

A STUDY OF ALLOTROPES OF SELENIUM BY THE X-RAY DIFFRACTION METHOD *

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Plate IX

ABSTRACT. The transformation of monoclinic selenium into metallic (hexagonal) form has been studied by the X-ray diffraction method and it has been found that the period of transformation depends on the temperature, *e.g.*, at 120°C it takes one hour, at 80°C, 15 days, and at 65°C more than 17 days are required for complete transformation. The transition is monotropic.

The amorphous varieties soften even at 38°C (the melting point of metallic selenium being 217°C) and on X-ray diffraction analysis three broad bands coinciding in position and intensity with the three distinct groups of lines of the crystalline varieties are obtained. It has been found that the vitreous selenium devitrifies even at 28°C and the devitrified mass gives crystalline pattern. The rate of devitrification and the transformation into the crystalline modification depends very much on the temperature. The surface of the sample of vitreous selenium supplied by Dr. Gripenberg preserved in his laboratory in Finland for seven years (the maximum temperature throughout the year being below 27°C) when examined was found to be crystalline, while the internal portion of the sample gave diffuse broad bands.

It has also been shown that at a very low temperature the devitrified product is purely monoclinic and at a high temperature it is purely hexagonal. There are intermediate temperatures at which both monoclinic and hexagonal varieties are produced.

Accurate measurements of the spacings corresponding to the bands obtained with samples of vitreous selenium heated for different periods at 38°C show that the band spacing is a continuous function of the period of heating. Now as there is a regular growth of size of the crystallites present in vitreous selenium with the period of heating, it is clear that the band-spacing is a function of the size of the crystallite. Our experimental results thus satisfy the theoretical work of Lenard Jones, *viz.*, that the lattice constant should be a function of the particle size. The band spacing corresponding to the sample of amorphous selenium coagulated from the colloidal solution is 3.8 A.U. while that of the vitreous selenium heated for 60 hours at 38°C is 3.4 A.U. only.

INTRODUCTION

Vitreous selenium, the most well-known amorphous variety, obtainable in the form of black sticks, can be easily prepared by rapidly cooling molten

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selenium. Selenium thus obtained is a brittle black substance having average density of 4.28 gms./c.c. On heating, gradual softening commences at 50°C. The red precipitated selenium or red amorphous selenium is prepared by the reduction of selenious acid with sulphurous acid, glucose, etc. Its behaviour on heating is the same as that of the vitreous selenium. The density of this variety is 4.26 gms./c.c. Both of the foregoing varieties are partially soluble in carbon disulphide.

Red monoclinic selenium is obtained when CS₂ solution of amorphous selenium is allowed to crystallise by evaporation at the room temperature. The density of this variety is 4.44 gms./c.c. at 0°C. It melts at 170°C and the transformation into metallic or hexagonal form begins slowly at 120°C. Metallic selenium, the hexagonal variety, is the most stable form and is obtained by the transformation of the above-mentioned forms of selenium. The density is 4.78 gms./c.c. at 0°C and melts at 217°C. The boiling point is 690°C. The electrical conductivity of metallic selenium is exceedingly small in the dark but on exposure to light the resistance diminishes in a remarkable manner. Selenium can also be obtained in colloidal state by the reduction of aqueous solution of SeO₂ by means of requisite quantity of SO₂ or glucose.

Bradley¹ has determined the structure of the hexagonal selenium (the metallic variety). The structure of the monoclinic selenium has been determined by Klug.² Prins and Dekeyser³ studied by X-ray diffraction method the crystallisation of vitreous selenium. Their conclusions may be summarised as follows : (a) The transformation of the vitreous selenium into the hexagonal variety may take place at 60°C if a thread of vitreous selenium be kept under tension at that temperature. (b) In the absence of any tension the crystallisation does not take place below 73°C.

The representation made in this paper comprises the results obtained during the course of a systematic study of the various modifications of selenium, under different physical conditions by X-ray diffraction method.

