CHAPTER 11

OPTICAL STUDY OF MICROHARDNESS OF CALCITE CLEAVAGE FACES.

11.1 Introduction:

Many workers have studied the variation of hardness with load in case of metals as well as minerals. However, no systematic study appears to have been made on the microhardness of calcite cleavage faces. This chapter reports systematic study of variation of hardness with load (direction constant) and along different directions (load constant) on calcite cleavage faces. This study has been made for examining the anisotropic character of the surface and the effect of localized plastic deformation on the structure sensitive properties of crystal. Further the later part is also utilized in etching technique to delineate dislocations by the formation of etch pits on them.

Tertsch (1950) observed different shapes of indent marks on rhombohedral faces of calcite by changing the orientation of the indenter with respect to a reference line on the cleavage face. Onitsch (1950) found the change in diagonal length with respect to loading time on calcite cleavages. In the present work the loading time is kept constant for all indentations. The hardness variation of the cleaved faces of calcite was studied in a range of loads 1 - 100 gms at room temperature by using vickers hardness tester.

11.2 Experimental procedure:

The specimens for which hardness values were to be evaluated for different loads and different orientations were freshly cleaved. The cleavage surfaces were mounted by fixing them on aluminium circular disc using galva-cement or araldite. The specimen should be properly levelled at the time of fixation. Indentations were made on the surfaces by the indentation technique after taking usual precautions mentioned in the previous chapter.

11.3 Observations, Results and Discussions:

11.31 Variation of microhardness with load:

Many sets consisting of a large number of observations on freshly cleaved surfaces of calcite indented by various loads were taken for detailed graphical study of the following relations:

$H_V = 1854\ {}^{p}/_{d^2}$ H_V = microhardness in Kg/mm^2

p = load in gms.

d = diagonal of indent mark in Microns.

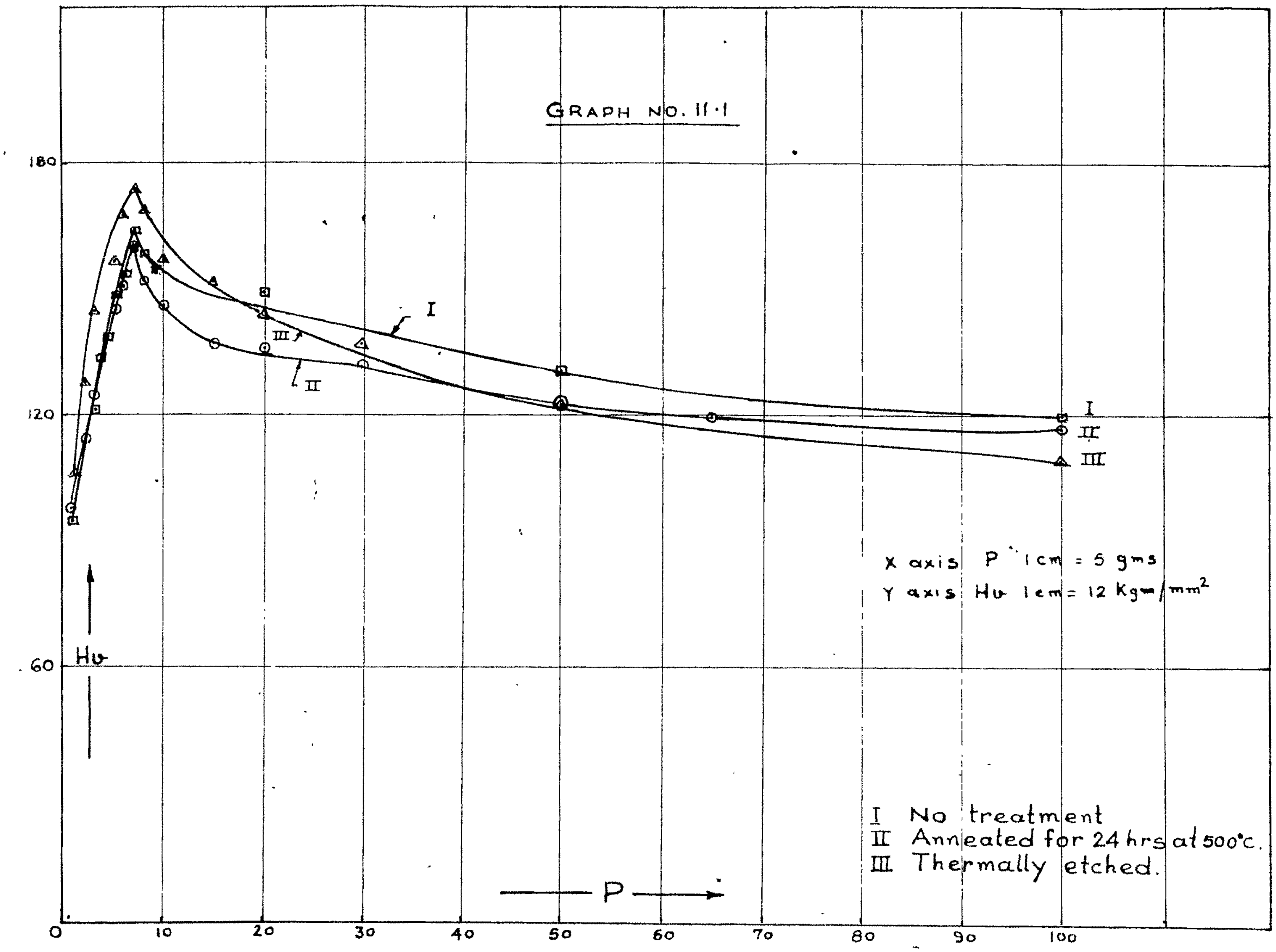
$p = ad^n$

$A = Bd^2$ A = Area of indent mark in $Microns^2$

n, a, and B are constants.

The indentation marks were produced by the diamond pyramidal indenter on the surface in such a way that the diagonals of these marks always remained parallel to a specific direction, say $[110]$ and $[1\bar{1}0]$ in the present case because these directions are of paramount importance for the calcite structure. A typical set of observations are presented in table 11.1. The graph of H_V versus P gives a direct idea of the nature of the hardness variation with load (graph 11.1). It showed an increase from 1 gm load onwards upto 8-12 gms and then it showed a gradual decrease, thereafter the graph was nearly smooth and straight

