of the salt crystals or salt metal complex embedded in the truly amorphous metal.

The external appearance of a deposit of explosive antimony is often such as to suggest a fibrous texture. The macroscopic stalactitic structure resembling certain geological growths (*e.g.*, limonite) made up of fibres radiating from a line is, for example, shown in the photographs published by Cohen and Ringer.‡ The central line is here the platinum

* Cohen and Ringer, ' Z. phys. Chem.,' vol. 47, p. 1 (1904).
† Steinwehr and Schulze, ' Z. Physik,' vol. 63, p. 815 (1930).
‡ *Loc. cit.*

wire upon which the antimony was deposited. Figs. 12 and 13, Plate 2, are microscopic views of two different types of cathode surface. The botryoidal structure usually due to the growth of fibres radiating from points is plainly visible. It should be pointed out that this globular structure is not characteristic of all deposits of explosive antimony. High-current densities and stirring speeds appear to inhibit its formation, and in the work being reported the great majority of the deposits were perfectly smooth and in appearance resembled polished steel.

The extremely friable nature and the earthy fracture of explosive deposits with a high $SbCl_3$ content also indicates that there is an aniso-tropic texture characteristic of the material. A bar of the substance is readily crumbled in a way that suggests a bundle of short, not very cohesive, fibres. Such a fibre-like orientation parallel to the current lines has been observed also in several electrolytically deposited crystalline metals,* where it is evidently due to the growth of crystallites in the direction of highest conductivity.

That the radial figures parallel the current lines is particularly evident if a cylindrical deposit formed upon a copper wire be sectioned, polished, and etched. In such a deposit the markings are truly radial with the wire as the hub of the wheel. If the cathode is smooth and uniform in thickness the etch figures are everywhere parallel to a radius. If the deposit is markedly botryoidal in structure the figures change direction as the cathode grows and always end approximately normal to its surface. The appearance of such a section under the microscope is strongly suggestive of a iron filing " map " of a part of a magnetic field, *e.g.*, fig. 7, Plate 1. In this case the deposit grew from N. to S. No change could be observed in the direction of the etch figures from the centre to the edge of smooth cylindrical deposits formed upon copper wires rotated at a high speed about their own axis during the electrolysis.

The question whether the radial and random figures brought out by treatment with ammonium sulphide or with chloride ions are due to the solution of the $SbCl_3$ or to some such mechanism as a differential solution of the metal itself in different states of strain will be discussed in a later paragraph. It is obvious, however, from figs. 4–11, Plates 1 and 2, that the density of both the radial and random markings increases with the amount of salt in the metal. Figs. 4, 5, 6, and 7 are etched deposits from a 70% $SbCl_3$ solution and therefore contain about 10% $SbCl_3$. Figs. 8, 9, and 11 are deposits from a 15% solution and so contain about 5%.

* *E.g.*, Glocker and Kaupp, ' Z. Physik,' vol. 24, p. 121 (1924); Bozorth, ' Phys. Rev.,' vol. 26, p. 390 (1925).

$SbCl_3$. All the surfaces were etched for the same length of time in the same ammonium sulphide solution. The markings are plainly larger and more numerous in the metal containing 10% $SbCl_3$. Attempts to " photometer " the negatives of such photographs by means of a Weston " photronic " cell have shown that there is a parallelism between salt content and amount of etching, but as yet have given no reproducible quantitative data with regard to the relative density of the etch figures on the different kinds of amorphous antimony.

Another type of visible heterogeneity is sometimes found in the explosive metal. Long, narrow, light-coloured bands extend throughout the deposit, as in fig. 15, Plate 2. (In this case the band runs about N.E. by E. and on the negative is very distinct.) These bands usually appear to be parallel to the electrode length and are therefore probably due to some irregularity in the deposition.

4—The Electrical Conductivity

The technique of preparing and mounting the specimens of explosive antimony for the resistance measurements has already been described. As the same resistance was obtained by the use of either alternating current (1000 $\backsim$) and telephones or direct current and a galvanometer the latter method was finally adopted. That Ohm's law holds at all measurable voltages is shown by the fact that the resistance of a given specimen is independent of the bridge current.

The results of the specific resistance measurement at $0°$ (ρ_0) are given in Table I. The dimensions and actual resistance of each specimen are listed in columns 3, 4, and 5. Column 1 gives the $SbCl_3$ content of the solution from which the metal was deposited and column 2 the amount of $SbCl_3$ in the specimen as interpolated from the data of Cohen and Ringer (*loc. cit.*). For the first eight specimens the resistance was measured in the direction at right angles to the lines of the depositing current. The resistance of the last four specimens is that parallel to the current lines. As the dimensional error in these latter measurements is much larger than in those preceding, they are not taken into account in calculating the average ρ_0, column 7. The values obtained, however, are not greatly different from the others, so that it appears that the conductivity of explosive antimony is the same, or is at least of the same order of magnitude, in all directions.