Experimental method.—The usual "powder photograph" method was adopted in our investigation. The tube was operated at 35-40 K.V. with a current of 5-6 M.A. Hemicylindrical cameras were used since the usual method of comparison of intensities of different rings are tenable only when the rays travel the same distance before falling on the X-ray film. Two hemicylindrical cameras, having radii 2.888 cms. and 1.814 cms. respectively, were used. In order to heat the sample during X-ray exposure, the sample was pressed against the slit cap or introduced within a thin-walled capillary which was surrounded by an electric heater. The electric heater consists of a syndanio bobbin, wound with a nichrome wire resistance, tightly fitting the slit tube. The temperature of the sample was measured by a calibrated copper-constantan thermocouple. For high temperature work, the film was cooled by circulating water through a metallic jacket pressing the film.

Allotropes of selenium.—*Black vitreous* selenium was prepared by rapidly quenching boiling liquid selenium in ice-cold water. Selenium thus obtained formed a hard shining black vitreous mass showing conchoidal fracture. The powdered vitreous selenium softens even at 38°C (melting point of the most stable hexagonal variety being 217°C) and the powdered mass coalesce. Vitreous selenium is partly soluble in CS₂ which on evaporation gives red monoclinic crystals. *Red precipitated selenium* was prepared by passing pure SO₂ gas through aqueous solution of SeO₂. In order to avoid the transformation of the red precipitated selenium into the metallic variety due to heat evolved in the process, the cylinder containing the aqueous solution of SeO₂ was kept cooled by surrounding it with a cold water jacket. It was found that at 40°C the red amorphous selenium turns black within half an hour. Its behaviour with CS₂ is the same as that of vitreous selenium.

Metallic (hexagonal) selenium can be prepared by heating any variety of selenium at 130°C for 12 hours. It can also be prepared by the following sublimation process. Vitreous selenium was taken in long glass tube which was carefully evacuated and sealed. The lower part of the tube was maintained at 73°C by means of an electric heater. After several days crystals appeared in the cooler part. It is insoluble in CS₂ and melts at 217°C.

X-ray diffraction photographs of these allotropes were taken. The interplanar spacings calculated for the rings obtained with the metallic variety correspond to that obtained by Bradley, in the case of hexagonal selenium. (Table I). The spacings obtained with the monoclinic variety is also given in Table I.

TABLE I

Hexagonal Selenium			Monoclinic Selenium		
Intensity	Bragg angle θ	Spacings in A.U.	Intensity	Bragg angle θ	Spacings in A.U.
W.	10 35'	3.781	W.	10 25'	4.256
S.	11 50'	3.753	W.	11 34'	3.837
W.	13 30'	2.976	S.	12 30'	3.555
V.S.	15 0'	2.973	W.	13 34'	3.281
V.W.	19 44'	2.057	S.	14 32'	3.066
W.	20 41'	2.178	S.	16 4'	2.781
M.S.	21 53'	2.065	W.	18 20'	2.446
W.	22 54'	1.977	V.W.	19 9'	2.346
M.S.	25 59'	1.756	V.W.	20 8'	2.236
M.S.	28 2'	1.637	V.W.	21 21'	2.115
M.S.	30 48'	1.503	W.	22 49'	1.985
M.S.	32 46'	1.422	W.	23 56'	1.897
V.W.	34 2'	1.375	V.W.	25 28'	1.785
			V.W.	30 0'	1.583
			V.V.W.	30 47'	1.56

The vitreous and the red amorphous selenium give three broad bands. The ring system of the crystalline (hexagonal) variety of selenium can also be broadly divided into three groups, each group containing several lines of fair intensity. The pattern obtained with the monoclinic selenium contains only one such group which approximately corresponds in position with the first group of the hexagonal variety. The bands obtained with the amorphous varieties correspond approximately in position and intensity with the *groups* mentioned in the hexagonal variety. This 'line-band' correspondence suggests that there is some relation existing between the crystalline and the corresponding amorphous state. In Table II the band spacings of the vitreous and red amorphous selenium are given. It will be seen from the table that the band spacing of the vitreous and the red amorphous selenium are somewhat different. The cause of the discrepancy will be discussed later on.

TABLE II

Black Vitreous Selenium			Red Amorphous Selenium		
Intensity	Bragg angle	Spacings in A.U.	Intensity	Bragg angle	Spacings in A.U.
S.	12 31'	3.551	S.	12 14'	3.633
W.	25 59'	1.757	W.	24 54'	1.828
V.W.	36 43'	1.406	V.W.	36 55'	1.281

Conversion of Monoclinic Selenium into the Hexagonal Modification :— From the thermo-chemical data⁷ a quantity of heat (about 2.2 Cal. per gm.) is evolved when monoclinic selenium converts into the hexagonal form at higher temperature. Again the heat of formation of SeO_2 from the monoclinic selenium is greater than that of the same from the hexagonal variety.

