PART II

STUDIES ON ANTIMONY CRYSTALS

CHAPTER V

A STUDY OF THE EFFECT OF TEMPERATURE GRADIENT AND GROWTH VELOCITY ON THE ORIENTATION OF ANTIMONY SINGLE CRYSTALS

Existence of preferred orientation in metals is a well known phenomenon. However, to date no general theory has been evolved, which can explain the observed behaviour of metals satisfactorily. This is because different metals having the same structure and similar physical properties are found to behave differently. While some metals do not show any preferred orientation, there are some other metals which prefer to grow along different crystallographic directions under different growth conditions. Theoretical explanation offered to the behaviour of a particular metal often contradicts the experimental observation and the behaviour of other metals with same structure. So far no study has been reported on the preferred orientation of antimony. The results of an attempt in this direction are presented in this chapter. Obviously, the experiments should be on single crystals and the necessity of allowing for random nucleation forbids the use of seed in growing the crystals. Hence the results refer to unseeded single crystals.

It is considered useful to present the various results on some of the metals and theoretical interpretations offered to explain their behaviour. That cast ingots of metals exhibit preferred orientation is well known for quite a long time. However, the first systematic work using single crystals was reported by Goss and Weintroub[1]. Crystals of tin, zinc, lead, bismuth, cadmium and indium were grown in a horizontal temperature gradient furnace. For slow rates of growth bismuth, cadmium and tin showed a preferred orientation which zinc and indium did not. The preferred orientation was that for which the direction of maximum thermal conductivity liesalong the axis of the specimen - the direction of heat flow. For zinc and indium the thermal conductivity is only slightly anisotropic and this is believed to be the reason for the absence of preferred orientation. Goss[2], in a subsequent publication pointed out that for faster rate of growth zinc showed a marked preference for the hexagonal axis to be normal to the specimen axis, bismuth still showed a preference for the [111] direction to be normal to the specimen axis and tin showed no preferred orientation at all. Generally it can be concluded that it is not a single factor which is responsible for the existence of preferred orientation but a number of factors like anisotropy of thermal conductivity of the metal, growth rate, temperature gradient, impurities and state of stress are contributory factors for the existence of preferred orientation.

The work of Goss and Weintroub is not mainly concerned with the orientation of the crystal but with the actual process of growth. In this respect it deserves credit in that a number of metals have been studied under different conditions. However, the data available in the lowest range of growth velocity is insufficient to give a conclusive result on the effect of growth velocity and temperature gradient on the orientation of crystals.

Grinberg[3] has studied the effect of growth rate on the orientation of the basal plane of cadmium with respect to the crystal axis. The crystals were grown by Bridgman's method in a vertical furnace at a temperature gradient of 15°C/cm. Various growth rates were tried in the range 2-10 cm/hr. It was observed that as the rate of lowering of crucible was decreased from

10 cm/hr, the angle between basal plane and the crystal axis increased until it reached a critical value at which it became random. When the mould was changed to graphite the nature of variation remained the same except for a shift in the curve. The results were interpreted as follows: For fast growing crystals the isotherms inside the mould are ellipses elongated in the direction of the mould axis. Therefore the basal plane is parallel to the major axis of the ellipse. When the rate of travel slows down the ellipse becomes circular and the orientation becomes random. The shift in the curve due to graphite mould is attributed to the larger conductivity of graphite. One conclusion drawn is that thermal conductivity has a marked effect on the orientation of the crystals. Bridgman[4,5] observed that zinc crystals grown in a temperature gradient furnace tend to orient in such a way that the c-axis makes large angles with the axis of the mould. Jillson[6] attributes preferred orientation in zinc crystals to small amounts of impurities. These results have been contradicted by Slifkin[7]. His experiments indicate that the geometry of crucible may have some effect on

the orientation of zinc single crystals.

Balasubramanian[8] has shown that zinc crystals have preference for the c-axis to be perpendicular to the crystal axis for large velocities of growth and parallel for small velocities of growth. The observations are in agreement with the results of Goss and Weintroub[1]. Impurities do not have any effect on the orientation. However, changes in the interface morphology brought about by constitutional supercooling change the orientation of the crystal. Shah[9] working on bismuth crystals has obtained results in agreement with those of Goss and Weintroub and has shown that the strong preference of bismuth single crystals to orient the (111) plane along the axis of the crystals is not in any way affected by any of the growth parameters, geometry and material of mould, impurities and interface morphology as also the method of growth, either Chalmers method or Bridgman's method.