It is to be noted that the conductivity increases with decreasing $SbCl_3$ content and that at $0°$ explosive antimony containing 10% $SbCl_3$ has about 200,000 times the resistance of ordinary antimony, $\rho_0 = 4 \times 10^{-5}$.

The effect of temperature change on the resistance of typical freshly made (*i.e.*, practically pure amorphous) specimens is shown in fig. 2. Provided that crystallization has not taken place to any appreciable extent a straight line results from plotting log R against 1/T, so that the resistance at any temperature can be represented by the equation

$$2 \cdot 3 \log R = \frac{\alpha}{T} - \beta,$$

where the numerical value of the constant β is dependent upon the dimensions of the specimen and the amount of $SbCl_3$ it contains. The value of α (slope of the lines in fig. 2) is about $2 \cdot 0 \times 10^3$ for freshly made

TABLE I—THE SPECIFIC RESISTANCE OF EXPLOSIVE ANTIMONY AT 0°

% $SbCl_3$ in solution	% $SbCl_3$ in metal	Length cm	Cross-section cm²	R_0 ohms	ρ_0	Mean ρ_0
75	10	1·55	0·0516	220·6	7·4	
75	10	1·90	0·0312	457·4	7·5	7·5
75	10	2·00	0·0875	173·8	7·6	
50	8	0·93	0·0623	68·7	4·6	4·7
50	8	0·68	0·0660	48·9	4·8	
15	5	1·35	0·0725	43·2	2·3	
15	5	1·30	0·0973	34·0	2·5	2·5
15	5	0·97	0·1038	25·7	2·7	
75	10	0·378	0·156	15·50	6·4	
75	10	0·263	0·101	13·61	5·4	
15	5	0·242	0·185	6·50	5·0	
15	5	0·180	0·145	4·70	3·8	

deposits, irrespective of the amount of salt present, and remains constant down to liquid air temperatures where the resistance becomes too high to measure on a Wheatstone bridge, 10^7–10^8 ohms. If the specimen is not allowed to remain at room temperature for any length of time the resistance at lower temperatures is accurately reproducible. As the specimen ages at room temperature, however, and the degree of crystallization increases, the value of α diminishes and ceases to be constant. The curve of log R versus 1/T bends down and tends to become more and more nearly parallel to the 1/T axis as the temperature is lowered. In Table II are given some typical results of resistance measurements made on specimens aged at room temperature. It is to be noted that the resistance at −78° has decreased to a much greater extent than that at 0°.

This decrease of α with increase of crystallization is presumably due to a tendency on the current lines to converge toward the crystalline
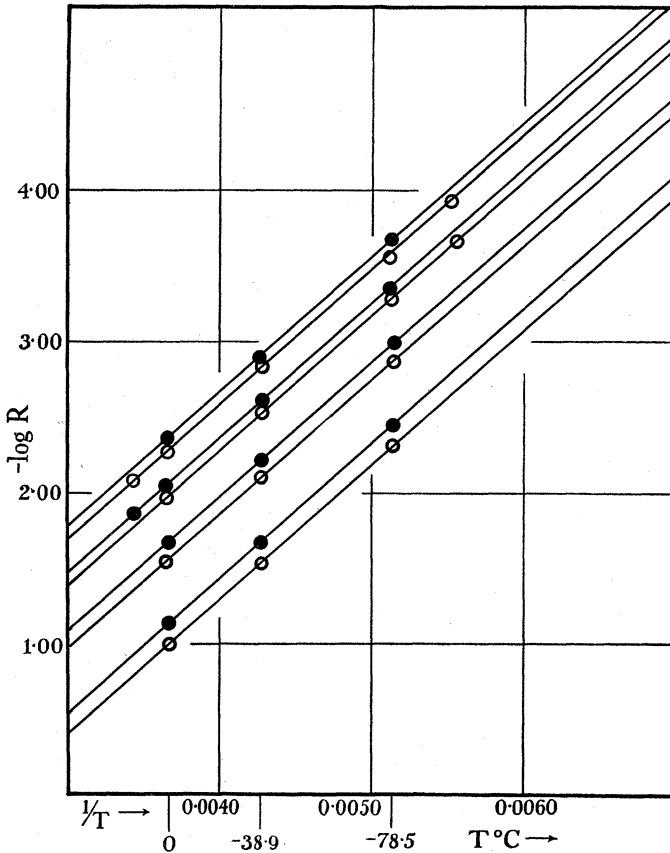
FIG. 2—Change of resistance with temperature.