This suggests that the monoclinic selenium has got a greater energy content than the hexagonal form and thus the former will have a tendency to pass into the hexagonal state.

It has been found that heated for 12 hours at 120°C, monoclinic selenium is completely converted into the hexagonal form. The conversion was then studied at 80°C. With the sample, heated for 12 hours at 80°C, no sign of transformation, from the monoclinic to the hexagonal form, was detected. The sample of monoclinic selenium was then maintained at 80°C and photographs were taken with the sample heated for 168, 200, 300 hours. In the photograph of the sample heated for 200 hours at 80°C, faint lines corresponding to the

hexagonal pattern were indicated. The sample was then maintained at 80°C continuously for 15 days and on X-ray analysis it was found that complete conversion into the hexagonal form has occurred (Plate IX). With the sample of monoclinic selenium heated at 65°C for 17 days a photograph was obtained in which the rings corresponding to both monoclinic and hexagonal selenium are present. The interplanar spacing corresponding to above-mentioned photographs are given in Table III.

TABLE III

Monoclinic selenium converted at 80°C			Monoclinic selenium partially converted at 65°C		
Intensity	Bragg angle θ	Spacings in structure*	Intensity	Bragg angle θ	Spacings in structure*
W	10 34'	3.782 H	W	10 22'	4.276 M
S	11 39'	3.81 H/M	M. S.	11 45'	3.779 H
V. W.	12 30'	3.555 M	M. S.	12 32'	3.546 M
W	13 23'	3.325 H	W	13 37'	3.270 M
V. S	14 52'	2.995 H/M	V. S.	14 51'	3.004 H
W	15 55'	2.805 M	M. S.	16 5'	2.778 M
V. W.	19 39'	2.289 H	—	—	—
W	20 41'	2.179 H	—	—	—
S	21 57'	2.062 H	—	—	—
W	22 40'	1.985 H	—	—	—
V. W.	23 49'	1.905 H	—	—	—
M. S.	25 54'	1.762 H	—	—	—
M. S.	28 8'	1.632 H	—	—	—
M. S.	30 51'	1.501 H	—	—	—
M. S.	32 38'	1.427 H	—	—	—

We should mention in this connection that transition of monoclinic selenium into the hexagonal variety is monotropic. The case is similar to that of S_w which passes into S_a even at the ordinary temperature, and more quickly at higher temperatures. Again, we see that in these cases of monotropic transition, apparently there is no sharply defined transition temperature. The transformation takes place practically at all temperatures but the rate depends on the temperature at which the transformation takes place. Monoclinic selenium converts into the hexagonal form and the reverse process cannot occur, since the hexagonal variety has got the minimum crystal potential energy. But it will be seen, later on, that in the case of crystallites or minute crystals of the hexagonal type, its conversion into the bigger monoclinic variety is quite possible.

VITREOUS SELENIUM

Devitrification of Selenium:—Powders of vitreous selenium were heated at temperatures 55°, 70°, 120°, 170°C with the help of an electric heater.

* H=Hexagonal, M=Monoclinic, H/M=Both H and M superposed.

At any temperature as the heating was continued and sample specimens were taken out of the heated mass at suitable intervals of time and the corresponding X-ray powder-diagrams were taken. The results of the X-ray study are summarised in the chart presented below.

Period of heating	55°C	70°C	120°C	170°C
0 hr.	3 amorphous bands.	3 amorphous bands.	3 amorphous bands.	3 amorphous bands.
12 hrs.	amorphous band with some indication of structure in the band.	A pure crystalline pattern with no indication of bands. The pattern corresponding to that of hexagonal selenium.		
24 hrs.	amorphous band and two faint rings superimposed on the 1st band.	„		
36 hrs.	amorphous band and four rings superimposed on the 1st band.	„		
72 hrs.	weak amorphous bands, four rings on the 1st band and several other rings in the position of the 2nd band.			

From the above chart it is evident that the gradual devitrification of vitreous selenium is due to its gradual crystallisation and the rate of crystallisation is found to be slower at low temperature.