Tamman[10] has used his theory of anisotropy of growth rate to account for the preferred orientation in ingots. A grain having a greater velocity of growth is able to encroach over its neighbour and eventually suppress it out. In order that the velocity of growth of a particular grain may be greater than another grain, it should have a higher thermal conductivity along the direction of thermal gradient and hence the crystal will have an orientation such that the planes having highest thermal conductivity will lie along the axis of the specimen. This theory can be applied only to anisotropic crystals and is not applicable to cubic crystals.

Chalmers' experiments[11,12,13] on the bicrystal boundaries of tin indicate that the equilibrium temperature of a crystal in contact with its melt is a function of the crystallographic orientation of the interface. From this an explanation for preferred orientation of isotropic crystals could be derived. However, if equilibrium temperatures for different crystal faces are different, the free energy per unit volume must be different in the two crystals, which is rather unreasonable. Chalmers has reconsidered this mechanism whereby one crystal grows ahead of its neighbour of different orientation. This explanation is given in terms of the ease with which an atom from the melt be accomodated on crystallographically different interface. A crystal interface grows ahead of its neighbour when atoms are more easily accomodated on it than on the neighbour by virtue of the fact that its growth can proceed at lower amounts of supercooling.

Tiller[14] has attempted to explain the observed preferred orientation in pure metal, metal with small amounts of impurities and alloys containing large amounts of impurities sufficient to produce constitutional supercooling. Basically the theory attempts to explain the preferred orientation in the cubic system and is applicable to other systems also with reasonable modification. Theory considers again the competitive growth of two nuclei of different orientations and the free energy of the resultant boundary. However, the explanation offered is not very clear in the case of pure metals.

From the discussion presented so far, it is clear that there are experimental differences among various workers. No single theory so far presented is capable of explaining the observed results. Basically the phenomenon of preferred orientation is essentially a process of easy adherence of the atoms on solid-liquid interface consisting of differently oriented grains and fundamentally the problem reduces to whether and how this adherence is affected by the growth conditions. Experimental work in the problem should cover detailed studies on the preferred orientations in metals of different crystal structures grown under controlled conditions of growth with a view to assess the relative importance of thermal conductivity, stress and solute concentration and interface morphology. Such study will be the cumulative and joint effort of various workers. The results presented in this chapter are obtained in an attempt to study the preferred orientation in antimony crystals.

While the results may not be exhaustive, the author has chosen to focus attention on some of the pertinent parameters of growth and sought answers to the following questions:

(1) Do antimony crystals grown under controlled conditions exhibit preferred orientation?

(2) Does this preference, if any, depend on (a) temperature gradient and (b) velocity of growth?

(3) Does this metal behave similar to other metals like bismuth of the same crystal structure and physical properties?

(4) Do the results compare with the available data on other metals of different structures?

(5) Do the results agree or contradict the theoretical predictions or the observed results explainable on the basis of any available theory?

Crystals were grown in a horizontal furnace under externally imposed thermal gradient. The description of this method (Chalmers' method) is already given in Chapter IV. In all the experiments presented here the temperature gradient was changed by changing the temperature of the after-heating furnace. Crystals were grown in a graphite boat with one end tapered and having the dimensions 12.0 x 0.8 x 0.4 cm.

Crystals have been grown under three different temperature gradients 92°C/cm, 75°C/cm and 52°C/cm. In each case the growth velocity has been varied from 1.5 cm/hr to 9 cm/hr. Orientation of the crystals is measured by measuring the angle between the (111) cleavage plane and the mould axis. For this purpose the crystals were cooled in liquid nitrogen and cleaved in the normal way using a sharp blade. It has not been possible to obtain single crystals in all cases especially at higher growth velocities. Table I gives the percentage of single crystals obtained in each case. It is observed that generally the probability of obtaining a single crystal is more when the temperature gradient is large and the rate of growth is slow.

