

THE ACTINIDES: PROSPECTS OF HIGH PRESSURE RESEARCH

K. GOVINDA RAJAN

Materials Science Laboratory, Reactor Research Centre, Kalpakkam 603 102, India.

ABSTRACT

The actinide elements starting from actinium (atomic number 89) and ending with lawrencium (at. no. 103) are obtained by the progressive filling of the $5f$ electron shell. In spite of their unique application in nuclear technology, an understanding of their solid state properties has a long way to go. From the work done so far on the actinides the following picture emerges: the early actinides (Ac-Pu) resemble the transition metals quite closely, and possess itinerant, bonding, non-magnetic $5f$ electron states; the later actinides (starting from curium) on the contrary, resemble the rare earths (lanthanides) and possess localized, non-bonding, magnetic $5f$ states. Americium is located on the transition regime, and consequently displays very interesting phenomena. High pressure is the cleanest way of bringing about overlaps of electronic states and it is the purpose of this article to first summarize how high pressure studies have helped in reaching the above conclusions on actinides. Future prospects for high pressure research on the actinides are then explored.

INTRODUCTION

THE study of crystal structure, phase transition and electronic band structure constitutes an important activity in solid state physics. Experimental data accumulated on the above aspects on, for example, the commonly occurring metals combined with the quantum theory of solids, enabled us to gain a good understanding of the thermal, electric, superconducting, optical, magnetic and mechanical behaviour of these solids. Moore¹ has written a delightful book to elaborate this approach. In the study of the physics of solids, high pressure experiments have proved very valuable. This can be appreciated if we realize that what makes the solid state exclusive is its lattice structure, and that the lattice parameter enters the description of all its properties. Applying high pressure to the samples provides the most direct way of reducing the lattice parameter, and thus high pressure experiments can be used to confirm the various models used for describing the solid state at *ordinary pressure*. In addition, at high compressions, the overlap of electron clouds between neighbouring atoms is enhanced. This gives rise to many spectacular phenomena. Formation of metallic hydrogen,

and insulating nickel at ultrahigh pressures have been predicted^{2, 3}. Today, high pressure research forms a specialized branch of experimental physics and the various methods of producing and measuring hydrostatic pressure ranging from 1 kbar and above are described in text books⁴. The methods developed for studying the actinides are described in the third section. The questions arise: what are the prospects of doing high pressure work on the actinide elements, what are the challenges, and what kind of results can be obtained?

RESUME ON ACTINIDES ELEMENTS⁵

The actinides starting from the element actinium ($Z = 89$) are the second rare earth series of elements, and are obtained by the progressive filling of the $5f$ shell. Figure 1 reproduces the portion of the periodic table, showing the actinides and the lanthanides. Being the heaviest elements in the periodic table, they are all radioactive and their nuclei spontaneously decay by the emission of α or β particles or by fission. While U and Th are available in vast quantities (thorium from monazite—containing 10%.

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	4f (LANTHANIDES)
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	5f (ACTINIDES)

Figure 1. Part of the periodic table to show the position of the actinides. The lanthanides are also shown for comparison.

Th_2O_3 ; uranium from pitchblende—approx. U_3O_8) and Np and Pu in considerable amounts from spent uranium fuel elements, the other members are available only in much smaller amounts—americium and curium in gram quantities, californium and berkelium by the milligram, and the rest in microgram or even smaller amounts. Some investigations have been carried out on samples containing only a few dozen atoms of the actinide! Table 1 summarizes the known routes of producing these actinides. The crystal structure data on the actinide metals is collected in table 2, and the results show considerable variety with all the elements excepting californium existing in at least two forms. The extreme example is Pu which has six different polymorphs, each stable over a considerable temperature range (100–150°C). Except for the later actinides, the structures are not related to those of the lanthanides and this difference shows up clearly, for example, in the metallic radii. In order to learn more about the actinides, it is necessary to investigate their electronic structure.

ELECTRONIC STRUCTURE OF ACTINIDES AND ROLE OF HIGH PRESSURES

Much progress on the electronic structure of the actinide metals has been made by comparing them with the lanthanides. The lanthanides are

obtained by the gradual filling of the 4f shell and since the 4f level in them is deeply located, the outer valence regions are very similar between all elements. In the metallic state the open 4f shell retains an integral occupation number and this results in a well-defined magnetic moment. In contrast, the (Sd) states form transition-metal-like conduction band states. The number of (Sd) valence electrons is 3, except for Eu and Yb where only 2 electrons participate in the bonding. For these two (anomalous) metals the third valence electron goes into the f-shell. Since the actinides are distinguished by their 5f shell we ask the question whether a similar description is possible for the actinide group of elements? In answering this, we note that the 5f shell, although fairly localized, forms a more extensive part of the actinide atom compared to the 4f shell in the lanthanides. The band width of the 5f (at equilibrium volume) is the largest in actinium ~ 5 eV, and is about 3 eV for the elements Th-Np. For Pu, the 5f bandwidth is about 2 eV, and it is less than 1 eV for Am. This progressive decrease is due to the well-known orbital contraction in a series of elements. The relative spatial extension of the 5f orbitals in the actinides compared to the 4f in the lanthanides also is due to the orthogonality of the 5f to the 4f core. This orthogonality can be effectively looked upon as a repulsive contribution to the atomic potential experienced by the 5f electron. The difference between the electronic structure of the 5f and 4f series of metals is illustrated by the behaviour of the metallic radius. As can be inferred from figure 2, the smooth variation in the RE series (except for Eu and Yb) does not seem to be true with the actinides. The actinides, instead, show a trend similar to 3d or 4d transition metal in the early actinides. Thus the early actinides are called the 6d transition metal series having no 5f occupation. Only when arriving at Pu some occupation of the 5f shell has to be introduced and the 5f electron (S) are then assumed to be of non-bonding, localized RE type. This "valence picture", however, was not universally accepted, for, the exceptional crystal structures found U, Np and Pu led one to believe that there is a substantial covalent (df) bonding present in these metals.

Table 1 The known routes for the production of the actinide elements. The half-life is expressed in years (y), days (d), minutes (m) or seconds (s) for the elements.

Isotope	Decay mode	$t_{1/2}$	Production
$^{227}_{89}\text{Ac}$	α	21.6 y	$^{226}_{88}\text{Ra} (n, \gamma) ^{227}_{88}\text{Ra} \xrightarrow{\beta^-}$; natural
$^{232}_{90}\text{Th}$	α	1.4×10^{10} y	natural
$^{231}_{91}\text{Pa}$	α	3.2×10^4 y	Fuel element residues; $^{230}_{90}\text{Th} (n, \gamma) ^{231}_{90}\text{Th} \xrightarrow{\beta^-}$
$^{238}_{92}\text{Th}$	α	4.5×10^9 y	natural
$^{237}_{93}\text{Np}$	α	2.17×10^6 y	Fuel elements; $^{235}_{92}\text{U} (n, \gamma) (n, \gamma) ^{237}_{92}\text{U} \xrightarrow{\beta^-} ^{238}_{92}\text{U} (n^+, 2n) ^{237}_{92}\text{U} \xrightarrow{\beta^-}$
$^{239}_{94}\text{Pu}$	α	2.4×10^4 y	Fuel elements; $^{238}_{92}\text{U} (n, \gamma) ^{239}_{92}\text{U} \xrightarrow{\beta^-} ^{239}_{93}\text{Np} \xrightarrow{\beta^-}$
$^{241}_{95}\text{Am}$	α	458 y	$^{242}_{94}\text{Pu} \xrightarrow{\beta^-}$
$^{242}_{96}\text{Cm}$	α	162.5 d	$^{241}_{95}\text{Am} (n, \gamma) ^{242}_{95}\text{Am} \xrightarrow{\beta^-}$
$^{247}_{97}\text{Bk}$	α	14×10^3 y	$^{244}_{96}\text{Cm} (\alpha, p)$
$^{249}_{97}\text{Bk}$	α	314 d	$^{239}_{94}\text{Pu} [(n, \gamma)/\beta^-] ^{249}_{96}\text{Cm} \xrightarrow{\beta^-}$
$^{249}_{98}\text{Cf}$	α	360 y	$^{249}_{97}\text{Bk} \xrightarrow{\beta^-}$
$^{254}_{99}\text{Es}$	α	250 d	$^{239}_{94}\text{Pu} [(n, \gamma)/\beta^-] ^{253}_{99}\text{Es} (n, \gamma) \rightarrow$
$^{257}_{100}\text{Fm}$	α	~ 85 d	$^{239}_{94}\text{Pu} [(n, \gamma)/\beta^-] ^{256}_{100}\text{Fm} (n, \gamma)$
$^{256}_{101}\text{Md}$	EC	90 m	$^{253}_{99}\text{Es} (\alpha, n)$
$^{255}_{102}\text{No}$	α	180 s	$^{239}_{94}\text{Pu} (n, \gamma)^7 ^{246}_{94}\text{Pu} \xrightarrow{\beta^-} ^{246}_{95}\text{Am} \xrightarrow{\beta^-} ^{246}_{96}\text{Cm} (^{13}_6\text{C}, 4n) \rightarrow$
$^{256}_{103}\text{Lw}$	α	35 s	$^{243}_{95}\text{Am} (^{18}_8\text{O}, 5n)$

$[(n, \gamma)/\beta^-]$ signifies multiple electron capture and β^- decay process; EC-electron capture.