The question naturally arises whether such crystallisation of vitreous selenium is at all possible at a still lower temperature. To investigate this point we analysed specimens of vitreous selenium heated at 43°C for 36, 60, 84, 182, and 200 hours. It was found that the diffraction patterns of the specimens heated for less than 182 hours showed only the amorphous bands. The patterns obtained with specimens heated for longer periods showed indications of rings, corresponding to the hexagonal form, but two faint rings of the system correspond to the two strong lines of the monoclinic pattern. After 20 days of continuous heating the pattern (plate IX) obtained with the specimen consisted only of sharp rings showing complete crystallisation. The next experiment was conducted with a specimen heated at 38°C. In this case the first indication

of crystallisation was observed in the specimen heated for 200 hours and even when the sample was kept at that temperature for 1100 hours we obtained (plate IX) both rings and amorphous bands in the diffraction pattern. It is peculiar that in this case the spacings of the rings suggest transformation both to the hexagonal and monoclinic form.

It has been mentioned before that vitreous selenium converts itself only to the hexagonal form above 43°C. But at 43°C two faint rings corresponding to the monoclinic form is just observed along with the strong lines of the hexagonal variety. But when the vitreous selenium is heated at 38°C for 1100 hours a different picture appears on the plate. In this transformation the percentage of monoclinic selenium in the transformed product is much greater than that obtained at 43°C. This is clearly evident not only from the number of rings of the monoclinic variety but also from the relative intensities of the rings of the two crystalline types.

Dr. Grippenbergs of Masaby, Finland, supplied us with a stick of vitreous selenium which had been preserved in his laboratory for seven years. The temperature of his laboratory does not rise on an average above 28°C throughout the whole year. The stick was analysed on the very day it was received here in Calcutta ; the temperature of our laboratory was 30°C ; a quantity of fine powder was scraped from the surface of the stick and the diffraction photograph was taken. Sharp Debye pattern was obtained showing sign of complete crystallisation into the monoclinic form. It is peculiar that at 28°C vitreous selenium converts only into the monoclinic form (plate IX).

TABLE IV

Vitreous Selenium devitrified below 28°C

Specimen	Intensity	Bragg angle θ	Spacings in A.U.	Structure
Grippenbergs sample of vitreous selenium scraped from the surface of the stick, 7 years after its preparation (temp. below 28°C).	V.W.	10 24'	4.264	M
	V.W.	11 39'	3.810	M
	S	12 30'	3.514	M
	W	13 30'	3.298	M
	S	14 32'	3.066	M
	S	16 5'	3.778	M

To examine the nature of selenium in the body of the stick, the stick was broken and a sample was taken from its central portion. On X-ray analysis three broad bands were observed and their spacings correspond to that of the vitreous or amorphous selenium.

Dependence of the Band Spacings on the period of heating :— From the powdered vitreous selenium maintained at 38°C, samples were taken at intervals of 12 hours and X-ray photographs were taken with these samples. The diameters of the bands of different photographs were accurately measured and corresponding band spacings calculated. Table V shows that the value of the spacings of the first band gradually increases with the period of heating. The intensities of the second and third band are very weak and it is difficult to measure accurately the diameter of the outer bands and further experiments with the microphotometer records will be taken up to investigate the mode of their change with the period of heating.

TABLE V
BAND SPACINGS OF VARIOUS FORMS OF SELENIUM

Specimen	Bragg angle θ	Spacings in A.U.
Red selenium coagulated naturally from colloidal selenium solution.	11 41'	3'80
Red selenium coagulated naturally from another sample of colloidal solution.	11 50'	3'753
Red precipitated selenium prepared in the Laboratory.	12 14'	3'633
Black vitreous selenium.	12 21'	3'551
Black vitreous selenium heated for 12 hours at 37°-39°C.	12 38'	3'519
Black vitreous selenium heated for 24 hours at 37°-39°C.	12 48'	3'474
Black vitreous selenium heated for 36 hours at 37°-39°C.	12 50'	3'465
Black vitreous selenium heated for 60 hours at 37°-39°C.	13 4'	3'404

Photographs of Red selenium coagulated naturally from colloidal solution and of Black Vitreous Selenium heated for 60 hours at 37°-39°C are reproduced in Plate IX. The differences in the diameters of the band in the photographs (a & b) can be easily seen.