GRAPH NO. 11·1



180
120
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50
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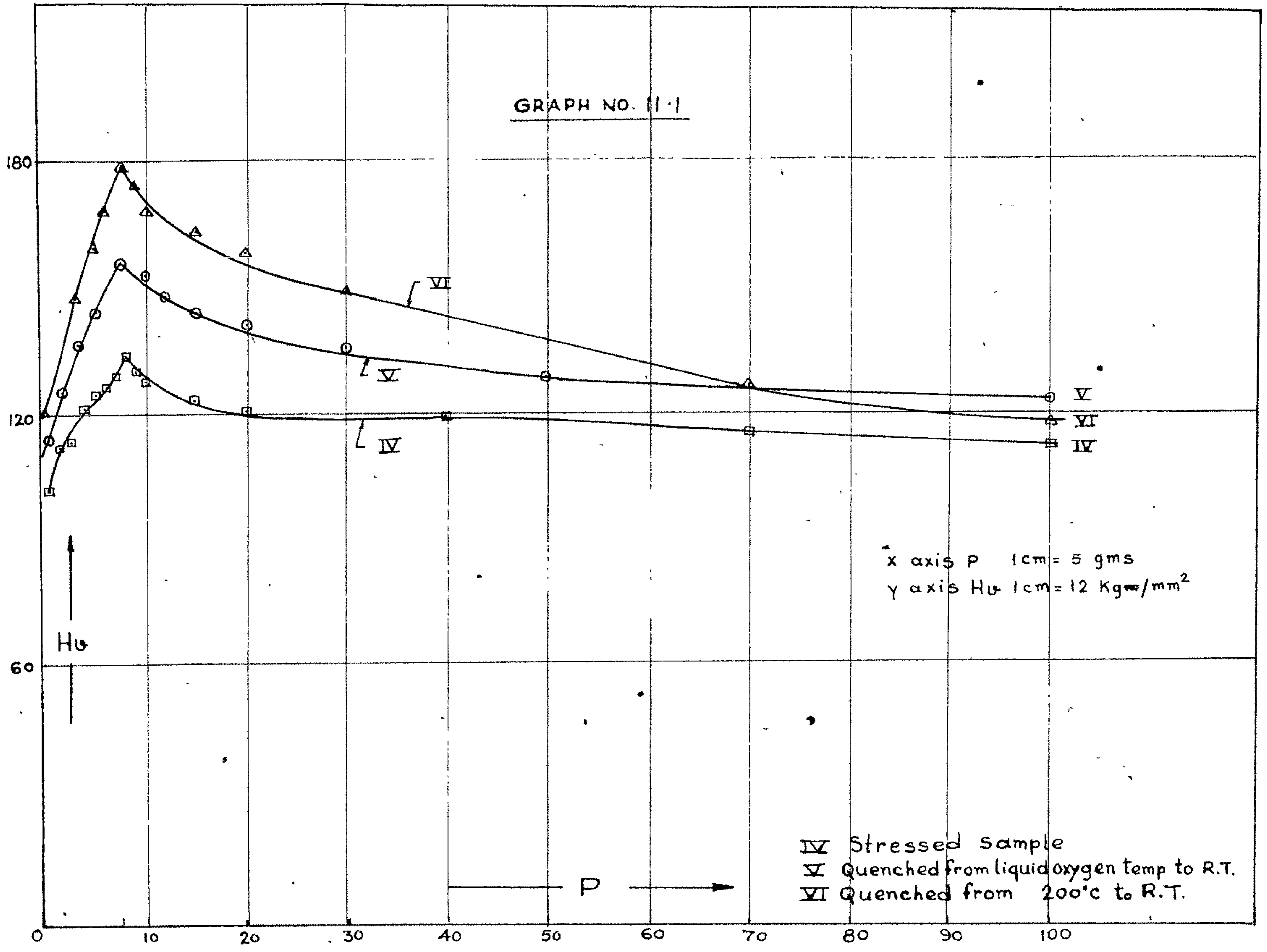
70
80
90
100
Hv
P
I
II
III
X axis P 1 cm = 5 gms
Y axis Hv 1 cm = 12 Kgm/mm²
I No treatment
II Annealed for 24 hrs at 500°c.
III Thermally etched.

GRAPH NO. II·I



180
120
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20
30
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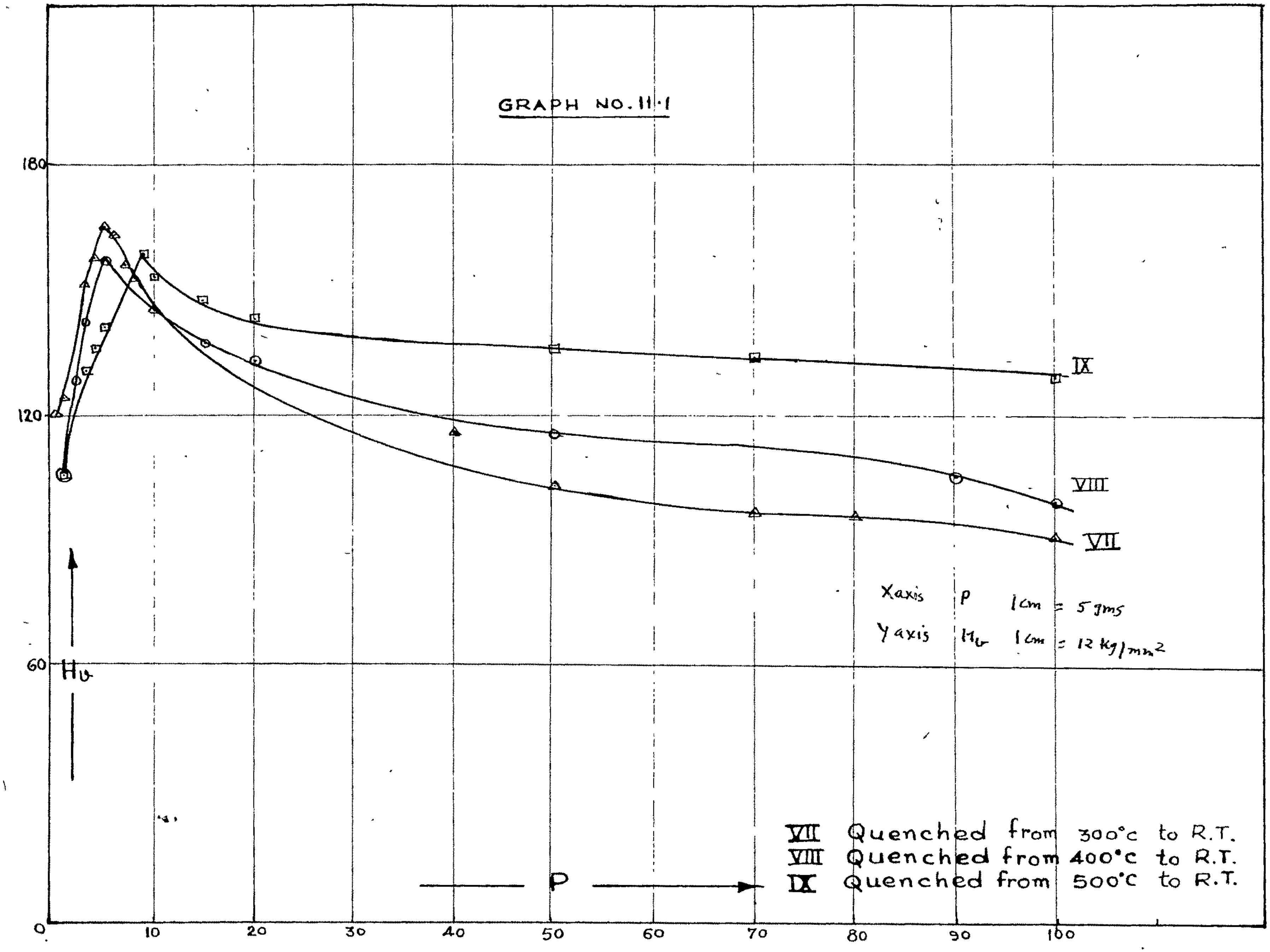
50
60
70
80
90
100
Hv
P
VI
V
IV
x axis P 1cm = 5 gms
Y axis Hv 1cm = 12 Kg/mm²
IV Stressed Sample
V Quenched from liquid oxygen temp to R.T.
VI Quenched from 200°c to R.T.