But with the advent of relativistic energy band calculations it is clear that the 5f in the early actinides shows metallic behaviour. Also a comparison of cohesive energy, room temperature entropy, absence of both localized magnetic moment and magnetic contribution to entropy and finally valence band photoelectron spectrum all show evidences of delocalized 5f shells. The current understanding can be summarized as follows⁶:

- bonding in Pa-Pu is dominated by the 5f electrons
- abnormal crystal structures found in Pa through Pu can be explained as due to bonding dominated by f electrons
- since 5f electrons prefer short bonds, a qualitative understanding of the occurrence of exotic and distorted crystal structure in the

(P,T) phase diagram of these elements —arriving at Americium in the actinide series a drastic change in the properties occurs. This can be seen from figure 2. Already the crystal structure of Americium corresponding to its atomic volume is dhcp, similar to the behaviour of the rare earths. As a trivalent metal, it will have a non-magnetic ground state. Also, superconductivity in Am was recently discovered.

The above account is a highly condensed version of what is understood about the electronic structure of the actinides. Given this situation, high pressure studies become very fundamental, and enable us to make major strides in the further understanding of the actinides. One way of appreciating this is to recall the very interesting speculation put forward by Johansson⁷. Those

Table 2 Present data on the crystal structure of the actinide elements. Also shown for comparison is the data on the lanthanides.

Element	Melting Point C	Ionic radius in metal A	Crystal structure
Ac	1050	1.88	FCC
Th	1750	1.79	FCC(α), BCC(β)
Pa	1560	1.63	BCT(α); BCC(β)
U	1132	1.56	ORTHORH(α); TETRAG(β)
Np	637	1.55	ORTHORH(α); TETRAG(β); BCC(γ)
Pu	640	1.59	MONOCL(α); MONO(β); ORTHO(γ); FCC(δ); BCT(δ'); BCC(ϵ)
Am	994	1.73	DHCP(α); FCC(β)
Cm	1340	1.74	DHCP(α); FCC(β)
Bk	986	1.70	DHCP(α); FCC(β)
Cf	—	—	DHCP

Element	Crystal structure	Element	Crystal structure
La	DHCP	Gd	HCP
Ce	FCC	Tb	HCP
Pr	DHCP	Dy	HCP
Nd	DHCP	Ho	HCP
Pm	DHCP	Er	HCP
Sm	DHCP	Tm	HCP
Eu	BCC	Yb	FCC
		Lu	HCP

who have been following the "Ce-problem" can recall how high pressure experiments were responsible for initiating wide interest in the phenomenon of valence fluctuations. The phase diagram of cerium is reproduced in figure 3, and along with the phase diagram, the "Johansson diagram" is also drawn. This simply is the plot of the melting point *vs* atomic number of the actinides. There is a remarkable similarity between the Johansson diagram and the phase diagram of cerium. Johansson proposes to replace the atomic number axis by a suitable pressure axis, and to introduce the new idea of a Mott transition as a function of atomic number.

Thus the high pressure studies are crucial to the understanding of the 5f state that characterizes the actinide series, and to the elucidation

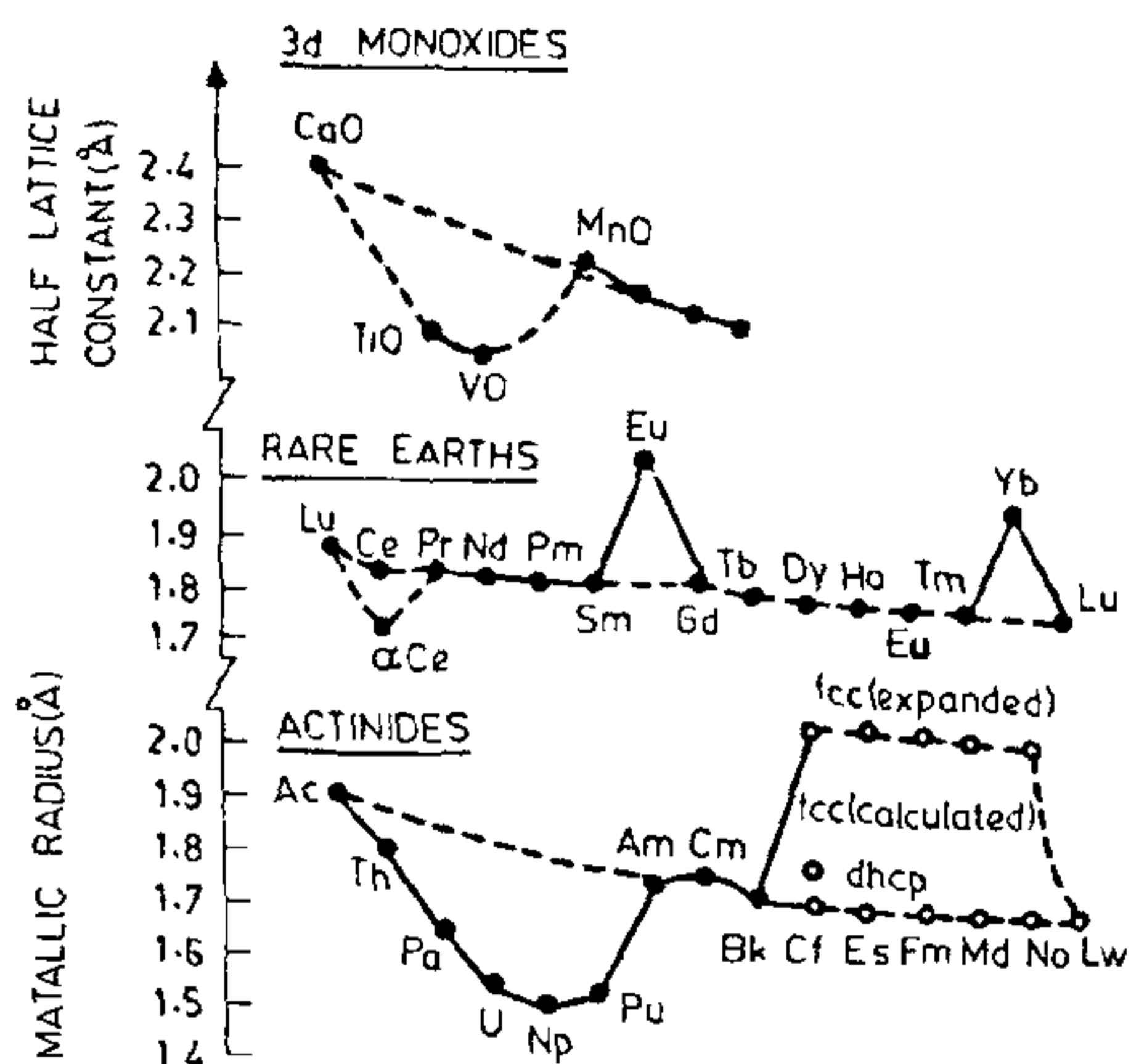


Figure 2. The metallic radius of the actinides, lanthanides and the early 3d transition elements. The striking feature is that the early actinides show a TM-like trend, whereas the latter actinides are more RE-like.

of the physical properties of the actinide. We have to remember, of course, that only a very few laboratories are specially equipped to handle the health hazard when dealing with the generally highly radioactive actinides. However, for the high pressure physicist interested in valence instabilities and delocalization phenomena the rare earths continue to provide many challenges!