Generally we know that the diffraction pattern of liquids and amorphous substances consists only of broad diffuse bands but the investigations of Laue⁴ and others proved that considerable broadening of the diffraction lines may take place on the diminution of the size of the diffracting crystallites. If the size of the particles be sufficiently small, the line may become broad enough so as to appear as bands resembling those of the liquids and the truly amorphous

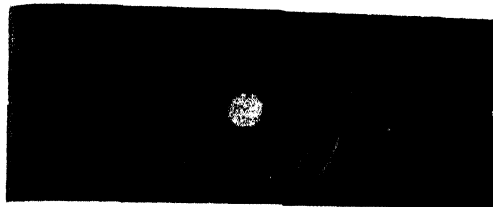


Fig. 1.

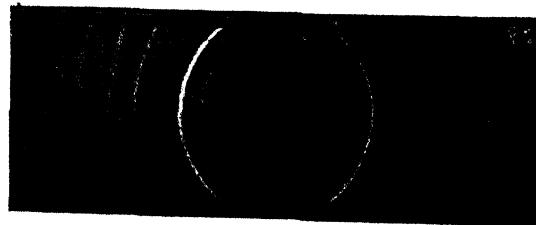


Fig. 2.

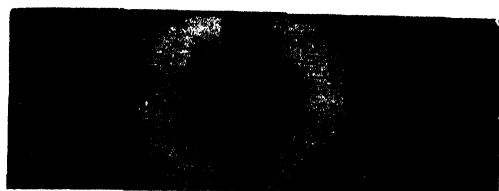


Fig. 3.

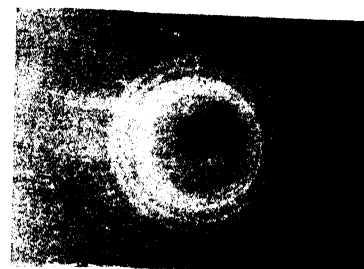


Fig. 4.



Fig. 5 (a)

Fig. 5 (b)

1. Monoclinic selenium transformed into the hexagonal form at 80°C.
2. Black vitreous selenium transformed into the hexagonal form at 43°C.
3. Partial transformation of vitreous selenium into both monoclinic and hexagonal form at 38°C. Lines superimposed on the band.
4. Vitreous selenium transformed into the monoclinic form at 28°C.
- 5.(a) Spontaneous coagulum of colloidal sol of selenium on ageing.
- (b) Vitreous selenium heated at 38°C for 60 hours. The difference in the diameter of the band in plate V(a) & V(b) is to be noted.

substances. The positions of the bands approximately coincide with the positions of the groups of intense lines in the pattern from crystals of larger sizes of the same substance. Generally, in order to have a sharp continuous Debye-Scherrer pattern the particle size should lie between 10^{-3} cm. to 10^{-4} cm. Thus the line-band correspondence indicate that the bands are due to the substance in an extremely subdivided state. Another effect, which is produced by the diminution in the size of diffracting crystallites, is the change in the diameter of the bands. This change may correspond either to an increase or decrease of the inter-atomic distances in the crystallites. That the lattice dimension is a function of the size of the crystallites was first theoretically investigated by Prof. Lenard Jones⁵ in the case of non-ionic crystals. The order of this change may be understood from the consideration of an ideal case in ionic crystals (such as NaCl), if the size of a simple cubic crystal be reduced to 500 atoms deep only, the lattice dimension changes by about 5% and in 3 atoms deep the change is about 14%.

Lowry and Bozorth⁶ while agreeing with the general resemblance between the patterns for graphite and amorphous carbon (which is assumed to consist of small crystallites of the graphite) pointed out that the spacings of the basal planes increased as the average particle size diminished.

DISCUSSION

When the molten selenium is suddenly cooled down so as to pass into the vitreous state, the mass solidifies before it can liberate the whole amount of its latent heat. The atoms of a solid body tend to arrange themselves in such positions that the crystal potential energy is minimum. In the case of selenium such a process of formation of crystal also happens by the marshalling of atoms in liberating the latent heat; but by the time the crystals have grown a little, the substance becomes too viscous to allow of any further marshalling or crystallisation. Thus instead of bigger crystals of the order of 10^{-3} - 10^{-4} cm. in size, we get minute crystals or crystallites of lesser dimension. If the formation of crystals would not have been thus checked, the molten selenium would easily pass into the crystalline state by giving up the whole of its latent heat, as is usual in the case of solidification of most of the substances. From the above argument, it is clear that some heat energy is actually retained by the crystallites present in the vitreous selenium, and the whole amount of the latent heat has not thus been liberated. In consequence, the crystallites present in vitreous selenium will have a greater energy content than ordinary crystals, *i.e.*, crystals of larger dimensions, in the formation of which, the whole amount of latent heat has been liberated. These crystallites, therefore, are in unstable