TABLE II—EFFECT OF AGEING ON THE RESISTANCE OF EXPLOSIVE
ANTIMONY

Age	Several hours		4 weeks		8 weeks	
% SbCl$_3$ in metal	Ro°	R − 78°	Ro°	R − 78°	Ro°	R − 78°
10	220·6	4546	216·3	3895	199·0	2485
10	90·0	1838	89·3	1691	83·0	1192
10	33·5	7155	32·5	649·7	31·0	176·0
10	44·5	9401	43·3	759·9	39·0	555·0
5	—	—	43·2	571·7	35·5	395·0
5	—	—	34·0	472·7	32·0	431·0
5	—	—	25·7	324·9	20·7	139·0

regions as the conductivity of the surrounding medium diminishes, *i.e.*, as the temperature is lowered. In other words, the current density in the crystals increases and that in the amorphous matrix decreases as the temperature falls. Thus the tendency of the crystals to act " in parallel " and cause what might be called " internal short circuiting " increases as the temperature is lowered.

The assumption that there is a distortion of the current lines caused by a heterogeneity of the medium is supported also by the fact that the passage of a relatively small current results in the explosion of a partially crystallized specimen. Current densities of the order of 1 amp/cm² will explode a piece of the amorphous metal even if it is directly immersed in running tap water. If a specimen exploded in this way be polished and etched the concentric crystallization lines are plainly visible under the microscope and by their curvature may be followed back to a " crater " (occasionally more than one) somewhere in the interior of the metal. It thus appears probable that current densities sufficient to bring the temperature up to the explosion point (100°–120° C) obtain at one or more points within the specimen. It should be pointed out here that the explosive crystallization wave will still travel at room temperature in specimens already 60–80% crystallized. The speed of the wave decreases and the spacing of the explosion lines increases with the degree of crystallization.

As already stated, the value of β in the above equation depends upon the dimensions and $SbCl_3$ content of the specimen. For a cube 1 cm on the edge β has the values 5·31, 5·78, and 6·41 for explosive antimony containing respectively 10, 8, and 5% $SbCl_3$. As this relationship is roughly linear the specific resistance of any specimen of freshly made explosive antimony at any temperature may be approximately represented by the equation

$$\log \rho = \frac{870}{T} + 0 \cdot 095\,C - 3 \cdot 26,$$

where C is the percentage of $SbCl_3$ in the metal.

From the behaviour outlined in the preceding paragraphs it might appear that the conductivity of explosive antimony is electrolytic in character. The high specific resistance, the negative exponential temperature coefficient of resistance, and the fact that the above equation is the same as the one that fits the electrolytic conductivity of dielectric crystals* all point to this conclusion. Moreover, the fact that the values of α for the molecular type of crystal lattice, 3×10^3,* and for explosive antimony,

* Joffé, " The Physics of Crystals," McGraw-Hill Book Co., N.Y., 1928.

$2 \cdot 0 \times 10^3$, are of the same order of magnitude suggests that the mechanism of conduction is the same in each case.

There are other data, however, which indicate that the conductivity is purely metallic. For instance, no detectable transfer of matter occurred during several prolonged attempts at " electrolysis " in directions both parallel and perpendicular to the face of the deposit. Ohm's law is obeyed at all measurable voltages; the same value for the resistance is obtained by using either direct or alternating currents, while increase in salt content, *i.e.*, increase in the number of possible electrolytic carriers, actually lowers the specific conductivity. It is indeed difficult to imagine any ionization in a medium of such electrical and optical properties. It would seem, therefore, that in spite of a small polarization effect at the higher temperatures the conductivity is mainly if not wholly metallic in character, in keeping with the fact that the material is opaque and when polished exhibits the unmistakable metallic lustre.

The experiments of Steinwehr and Schultz* on the galvanic polarization of explosive antimony were repeated and extended. By means of a quickly operated double-pole double-throw switch a specimen con-nected across a measured voltage drop and kept at a constant temperature could be disconnected and thrown into a galvanometer circuit. The total resistance of this circuit was kept equal to the critical damping resistance (300 ohms) of the galvanometer—a 30-ohm instrument with a sensitivity of $1 \cdot 5$ microvolts per mm of scale.