REVIEW OF HIGH PRESSURE TECHNIQUES

For exploring the solid state an impressive arsenal of experimental techniques are available. It is fortunate that many of them have been adapted for investigation at high pressure. The methods already developed for studying the actinides at high pressure are: x-ray and neutron diffraction, magnetic measurements, Mossbauer spectroscopy, electrical resistivity and Hall measurements, determination of the superconducting transition temperature, NMR, melting curve determination and the de Hass-van Alphen resonance for Fermi surface studies. Very painstaking measurements on the pressure dependence of self-diffusion coefficients in actinides have also

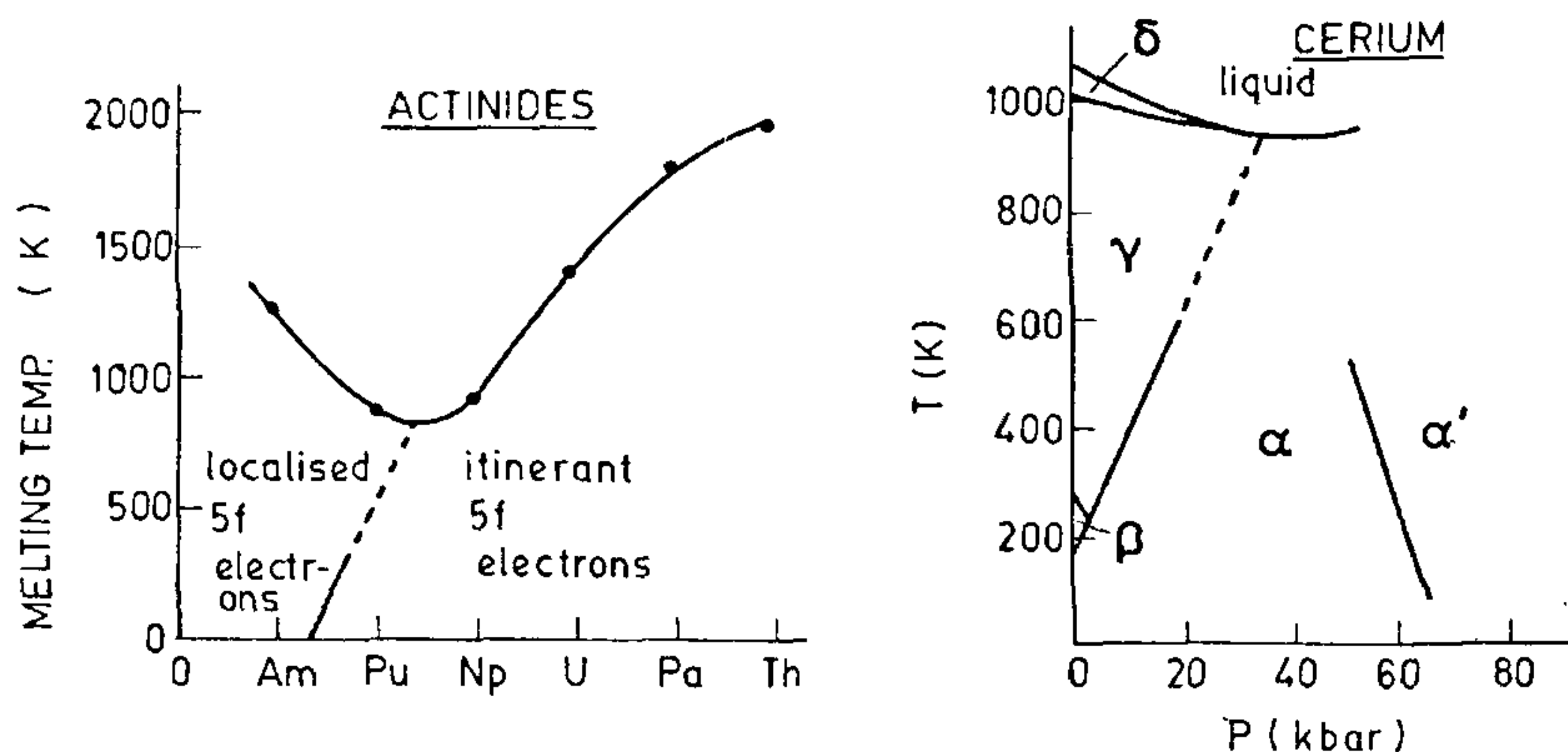


Figure 3. The "Johansson diagram"—the melting point variation of the actinides—plotted above the well-known phase diagram of cerium. The similarities tempt one to talk of a Mott transition with atomic number variation.

been reported. It is not the purpose of the present article to exhaustively discuss the methods. Only a few of them are described so as to give the reader some feel for the high pressure techniques.

X-ray diffraction constitutes the natural starting point in the study of the actinides. This is because when one deals with the actinides the (P, T) terrain is virtually uncharted. Obtaining the crystal structure constitutes the first step whenever a new phase is formed under high pressure. To be able to solve the structure with the actinide sample in the high pressure environment one has to overcome numerous problems. We recall that if the single crystal of any material is available, then one can determine its crystal structure with a high degree of certainty. In the case of actinides, excepting for thorium and uranium, no single crystal specimens are yet available, and the samples are best thin polycrystalline foils, which are sometimes mounted on a substrate. Thus from the so-called "powder data" the crystal structure has to be deduced. The x-ray structure specialists have long since solved this problem adequately, and powerful computer search programs are currently available. The high pressure physicist faces an additional problem. This concerns the quality of data obtained from the sample at high pressures. Because of the

complication of the cell design, the data obtained from a sample at high pressure is generally of much poorer quality than what is obtained from standard diffraction cameras operating at NTP.

The most widely used high pressure x-ray camera is the so-called diamond anvil camera. In this method of generating very high pressures, the sample is contained in a gasket which, in turn, is clamped between a pair of diamonds. The gasket has a small central hole into which the sample and the hydrostatic pressure medium (liquid or gas) are loaded. Figure 4 shows the arrangement. High pressure is generated by squeezing the gasket by a compressive load applied through the lever-arm. Figure 5 shows the overall arrangement. Pressure is measured by the ruby-fluorescence method. This is an elegant method and employs the result that the wavelength of the R_1 -fluorescence line (6927 Å) shifts linearly with pressure [$P = 2.746 \Delta\lambda$, P in kbar and $\Delta\lambda$ in Å]. The linearity has been checked up to 800 kbar, after which a perceptible curvature emerges. With carefully selected gem-quality diamonds and with proper gasketing, the cell can generate close to a megabar. With the provision for *in-situ* pressure calibration, and with the great advantage that diamond is transparent to visible and x-rays, the DAC is unparalleled in its capa-

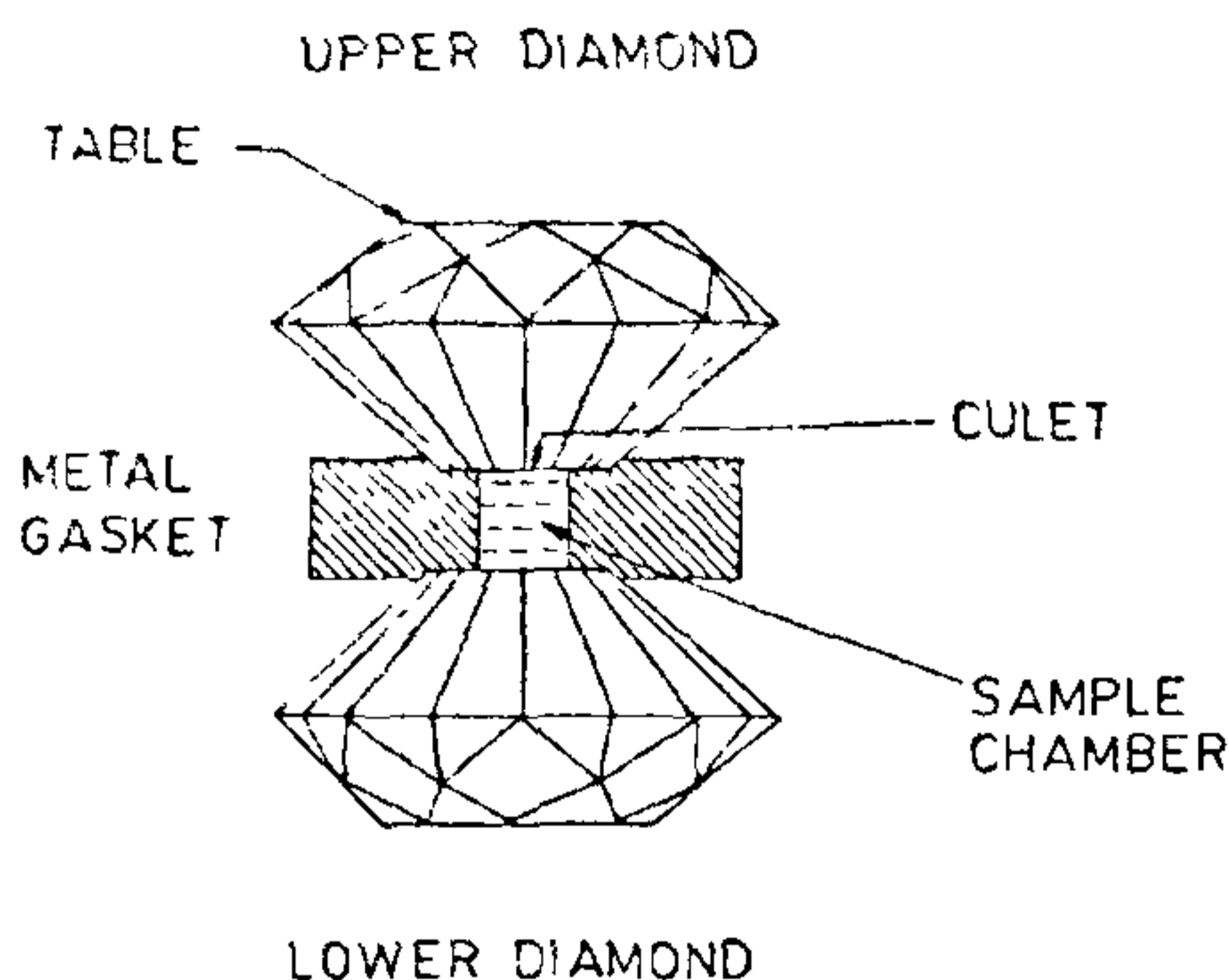


Figure 4. Principle of a diamond anvil cell (DAC). The mating faces of the diamonds will be typically, 1 mm across, and the sample chamber $100\ \mu$ across. The diamonds are approximately 1/5 carat each.

