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TRANSITION PRESSURES OF Bi_{3-5}, Sn and Fe

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ABSTRACT :

Transition Pressures of Bi 3 - 5, Sn and Fe. Mr CONTRE.

Making use of "X type anvil", the change in resistance of two reference metals in each run were simultaneously recorded in order to compare their transition pressures. A linear extrapolation through the well known points below 60 kbar showed inconsistencies in the most commonly used high pressure scales. The recording of the pistons displacements lead to an exponential extrapolation which gave transition pressures of 78 ± 2 kbar for Bi 3 - 5, of 102 ± 4 kbar for Sn and of 140 ± 15 kbar for Fe.

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I - INTRODUCTION

The exact measurement, or even the simple evaluation of the pressure which is built up inside a high pressure solid medium apparatus, has from the beginning always been a problem. It was only in piston-cylinder apparatus that a direct measurement of the pressure was possible. Thus it became feasible, making use of the phase transitions of a number of metals, to evaluate the pressure which was built up in more intricate apparatus like "belt" below 60 kbar.

Above 60 kbar there is much confusion taking into account the various datas that have been published to day (table 1). Lately, during the same year 1966, two teams, one from U. S. A. working with Professor HALL, (II) the other from Soviet Union working with Professor VERESCHAGIN (13) published in earnest that the high Bismuth transition occured at 76. 5 $\pm$ 2 kbar for the first one, at 89. 3kbar $\pm$ 1 % for the second one.

The research workers in the high pressure field cannot remain unconcerned by that state of the art, if they wish to make more precise measurements.

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APPARATUS	YEAR	AUTHORS	REF.	PR[illegible]URE [illegible]NSIT[illegible] IN [illegible]LOBA[illegible]								
				Bi I-II	Bi II-III	Tl II-III	Ba II-III	Yb	Bi III-V	Sn I-II	Fe α-ε	Ba
Piston-cylinder	1941 1942	BRIDGMAN -in volume change (vol)	1	25		39,2 / 40	58,8 / 60	-	88,2 / 90	-	-	-
Bridgman's anvil	1952	BRIDGMAN-by resistance (res) (res)	2	25,65	27,08	45	78,4 /80	58,8		no data below 100 kbar		
Shock	1956	BANCROFT & al	5								131	
Belt	1958	BUNDY (res)	17	25,65	27,08	45	78,4 /80	58,8	122,5	114	-	-
Shock	1960	BOYD & ENGLAND (res)	14	25,2		37,1						
Drickamer's anvil	1961	BALCHAN & DRICKAMER (res)	4	-	-	-	59 ± 1	-	90 ± 2	-	133 ±1,5%	144
Piston-cylinder	1962	KENNEDY - LA MORI (vol)	3	25,38 ±0,02	26,96 ±0,18	36,7 ± 0,1	59,6 ± 1	-	-	-	-	-
Drickamer's anvil	1962	BALCHAN & DRICKAMER (res)	9							113 / 115		
Piston-cylinder	1963	KLEMENT-JAYARAMAN-KENNEDY	10						~78			
Tetrahedral press	1963	HALL & MERRILL (res)	18					39,5				
Bridgman's anvil	1964	STARK & JURA	6						81 ± 4	99 ± 4	118 ±6	
Bridgman's anvil	1964	STROMBERG & al	24							107		
Piston-cylinder	1965	ROUX	21	25,5 ±0,15	27,6 ±0,15	36,8 ±0,6						
Tetrahedral press	1965	JEFFERY (vol) (res)	8	25,0 ±0,5	28,0 ±0,6	35,6 ±1,3	54,5 ±1,5	38,1 ±1,3	76,5 ±2	92 ±3,5	-	-
Cubic press	1965	GIARDINI & SAMARA (ind.vol)	19						81-82			
Tetrahedral press	1966	JEFFERY (res) BARNETT - sheet VAN FLEET HALL - wire	11	26,2 ±0,8 26,5 ±1,3	29,1 ±0,8 29,7 ±1,4	35,4 ±2,1	54,6 ±0,9	38,2 ±1,5	75,7 ±1,3	92 ±3		
Piston gauge	1966	VERESHCHAGIN, ZUBOVA & al	13	25,4 1 %	26,9 1 %	36,9 1 %	58,5 1 %		89,3 1 %			
Dead-weight piston jauge	1967	HEYDEMANN (vol)	20	25,31 25,50	±0,06	according to grain size and purity						
Piston-cylinder	1967	KENNEDY & al	29				55,0 ±0,5					

TABLE 1 - PRESSURE TRANSITION DATAS

The present work is an attempt to show the inconsistencies of the main pressure scales in the particular case of an apparatus called "X type anvil", and to suggest possible values for the transition pressures of Bismuth 3 - 5, of Tin an Iron. The four most widely used pressure scales, called A, B, C, D, (table 2) have been chosen so as to be compared. Making the asumption that the transition pressures below 60 kbar are accurate, a linear extrapolation reveals a few inconsistencies From the piston displacement recording, an analytical expression of the calibration curve is then derived. It is thus possible to evaluate the higher transition pressures.