Table II lists the observed orientations of the crystals in each case. It is seen that for any particular velocity the orientation is found to fluctuate within certain limits. However, it is observed that there is a direct relationship between growth velocity and orientation in each case. The best way of studying such a data is by using a regression analysis. Figures 1,2 and 3 are the scatter diagrams for the three temperature gradients in which individual values of orientation Y is plotted against growth velocity X. It is seen from these scatter diagrams that the relationship between the two variables X and Y approximates to be straight line. If we assume a linear regression of the form

$$Y = a + bX \qquad \dots \qquad \dots \qquad \dots \qquad (1)$$

TABLE I

PERCENTAGE OF SINGLE CRYSTALS

Temperature gradient		Growth velocity X cm/hr.							
		9	8	6	5	4	3	2	1.5
92°C/cm	No. of crystals grown	6	4	5	6	7	10	7	7
	No. of single crystals	2	2	3	5	7	8	7	6
	% single crystals	33	50	60	83	100	80	100	84
75°C/cm	No. of crystals grown	6	5	6	6	7	6	6	6
	No. of single crystals	1	2	4	5	6	6	6	6
	% single crystals	16	40	67	83	84	100	100	100
52°C/cm.	No. of crystals grown	2	2	2	2	2	2	2	2
	No. of single crystals	0	1	1	2	2	2	2	2
	% single crystals	0	50	50	100	100	100	100	100

TABLE II

ORIENTATIONS OF THE CRYSTALS

Temperature gradient	Growth velocities in cm/hr X	observed orientations in degrees Y							
		1	2	3	4	5	6	7	8
92°C/cm	9	62	60						
	8	60	58	65					
	6	50	53	57					
	5	40	49	47	41	38			
	4	35	28	32	38	29	36	35	
	3	31	25	23	20	30	45	21	15
	2	3	5	12	20	15	12	15	
	1.5	8	5	13	7	3	11		
75°C/cm	9	67							
	8	61	57						
	6	60	65	58	63				
	5	54	45	51	43	48			
	4	42	35	38	46	39	35		
	3	22	32	28	30	35	20		
	2	13	22	18	15	14	20		
	1.5	4	7	5	12	5	8		
52°C/cm	9	-							
	8	70							
	6	63							
	5	50	53						
	4	37	42						
	3	18	28						
	2	10	18						
	1.5	7	12						