At $-78°$ no trace of a polarization E.M.F. could be observed after applying potential differences as high as 10 volts to the ends of a specimen for long periods of time. (Voltage drops greater than this cause the passage of currents large enough to heat the specimen.) At higher temperatures, however, measurable and reproducible galvanometer deflections were encountered, indicating that the material is polarized to a slight extent. At any one temperature this E.M.F. of polarization varies directly as the polarizing voltage, which has to be applied for 2–3 minutes before the galvanometer kick reaches a constant maximum. For any one voltage drop the polarization E.M.F. is a linear function of the temperature. Table III gives the results obtained with a typical specimen (No. 4 in Table I) of uniform cross-section. In column 2 are listed the polarization E.M.F.'s (in microvolts) caused by a potential drop of 1 volt per cm at each of four different temperatures. The linear relationship is evident. If left in the circuit the galvanometer returns to zero at a rate which is proportional to the magnitude of the deflection. The " half-life " of the polarization is given in column 3.

* ' Z. Physik,' vol. 63, p. 815 (1930).

The whole effect is very similar to that encountered in dielectrics and in all probability is due to an ionic displacement or orientation in the highly viscous medium. As is to be expected, the number of ions (polarization) and the ease of relaxation (ionic mobility) increase with increasing temperature.

TABLE III—POLARIZATION AND ITS RATE OF DECAY AT DIFFERENT TEMPERATURES

Temperature °C	Polarization volts $\times$ 10^6	$t\frac{1}{2}$ (sec)
22	202	24·7
0	147	28·9
−21	93	34·6
−78	0	—

5—THE RATE OF THE NON-EXPLOSIVE CRYSTALLIZATION

If a specimen of explosive antimony be kept at a temperature between 50° C and 100° C the electrical conductivity increases at a measurable rate. The higher the temperature the more rapid is the change. As has already been pointed out, an increase in conductivity at constant temperature is presumably due to an increase in the ratio crystalline phase/amorphous phase, so that resistance measurements may be used to follow the rate of crystallization. It is true that there exists at all temperatures a certain amount of what has been called " internal short-circuiting," so that a strict linear relationship between the concentration of the dispersed crystalline phase and the overall resistance of the specimen cannot be expected. However, as shown in Table II, the magnitude of this effect appears to increase exponentially with the difference between the specific conductivities of the amorphous and crystalline metal and to become less and less important as the temperature rises, *i.e.*, as the difference between the specific conductivities of the two phases diminishes. At the temperatures at which the resistance changes at a measurable rate there is thus, in all probability, no great error involved in assuming a linear relationship between the electrical conductivity of a specimen and the extent to which it has crystallized. The fact that the resistance changes at a rate which is proportional to its magnitude is indeed very good evidence that this assumption is justified.

Rates of resistance change were measured at 56·6° (acetone vapour), 80° (benzene vapour), and 100° (steam), and in the following are inter-

preted as rates of crystallization. The resistance always decreased according to the equation of a first-order reaction:

$$k = \frac{2 \cdot 303}{t} \log \frac{R_0 - r}{Rt - r}$$

in which r is the final resistance (leads plus crystallized specimen), R_0 is the resistance at the start, and Rt is the resistance at time t. Velocity constants ($k =$ slope $\times 0 \cdot 434$) were calculated from the slope of the straight line obtained by plotting $\log \frac{R_0 - r}{Rt - r}$ against t or by Guggenheim's method.* The results of these measurements of rate of crystallization are summarized in Table IV. The concentration of $SbCl_3$ in the solution from which the metal was deposited appears to have little or no effect upon the rate of crystallization. During the reaction $SbCl_3$ is liberated by the specimen which loses the fibrous characteristics of the explosive modification and becomes a definitely polycrystalline metal. A microscopic examination of polished and etched surfaces of the changed specimens has shown the crystallization to be perfectly random. No trace of the rhythmic orientation characteristic of the " exploded " metal is evident.

The slope ($\times 2 \cdot 303$ R) of the straight line obtained by plotting $- \log k$ against $1/T$ gives an activation energy of 27,300 calories per gm atom. The velocity constant of the crystallization at any temperature is given by the equation

$$\ln k = 31 \cdot 40 - \frac{27300}{RT} .$$

This 27,300 calories ($1 \cdot 2$ electron-volts) which must be acquired per gm-atom before crystallization can occur is of the order of magnitude of an ionization potential. It may be that the acquisition of $27,300/N$ calories per atom actually results in a sort of ionization, $i.e.$, liberation of a " conductivity " electron, and so makes possible the growth of the ordinary metallic lattice.

Recognition of the large temperature coefficient of the rate of crystallization makes possible a clearer picture of the explosion phenomenon. If the heat evolved in the reaction is not conducted away rapidly enough to prevent a rise in temperature the effect will, of course, be cumulative and a purely thermal explosion will result. It is thus meaningless to speak of a definite explosion temperature characteristic of the substance.

