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MICROHARDNESS MEASUREMENT OF UNIRRADIATED AND IRRADIATED BERYLLIUM OXIDE

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ABSTRACT

The measured Knoop hardness of beryllium oxide was found to depend on both the indenter load and the orientation of grains within the matrix. Single crystal measurements showed that both prism and basal planes exhibit hardness anisotropy, with a two– and six–fold symmetry respectively; these results were as follows:

Plane indented	Indentation direction	Hardness (100 g) (kg/mm²)
(10.0)	[00.1]	750
	[$\bar{1}$2.0]	1100
(00.1)	[10.0]	1070
	[11.0]	1340

All irradiated specimens except those of lowest density showed irradiation hardening. It is shown that density predominates over such properties as grain size, fabrication methods, and source of supply, in controlling the initial hardness of the material, and the rate and extent of the irradiation hardening. No correlation was evident between the extent of irradiation hardening and observable microcracking.

CONTENTS

1. INTRODUCTION

Neutron irradiation of beryllium oxide produces an anisotropic expansion of the crystal lattice. The two mechanisms considered responsible for this expansion are the formation of interstitial atoms and vacancies by knock–on reactions, and fast neutron transmutation reactions, the net result being a disturbance of the lattice regularity. This is discussed more fully by Hickman (1962).

Microhardness depends on the regularity of the crystal lattice, and irradiated beryllium oxide should therefore exhibit ''irradiation hardening''. The rate and extent of such hardening may well provide a simple means of assessing the degree of irradiation damage, and of comparing the behaviour of various types of material under irradiation.

This report describes a pilot investigation of the irradiation hardening of beryllium oxide. The specimens tested were originally prepared for metallographic examination to assess the extent of microcracking, and thus do not form a complete series. Some preliminary work was also done to assess the possible dependence of measured hardness on the load applied to the Knoop indenter, and the orientation of the beryllia grains within the matrix of the specimen.

2. REVIEW OF LITERATURE

The literature contains relatively little information on the microhardness of unirradiated beryllium oxide, and reviews which assess the effect of neutron irradiation on beryllia (for example Hickman 1962; Shields et al. 1962) generally do not consider this property.

Cline and Kahn (1963) have measured the Knoop hardness (100 g load) of the prism and basal planes of an unirradiated single crystal of beryllium oxide, and they obtained the following results :

Plane Indented	Indentation Direction	Hardness (100 g) kg/mm^2	
(00.1)	[10.0] , [11.0]	1300	no orientation dependence
$(00.\bar{1})$	[10.0] , [11.0]	1100	
(10.0)	[00.1]	1175	orientation dependent
(10.0)	[10.0]	917	

They observed no dependence of hardness on either indenter load over the range 15 g to 200 g, or rate of indentation over the range one second to 10 minutes; however, the incidence of cracking was higher for the greater indentation rates. An interesting observation was that ''cracking was essentially eliminated when an organic solvent such as kerosene was applied to the crystal prior to indenting it''.

Using a double–cone diamond indenter on razor blade steel and plate glass, Grodzinski (1954) endeavoured to separate the effects of the elastic and plastic components of strain during microhardness testing. He found that the measured hardness, which is determined from the size of the impression, and therefore measures only plastic deformation, bore a hyperbolic relationship to the indenter load. However, when the elastic deformation was also taken into account (by thinly coating the test surface and observing the total deformation produced by the indenter), the microhardness decreased with decreasing indenter loads. Grodzinski concluded that the elastic component of strain became relatively more dominant with lower indenter loads, and that this effect caused the observed hyperbolic relationship.

3. EXPERIMENTAL PROCEDURE

3.1 Description of Specimens

Details of the types of material tested in this investigation are given in Table 1. Each material has been given a code letter and this is used to identify specimens throughout the report. The fabrica–

tion methods used to prepare the specimens have been described by Reeve and Ramm (1961a, 1961b). The irradiation conditions for the various specimens are shown in Table 4, and Hickman (1962) has described the irradiation techniques used.

Measurements were also made on two unirradiated single crystals of beryllium oxide. One crystal was columnar, with well-developed prism faces; the other was a portion of a platelet, having only one basal plane suitable for testing. The external morphology of both crystals enabled the identification of various test planes and directions without the aid of X-ray techniques.

3.2 Measurement of Microhardness

All specimens except the single crystals were mounted in transverse section in bakelite, and metallographically polished. Microhardness measurements were performed on a Leitz Durimet Microhardness Tester. In several instances, the indentation lengths were measured on a calibrated metallograph; this was necessary for the single crystals, since the Durimet instrument is not equipped with a goniometer.

It was found that surfaces prepared using diamond paste on rotary laps were more satisfactory for microhardness testing than those prepared on vibratory polishers. The former surfaces are less susceptible to relief effects, particularly in coarse-grained materials, and are consequently less subjected to impression distortion. The diamond polished surfaces also appeared to be more resistant to cracking around the indentations; this tends to support the observation of Cline and Kahn (1963) concerning the inhibition of cracking by organic solvents, since kerosene is used as a lubricant during diamond polishing.

4. RESULTS

4.1 The Relationship Between Indenter Load and Measured Hardness

A series of Knoop hardness measurements, using indenter loads ranging from 15 to 300 grams, was made on each of the following materials:

(a) The prismatic unirradiated single crystal of beryllium oxide; measurements were made both normal and parallel to the c-axis on the prism planes.

(b) A standard hardened steel test block ($HV_{100} = 927 \pm 30$).

(c) An irradiated hot-pressed beryllia specimen (No. 671, type A, 1.1×10^{20} nvt at 610 - 630°C).

(d) An unirradiated cold-pressed and sintered beryllia specimen (No. 1207, type E control).

The results of these measurements are listed in Table 2, and are shown graphically in Figures 1 and 2. Whilst the scatter in measurements for each indenter load is relatively large, and inherently increases as the load decreases, the results nevertheless clearly demonstrate that the measured (plastic) hardness increases with decreasing indenter loads. Grodzinski (1954) noted that such hyperbolic relationships conform to a power law when the load is plotted against the plastic deformation in a log-log diagram, as in Figure 3.

Since the measured hardness is inversely proportional to a power of the load, it becomes necessary to specify the indenter load used. Furthermore, the nature of the specimen imposes a limitation on the indenter load that can be used to give satisfactory results, but the use of differing loads prevents a direct comparison between such specimens.