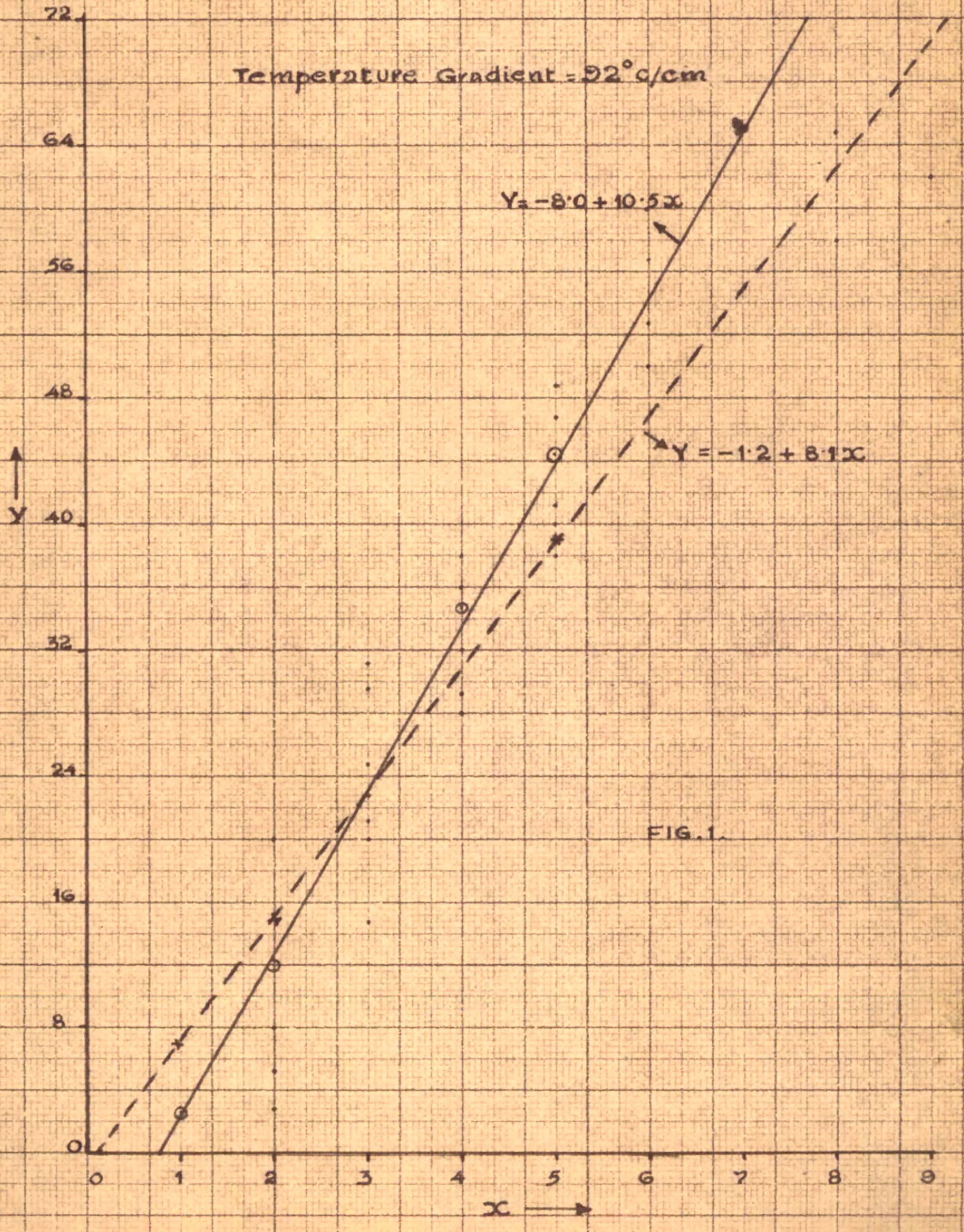
Temperature Gradient = 92°c/cm
Y = −8·0 + 10·5x
Y = −1·2 + 8·1x
Y
x
72
64
56
48
40
32
24
16
8
0
0
1
2
3
4
5
6
7
8
9

FIG. 1.