* ' Phil. Mag.,' vol. 7, p. 538 (1926).

The same would seem to apply to the transition temperature observed by Kramer and Zahn* for the amorphous → crystalline change in thin metallic films.

The fact that explosive antimony crystallizes slowly at room temperature throws doubt upon the reliability of previously determined physical

TABLE IV—RATE OF CRYSTALLIZATION OF EXPLOSIVE ANTIMONY

% SbCl$_3$ in solution	R$_0$	$t\frac{1}{2}$ (min)
	56·6° C	
60	28·0	363
40	28·9	377
60	44·5	350
40	15·5	325
60	40·5	380
40	9·85	380
15	9·74	360
15	9·37	350
15	19·6	373
75	75·4	353
		Mean=363; $k = 3·2 \times 10^{-5}$ sec^{-1}
	80·0° C	
60	25·2	23
40	28·8	24
60	15·1	21
40	4·88	19
75	40·0	20
75	26·0	20
75	7·02	23
		Mean = 21; $k = 5·5 \times 10^{-4}$ sec^{-1}
	100·0° C	
40	10·8	3·2
15	1·57	3·0
15	19·6	3·2
75	26·0	2·4
75	23·2	2·3
		Mean = 2·8; $k = 4·1 \times 10^{-3}$ sec^{-1}

constants of the substance. An example from this laboratory will serve as an illustration. It was stated in Part I that the speed of the explosion wave was being determined by measuring the distance from each of two "craters" (one of which was made a known fraction of a second after the other) to the line of meeting of the two sets of waves (*see* figs. 11 and

* ' Naturwiss.,' vol. 43, p. 792 (1932); ' Z. Physik,' vol. 86, p. 413 (1933).

12, Plate 7, Part 1). The method was to drop two red-hot needles from different heights on to the polished specimen. The needles were released simultaneously from electromagnets connected in series. Distances of fall were measured with a cathetometer; " crater-to-crater " and " craters-to-line " distances were measured with a microscope and mechanical stage. Fairly consistent results (10 to 40 cm/sec), which showed that the speed of explosion depended largely upon the temperature, salt concentration, and thickness of the deposit, were obtained. The age of the specimens used ranged from several weeks to several months.

As soon as it was found that the deposits should be 50% crystalline after about a month at room temperature the experiments were repeated with specimens no more than several hours old. It was then found that under all conditions (of temperature, etc.) the explosion was so violent that the deposits were shattered and stripped from the copper or so distorted that microscopic measurements were impossible. Fig. 14, Plate 2, is a photomicrograph of a fragment of a thick specimen that was badly shattered by the explosion. The hot needle struck at the centre of the concentric cracks, and the manner in which the deposits are split up into spherical shells is evident. As is to be expected, the speed and violence of the explosion is greatly reduced by partial crystallization. The point stressed here is that other properties also must be affected by ageing.

The actual rate of crystallization at room temperature is, however, much slower than that calculated from the high-temperature data. The resistance at $0°$ of the specimens listed in Table II has diminished only 8–12% (instead of the calculated 60%) after 8 weeks at room temperature. It appears also that thin pieces crystallize more rapidly than thick ones, and that lacquered specimens crystallize more slowly than those from which the lacquer has been removed. Moreover, by grinding off the surface layers of a fairly thick partially crystallized specimen it is possible to raise its resistance temperature coefficient—in favourable cases α can be brought up almost to that $(2·0 \times 10^3)$ of the freshly made material. It would seem, therefore, that at the lower temperatures the crystallization tends to work inward from the surface and that its rate may be influenced to some extent by the rate of escape, i.e., by the vapour pressure, of the $SbCl_3$. The fact that the crystallization at the higher temperatures is a precise first-order reaction indicates that it is here a uniformly random process—possibly because the escape of $SbCl_3$ no longer determines the rate. If, at these temperatures, the surface layers crystallized much more rapidly than the interior complications due to short-circuiting and dependence of velocity constant on the surface, volume ratio of the specimen would be expected. The fact that deposits of sublimed $SbCl_3$ are to

be observed on the walls of stoppered bottles in which massive deposits have been stored for several years shows that the salt can and does leave the metal as it crystallizes at room temperature.