The beryllium oxide specimens (particularly those which have been irradiated to higher doses) become increasingly susceptible to cracking as the indenter load increases. This effect is less noticeable with fine-grained specimens, and in such cases the larger loads are to be preferred, since the resulting impressions are larger and more accurately measured, and orientation dependence effects are thus more nearly eliminated. The larger impressions more readily produce cracking or chipping within the coarser-grained matrices and, since they occupy only a few grains, they are regularly distorted in shape. Thus for coarse-grained specimens, lower indenter loads are more satisfactory, preferably such as will allow the impression to be contained within a single grain.

It will be noted from Table 4 and Figure 7 that some type C specimens were tested at loads of both 50 and 300 grams, and that the former measurements are the lower, contrary to the relationship found above. These anomolous 50 g results probably stem from the use of a metallograph to measure the indentations, and the better resolution thereby attained.

4.2 The Relationship between Crystal Orientation and Measured Hardness

During the above tests on the prismatic single crystal, no cracking was observed at the indentation normal to the c-axis. For indentations made approximately parallel to the c-axis cracks were observed with the 200 g and 300 g loads, and an indenter load of 100 g was therefore used to investigate the effect of crystal orientation on hardness.

The results of these measurements are shown in Table 3 and in Figures 4 and 5. Hardness was found to be anisotropic in both orientations.

In the prism plane tests, plotted in Figure 4, the reference direction chosen was the c-axis, that is [00.1]. As the indentation direction changed through 90° from [00.1] to [$\bar{1}$2.0], the measured hardness increased non-linearly from about 750 to 1100. This order of variation of hardness with orientation was also observed by Cline and Kahn (1963); however, whereas they record [00.1] as the "harder" direction, the present investigation suggests that this is in fact the "softer" direction. It is here assumed that their direction "[10.0]" should be read "[$\bar{1}$2.0]" or "[11.0]".

In the basal plane tests, carried out on the second crystal, and plotted in Figure 5, the reference direction chosen was the normal to the prism plane, that is [10.0]. As the indentation direction changed through 30° from [10.0] to [11.0], the measured hardness increased linearly from about 1070 to 1340. Whilst Cline and Kahn reported no hardness anisotropy within the basal plane, they observed a variation of a similar order between "(00.1)" and "(00.$\bar{1}$)" - that is, presumably, between the "beryllium" and "oxygen" planes. Although the type of basal plane tested in the present work was not identified, it does not seem likely that its surface was inhomogeneous since intermediate hardness results were obtained at angles between 0° and 30°.

The hardness anisotropy of the prism plane has apparently a two-fold symmetry, and that of the basal plane a six-fold symmetry. The minimum range of hardness measurements arising from random grain orientation within unirradiated polycrystalline matrices could be expected to be at least 750 to 1340 for individual grains (with an indenter load of 100 g). In fine-grained material, where the indentation covers a number of grains, this range would be modified by such factors as microporosity and grain boundary reactions, as well as by grain orientation.

4.3 The Relationship Between Irradiation Dose and Measured Hardness

Results are given in Table 4 of the microhardness tests made on a number of irradiated and and unirradiated polycrystalline beryllium oxide specimens of both hot-pressed and cold-pressed and sintered material. Some of these results are also plotted in Figures 6, 7, and 8.

4.3.1 The unirradiated control specimens

In Figure 8, hardness is plotted against nominal theoretical density for the unirradiated control specimen of each type of material.

As could be expected, the hardness of the specimens generally increases with increasing density; furthermore, the following observations indicate that the density is the dominating property governing the hardness of the materials, to the practical exclusion of source of supply, method of fabrication, and grain size.

(a) The results from cold-pressed and sintered materials D and E suggest that the hardness is nearly constant over the range of 90-97 per cent. of theoretical density. The density of the similar material F also lies within this range, and this material is found to have a similar hardness, although the grain size is much coarser.

(b) Material C, also cold–pressed and sintered, with an intermediate grain size, is a few (critical) per cent, denser, and has a somewhat higher hardness. Its hardness is, however, similar to that of the hot–pressed material A, which is from a different source of supply, but has a similar grain size and density.

(c) The type B control specimen was tested at a different indenter load but, if due allowance be made from Figures 1 and 2, a conversion to about 1000 to 1200 results. With this allowance, the increase in hardness can be readily attributed to the increase in density, as in (b).

(d) The type G control specimen is similar to types D and E in most respects, but it has a much lower density, and a correspondingly lower hardness. It is obvious that the measured hardness of this particular specimen is markedly affected by its low density.

4.3.2 The neutron irradiated specimens

(a) Hot–pressed material

From the few type A specimens tested, it is apparent that doses of from 0.2×10^{20} to 1.2×10^{20} nvt result in an increase in hardness of the order of 10 – 20 per cent., and that the degree of hardening is greater for irradiation at the lower temperature.

The results obtained from the three type B specimens show a simple linear relationship (Figure 6). Although the individual grains in specimen 1134 (irradiated to 3×10^{20} nvt) had withstood hardening to the extent of some 125 per cent., there was very little integrity remaining in the matrix, and most grain boundaries were cracked. No high–temperature irradiated specimens of material B were available for microhardness testing.

(b) Cold–pressed and sintered material

Owing to the restricted range of specimens available for testing, the relationship between the hardness and irradiation dose was not clearly defined by the results obtained.

In all cases except material E, the hardness increase appears to saturate at doses around $3–5 \times 10^{20}$ nvt and there may be a reversal above this value. However, the reversals shown in Figure 7 are not significant in terms of the accuracy of measurements.

5. CONCLUSIONS

The measured Knoop hardness of beryllium oxide depends on the indenter load; this is contrary to the results of Cline and Kahn (1963), but in agreement with results obtained by Grodzinski (1954), who suggested that the observed hyperbolic relationship stems from the increasing elastic component of the deformation at lower loads. This dependence of hardness on load complicates the comparison of results obtained during testing, since the properties of the various types of matrices dictate the most suitable loads. The larger indentations are the most suitable from the point of view of accuracy of measurement; but whilst these are satisfactory for fine–grained materials, coarser specimens require the use of lower loads to prevent or minimise cracking and distortion of the indentation.

Knoop hardness also depends on crystal orientation; both of the simple lattice planes exhibit hardness anisotropy, with two–fold symmetry on the prism planes, and six–fold symmetry on the basal plane. These results also are at variance with results obtained by Cline and Kahn, who observed no basal plane anisotropy, and the reverse anisotropic effect to that here described for the prism plane.