GRAPH NO. 11·1


180
120
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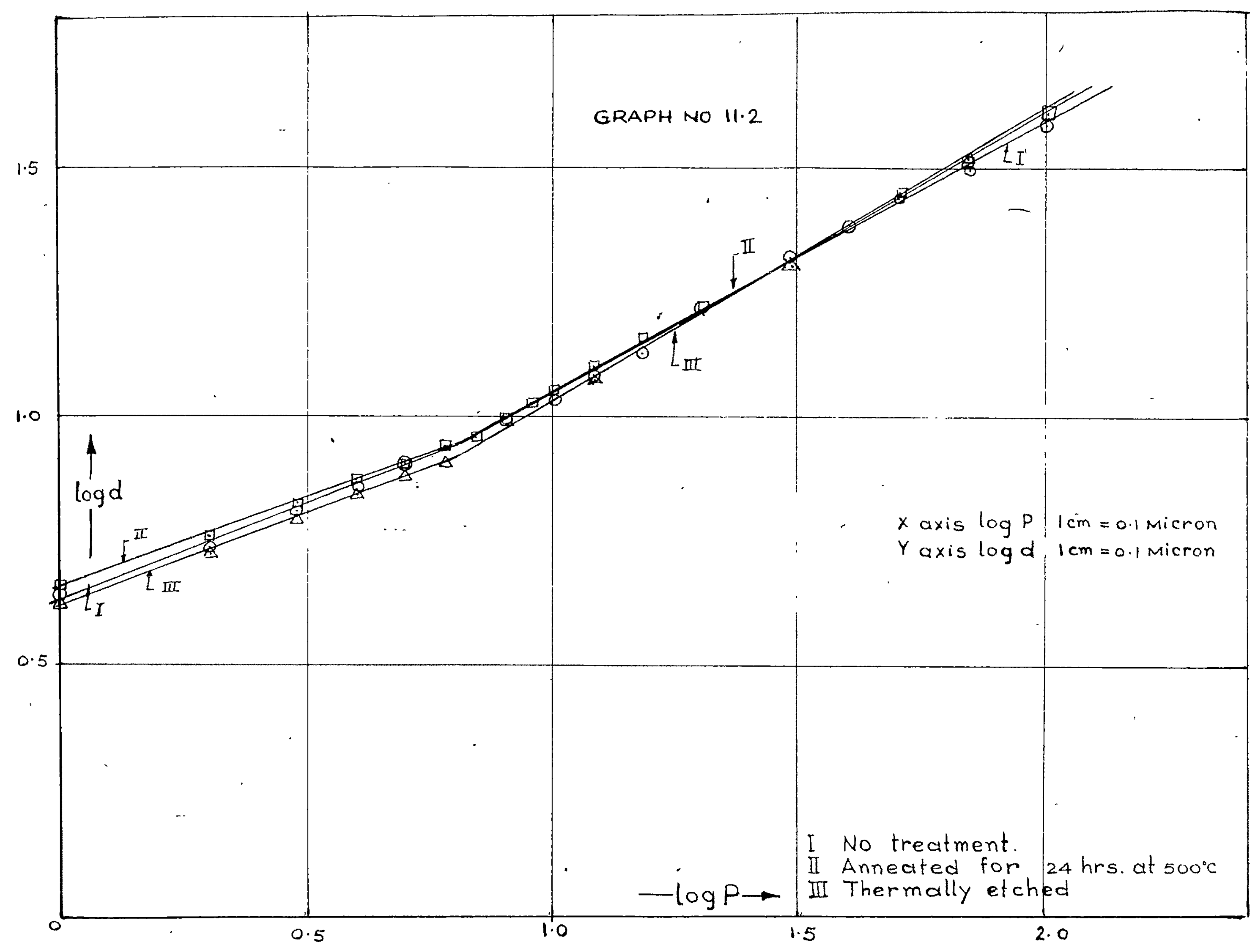
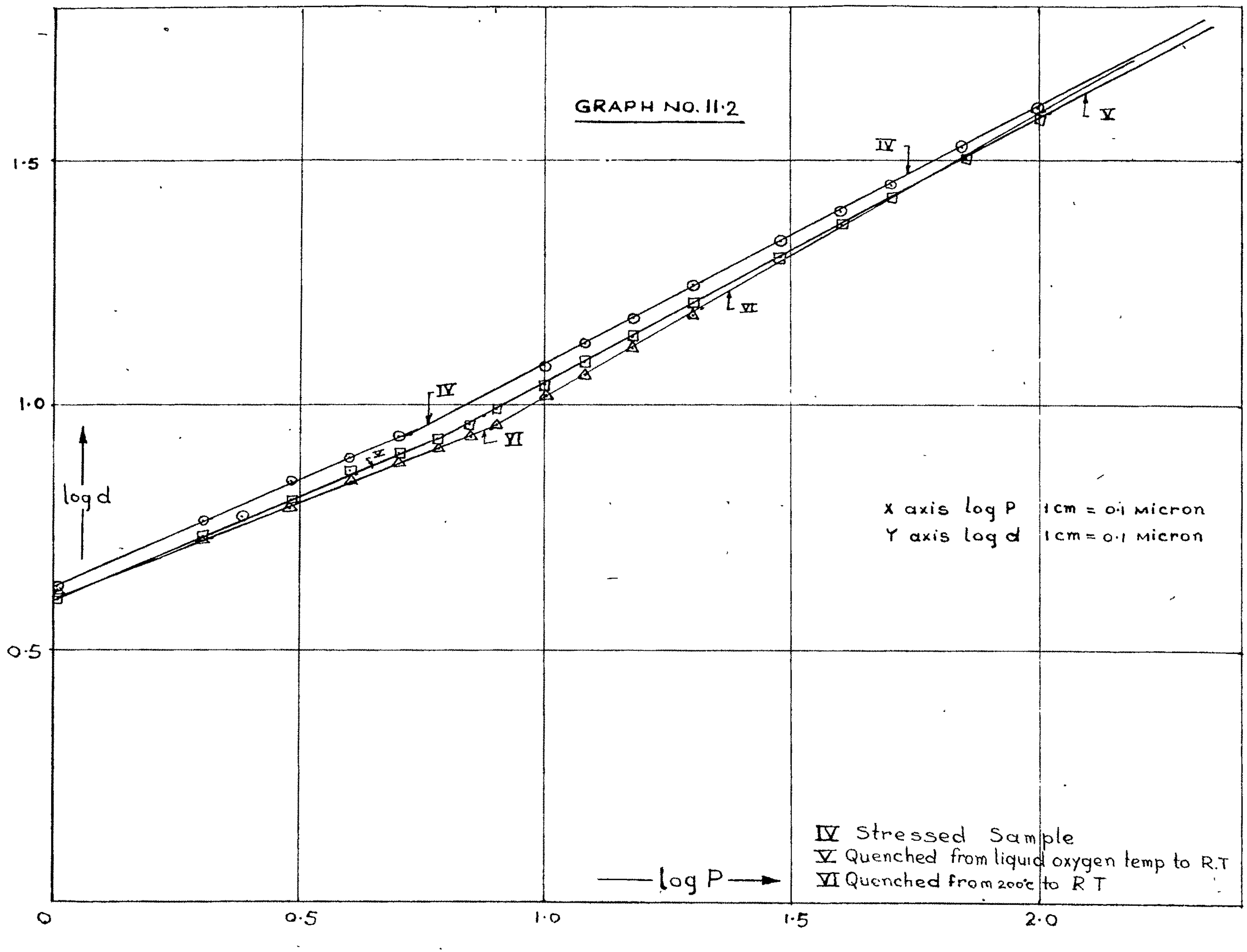
70
80
90
100
IX
VIII
VII
Hv
P
X axis P 1 cm = 5 gms
Y axis Hv 1 cm = 12 kg/mm²
VII Quenched from 300°c to R.T.
VIII Quenched from 400°c to R.T.
IX Quenched from 500°C to R.T.