In this connexion it is a peculiar fact that a specimen partially crystallized by storage at room temperature will regain part of its resistance when kept at $0°$. In fig. 3 the percentage change in the resistance at $-78°$ is plotted against time for four typical specimens, the initial resistance of which ranged from 715 to 4546 ohms. During the periods covered by the continuous lines the specimens were kept at $20°$; between the points connected by the broken lines they were kept in ice. An unmistakable uniformity of behaviour is evident. The resistance always diminishes at
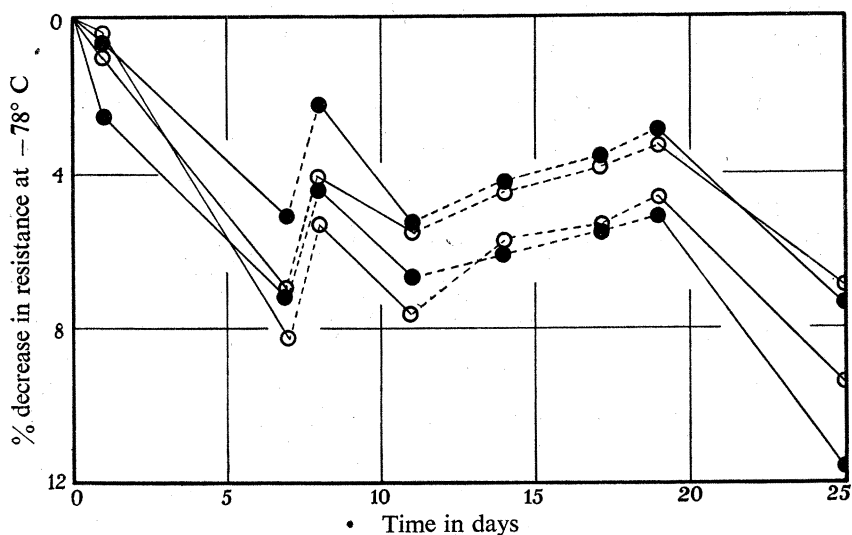
Fig. 3—The effect of storage temperature on resistance change.

$20°$ and increases at $0°$. The resistance of a fresh specimen does not increase when kept in ice (as is to be expected, a very slow decrease occurs), nor can the original resistance of an aged specimen be completely recovered by storage at $0°$.

DISCUSSION

As has already been pointed out in Part I, there is good evidence for believing that the explosive deposits consist of amorphous antimony containing 2 to 10% $SbCl_3$. The part played by the salt in this peculiar form of matter is still obscure. The etch figures, Plates 1 and 2, may be due to increased reactivity along lines of internal stress in a homogeneous medium or they may be caused by a difference in the solubility of the two

phases of a heterogeneous system. The peculiar growth and the oriented fibrous structure of the deposits suggest that the latter is the correct interpretation. While it seems probable that the amorphous metal constitutes one phase, the nature of the other, if indeed it exists, is not clear. Although the etch figures increase in density with increasing $SbCl_3$ content they cannot be due to the removal of $SbCl_3$ as such since they do not appear during prolonged immersion in such excellent $SbCl_3$ solvents as alcohol and ether and aqueous HCl. The hypothesis suggested for further investigation is that this second phase consists of an Sb-$SbCl_3$ complex resulting from the deposition of a complex ion. The important point at the moment is that explosive antimony is probably a hetero-geneous " gel " and not a homogeneous solid solution of $SbCl_3$ in the amorphous metal as has previously been supposed.

It is questionable whether or not the explosive deposit should be referred to as a " metal." A consideration of the electrical conductivity —probably the most useful criterion of the metallic state—leads to no decision. Increase in the $SbCl_3$ content, however, increases the resistance, so that there is probably a small but real metallic conductivity character-istic of the amorphous phase; but amorphous antimony should not be likened to the super-cooled liquid. While both are " amorphous " the binding in the former must be predominantly homopolar and in the latter metallic.

Summary

A microscopic study of polished and etched surfaces has shown that the explosive electrolytic deposit of antimony possesses a heterogeneous gel-like structure in which one phase is oriented parallel to the lines of the depositing current. This oriented phase, which is soluble in ammonium sulphide solution, is regarded as an $SbCl_3$-Sb complex resulting from the deposition of a complex ion. The other phase is probably amorphous antimony.

In the case of fresh deposits the specific resistance, which is about 10^5 times that of ordinary antimony and which has a negative exponential temperature coefficient, is given by the equation