In polycrystalline beryllium oxide, the density predominates over such properties as the grain size, method of fabrication, and source of supply, in controlling the hardness of the material. The density also seems to control both the rate and extent of the hardening induced in the beryllia by neutron irradiation.

The rate of irradiation hardening is higher for the denser materials. It appears also that for the denser specimens the rate tends to be constant, at least for lower doses, and that there is a linear relationship between hardness and dose; this is observed for material B (Figure 6), and could well occur for the other materials below a dose of 3×10^{20} nvt.

The extent of irradiation–induced hardening is also governed by the density of the material. The densest material (type B) shows hardening to the extent of 125 per cent. at 3×10^{20} nvt, whereas the less dense materials (except type E) have, at between 3 and 7×10^{20} nvt, obtained maximum hardnesses which represent increases of less than 75 per cent., and which are progressively lower for the less dense materials. Evidently it is the grain boundaries which are the main factor determining the hardness in these low density materials, rather than the grains themselves.

Microcracking was not observed in specimen types D, E, and G, although it had occurred in types B, C, and F at doses of less than 1, 5, and 5 x 10^{20} nvt respectively. No correlation was therefore evident between the irradiation hardening relationship and the onset of metallographically observable microcracking.

6. REFERENCES

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TABLE 1

MATERIALS USED IN THE INVESTIGATION

Code	Starting Material	Fabrication Method	Density (% T.D.)	Nominal Grain Size (Microns)
A	Pechiney	) hot pressing	96–98	10–20
B	Berylco No. 1	)	>99.5	25–30
C	) Brush UOX	) cold pressing	97–98	7½–15
D	) (pre–ground)	) and	90–93	<2
E	)	) sintering	94–97	<3
F	) Brush UOX	)	95–96	20–30
G	)	)	72–75	<1

The reference code in column 1 is used throughout the text for referring to the various materials.

TABLE 2

RELATIONSHIP BETWEEN INDENTER LOAD AND MEASURED HARDNESS

Specimen	Results	Indenter load (g)					
		15	25	50	100	200	300
No. 1207, Type E, Unirradiated	Knoop Hardness	1481	1481	1235	935	907	884
		1365	1231	1093	1039	907	910
		1613	1231	1138	935	976	937
		1936	1098	1138	1011	924	896
		1262	1481	1013	985	924	923
	Mean	1531	1304	1123	981	928	910
	Range	1262–1936	1098–1481	1013–1235	935–1039	907–976	884–937
No. 671 Type A 1.1×10^{20} nvt at 610–630°C	Knoop Hardness	1613	1691	1288	1231	1185	1042
		1765	1581	1539	1231	1013	1111
		1481	1581	1470	1307	1116	1093
		2135	1481	1539	1231	1138	1042
		1936	1815	1405	1098	1052	995
	Mean	1786	1630	1448	1220	1101	1057
	Range	1481–2135	1481–1815	1288–1539	1098–1307	1013–1185	995–1111
Hardened Steel Test–Block	Knoop Hardness	1089	1098	1093	1011	891	884
		1262	1161	1093	985	924	871
		1171	1161	1053	1011	907	859
	Mean	1174	1140	1080	1002	907	871
	Range	1089–1262	1098–1161	1053–1093	985–1011	891–924	859–884
Single Crystal, Prism Plane Normal to c–axis	Knoop Hardness	1481	Not taken	1288	1098	1052	1042
		1365		1185	1074	1046	1026
	Mean	1423		1236	1086	1049	1034
Single Crystal, Prism Plane Parallel to c–axis	Knoop Hardness	1015	Not taken	908	870	804	812
		1015		969	846	790	740
	Mean	1015		940	858	797	776

Additional readings on the hardened steel test–block:

(i) 500 g load : 850, 850, 832.

(ii) 1000 g load : 805, 817, 817.

TABLE 3

RELATIONSHIP BETWEEN CRYSTAL ORIENTATION

AND MEASURED HARDNESS

Plane Indented	Indentation Direction	Hardness (100 g) (kg/mm^2)
(10.0)	[00.1]	750
	[$\bar{1}$2.0]	1100
(00.1)	[10.0]	1070
	[11.0]	1340

TABLE 4

RESULTS OF HARDNESS MEASUREMENTS

Specimen		Irradiation		Indenter Load	Knoop Hardness			
No.	Type	Dose (x 10^{20} nvt)	Temp. (°C)	(g)	No. of Readings	Range	Mean	r.m.s.
704	A	Control	–	300	6	923–1111	1029	±72
668	A	1.2	500–520	300	6	1093–1268	1228	68
671	A	1.1	610–630	300	6	1042–1206	1107	61
672	A	1.1	610–630	300	6	995–1206	1120	78
674	A	1.1	650–670	300	6	1147–1291	1224	57
682	A	0.2	75–100	300	6	1147–1291	1238	50
684	A	0.2	75–100	300	6	1058–1386	1240	115
745	A	1.2	75–125	300	6	1186–1291	1262	41
1148	A	Control	–	300	6	910–1058	977	54
1139(a)	B	Control	–	50	11	1055–1405	1245	127
1228	B	1	50–100	50	11	1540–1970	1723	122
1134	B	3	50–100	50	11	2460–3380	2782	287
1169	C*	Control	–	50	11	785–927	876	43
1156	C*	3	50–100	50	11	1225–1583	1378	135
1155	C*	5	50–100	50	11	1235–1629	1413	137
1169	C	Control	–	300	11	923–1026	982	36
1156	C	3	50–100	300	11	1437–1609	1513	63
1187	D	Control	–	300	11	826–903	861	30
1175	D	3	50–100	300	11	835–1007	914	50
1173	D	5	50–100	300	11	769–995	863	64
1181	D	15	~100	300	2	590–605	598	~11
1207	E	Control	–	300	11	815–899	856	30
1195	E	3	50–100	300	11	1218–1286	1257	26
1193	E	5	50–100	300	11	1391–1480	1433	33
926	F*	5	580–600	50	11	1093–1369	1211	76
931	F*	7	650–690	50	11	1102–1321	1181	59
925	F	Control	–	300	6	779–937	857	62
946	G	Control	–	300	6	296–317	306	7
947	G	5	580–600	300	6	200–261	241	26
942	G	6	510–540	300	6	236–329	283	34

* Indentations measured on metallograph.