suggesting a nearly constant hardness value for the higher values of loads. The above variation can be explained on the basis of the depth of penetration of the indenter. At small loads, the indenter pierces only the surface layers, hence the effect is shown more sharply at those loads. However, as the depth of the impression increases the effect of the surface layer of the crystal becomes less sharp and hence the variation of load with microhardness becomes less sharp. After a certain depth of penetration, the effect of inner layers becomes more and more prominent than those of surface layers and ultimately there is practically no change in the value of hardness with load.

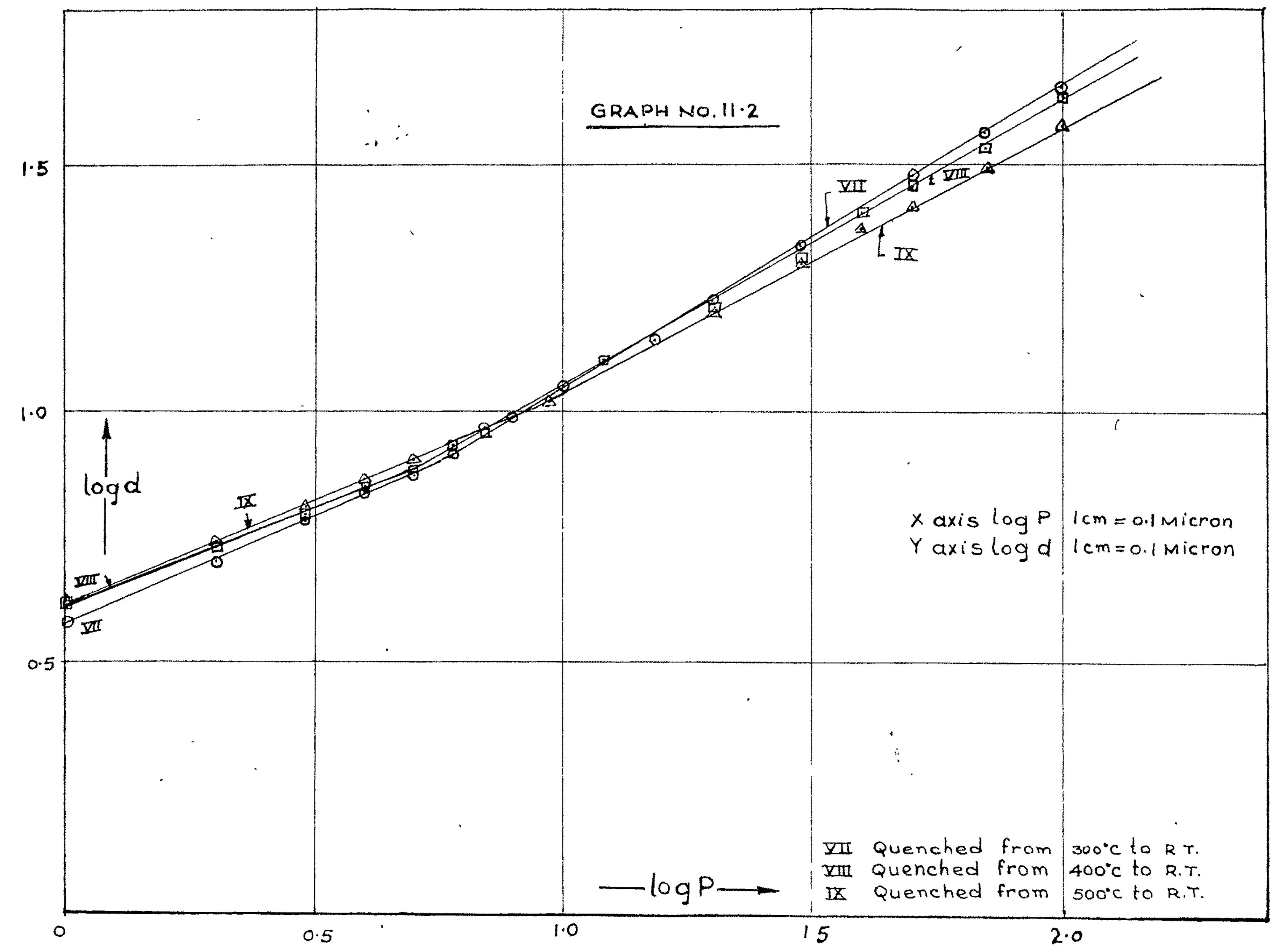
The equation (2) is Kick's law which states that the load p is related to the diagonal length and 'a' and 'n' are constants of a material; 'a' represents the "Standard Hardness" for an indenter of fixed diameter and 'n' giving the measure of the variation in hardness as a function of 'p' ~~and~~ or 'd'. The values of these constants are evaluated by plotting log. p against log. d. The graph obtained is a straight line and the slope of this line gives the value of 'n'. For all indenters that give geometrically similar shapes (impressions), Kick's law postulates a constant value $n = 2$ which implies a constant hardness value. However, in general 'n' is not equal to 2 which means that hardness is usually dependent on the applied load.