$$\log \rho = \frac{8 \cdot 7 \times 10^2}{T} + 0 \cdot 095 \, C - 3 \cdot 26,$$
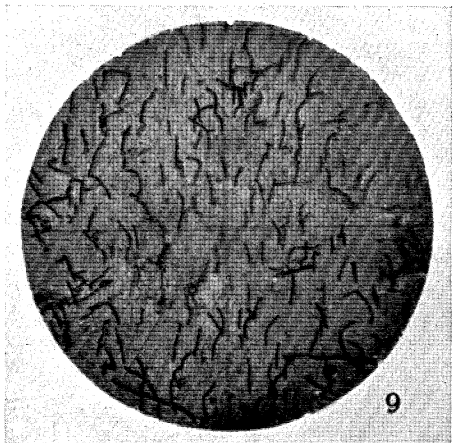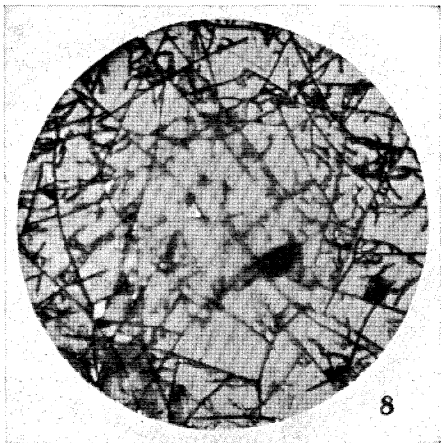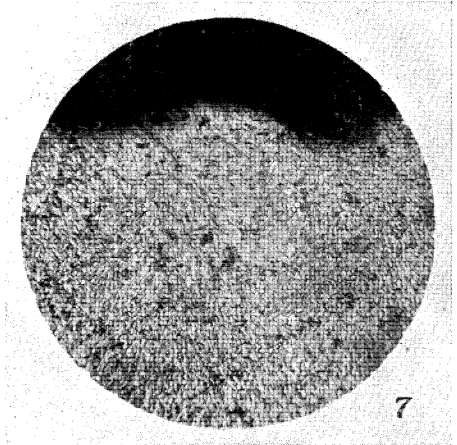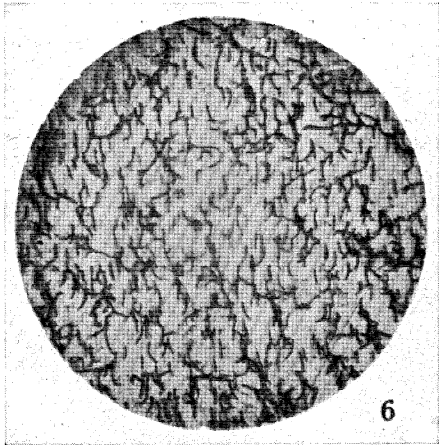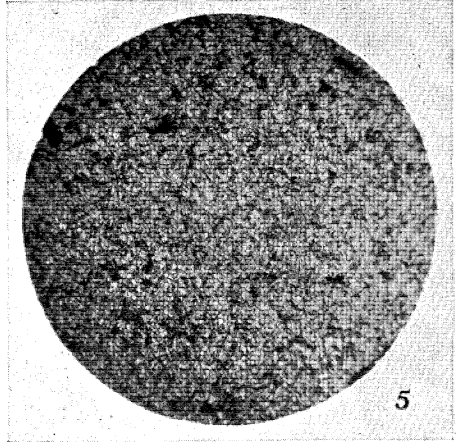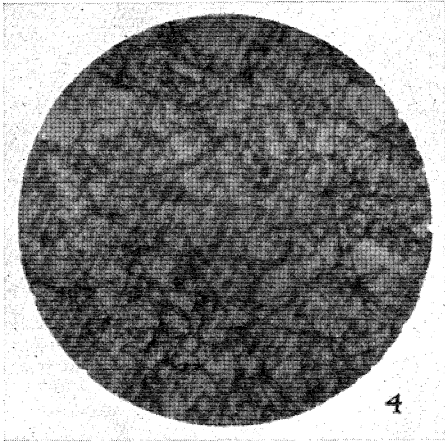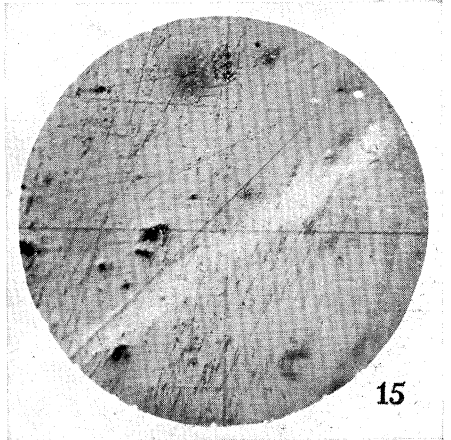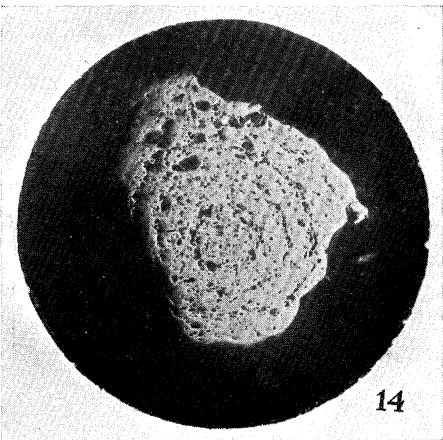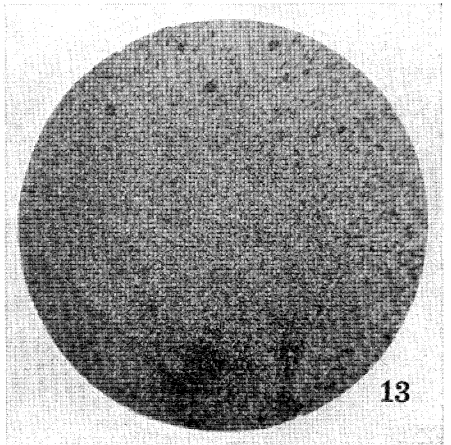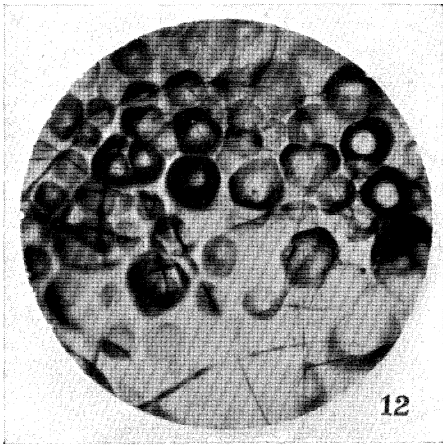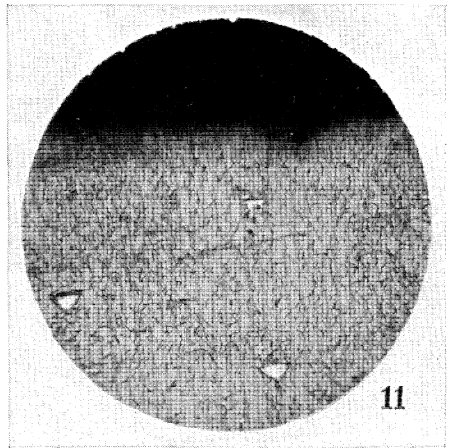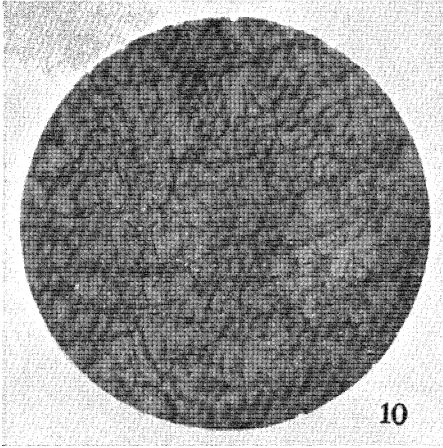
where C is the percentage of $SbCl_3$ in the metal.   (This equation does not apply to partially crystallized deposits.)   Ohm's law is obeyed and Faraday's law is not involved, so that, in spite of the resistance temperature coefficient and a small polarization which appears at the higher temperatures, the conductivity is probably metallic.