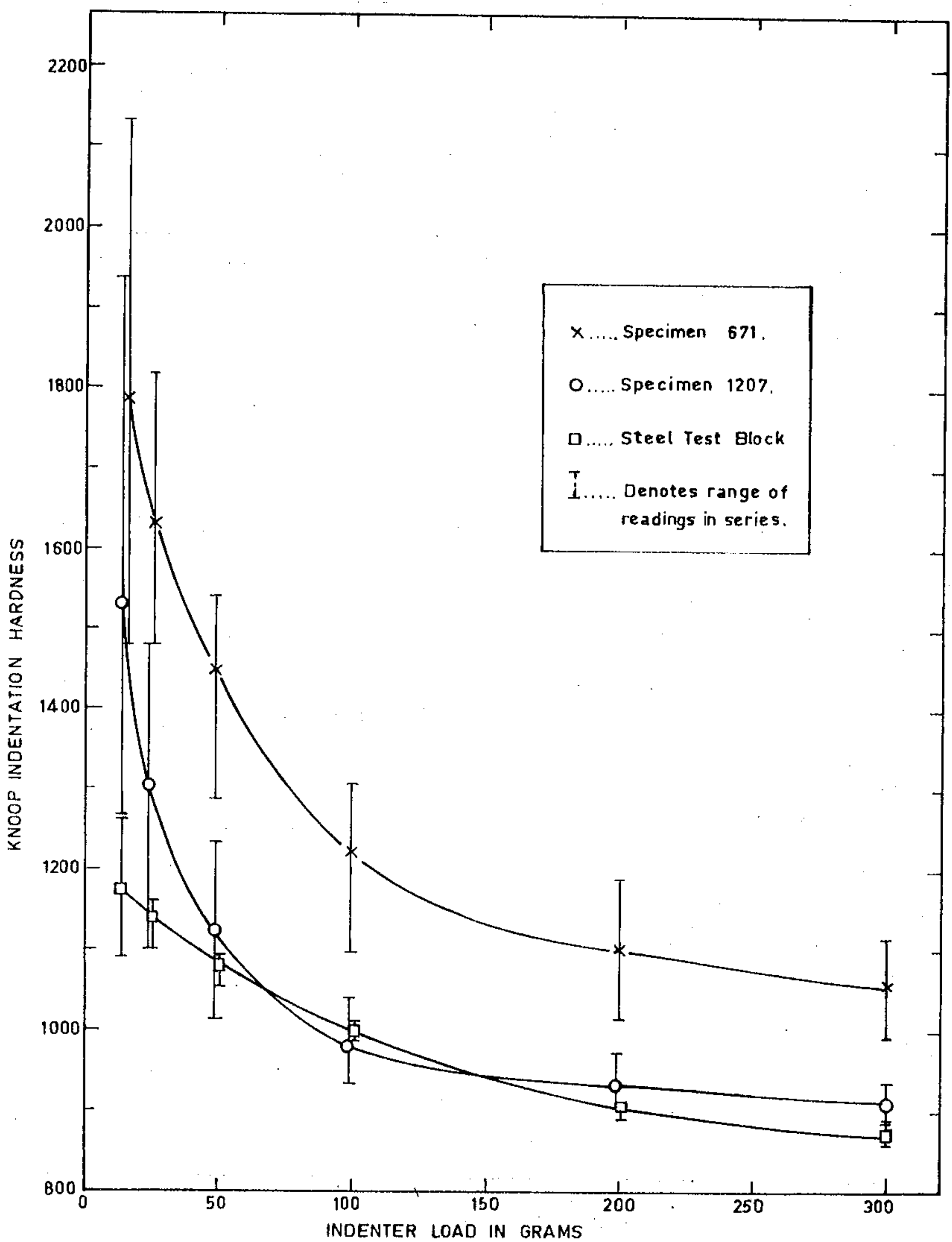

FIGURE 1 VARIATION OF KNOOP HARDNESS WITH INDENTER LOAD

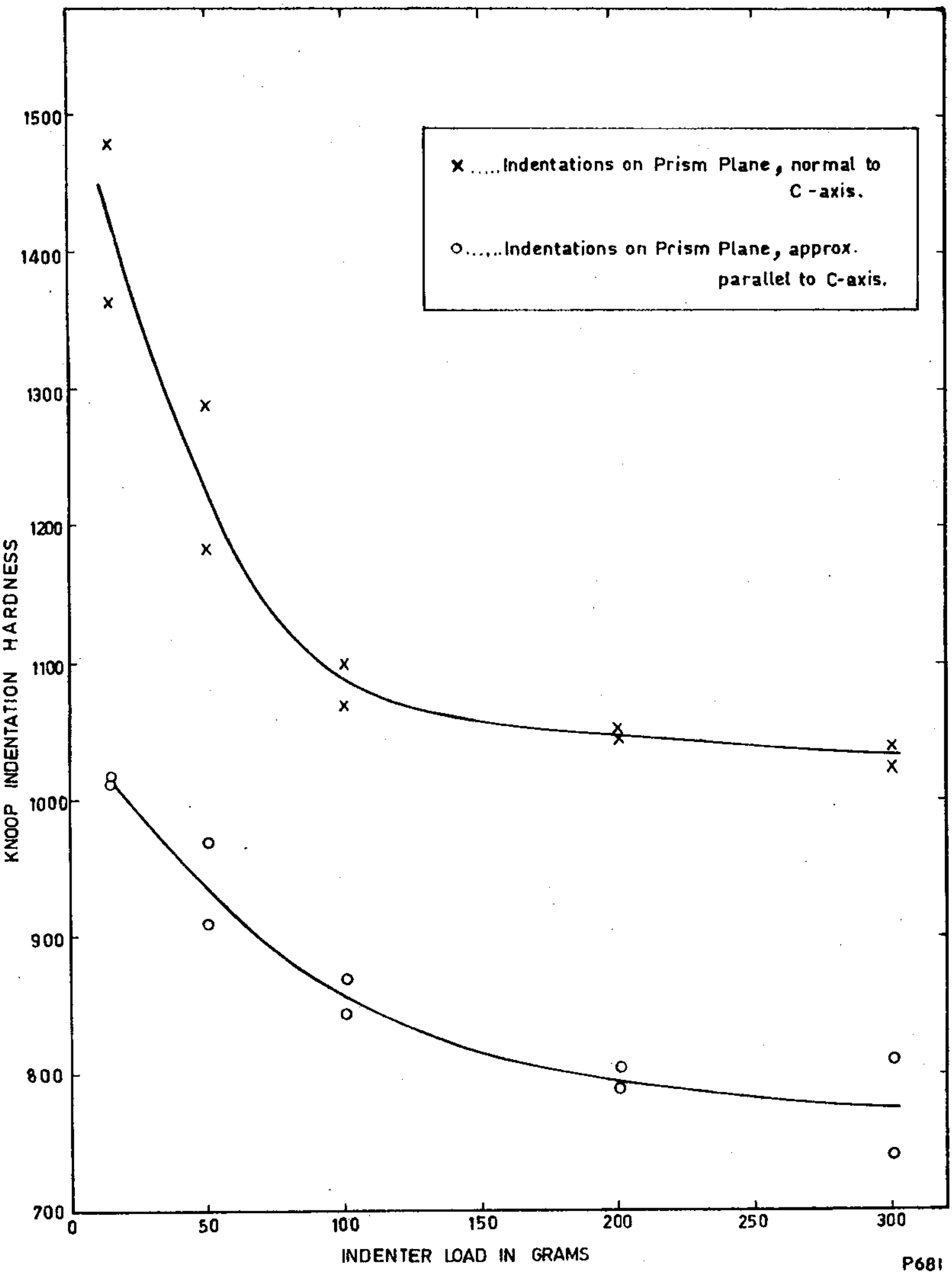

FIGURE 2 KNOOP HARDNESS VERSUS INDENTER