GRAPH NO 11·2
X axis log P 1cm = 0·1 Micron
Y axis log d 1cm = 0·1 Micron
I No treatment.
II Annealed for 24 hrs. at 500°C
III Thermally etched
log d
log P
I
II
III
0
0·5
1·0
1·5
2·0



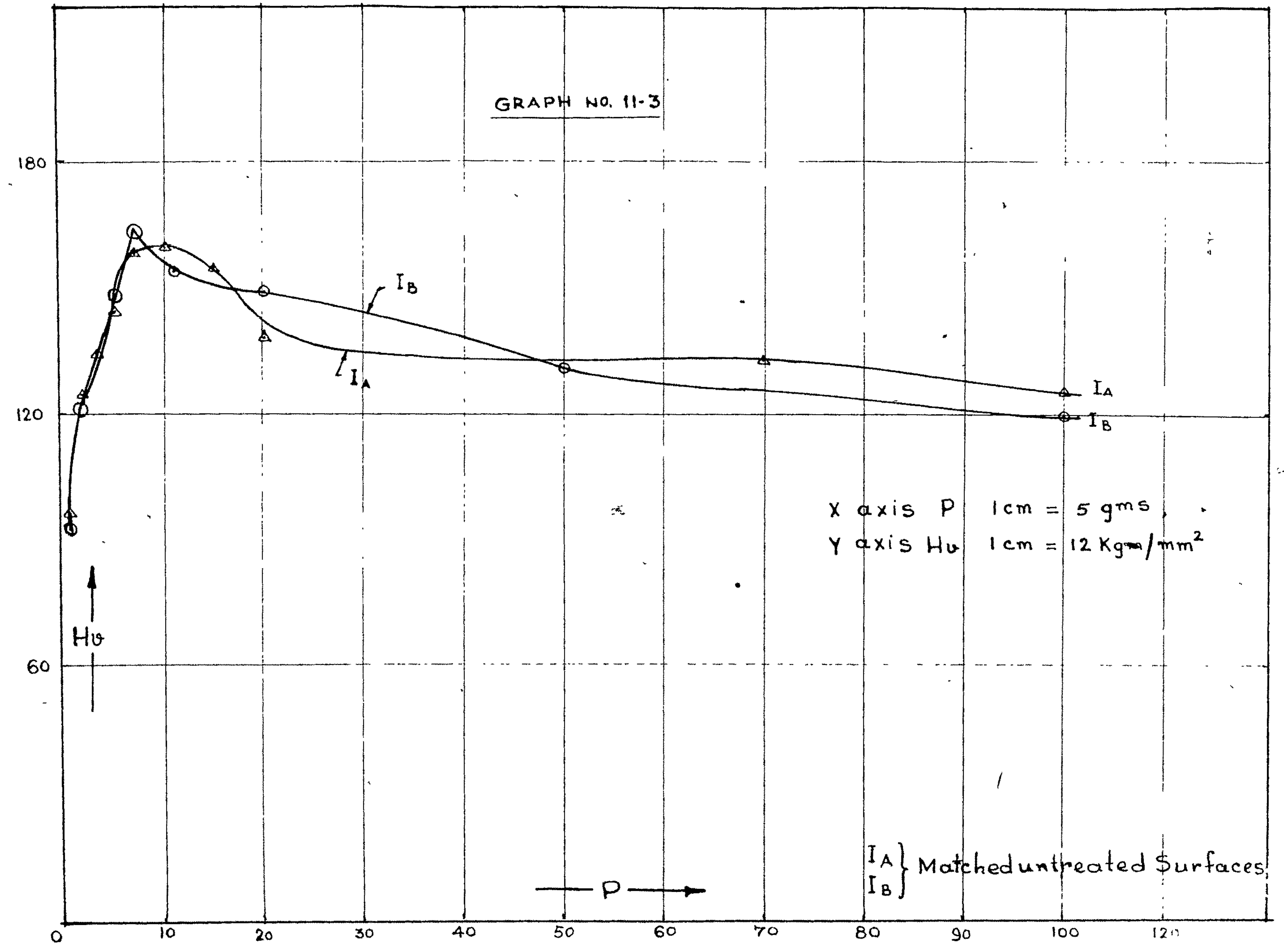
GRAPH NO. 11·2
IV
V
VI
log d
log P
X axis log P 1cm = 0·1 micron
Y axis log d 1cm = 0·1 micron
IV Stressed Sample
V Quenched from liquid oxygen temp to R.T
VI Quenched from 200°c to R T
0
0·5
1·0
1·5
2·0