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- TABLE 2 -

- PRESSURE SCALES -

REF	YEAR	AUTHORS	PRESSURE TRANSITION IN KILOBARS						
			Bi I-II	Bi II-III	Tl II-III	Ba II-III	Bi VI-VIII	Sn 1-2	Fe
		BRIDGMAN	25,4	26,8	36,7	58,5	89	113/	133
A	1962	KENNEDY-LA-MORI						115	
		BALCHAN-DRICKAMER	± 0,1	± 0,1	± 0,1	± 0,6	± 1		
	1965	STARK	25,4	26,8	36,7	59	81	107	133
B		JURA - STROMBERG							
	1966		± 0,1	± 0,1	± 0,1	± 1	± 4	± 4	
		JEFFERY	25,0		35,6	54,5	76,5	92	
C	1965	BARNETT							
		HALL							
D	1967	VERESHCHAGIN & al	25,4		36,9	58,5	89,3		
			± 1 %		± 1 %	± 1 %	± 1 %		

II - EXPERIMENTAL PROCEDURE.

The apparatus called "X type anvil" has already been described (31) (32) (35) and first presented at the Eindhoven meeting of the European High Pressure Research Group (1966). It consists of a die and of pistons with a special shape as shown on figure 1. It allows to build, inside a volume which is identical to that of a "belt", higher pressures without damage. The cell body is made of pyrophyllite and the gaskets are of a mixed type, that is to say they consist of a pyrophyllite ring and of a teflon ring (figure 1).

The experiments have been carried out by recording simultaneously the resistance of two reference metal samples at room temperature. This procedure eliminates the lack of reproductibility of the calibration curve. The specimens located side by side, at 1 mm from each other, inside a teflon cylinder (Ø = 4 mm h=3mm) which was in the center of the cell. (figure 2). The metal samples were 0,5 mm in diameter and 4 mm long wires. The electrical connections were established between the pistons and the chamber. The chemical analysis of the samples is given in table 3.

At the same time that the resistance changes were recorded, the displacements of the pistons towards each other were measured, making use of 4 dial gages located at 90° angle around the high pressure apparatus (figure 3). All the measurements have been carried out during the first increase in pressure run and the loads have been measured with strain gage dynamometer.

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- TABLE 3 -

- CHEMICAL ANALYSIS OF THE SAMPLES -

SAMPLES TOTAL PURITY	Bi 98,5 %	Tl 99,99%	Ba 99,2%	Sn 99,9 %	Fe 99,8 %
Impurities					
Li			< 10		
Na			100	< 10	< 25
Mg	10 à 50	< 10	400	25	< 50
Al	< 50	< 10	300	< 50	< 25
Si	Traces	< 50	80	200	80
K			< 10	< 10	< 10
Ca	< 100		0,1%	< 50	< 50
Ti	< 100		< 100		
Cr	< 50				< 50
Mn	< 25		250		230
Fe	< 50	< 10	< 50	< 50	---
Co					< 10
Ni	< 100		< 100		350
Cu		< 10	< 50	< 50	
Zn			< 200		< 100
As					Traces
Sr			0,5%		
Zr					Traces
Mo	< 250			< 250	800
Ag	< 10				< 10
Cd		< 10			
Sn	1000 à 2000		< 50	---	< 50
Pb	1 à 1,5%	< 10	< 50		< 50