state and will always have a tendency to liberate the heat retained in the so-called amorphous state and form bigger crystals. This can only happen if, by heating the vitreous mass, we increase the mobility of the molecules of selenium, so that marshalling or crystallisation can again begin and the size of the crystallites increase gradually. The rapidity of crystallisation will depend on the degree of mobility or softening of the mass, which again will evidently depend on the temperature at which selenium has been maintained. This explains the increase in the rate of crystallisation of vitreous selenium with the rise of temperature. A portion of the vitreous selenium is soluble in CS_2 and monoclinic selenium is the only variety of selenium which is soluble in CS_2 . Thus vitreous selenium contains crystallites of both monoclinic and hexagonal selenium. From the consideration of experimental results on transformation of vitreous selenium into monoclinic at low temperature and into hexagonal at high temperatures, both with the evolution of heat it follows that both of these crystallites have got greater energy content than either of ordinary bigger monoclinic or hexagonal crystals. Also from thermochemical data⁷ it will be found that the heat content of vitreous selenium (containing both hexagonal and monoclinic crystallites) is greater than that of the ordinary monoclinic crystals which again has got greater heat content than the stablest hexagonal variety. Thus, both monoclinic and hexagonal crystallites present in vitreous selenium can pass either into purely hexagonal form or purely monoclinic form. And it has been found experimentally that at temperatures below 28°C vitreous selenium converts only into the monoclinic form. At temperatures above 43°C vitreous selenium is converted only into the hexagonal form and at intermediate temperatures, *viz.*, between 28°C and 43°C both monoclinic and hexagonal crystals are found in the transformed product.

The gradual growth of the size of the crystallites with the period of heating has got two experimental evidences. The diffraction photograph of a sample of vitreous selenium heated for a certain period at a particular temperature gives sharp lines superimposed on broad bands. The broad bands, as has been explained before, are due to crystallites still present in the vitreous selenium and the sharp rings are due to ordinary crystals, formed by the gradual growth of size of the crystallites, and lines superimposed on the bands directly shows the line-band correspondence.

According to the theoretical investigation of Lenard Jones, in the case of non-ionic crystal, lattice dimension increases as the particle size diminishes. This has been verified by Lowry and Bozorth in the case of carbon. The increase in the band spacings of vitreous selenium, with the period of pre-heating of the sample suggests, therefore, a gradual growth of size of the crystallites with the period of heating.

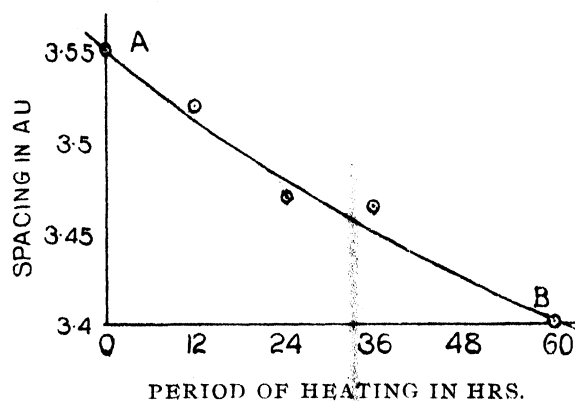


FIG. 1

The different band spacing obtained in the case of red amorphous selenium, red selenium coagulated from colloidal solution of selenium, can also be ascribed to the different sizes of the crystallites in these varieties. If these varieties of selenium are now arranged in the order of diminishing crystal sizes, based on X-ray determination, it will be observed that the same arrangement is again obtained, based on the colour of the specimen. As the grains get finer, the colour changes from black to red. Table V shows the various types of selenium arranged in order of increasing size of the crystallites against corresponding band spacings. From the smooth graph AB (Fig 1) in which abscissa represents the period of heating of vitreous selenium, in our experiment, and the ordinate being the spacings in A.U., it will be evident that there exists a relation between band spacings of vitreous selenium and the period of heating.

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