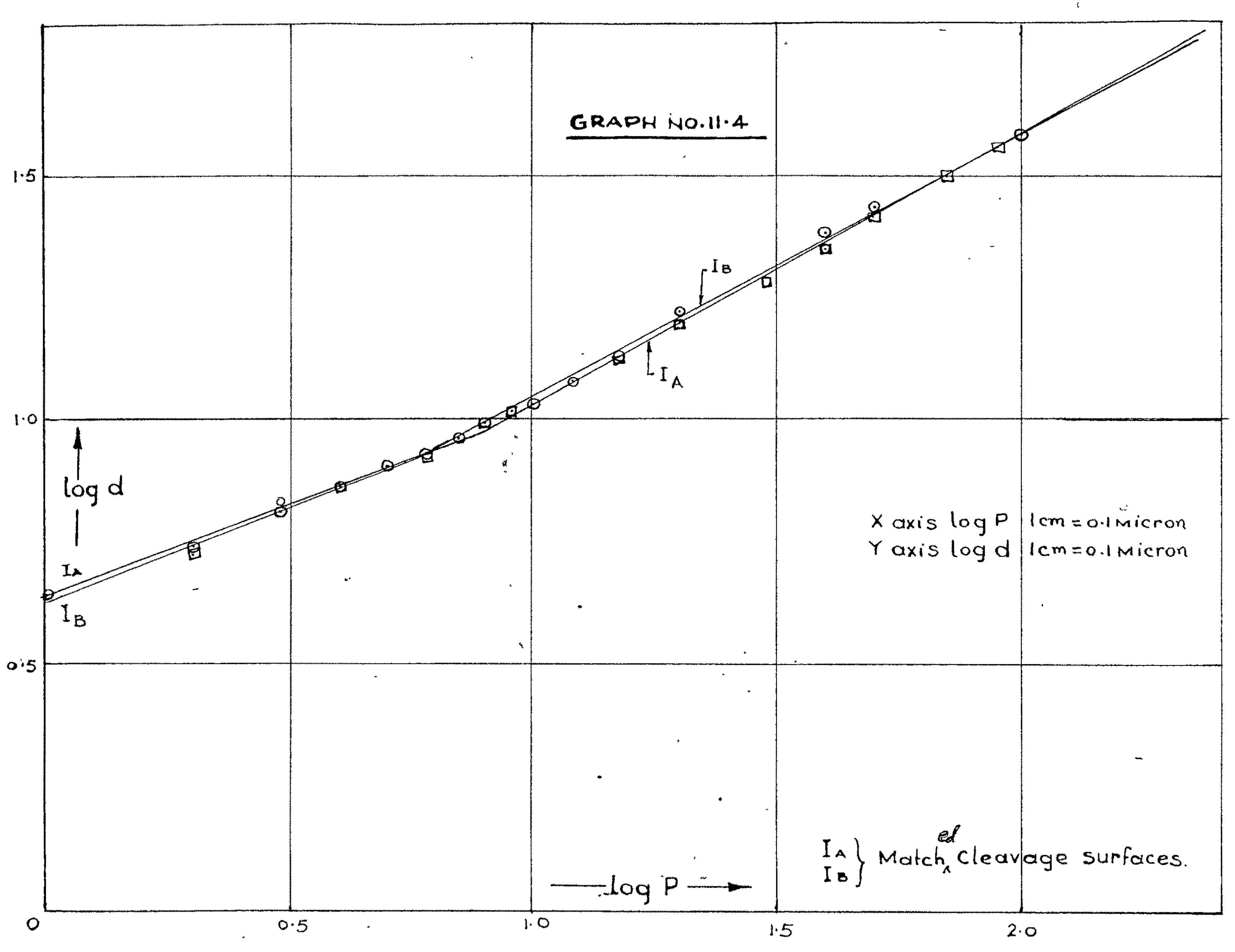


GRAPH No. 11·2
1·5
1·0
0·5
0
0·5
1·0
1·5
2·0
log d
log P
VII
VIII
IX
X axis log P 1cm = 0·1 Micron
Y axis log d 1cm = 0·1 Micron
VII Quenched from 300°c to R.T.
VIII Quenched from 400°c to R.T.
IX Quenched from 500°c to R.T.

A careful study of the graph (log P versus log d) (graph 11.2) shows that, there are two clearly recognizable straight lines of different slopes meeting at a kink which is obtained at a load of about 6 to 9 gms. Besides the straight line corresponding to observations taken at loads less than 6 gms gives a slope n_1 of higher values whereas for the second straight line (load more than 9 gms) slope is nearly equal to 2 or a little less than two. Since 'n' values are different in different regions being greater in the first region, the 'a' values also vary in the two regions being less in the first region and more in the second one (i.e. higher load region) of the graph. When both the regions of these graphs are considered the kink represents a transition point or a narrow transition region which lies in the range of 6 to 9 gms. It is only in the transition region that there is an observable effective change in the values of the constants 'a' and 'n'. The transition region in the graph of log p versus log d in many cases corresponds to the peak value H_v obtained in the graph of ~~the~~ H_v against P. The above observations (graph 11.1) also suggest the two values of slope, one is greater than two and other is less than two.

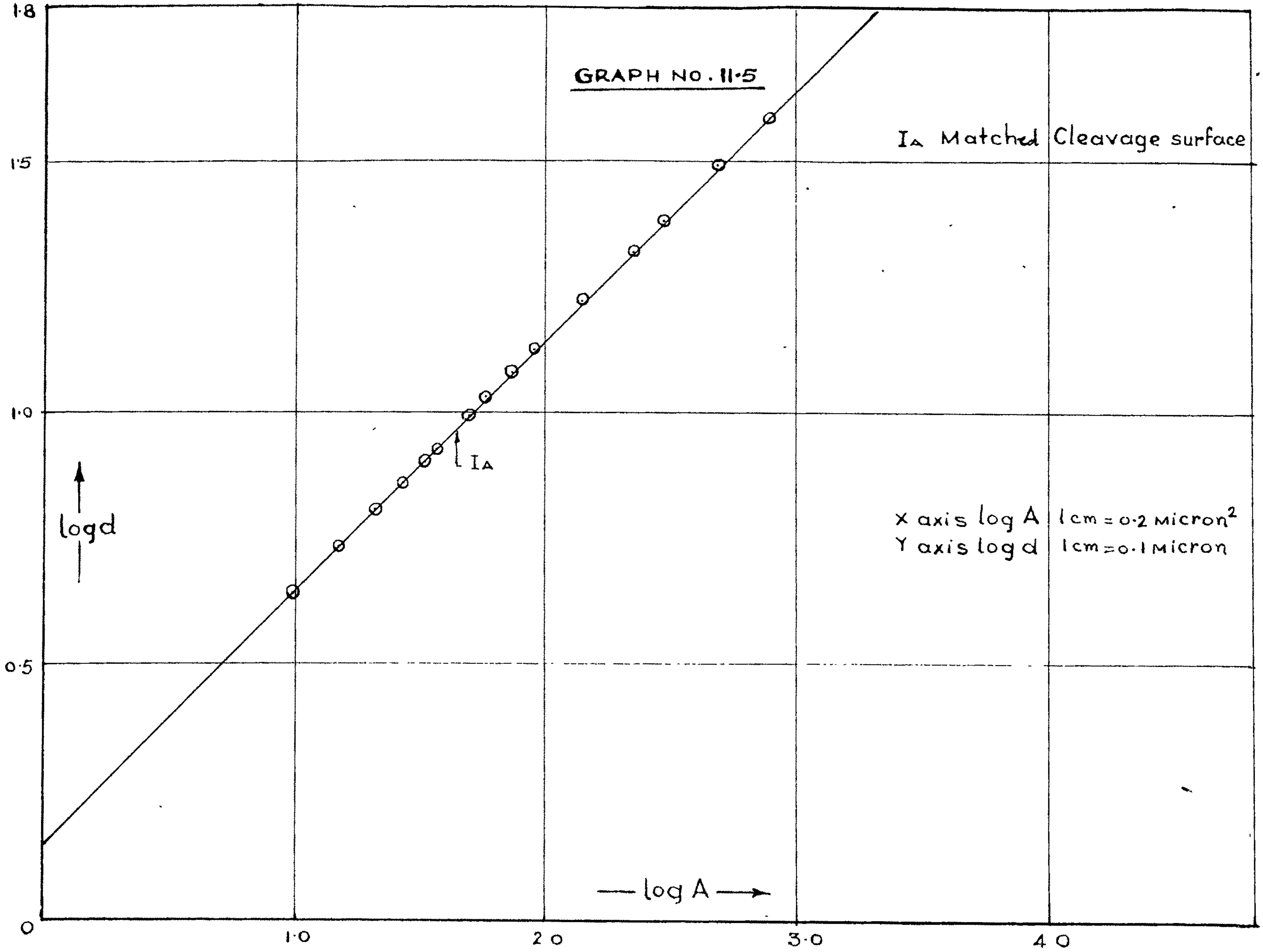
It is now well established that there is a perfect correspondence of cleavage microstructures on the oppositely matched cleavage faces. This property is also reflected in the study of microhardness of matched cleavages. The


GRAPH NO. 11-3
180
120
60
0
10
20
30
40
50
60
70
80
90
100
I_A
I_B
Hv
P
X axis P 1cm = 5 gms
Y axis Hv 1 cm = 12 Kgm/mm^2
I_A } Matched untreated Surfaces
I_B


GRAPH NO. 11·4
1·5
1·0
0·5
0
0·5
1·0
1·5
2·0
log d
log P
I_A
I_B
X axis log P 1cm = 0·1 Micron
Y axis log d 1cm = 0·1 Micron
I_A I_B Matched Cleavage surfaces.

graphs 11.3 and 11.4 represents the observations taken on the oppositely matched cleavage faces. There is almost a complete correspondence between graphs 11.1 and 11.3 (H_v versus P) and graphs 11.2 and 11.4 (log P versus log d). Sometimes this property was utilized for comparing the behaviour of matched counterparts which were given different treatments.