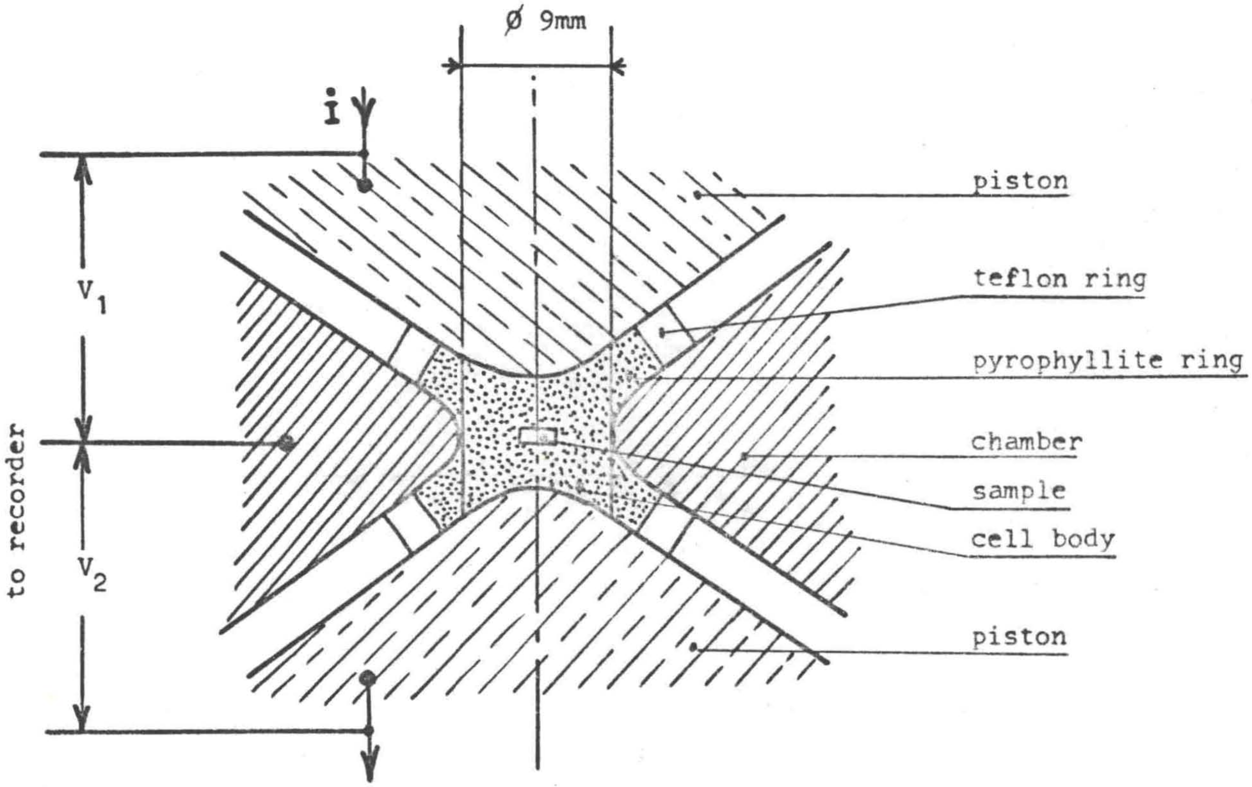

Figure 1 . Cross section of the cell inside the X type anvil

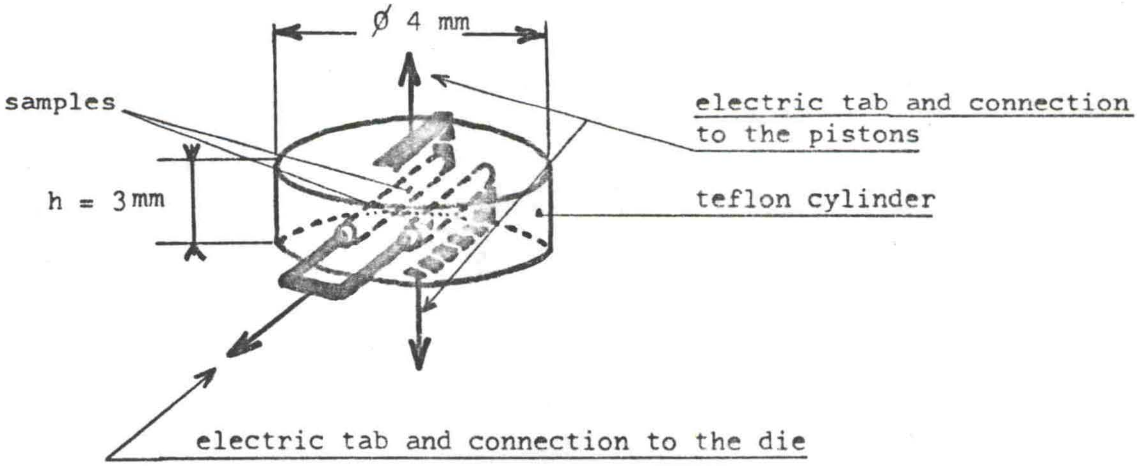

Figure 2 . Samples assembling, schematic

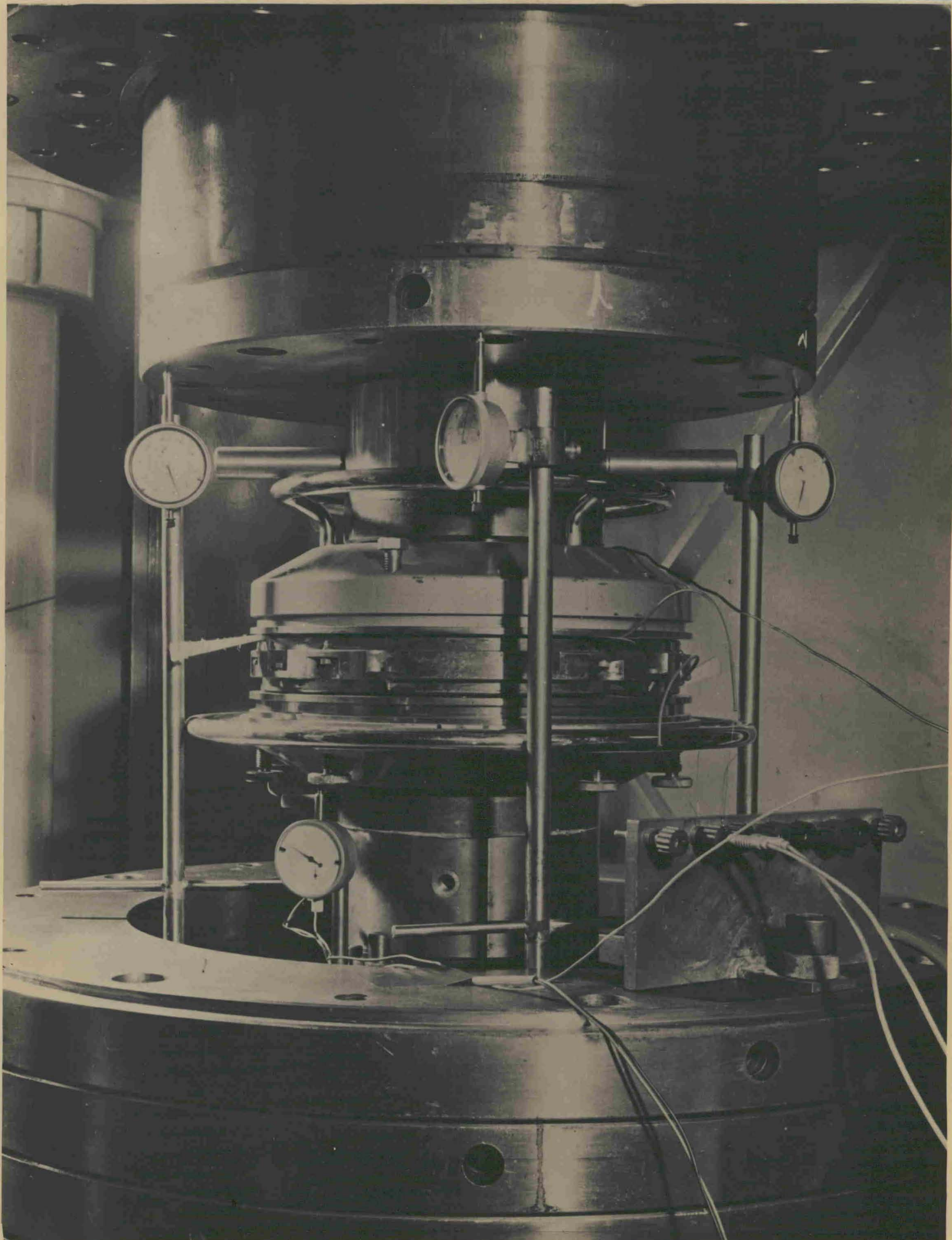

Fig.3 Photograph of the "X type anvil" showing the four dial gages used to record the piston displacements

III - EXPERIMENTAL RESULTS.

Fifty runs have been carried out under those conditions, among which the Fe transition was obtained 3 times, the Sn transition 10 times and the Bi 3 - 5 transition 20 times. A typical resistance recording is shown on figure 4. The displacement of the pistons, as measured during each run, has the shape which is shown on figure 5. The lower part corresponds to the extrusion of the gaskets without much increase in the pressure, where as the upper part corresponds to the real compression of the cell. Calibration curves, based on the B scale (table 2), are shown on figure 6 for two different die diameters. It is to be noted that the lower part is approximately a straight line which goes through the origin of coordinates.

From those experimental results, two types of extrapolations have been made to get the transition pressures of Bi 3 - 5, Sn and Fe.

The first one is a simple linear extrapolation. The second one makes use of an analytical function. The piston displacement recordings give a clue as to the kind of function which is to be chosen. When plotted on a semilogarithmic scale those recordings are quite linear in their upper portion. (Fig. 7) With a slope K thus the piston displacement $\mathcal{E}$ can be expressed as :

$$\mathcal{E} = \mathcal{E}_o \, e^{-F/K}$$

Where $\mathcal{E}_o$ is a constant
F is the load.