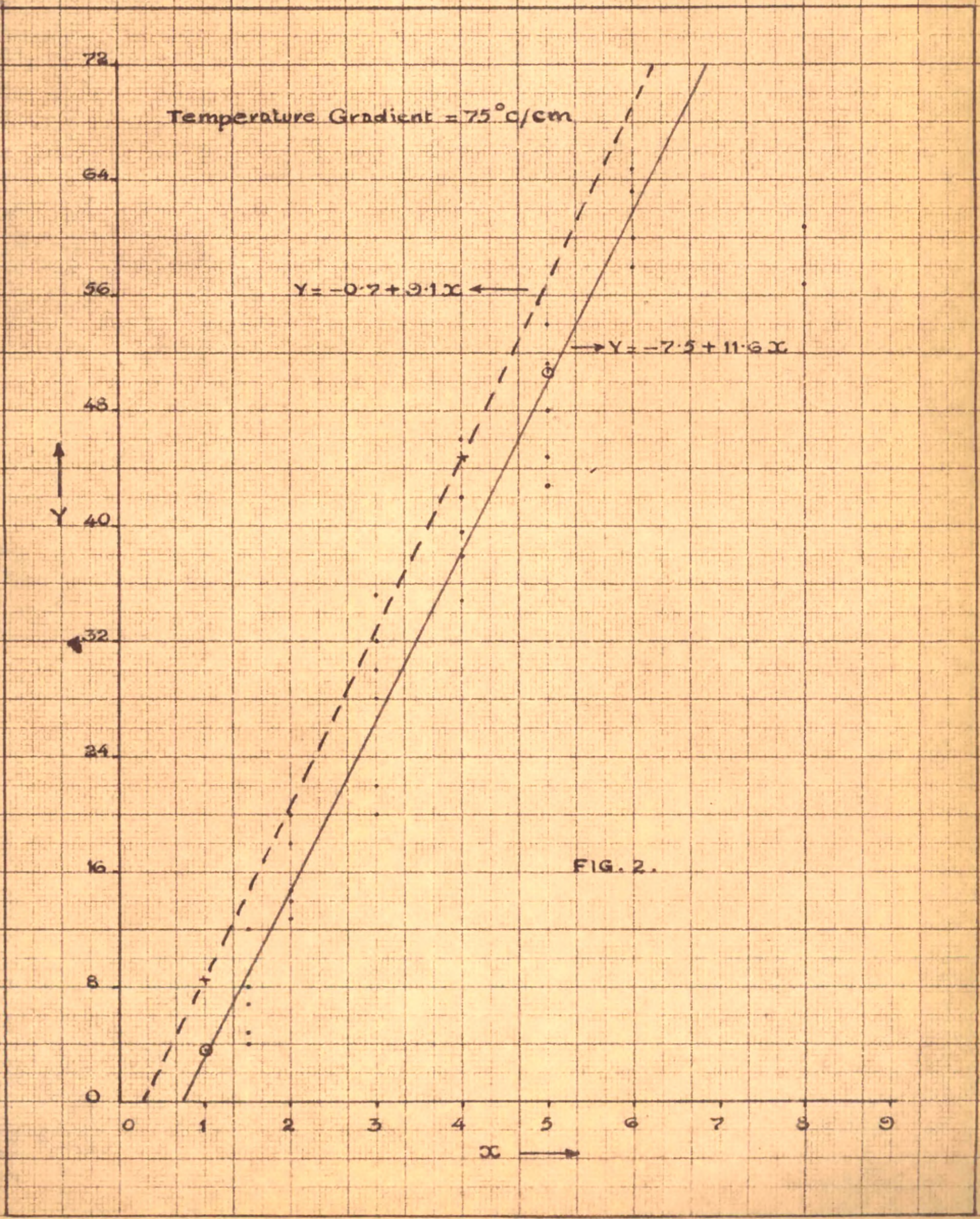
Temperature Gradient = 75°C/cm
Y = -0·7 + 9·1 x
Y = -7·5 + 11·6 x
Y
x
72
64
56
48
40
32
24
16
8
0
0
1
2
3
4
5
6
7
8
9

FIG. 2.