LOAD FOR TWO DIRECTIONS IN A SINGLE CRYSTAL TEST-PIECE

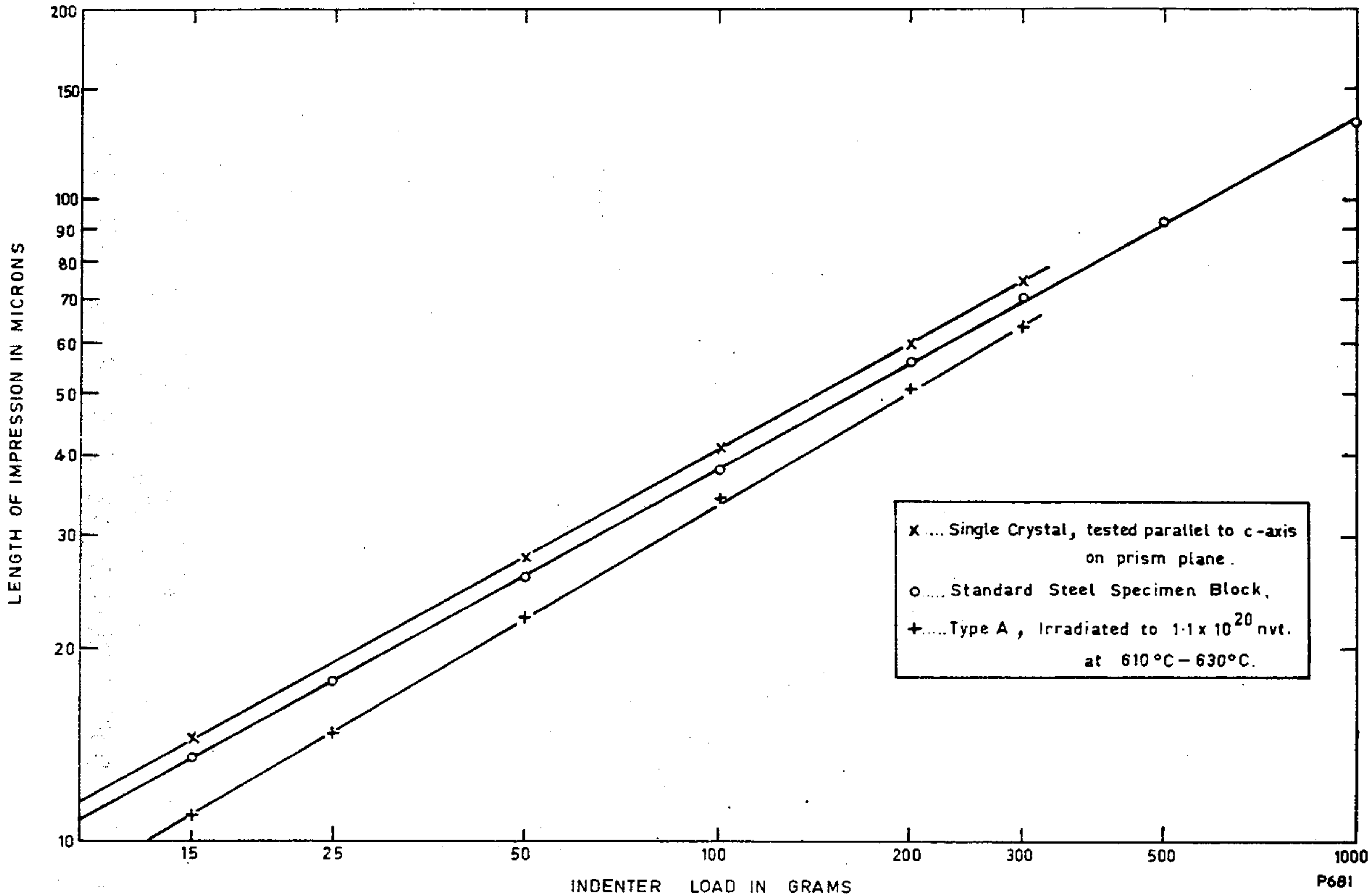

FIGURE 3 LOG-LOG PLOT OF LOAD VERSUS PLASTIC DEFORMATION

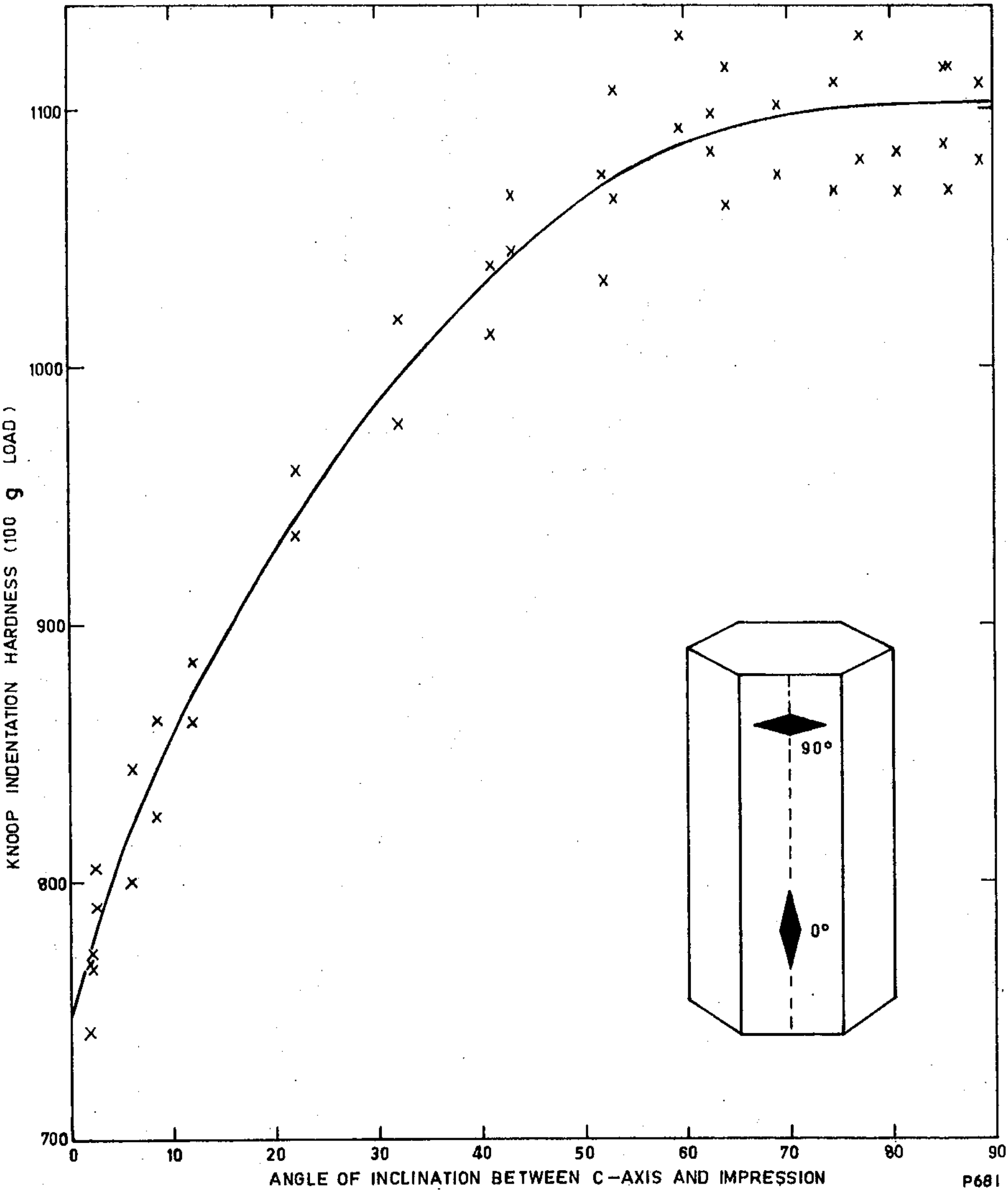