Between 55° C and 100° C amorphous antimony crystallizes at a measurable rate which is independent of the amount of salt in the metal and which can be represented by the equation of a first-order reaction. The Arrhenius equation applies and gives an energy of activation of 27,300 cal/gm atom.   The rate of crystallization is given by the equation

$$\ln k = 31 \cdot 40 - \frac{27,300}{RT} \, .$$

EXPLANATION OF PLATES

PLATE 1

FIG. 4—Random etch figures on polished face of deposit from 70% $SbCl_3$ solution.   × 180.

FIG. 5—Same as fig. 4.   × 45.

FIG. 6—Radial etch figures on polished end of deposit from 70% solution.   × 180.

FIG. 7—Same as fig. 6 except that deposit is from a 60% solution.   × 45.

FIG. 8—Same as fig. 4 on deposit from a 15% solution.   × 180.

FIG. 9—Same as fig. 6 on deposit from a 15% solution.   × 180.

PLATE 2

FIG. 10—Same as fig. 6 on deposit from a 60% solution.   × 180.

FIG. 11—Same as fig. 6 on deposit from 15% solution.   × 45.

FIG. 12—Botryoidal structure on surface of deposit from a 70% solution.   × 180.

FIG. 13—Same as fig. 12 on deposit from a 15% solution.   × 45.

FIG. 14—Fragment of exploded deposit showing concentric cracks about crater.   × 10.

FIG. 15—White streak in explosive metal.   × 180.