bility. X-ray diffraction measurements can be carried out in a variety of ways. The simplest approach is to use a monochromatic x-ray source and record the diffraction lines on a photographic plate. This is very time-consuming and takes many tens of hours for obtaining a good diffraction pattern. The quality of data obtained is satisfactory, but the method is too slow for short-lived actinides. XRD data can be obtained much more rapidly if the monochromatic x-ray source is replaced with a white x-ray source, and the photographic plate with a solid state detector. Most recently, the DAC has been combined with a synchrotron radiation source for high pressure XRD. It is possible to generate powder diffraction pattern in a matter of seconds. Some workers have developed a position sensitive detector with the DAC and $\text{MoK}\alpha$ radiation and have shown that the method combines rapid data collection capability with a high signal to noise ratio. For further details on the diamond anvil cell, the recent exhaustive article by Jayaraman may be consulted⁸.

The electrical properties of actinides at high pressure can be conveniently studied by the opposed anvil technique, one version of which has been developed at the author's labora-

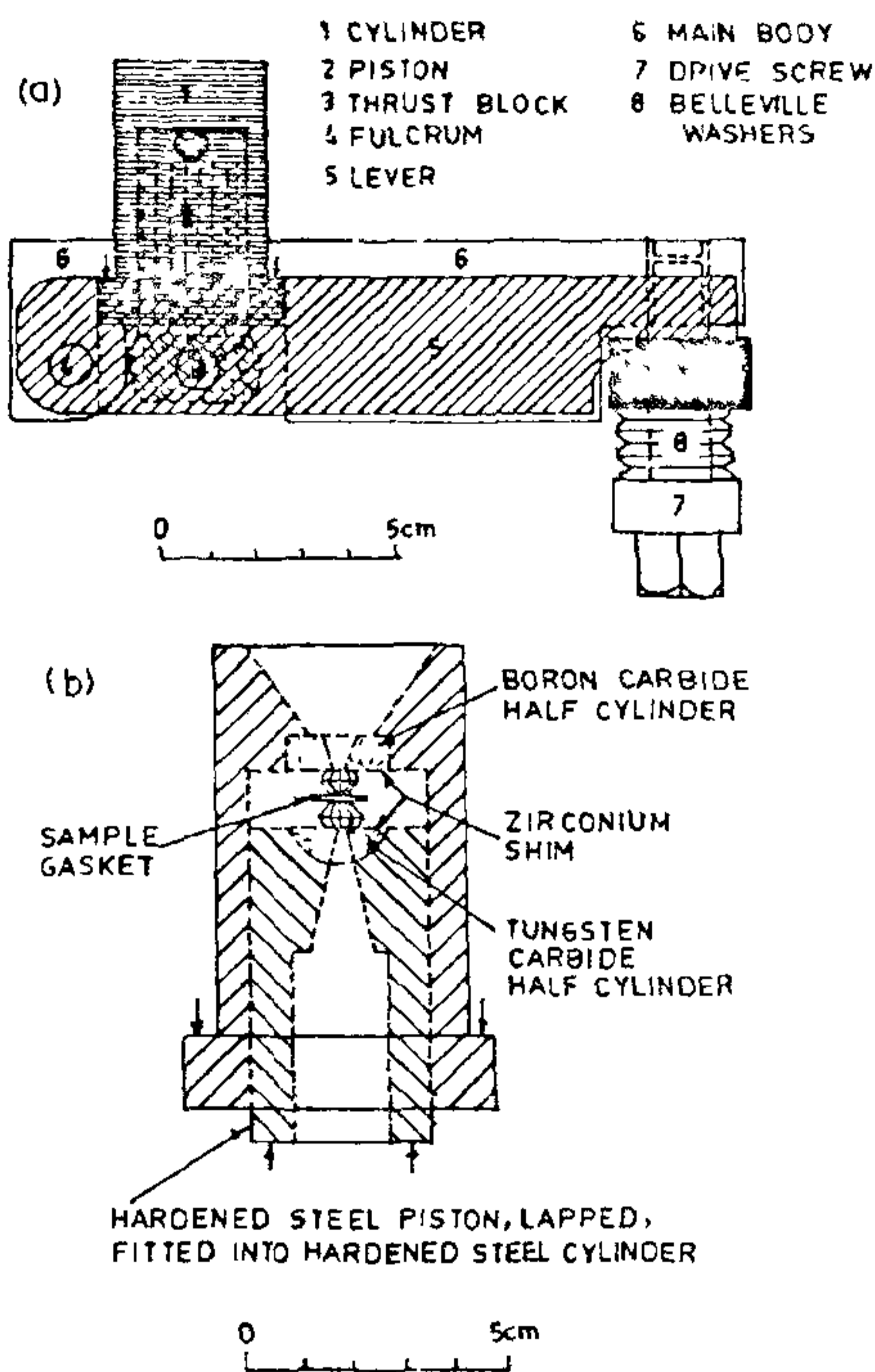
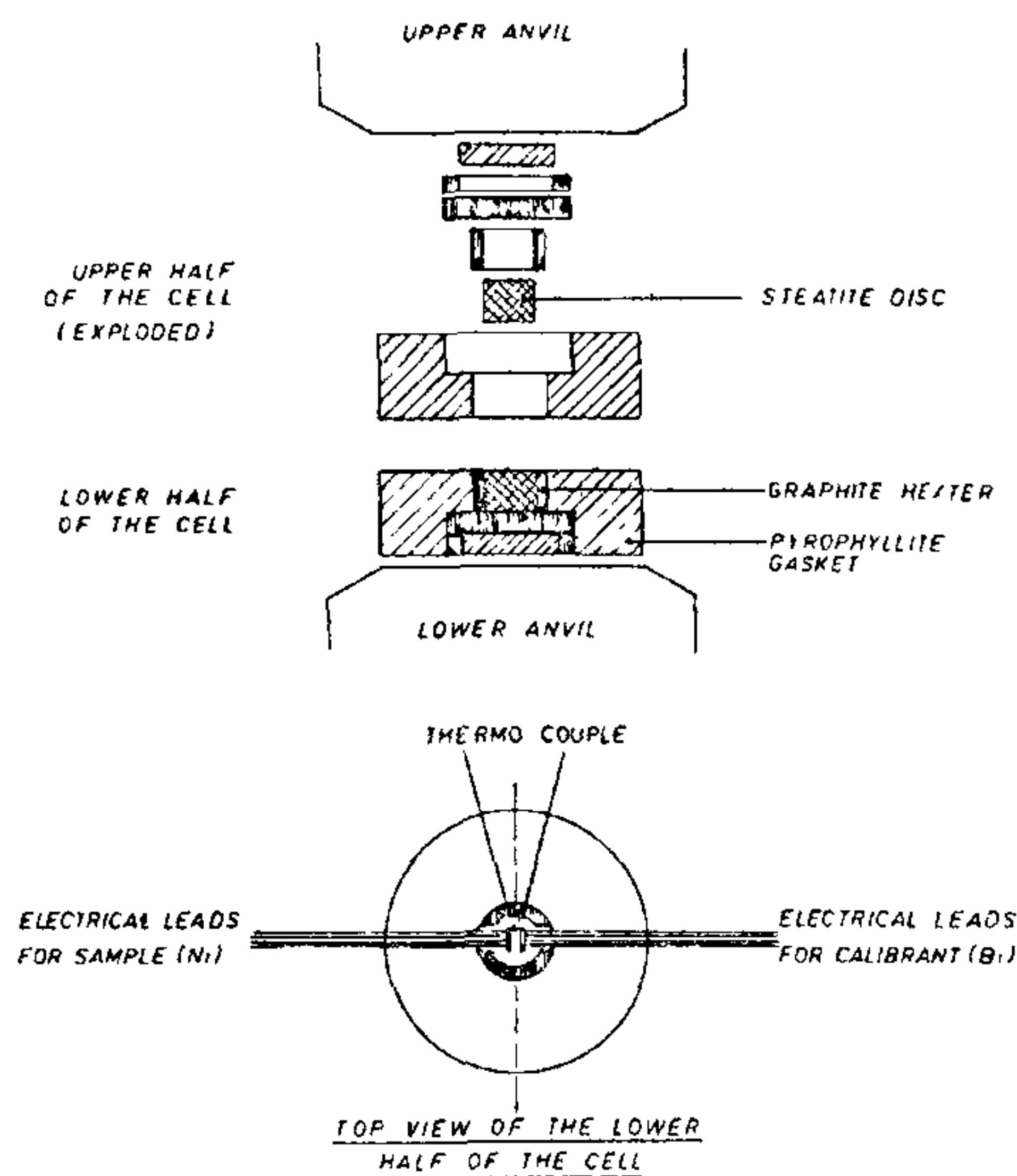