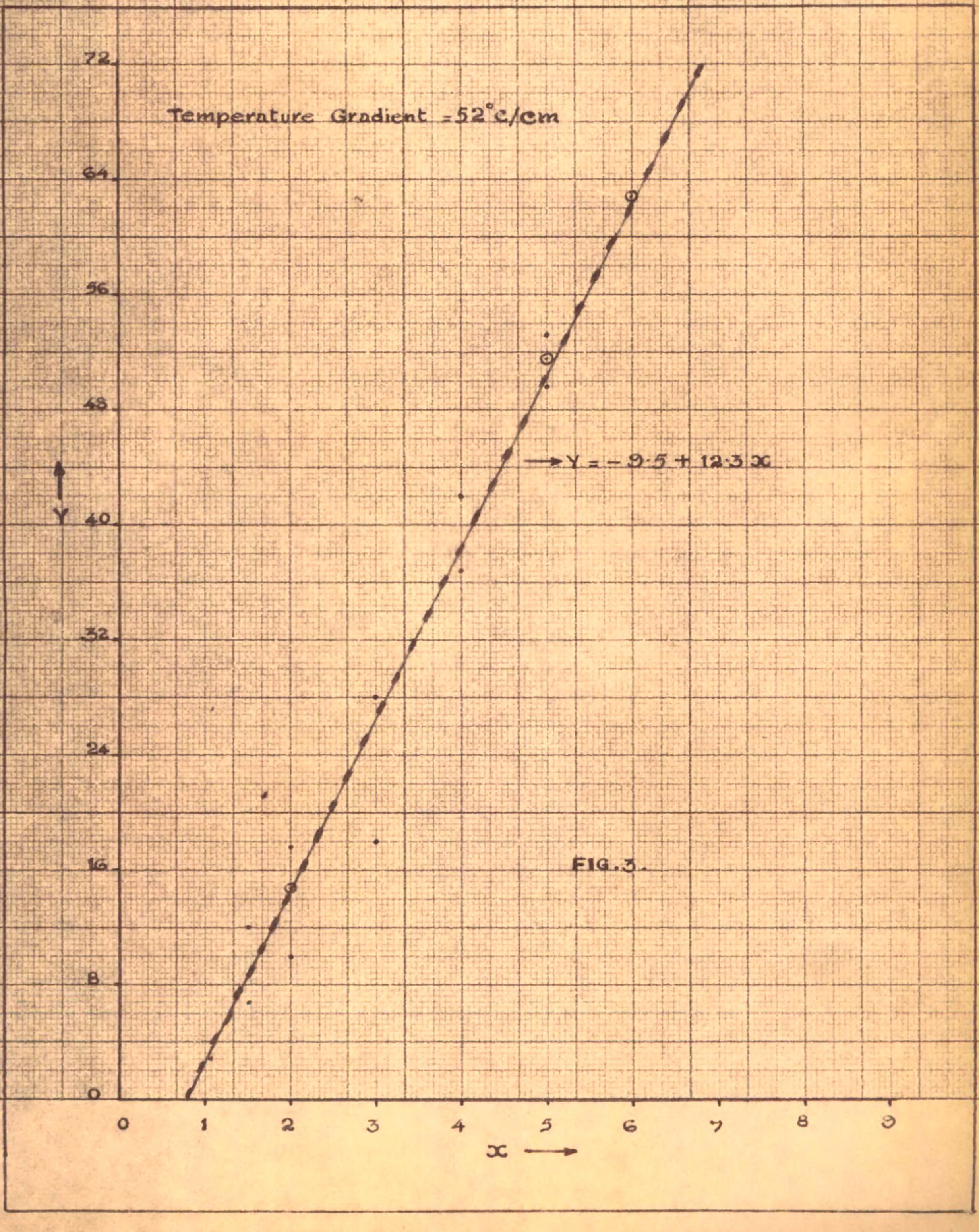
Temperature Gradient = 52°C/cm
Y = − 9·5 + 12·3 x
Y
72
64
56
48
40
32
24
16
8
0
0
1
2
3
4
5
6
7
8
9
x

FIG. 3.

where a and b are constants given by the equations

$$b = \frac{\Sigma XY - n\bar{X}\bar{Y}}{\Sigma X^2 - n\bar{X}^2} \qquad \dots \qquad \dots \qquad (2)$$

and $$a = \bar{Y} - b\bar{X} \qquad \dots \qquad \dots \qquad \dots \qquad (3)$$

where $\bar{X}$ = arithmatic mean of all values of growth velocities - X

$\bar{Y}$ = arithmatic mean of all values of orientation - Y

ΣXY = sum of products of X and Y

ΣX^2 = sum of squares of X

ΣY^2 = sum of squares of Y

Correlation coefficient r , which is a measure of the strength of relationship between X and Y is given by

$$r = \frac{\Sigma XY - n\bar{X}\bar{Y}}{\sqrt{(\Sigma X^2 - n\bar{X}^2)(\Sigma Y^2 - n\bar{Y}^2)}} \qquad \dots \qquad (4)$$

constants a, b and r are calculated in all three cases and shown in Table III. The results in the last column indicate the percentage variation of orientation explainable in terms of the variation of growth velocity. The regression lines given by equation (1) are drawn for all the temperature gradients (dotted lines in the figures). While the figure 3 shows a perfect dispersion of the points around the regression line, such a dispersion is not observed in figures 2 and 3. A closer inspection of the figures indicates a deviation from the general trend at velocities greater than 6 cm/hr. Another analysis is made eliminating these readings (above 6 cm/hr growth velocities) and results are summarised in Table IV.