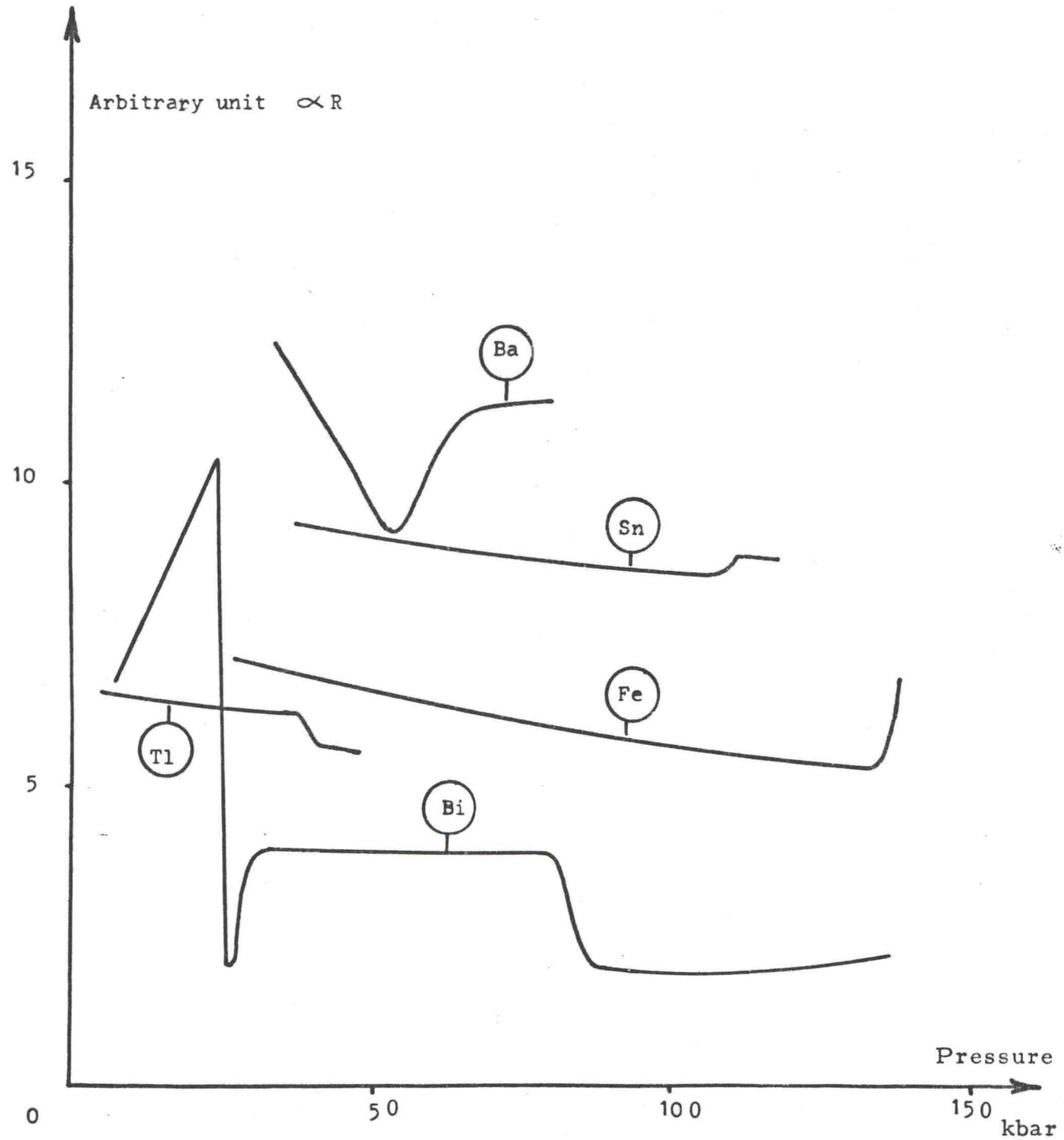

Figure 4 . Typical behavior of the resistance of the metals used to calibrate the pressure generated inside the cell