Figure 5. Cross section of the Mao-Bell DAC (after Mao and Bell).

tory^{9, 10}. True 4-lead electrical resistivity measurements can be made with the set up shown in figure 6. Here maraging steel or tungsten carbide anvils contain between them a pyrophyllite gasket in which the sample and a pressure calibrant are mounted. The chief merit of this technique is the provision for continuous *in situ* pressure calibration, and the incorporation of a small furnace for heating the cell. The technique was used to measure the electrical resistivity of U, Th, UC, ThS and ThSe.

Finally, a typical high pressure Mössbauer cell is described¹¹. Figure 7 is a cross-section of the Mössbauer cell developed by Moser *et al*¹¹ for their studies on neptunium intermetallics. The figure is self-explanatory, and it is possible to go



HIGH PRESSURE-HIGH TEMPERATURE
CELL ASSEMBLY

Figure 6. Sketch of the high pressure-high temperature cell. High pressure is generated by the opposed anvil technique, and high temperatures are realized by enclosing the sample in a graphite microfurnace.

upto 70 kbar with this cell. The 60 keV transition in ^{237}Np was used. The design is quite ingenious and uses well-supported pistons and a large sample volume.

It is expected that in the near future other techniques such as EXAFS, optical techniques, nuclear techniques such as positron lifetime, Compton scattering etc will be made available.

RESULTS OBTAINED SO FAR

The high pressure results obtained so far on the actinides can be discussed most conveniently by considering one element after another.

Actinium ($Z = 89$)

Ac has the fcc crystal structure, but the question whether Ac exhibits a distorted fcc structure

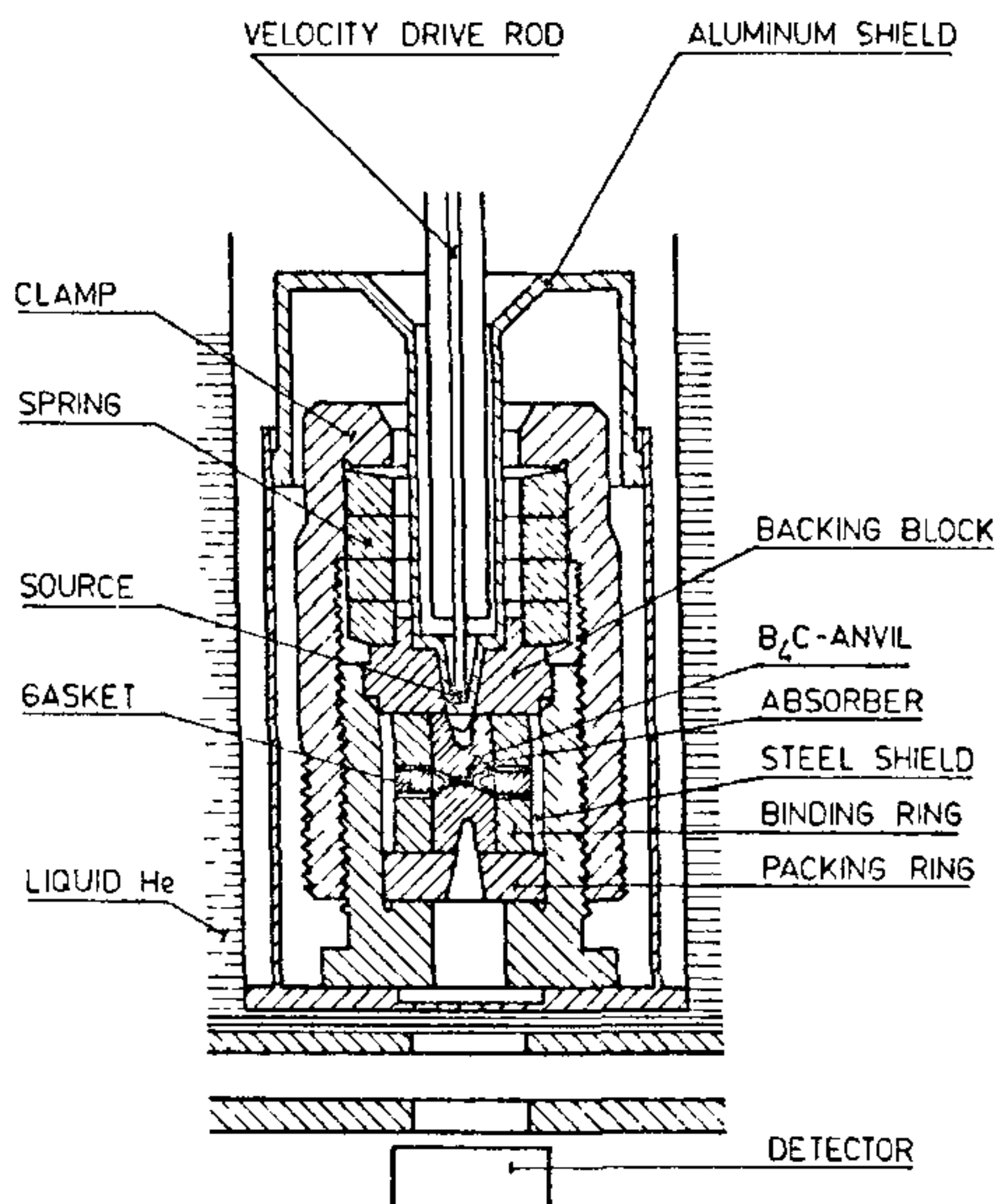


Figure 7. Clamp-type B_4C anvil Mössbauer cell (after Moser *et al.*)¹¹. The cell measures approximately 50 mm in diameter and 100 mm in length.

at normal pressure has been raised by some workers, and it is still unanswered. This metal poses several experimental problems. For example, just after one day of decay, one obtains completely black x-ray films. The situation on Ac was summarized in a recent conference as: "obtaining useful diffraction data is not possible without a major expenditure of money and effort, and, even then, with no guarantee of success". It thus appears that what is known on Ac can be written down on the back of a postage stamp!

The isothermal bulk modulus of the elements Ac through Am shows a trend as shown in figure 8. The only measurement on Ac to determine the bulk modulus gives a value around 0.3 Mbar.

Thorium ($Z = 90$)

The isothermal bulk modulus of Th is as shown in figure 8. The rare earths are also included for comparison. Only for thorium and americium band structure calculations and thence