The revised regression lines in all the figures are plotted (dark lines in the figures) and it is found that the dispersion of the points around the line is uniform within the ranges considered. The observations suggest that about 95% (r^2 x 100) of the variation in the orientation of the crystal is due to variation in the growth velocity. Constants a and b are found to be almost same for the three temperature gradients used in the experiments. These statistical tests for significance of the differences in a and b for the three temperature gradients give negative results. Thus the orientation of the crystals do not depend on the temperature gradient. The distribution of the points for higher growth velocities indicates that the orientation is no longer dependent on the growth velocity beyond 6 cm/hr. The

TABLE III

Temperature gradient	a	b	r	r^2 x 100
92°C/cm	-1.2	8.1	0.95	90
75°C/cm	-0.7	9.1	0.94	88
52°C/cm	-9.5	12.3	0.98	96

TABLE IV

Temperature gradient	a	b	r	r^2 x 100
92°C/cm	-8.0	10.5	0.97	94
75°C/cm	-7.5	11.6	0.97	94
52°C/cm	-9.5	12.3	0.98	96

observations can be summarised as follows:

(1) The probability of obtaining single crystals in the experiment is more when the growth velocity is low.

(2) Antimony exhibits a preferred orientation and is determined by the growth velocity when the latter is small in the range 1 cm/hr to 6 cm/hr.

(3) The temperature gradient doesnot have any observable influence on orientation within the ranges studied.

(4) Beyond 6 cm/hr, the crystals do not exhibit any preferred orientation.

Comparison of the results with the other available data on bismuth shows that the behaviour of antimony is contradictory to the behaviour of bismuth. Whereas the latter shows a strong preference for the (111) plane to lie parallel to the axis of the specimen which is independent of growth rate and temperature gradient as has been established by Goss and Weintroub[1] and Shah[9], the preference of antimony is dependent on growth rate. However for slow rates of growth behaviour of antimony is similar to that of bismuth where the (111) planes tend to make small angles with the specimen axis. As in the case of tin, antimony also does not exhibit preferred orientation at fast rates. Comparing with the results of Grinberg[3] on cadmium, though a linear relationship is observed, the nature of variation is quite reverse i.e. the angle between the (111) plane and crystal axis is found to increase with the increase in velocity of growth. Similarly the results contradict those on zinc also, so far as the orientation of the cleavage plane with the mould axis is concerned.

The temperature gradients in the experiments are generally high and in the case of lower growth rates it can be assumed that equilibrium conditions exist. Then, according to Tiller's theory[11] it should normally be expected that the (111) plane lie along the interface. The results obtained do not therefore agree with the Tiller's theory according to which we must expect (111) planes to be normal to the crystal axis. If we consider, after Chalmers[15], that preferred orientation is the result of the case with which atoms are attached to an interface, we have an explanation as to why the probability of obtaining single crystals is low at fast rates. Since it has been observed that at fast rates no preferred.

orientation is observed, differently oriented nuclei have the same probability of adhesion to the interface and in the freezing metal they can survive with equal probability resulting in a polycrystal. Thus the absence of preferred orientation and the predominence of polycrystals agree well.

The observed results thus do not completely fit into the theories, though explainable in part. Variables employed throughout the investigation being the ones connected with thermal conduction the explanation should be looked for in the thermal behaviour of the metal, though crystallographic features are also important. It is, however, surprising to note that the results do not show any significant change with the temperature gradient. Perhaps the variation employed is not sufficient to produce any observable difference. The experimental data also do not agree well with the behaviour of other metals. The deductions are thus tentative and much more experimental work is necessary before a reliable picture can emerge.

CONCLUSIONS:

The general conclusions of the experiments can be summarised as follows:

(1) Antimony single crystals exhibit preferred orientation for low velocities of growth when grown under externally imposed thermal gradient.

(2) The inclination of the (111) plane to the axis of the crystal shows a linear relation to the velocity of growth.

(3) For large growth rates the crystals do not show any preferred orientation.

(4) Within the range of the experiment the orientation is not dependent on the thermal gradient.

(5) Though the results compare with other metals in certain specified ranges, the behaviour of antimony is unique.

(6) The results do not agree well with Tiller's theory.

(7) Anisotropy of thermal conductivity appears to be an important factor in determining the orientation.

(8) To obtain single crystals, the growth velocity should be low.

(9) It appears possible to grow single crystals of desired orientation by proper choice of the growth rate.

(10) Absence of preferred orientation is the main cause for the domination of polycrystals at fast growth rates.

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