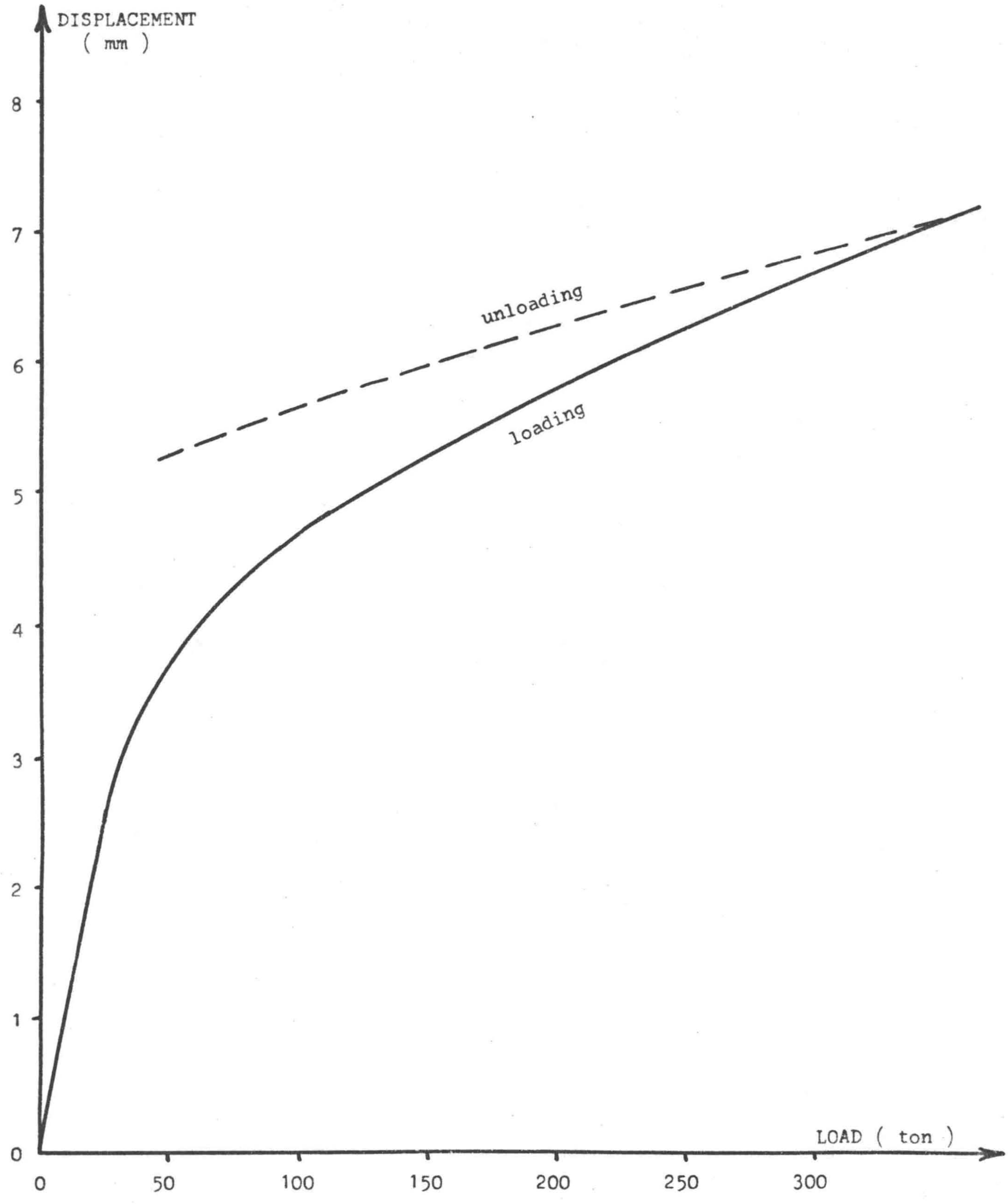

Figure 5. Piston displacement curve

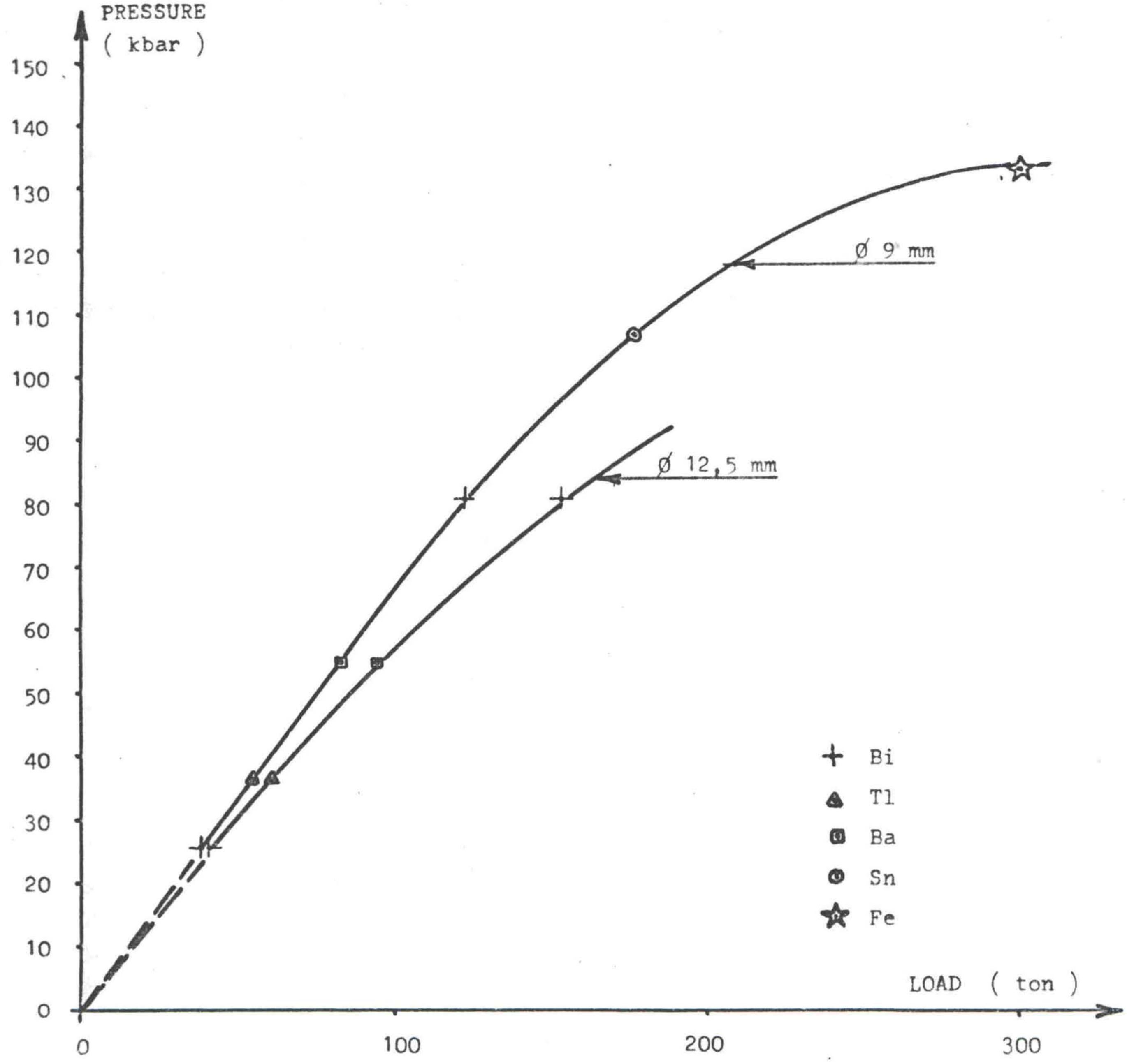

Figure 6. Pressure calibration curves for two different die diameters.

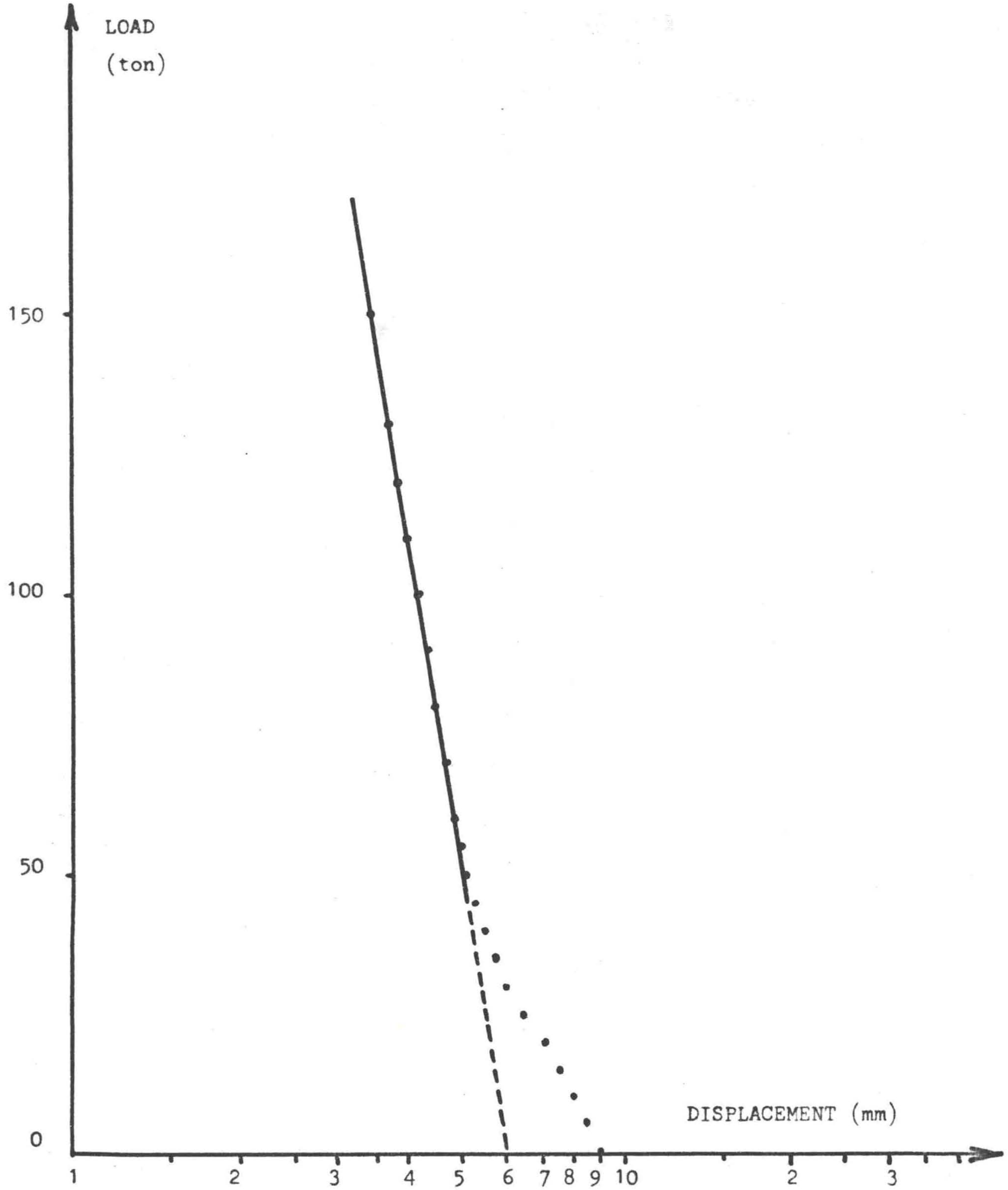

Figure 7 . Piston displacement curve

When this exponential stage is reached, the extrusion is considered as achieved and the asumption is made that the change in volume of the cell is proportional to the piston displacement. On the other hand, the pressures which are generated inside the cell are related the overall compressibility of its components through a law, which can be shown empiricaly to be close to an exponential with a good approximation within the range of experimentation. (28). From these considerations an expression of the calibration curve follow :

$$P = - A \log (B + \exp - F/k)$$

A, B and C are constants which can be evaluated knowing accurately at least three experimental values. They will be chosen among the best known transition points (Bi 1 - 2, Tl, Ba). It is obvious that when the load F is increased indefinitely the pressure P must go to a limiting value, which is the case with the above expression provided that B is positive. It also gives curves whose concavity is towards increasing load as expected.