FIGURE 4 KNOOP HARDNESS VERSUS PRISM PLANE ORIENTATION

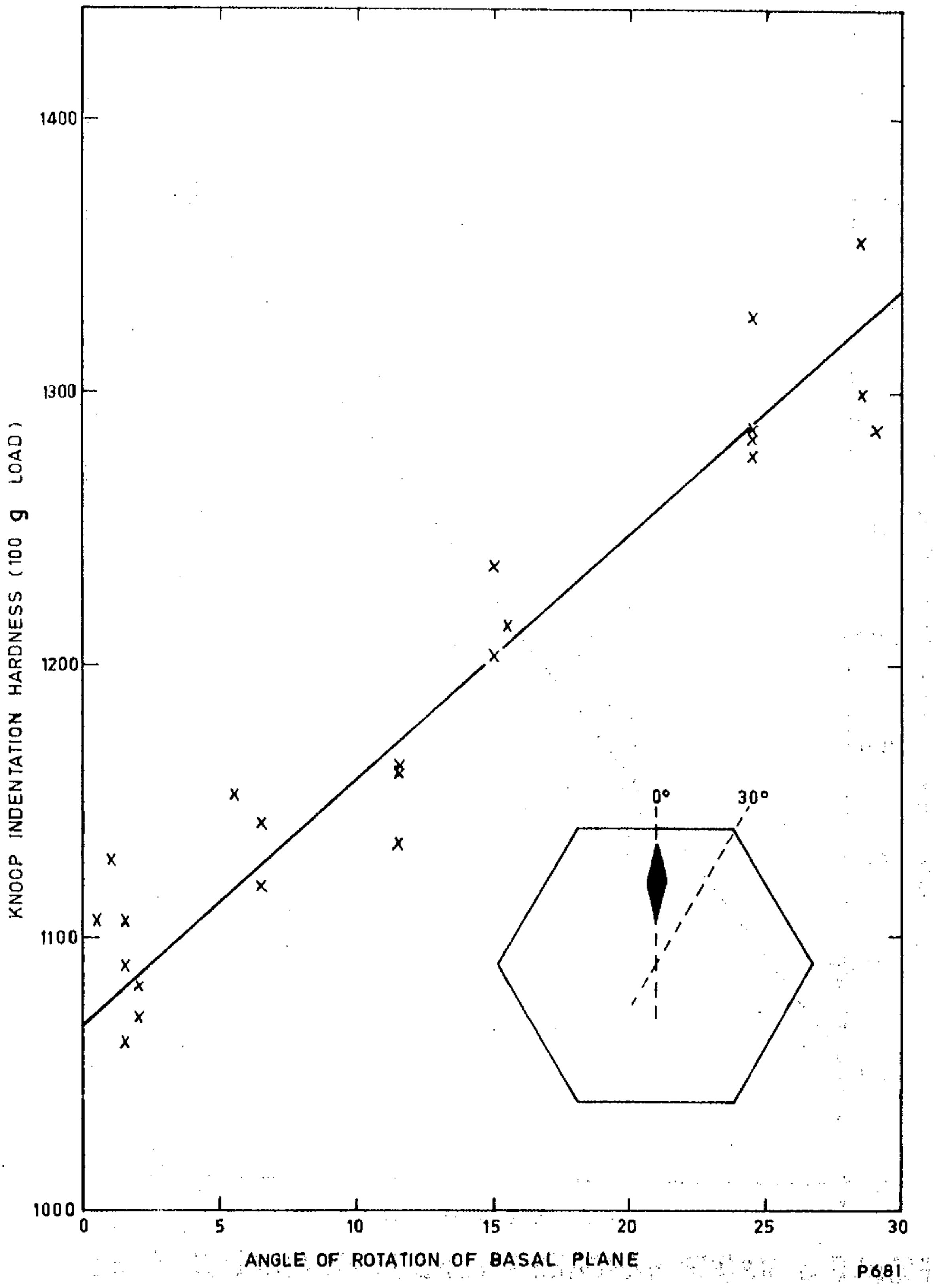

FIGURE 5 KNOOP HARDNESS VERSUS BASAL PLANE ORIENTATION