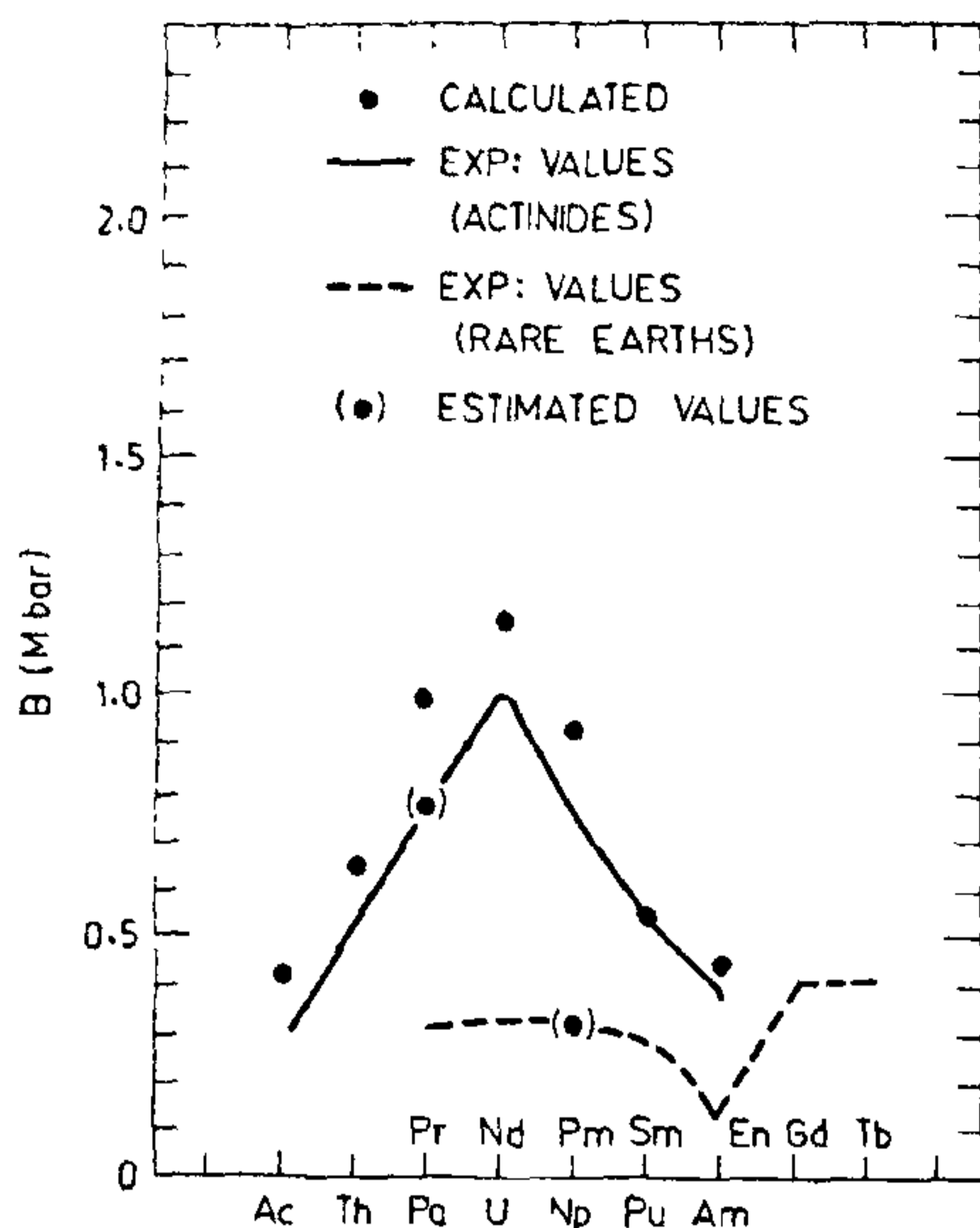


Figure 8. Comparison between the experimental and calculated bulk modulus for the actinide metals.

to compressibility have been made. The calculated value agrees very well with the experimental figure. The superconducting transition temperature of thorium has been found¹⁰ to decrease from about 1.4 K at atmospheric pressure to 0.7 K at about 160 kbar reaching a (broad) maximum of 0.6 K at about 80 kbar. There is some evidence from these measurements for a possible (but gentle) phase transition at < 100 kbar. It seems that this transition can be observed only at low temperatures, as the work on thorium at room temperature has failed so far to bring any evidence.

Pressure studies have proven to be important in the study of band structure and electronic properties of the early actinide metals. In the case of Th, reasonably good single crystals were prepared, and Schirber and coworkers¹¹ have made detailed measurements of the Fermi surface. It is worth noting that two experimental problems had to be successfully solved before reliable FS data could be generated. The first

concerns the pressure medium. As is well known, FS measurements are usually performed in high magnetic fields and at temperatures ~ 1 K. Under these conditions all pressure media solidify and impart strains to the sample. Schirber showed how very good hydrostatic pressure conditions (at least 10 kbar) could be achieved by careful isobaric freezing of helium so that reliable studies even on fragile and anisotropic single crystal could be made. The second problem relates to the dHVA technique. Thanks to the development of field modulation method, accurate FS cross-section determinations without the necessity of introducing leads, into the high pressure environment are now possible.

In the case of Th, the pressure studies of the Fermi surface yielded the unexpected result that all of the Fermi surface cross-sections of this fcc metal decreased with pressure.

High pressure measurements on cold-worked metals and alloys lead to valuable defect information. The actinides are no exception. In our laboratory some studies on the effect of hydrostatic pressure on highly cold-worked Th were carried out¹⁴. Electric resistivity measurements clearly showed pressure-induced recovery occurring (sharply) at about 20 kbar in Th. Observations in a TEM of the pressure-treated and recovered samples give indications of a dislocation rearrangement occurring sharply at 20 kbar. This recovery behaviour of Th can be interpreted in terms of a point-defect induced dislocation rearrangement and recovery.

A word on Th intermetallics and compounds: the thorium intermetallics like ThAl_2 are interesting since there is a possible transition to the Laves phase structure under pressure. On the compounds ThS and ThSe compressibility measurements were first made in our laboratory¹⁵ but there was no evidence for any structural transition upto 200 kbar. ThS was again studied by Benedict *et al*, this time using the synchrotron source DORIS at Hamburg, and have confirmed our findings.

Protactinium ($Z = 91$)

The measured bulk modulus of protactinium is 0.75 Mbar. No successful calculation exists for

the bulk modulus. One can observe from table 2 that starting with Pa, the crystal structure in the actinide series has already started deviating from the simple fcc to more complicated bct. There is at present lack of enough sample, and making larger quantity of Pa appears to be very expensive. The lattice parameter of PaN has been recently determined.

Uranium ($Z = 92$)

The low pressure (< 50 kbar) behaviour of U metal is by now well known. Recent results at higher pressures indicate no phase transition upto 250 kbar. It is rumoured that there is a phase transition (at room temperature) around 700 kbar, and laboratories having a few diamond anvils to spare can confirm this! The phase diagram of U upto 80 kbar appears on figure 9. The structure of the various phases has been determined, and table 2 summarizes the data.

High pressures played a rather curious role in the investigation of α -U. Direct experimental determination of the Fermi surface and other single crystal related properties was thwarted by several phase transitions that occur on cooling α -U below 43 K. But an application of about 8 k-bar on α -U suppressed all these phase transitions and retained α -U down to 1 K at which temperatures the Fermi surface studies were carried out.