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IV- DISCUSSION.

1° - LINEAR EXTRAPOLATION.

As the true calibration curve must go to an asymptotic value when F goes to infinity, the linear extrapolation gives excess pressures. The lowest among those are gathered in table 4 together with the corresponding values of the four chosen scales A, B, C and D.

- TABLE 4 -

- LINEAR EXTRAPOLATION -

Pressures in kbar.

SCALES		A	B	C	D	Alined Values
$Bi_{3\to 5}$	Nominal Values	89	81	76,5	89,3	$\leqslant 78 \pm 2$
	Extrapolated Values	77,7	77,7	75,3	78	
$Sn_{1\to 2}$	Nominal Values	115	107	92	(115)	$\leqslant 104 \pm 5$
	Extrapolated values	118	108	118	118	
$Fe_{\alpha\to\varepsilon}$	Nominal Values	133	133	118	(133)	$\leqslant 170 \pm 17$
	Extrapolated Values	182	170	144	182	

The following remarks can be made :

a) - For the Bi 3 - 5 transition all these excess values are below the corresponding values of the scales. It is a striking case of inconsistency, at least for the scales A, B and D. This results from the fact that the calibration curve of the present apparatus is nearly linear up to about 100 kbar.

The scale C is the more coherent.

b) - For the Sn transition the linear extrapolation does not reveal any inconsistency even if this extrapolation uses the scale value of the pressure transition of Bi 3 - 5.

c) - For the Fe transition the linear extrapolation gives a result which is very far off, even if the scale value of the pressure transition of Sn is used.

If a linear extrapolation is made through all the range the pressure transitions are found to be 78 $\pm$ 2 kbar for Bi 3 - 5, 104 $\pm$ 5 kbar for Sn, and 170 $\pm$ 17 kbar for Fe which is certainly very far for the true value.

2° - EXPONENTIAL EXTRAPOLATION.

The exponential extrapolation hopefully should give a better estimate of the transition pressures. Table 5 gives the calculated values.

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- TABLE 5 -

- EXPONENTIAL EXTRAPOLATION. -

Pressures in kbar.

SCALES		A - D	B	C
Sn $1 \rightarrow 2$	Nominal Values	115	107	92
	Extrapolated Values	110	101,8	97,7
Fe $\alpha \rightarrow \varepsilon$	Nominal Values	133	133	118
	Extrapolated Values	-	150	106

The accuracy given next to each value takes into account the uncertainty of the pressure transition of Bi 1 -2 (25. 4 $\pm$0.1 kbar) of Tl 2 - 3 (36. 7 $\pm$ 0. 1 kbar) and of Ba using the latest value given by Kennedy (29) (55 $\pm$ 0. 5 kbar) which fits better than others.

For the present apparatus it turns out that by using the following transition pressures the calibration curve is nearly linear.

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Bi 1 - 2	Tl	Ba	Bi 3 - 5	Sn
25.4 ± 0,1	36. 7 ± 0,1	55 ± 0,5	78 ±2	102 ± 4

The case of Fe is a little different because the nucleation of the transition seems to depend greatly upon the pressure gradients inside the cell, as shown by several people (26) the present apparatus gives stresses which are of a less uniaxial character as a Drickamer or a Bridgman anvil, which might explain the high value found : 140 ± 15 kbar.* It thus appears that Fe does not constitute a good reference metal

In order to fill up the gap in the high pressure scale , it would be desirable to find another reference element such as Germanium (30) (34).

* Recent experiments performed on Iron and Baryum samples lying side by side in the high pressure cell cast no doubt on the fact that the high baryum transition definitely occurs at a much lower load than the Iron transition, in our apparatus.

V - CONCLUSIONS

With a "X type anvil",inconsistencies in the high pressure scales which are currently used have been revealed. A new pressure scale which fits better this apparatus has been established, which would locate the transition pressures of Bi 3 - 5 at 78 ± 2 kbar and of Sn at 102 ± 4 kbar, and of Fe at 140 ± 15 kbar. However many authors have discussed the influence of the apparatus shape, of sample shape, (wire or ribbon) of the pressure transmiting medium, of the pressure gradients on the nucleation of the allotropic transformations under high pressure. Thus the above conclusions may be valid only for the apparatus which was used. Rather than calibrating it would be better to evaluate the pressure at all time by the continuous change in the property of a material such as the lattice parameter with X - ray diffraction. Provided the equation of state of the material is theoretically known, an apparatus such as a hexahedral press built in our laboratory (31) should bring in the future interesting results.

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