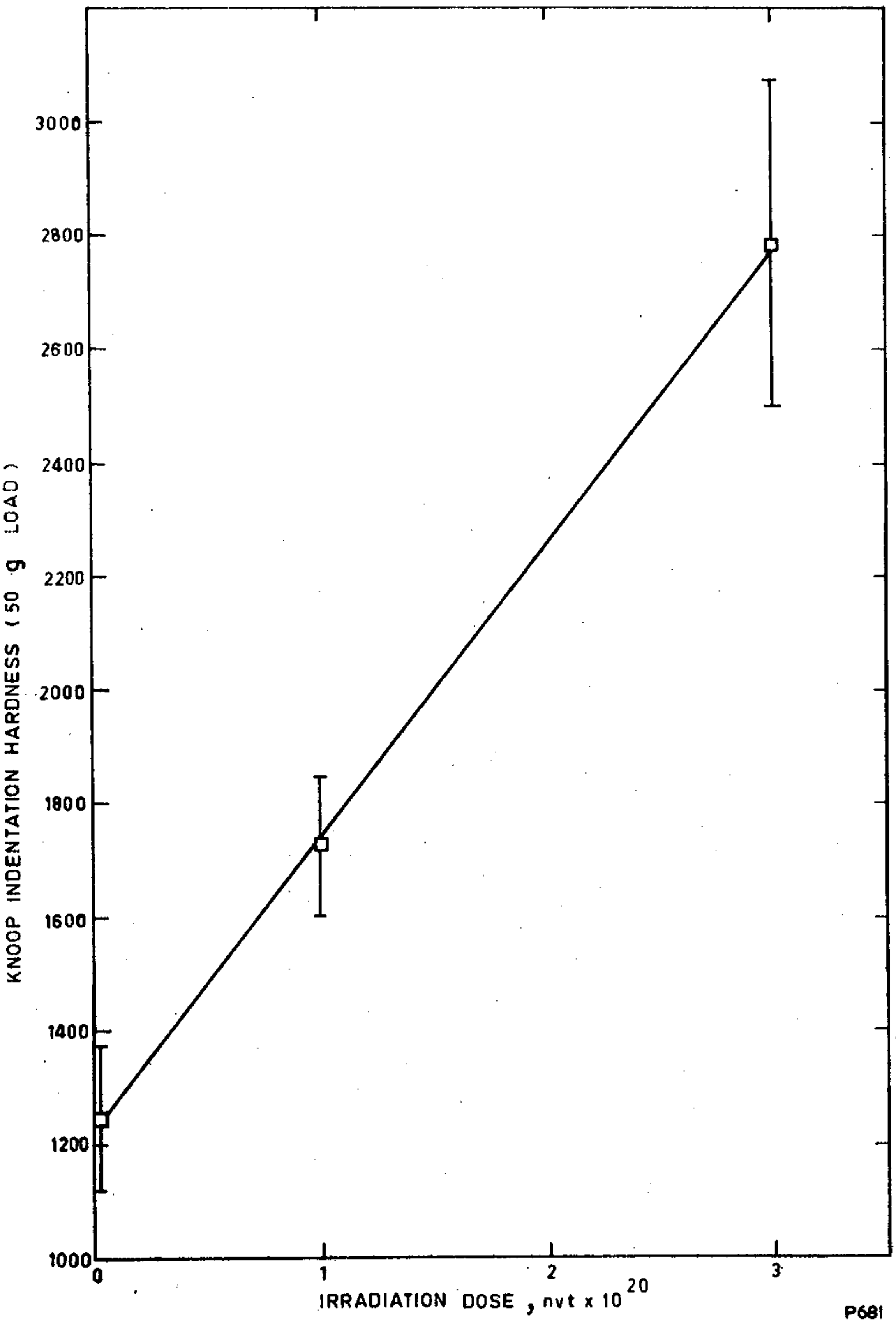

FIGURE 6 KNOOP HARDNESS VERSUS IRRADIATION DOSE FOR LOW TEMPERATURE IRRADIATION OF MATERIAL B

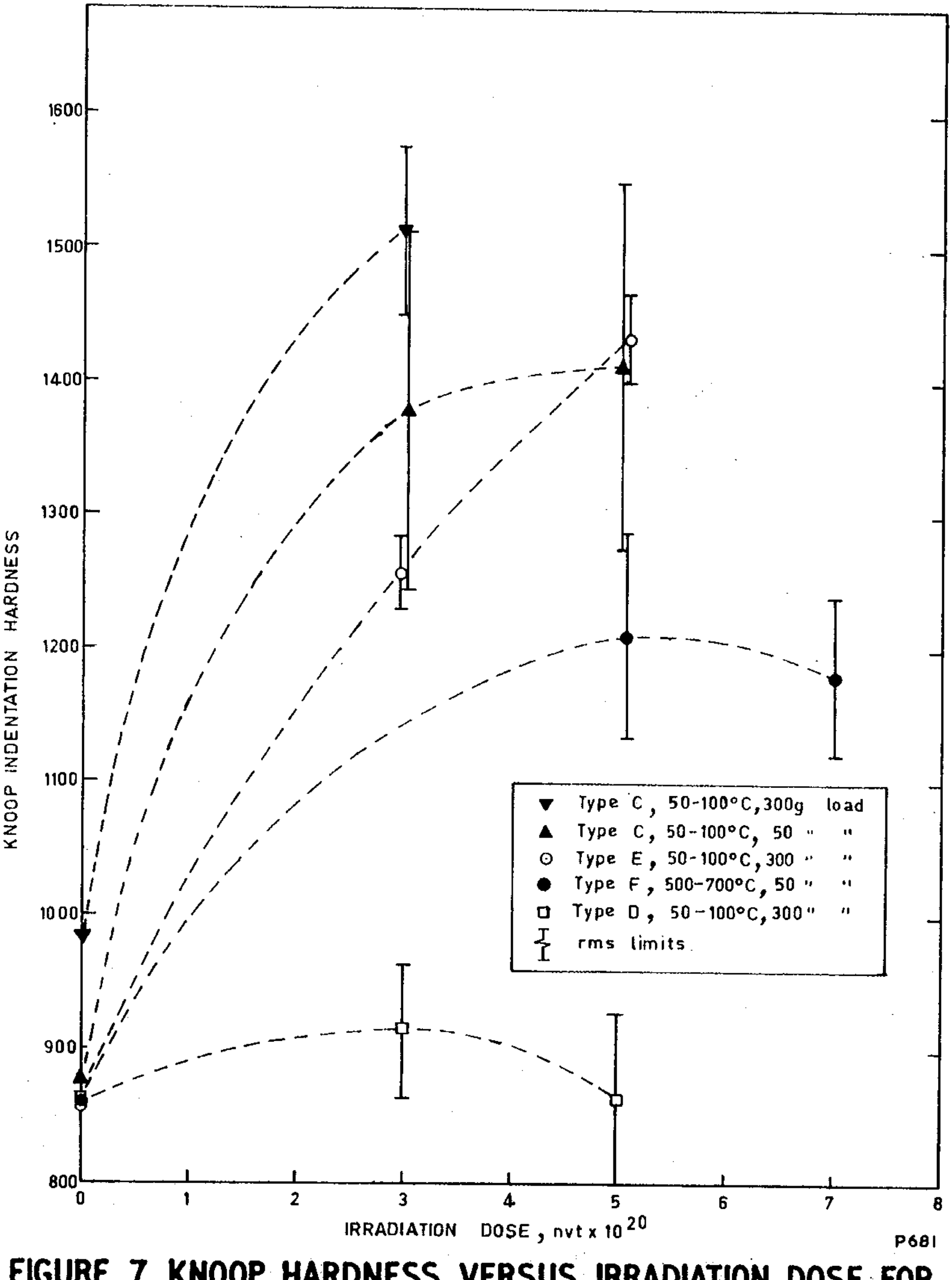