In order to verify whether the first region in the graphs is due to the deformation produced by the previous indentations or it is the characteristics of the load of indentation and its penetration, a series of experiments were undertaken on the oppositely matched faces of calcite cleavages. The indentations were made on different faces with different set of loads. Thus a face was indented with 10 - 100 gms. load while its corresponding region on the matched face was indented with 50 - 100 gms load. Similarly indentations were also made with 20 - 80 gms load while its corresponding region on the opposite face was indented with 70 - 100 gms load. In all these cases the graph between log p versus log d exhibited only one line having the value of slope, $n \sim 2$ and the first region in the graph corresponding to the higher value of slope 'n' was missing. These observations suggest that first region (upto 6 to 9 gms) is sensitive to surface


GRAPH NO. 11·5
IA Matched Cleavage surface
X axis log A 1cm = 0·2 micron²
Y axis log d 1cm = 0·1 micron
log d
log A
IA
1·8
1·5
1·0
0·5
0
1·0
2·0
3·0
4·0

layers whereas the second region which penetrates greater depths and gives hardness of the inner layers seems to be independent of applied load. This is in accordance with the graph of H_V versus p for the above observations. Thus it is not the effect of previous indentations made on the surface but it is only the particular loads, which in turn, means that the penatration depth at these loads is responsible for the variation of hardness with the load. For higher loads since the penetration is more, the increase in load does not effect the hardness values, whereas the indentations at low loads penetrate mostly the surface layers and hence represent the true microhardness values of the particular face under study.

The equation (3) expresses a relation between area of the indentation mark and the mean length of the diagonals. B is a constant whose value is unity when there is no recovery after indentation. The graph of log d versus log A (graph 11.5) gives a straight line with slope 2. Attention is drawn to the fact that the straight line is not passing through the origin. This shows the existence of a small amount ($\sim$ 3 microns^2) of recovery after the surface is indented.

In order to determine the factors affecting the values of 'n' and 'a', the study was carried out on crystal surfaces which were thermally or mechanically treated. The crystals were quenched from high temperature (up to 500°C just below decomposition temperature to room temperature), also crystals were quenched from room temperature to liquid oxygen temperature; some specimens were mechanically strained. In all these cases after the treatment was over, the crystals were cleaved in the usual way and freshly cleaved surfaces were used for indentation studies at room temperature. The typical observations are included in table 11.1 and for each set, graph of H_V versus p is plotted for all the above treated surfaces of the calcite cleavages. All these graphs showed that the microhardness varied with the load in a complicated manner, the variation being more prominent for small loads while for higher loads it becomes somewhat smooth. The nature of the graph is nearly same as that for the untreated cleavage surface of calcite; first hardness increases with load then decreases with load and afterwards the value of hardness is independent of load. The results on differently treated samples show a very small change in the peak values. The graphs of log d versus log p for these treated crystal surfaces are plotted (graph 11.2) . The mean value of 'n' and 'a'

TABLE No: 11.2

VALUES OF 'n' AND 'a' OBTAINED FROM THE Log.'P' VERSUS Log.'d' GRAPH FOR CALCITE CLEAVAGE FACES GIVEN DIFFERENT TREATMENTS.

Obs. No.	Treatment	n_1	a_1 $\times 10^{-3}$	n_2	a_2 $\times 10^{-2}$	$\frac{n_1}{n_2}$	$\frac{a_1}{a_2}$
I-A	Untreated	2.70	18.2	1.85	11.6	1.46	0.157
I-B	Counterparts	2.71	17.8	1.85	12.0	1.47	0.148
II	Annealed	2.77	16.0	1.81	10.2	1.53	0.157
III	Thermally etched	2.47	32.0	1.88	10.0	1.31	0.322
IV	Stressed	2.27	38.0	1.94	7.5	1.17	0.506
V	Liquid oxygen quenched.	2.50	29.00	1.83	12.6	1.36	0.230
VI	200°C quenched to room temp.	2.50	31.0	1.76	15.1	1.42	0.209
VII	300°C quenched to room temp.	2.40	41.0	1.66	18.9	1.44	0.217
VIII	400°C quenched to room temp.	2.38	34.0	1.81	11.9	1.31	0.293
IX	500°C quenched to room temp.	2.50	27.0	1.85	12.0	1.35	0.230

obtained from several sets of observations are given in table 11.2. The ratios $^{n_1}/_{n_2}$ and $^{a_1}/_{a_2}$ are also given in this table. It is obvious from table 11.2 that the values of n_1 and a_1 for treated and untreated crystal surfaces show some differences whereas for the second part of the graph there are less variations in the values of 'n_2' and 'a_2' of surfaces of crystals subjected to different treatments. This clearly indicates that n_1 and a_1 are dependent on the previous history of the specimen. Hence the two regions correspond with the structure sensitive and structure insensitive mechanical properties of crystals. Besides the initial indentations under low loads i.e. initial plastic deformation, produces cold working of the crystal. There will also be a certain amount of recovery from this deformation as shown by graph 11.5. As a result, the degree of hardening of crystal increases. Hence with increase in load for indentation beyond 10 gms. surface offers high resistance to indentation. The hardness in this region will therefore be lower than that in first region. The surface is therefore likely to follow Kick's law and the value of n_2 will be nearly two. It should be noted that in the case of mechanically strained samples n_1 is 2.1 i.e. has a different value as compared to the thermally quenched and untreated surfaces. It is apparent from the values of

$^{n_1}/_{n_2}$ and $^{a_1}/_{a_2}$ that quenching of crystals at increasingly higher temperatures lowers the ratio $^{n_1}/n_2$, but increases the value of $^{a_1}/_{a_2}$. However the variations donot appear to be systematic. This suggests that in addition to the cold working and recovery of deformed crystal surfaces, the other factors such as energy, nature and concentration of imperfections etc. are operating. It is therefore not desirable to conjecture the behaviour of surfaces from n_1 and a_1 values only. For the second part of the graph the values of n_2 are approaching two. This is more or less in accordance with kick's law. However, there are slight variations. The values of a_2 for differently treated surfaces donot differ significantly.

11.32 Orientation dependence of hardness:

The observations of the slip trace and microcracks along certain directions on a crystal surface indented by a diamond pyramidal indenter gives an idea about the anisotropic nature of the properties of crystals. Once a crystal surface is indented, the effects due to piling-up and sinking-in being crystallographic in nature are shown only along certain directions. Similarly the elastic recovery taking place in the impressions is more along the depth and the sides of the impression and negligible along the diagonals. Hence if there is any change in the orientation of the indentation mark with respect to a chosen crystallographic direction, some variations in the diagonals, as well as, sides of a given vickers impression are observed. These changes in the length of diagonals and sides and depths produce changes in the dimensions of the indentations which give rise to different values of hardness along different directions, thereby showing the anisotropic character of hardness. However, the crystallographic features like slip and twin bands etc. are not affected by the change in orientation of the indenter with respect to a given direction on a crystal face. The graphs plotted between H_V and the orientation of the indentation mark exhibit a number of hardness maxima and minima for complete rotation, which have some relation with the crystallographic symmetry of the plane indented, i.e. from the number of peaks obtained from the graph, number of symmetry element of the face may be found.