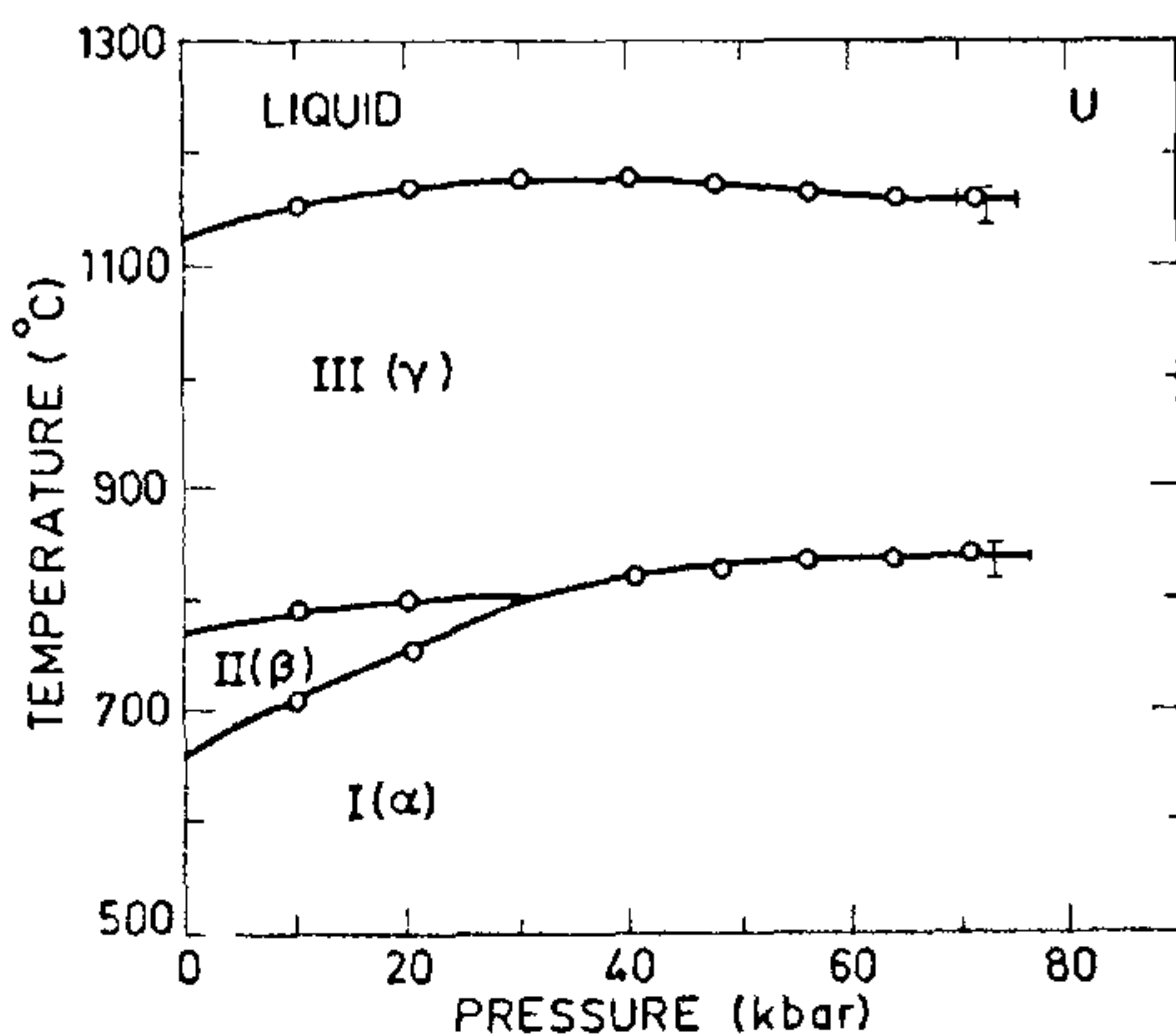


Figure 9. The phase diagram of uranium to 80 kbar.

Turning now to the uranium intermetallics, several high pressure studies on the magnetic properties of the type UX_2 ($X = Fe, Co, Ni, Pt, Ge, Ga$) have been carried out by Franse and coworkers¹⁶. The motivation is the useful role played by high pressure experiments on transition metals in establishing the type of ferromagnetic order in the TM. Since we argue that the 5f electrons in the first half of the actinide series are of an itinerant nature, high pressure studies can be of help in investigating the magnetic behaviour of intermetallic uranium compounds. The high pressure studies show that the magnetic properties of uranium compounds are strongly pressure-dependent thus confirming the itinerant nature of the 5f levels.

Interesting effects due to "vacancy squeezing" in uranium monocarbide were found when subjecting UC to high pressures¹⁷. The vacancies are present in UC to a concentration as high as 2%, and arise due to its ability to exhibit large deviation from stoichiometry. These vacancies become mobile under the application of high pressures, leaving behind a stiffer lattice. It was also found that the NaCl-type structure in this compound was stable upto the highest pressure studied, namely 120 kbar.

Neptunium ($Z = 93$)

The phase diagram of Np appears on figure 10. There is a lack of good electrical resistivity data. The intermetallics provide a sensitive way of changing the Np-Np distance widely (consistent with the phase diagram of Np and additive) and high pressure investigation on the neptunium Laves phases have been carried out. One exploits the correlation between the lattice constant and alloying behaviour. The Np intermetallics NpX_2 ($X = Al, Os, It, Mn, Ru$) all crystallize in the cubic Laves phase with the lattice constant varying from 7.785 Å for $NpAl_2$ to 7.320 Å for $NpMn_2$. Mössbauer experiments performed on these confirm the nature of the 5f level in actinides outlined so far. In particular, the Mössbauer results demonstrate how, for example, in $NpAl_2$ the 5f level which is initially localized progressively gets delocalized under pressure. An added advantage with the Mössbauer technique is that

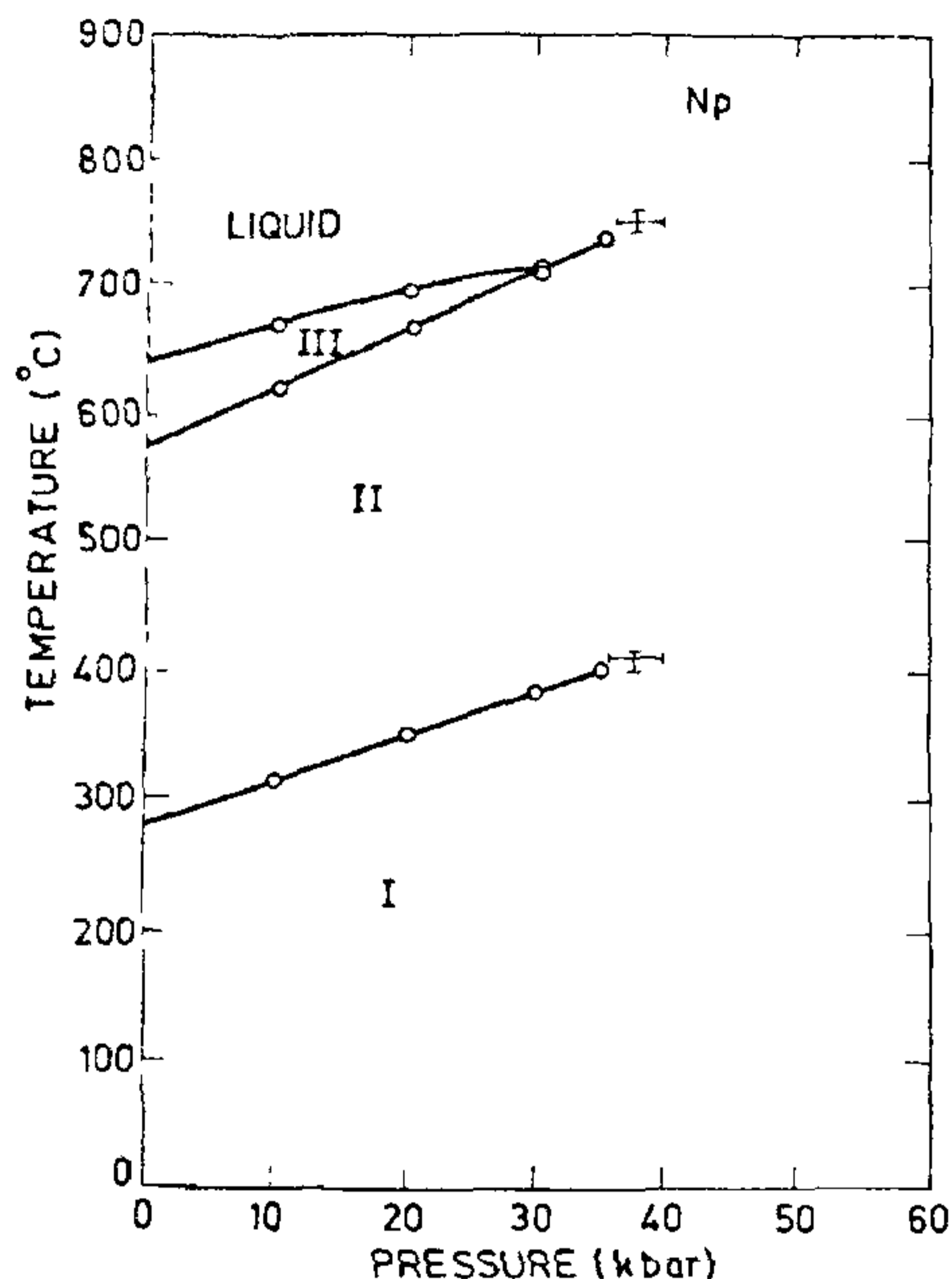


Figure 10. The phase diagram of neptunium to 40 kbar.

by monitoring the fluctuations in the hyperfine field one can investigate the dynamics of the delocalization process.

Very recently Zankert *et al*¹⁸ have measured the lattice parameter variation with pressure of NpAl_2 . The behaviour is shown in figure 11. The behaviour is anomalous and the resemblance to the lattice parameter variation in Cerium is not accidental! They confirm as in the case of Ce a gradual transformation toward more itinerant electron behaviour due to delocalization of 5f electrons. This is in accordance with the Mössbauer results outlined above.