FIGURE 7 KNOOP HARDNESS VERSUS IRRADIATION DOSE FOR VARIOUS MATERIALS

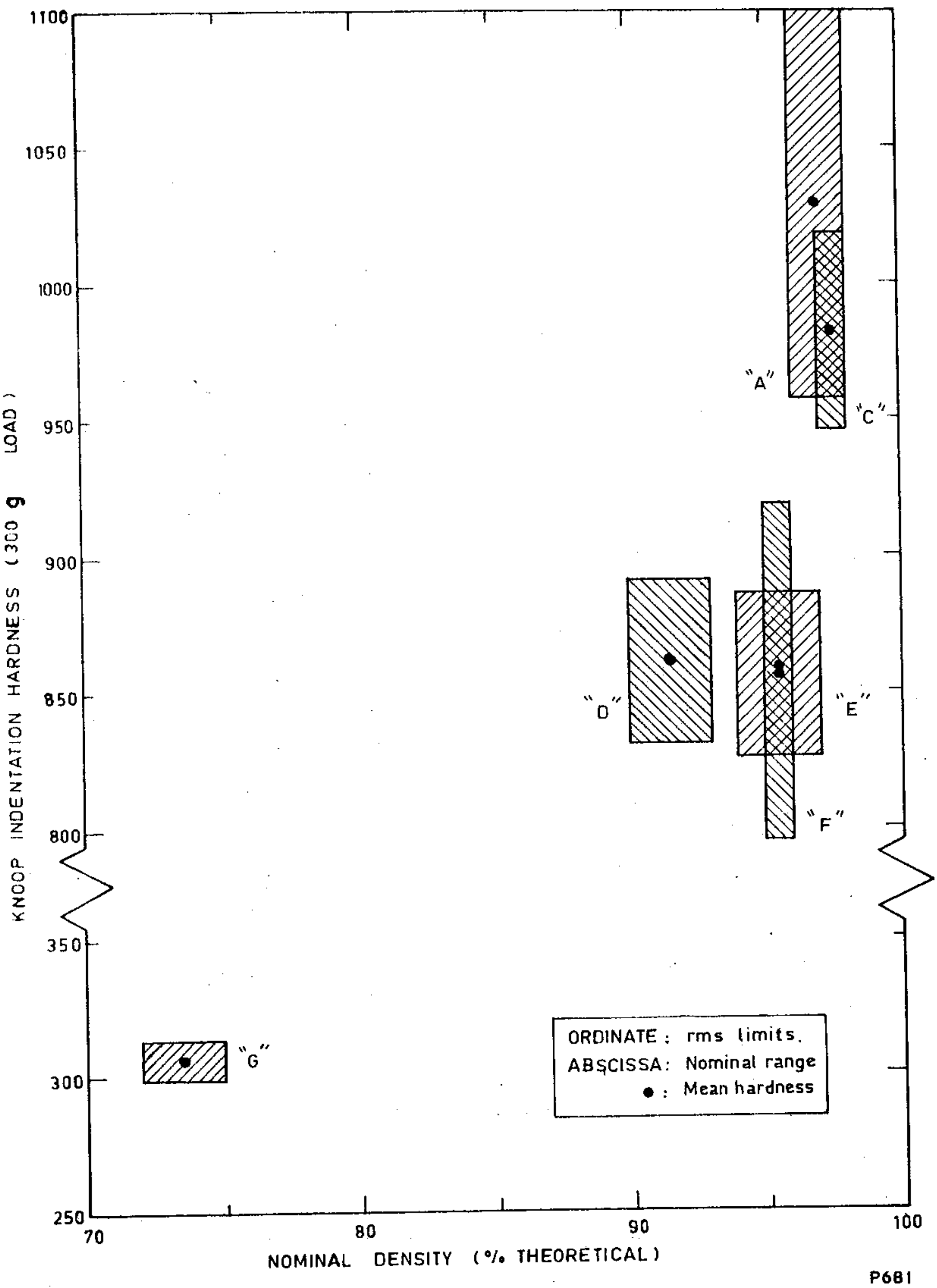

FIGURE 8 KNOOP HARDNESS VERSUS DENSITY FOR UNIRRADIATED CONTROL SPECIMENS