The orientation dependence of the microhardness was studied on freshly cleaved calcite faces keeping the diagonal of the indentation mark parallel to [110] as a standard reference direction. The indentations were made along different directions varying from 0° to 180° and in some cases from 0° to 360°. In addition to the change in the shape and sides of the indentation mark a change in the length of diagonals is also observed. The shapes of the

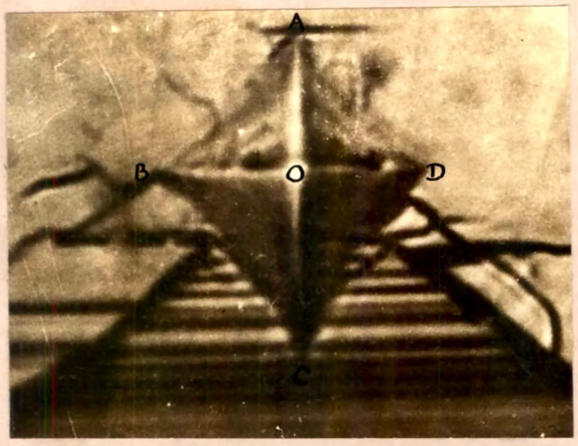


FIg. 11.1 (x170)

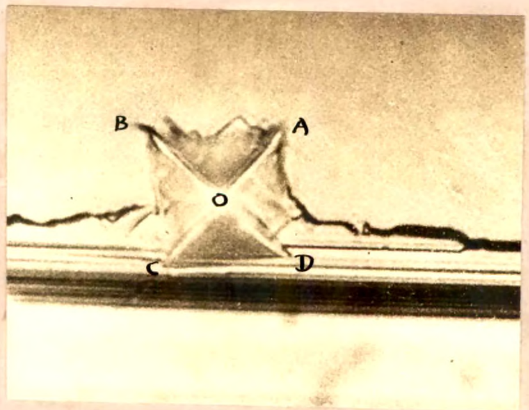


Fig. 11.2 (x170)

indentation marks are slightly different for various orientations.

The lines below the indent mark are parallel to $[1\bar{1}0]$ (fig. 11.1; x 170). If O is the point of maximum depth, OC is more than OA, whereas lines OB and OD are nearly equal. It is further observed that the sides BC and DC of the indenter are slightly concave. If diagonals of the indent mark is making 45° to the line $[1\bar{1}0]$ (fig. 11.2; x 170), i.e. indenter is rotated through 45° from the reference direction, the shape of the indent mark is changed. The lines AO and BO are equal where O is the projection of point of maximum depth on the observation plane. The lines CO and DO are also equal. The line AO is slightly more in magnitude than the line DO. It is clear that the lines $[1\bar{1}0]$ are generated more near CD of the indent mark. For all the above figures symmetry about the line parallel to $[1\bar{1}0]$ is preserved. It is noted that if the indent mark is etched with a dislocation etchant (see chapter 4), the rows of etch pits parallel to $[110]$ are produced. The length of the diagonals for 0° and 180° were found to be less than the diagonal lengths of the indent mark for 45° and 135° for same load. Since the hardness depends on the diagonal length, a change is observed in hardness at these orientations. The values of hardness were more for 0° and 180° and less for 45° and 135° indentations.

TABLE No: 11.3

VARIATION OF HARDNESS WITH RESPECT TO DIFFERENT ORIENTATION OF INDENT MARK ON CLEAVAGE FACES OF CALCITE.

Obs. No.	1 50 gms. load Orientation Degree	Dia. Micron	H_v Kgm/mm^2	2 20 gms. load Orientation Degree	Dia. Micron	H_v Kgm/mm^2	3 10 gms load Orientation Degree	Dia. Micron	H_v Kgm/mm^2
1	0	26.25	134.5	0	15.00	164.8	0	10.50	168.2
2	12	27.50	122.5	15	15.43	155.6	12	10.62	164.2
3	24	26.87	129.5	30	16.50	136.2	24	11.12	150.0
4	36	27.87	119.5	45	17.12	126.4	36	11.37	143.3
5	48	28.50	114.2	60	16.75	132.2	48	11.62	137.2
6	60	28.25	116.0	75	16.25	142.6	60	11.50	140.2
7	72	27.75	122.6	90	15.00	164.8	72	11.12	150.0
8	84	26.62	131.0	105	15.25	159.6	84	10.75	160.5
9	96	26.18	135.2	120	16.5	136.2	96	10.95	160.5
10	108	26.87	129.5	135	17.25	124.6	108	11.25	146.5
11	120	27.62	121.5	150	16.87	130.1	120	11.56	138.7
12	132	28.00	118.2	165	15.87	154.3	132	11.68	135.8
13	144	27.12	126.3	180	15.00	164.8	144	11.87	131.5
14	156	26.56	131.5				156	11.62	137.2
15	168	26.12	136.0				168	11.12	153.2
16	180	25.62	141.0				180	11.50	168.2

For various values of orientations of indenter ranging from 0^{o} to 360^{o}, the microhardness values were calculated from the diagonal measurements of the indentations on a cleavage face of calcite and summarized in table 11.3. The graph 11.6 plotted between the orientation θ and H_v for different loads showed five peaks in a complete rotation (or three peaks from the orientation ranging from 0^{o} to 180^{o}). Starting from 0^{o} for which diagonals of the indentation marks are parallel to the $[110]$ and $[1\bar{1}0]$. The graph shows decrease of 'H_v' from 0^{o} till it reaches a minimum at 45^{o} then it (hardness) increases and again shows a maximum at 90^{o}. It should be noted that the peaks at 0^{o}, 90^{o}, 180^{o}, 270^{o} and 360^{o} correspond to almost identical values of microhardness. In addition, for different orientation of the indentations, the individual diagonal lengths d_1 and d_2 were measured seperately. The nature of the graph between the ratio d_1/d_2 and orientations is too complicated nature to be related to the peaks of the graph of ~~the~~ H_v versus θ .

The range of hardness values with different orientations is 130-160 Kg/mm^2 at 10 gms. load, while it is 115-140 Kg/mm^2 for 50 gms. load. This is in accordance with the hardness variation with load which gave less value of hardness at higher loads.

11.4 Conclusions:

(1) Microhardness of calcite cleavages changes with load. In low load region (up to 10 gm) it increases then it decreases and attains constant value at about 40 gms load.

(2) There is very little effect of surface treatments on microhardness in high load region while surface treatments (such as straining) have significant effect on it in low load region.

(3) Microhardness is maximum if diagonals of indent mark are parallel to $\langle 110 \rangle$ (standard direction) and it is minimum when they are rotated through 45° from the standard direction.

(4) The value of microhardness is nearly same for oppositely matched cleavage faces of calcite.

(5) The characteristic lines parallel to $[1\bar{1}0]$ are observed near indent mark at $\geqslant 5$ gms. loads.