Plutonium ($Z = 94$)

The behaviour of Pu metal under pressure is expected to be like that of U, that is, at high pressure, one should be able to get away from the complexities of its structural behaviour at NTP,

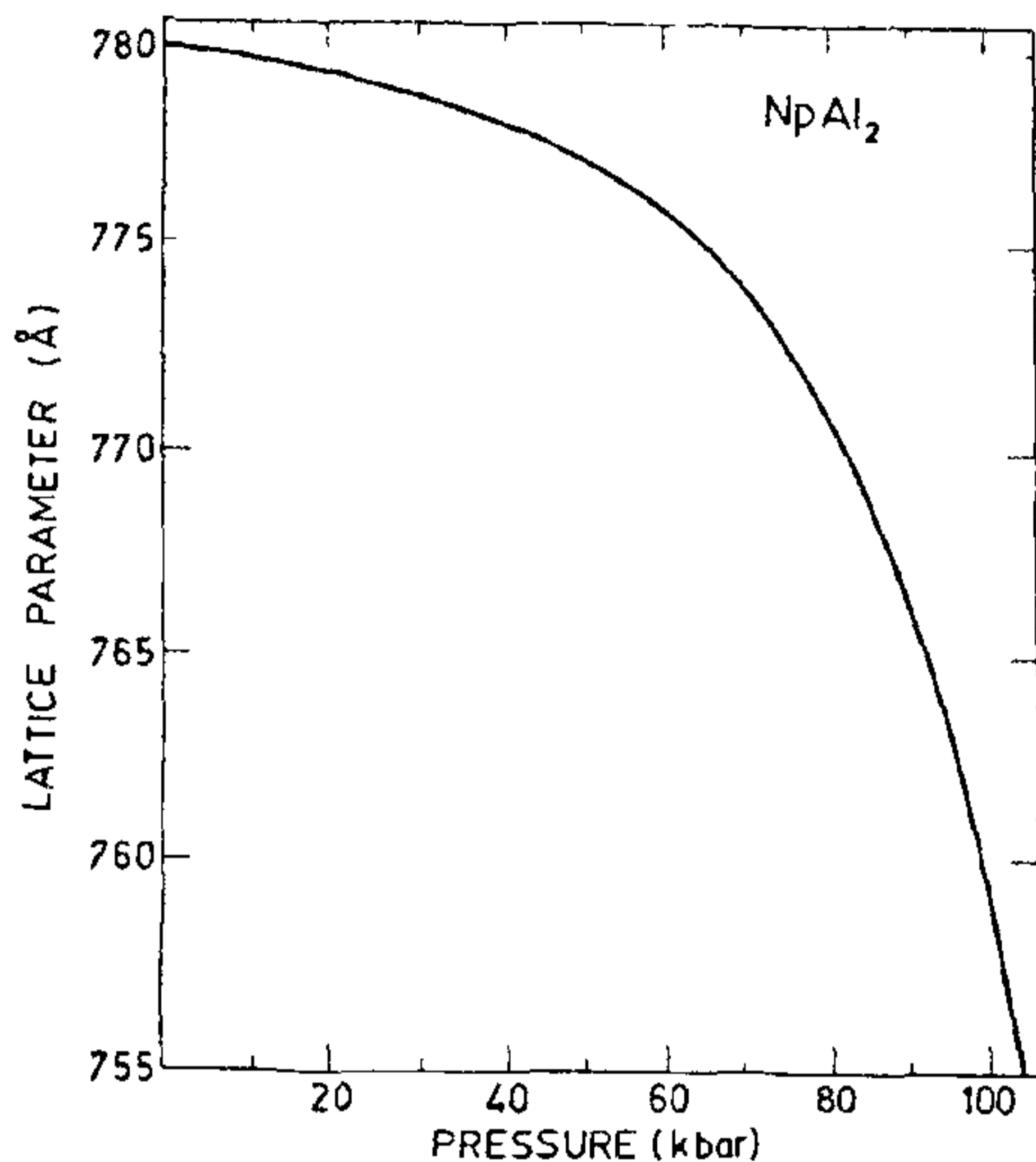


Figure 11. The lattice parameter of NpAl_2 at high pressure. The trend is very similar to that of cerium, and this anomalous behaviour is an indication of the delocalization of the 5f electrons in Np.

and then to exhibit fewer phase transitions. The phase diagram known to date is as shown in figure 12. Electrical resistivity data on Pu to high pressures will certainly clarify many issues. One should bear in mind that research on Pu comes under the "classified" nature, and thus it is possible that many of the studies one would like

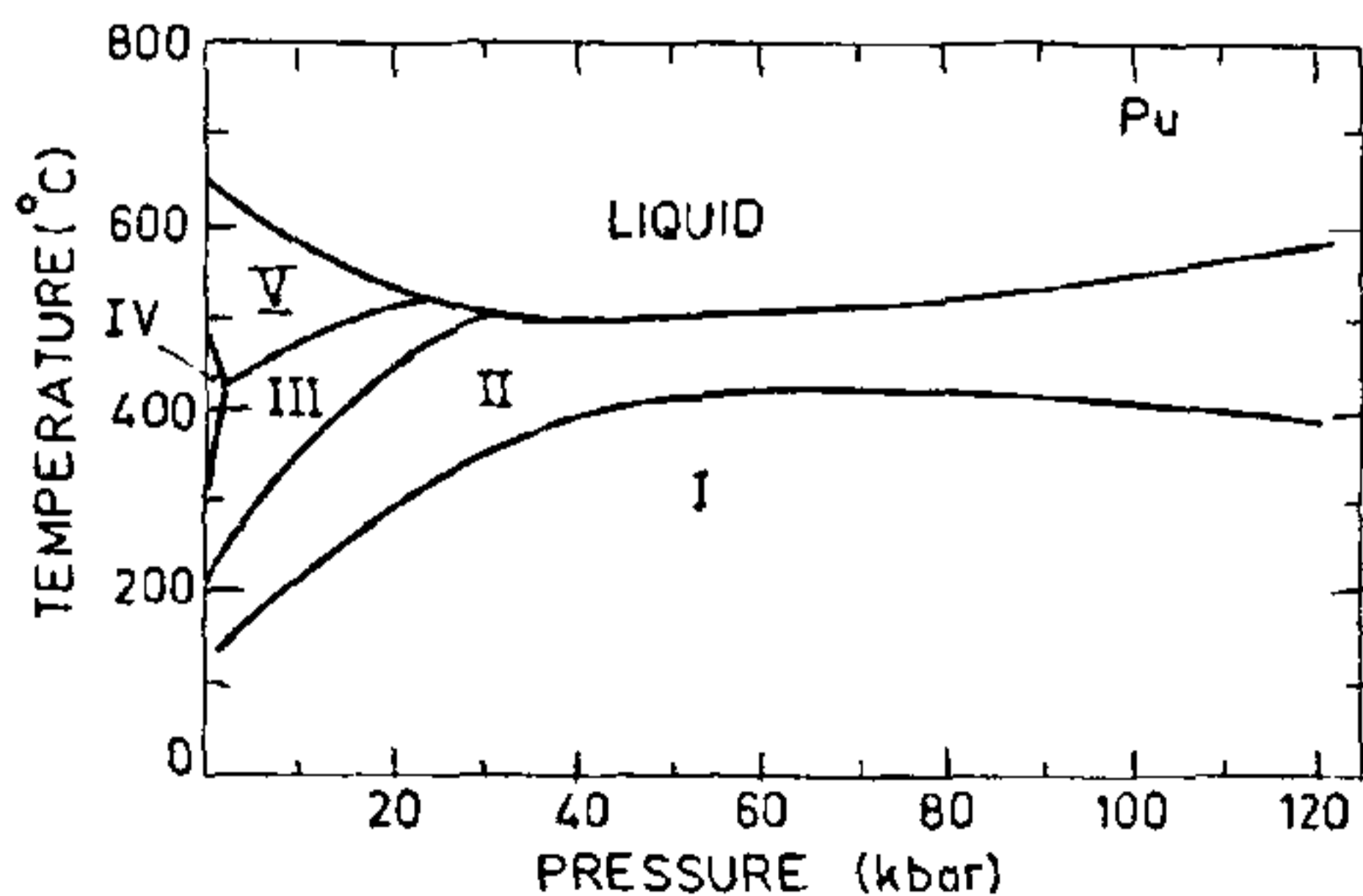


Figure 12. The phase diagram of plutonium to 120 kbar.

to see have probably been carried out, but results not still declassified.

Cornet has carried out self-diffusion measurements on ϵ -Pu, and especially, the pressure dependence of the diffusion coefficient. An unusual behaviour on the pressure dependence of D , namely, an increase with pressure was found. Such a result implies a negative activation volume for diffusion in a bcc system. The author himself has wondered whether his single crystals were completely perfect for, the presence of any flaw (like a grain boundary) can easily explain such an anomalous result. It would be very valuable to confirm this finding.

Americium ($Z = 95$)

In our story on the nature of the $5f$ levels in the actinides, we pointed out the unique position of Am. Naturally, considerable effort has gone in the study of the high pressure behaviour of Am. Figure 13 shows the calculated volume ratio V/V_0 as a function of pressure and how they compare with the experimental data. The most noticeable feature from this is, of course, the dramatic volume decrease accompanying the $5f$ delocalization process (Mott transition). At low pressures, the calculated compressibility agrees very well with the measured values. Am at NTP has the dhcp structure and this goes over to fcc at about 50 kbar. Recently, the crystal structure for the new phase appearing around 110 kbar was found to be the so-called α'' -U structure.

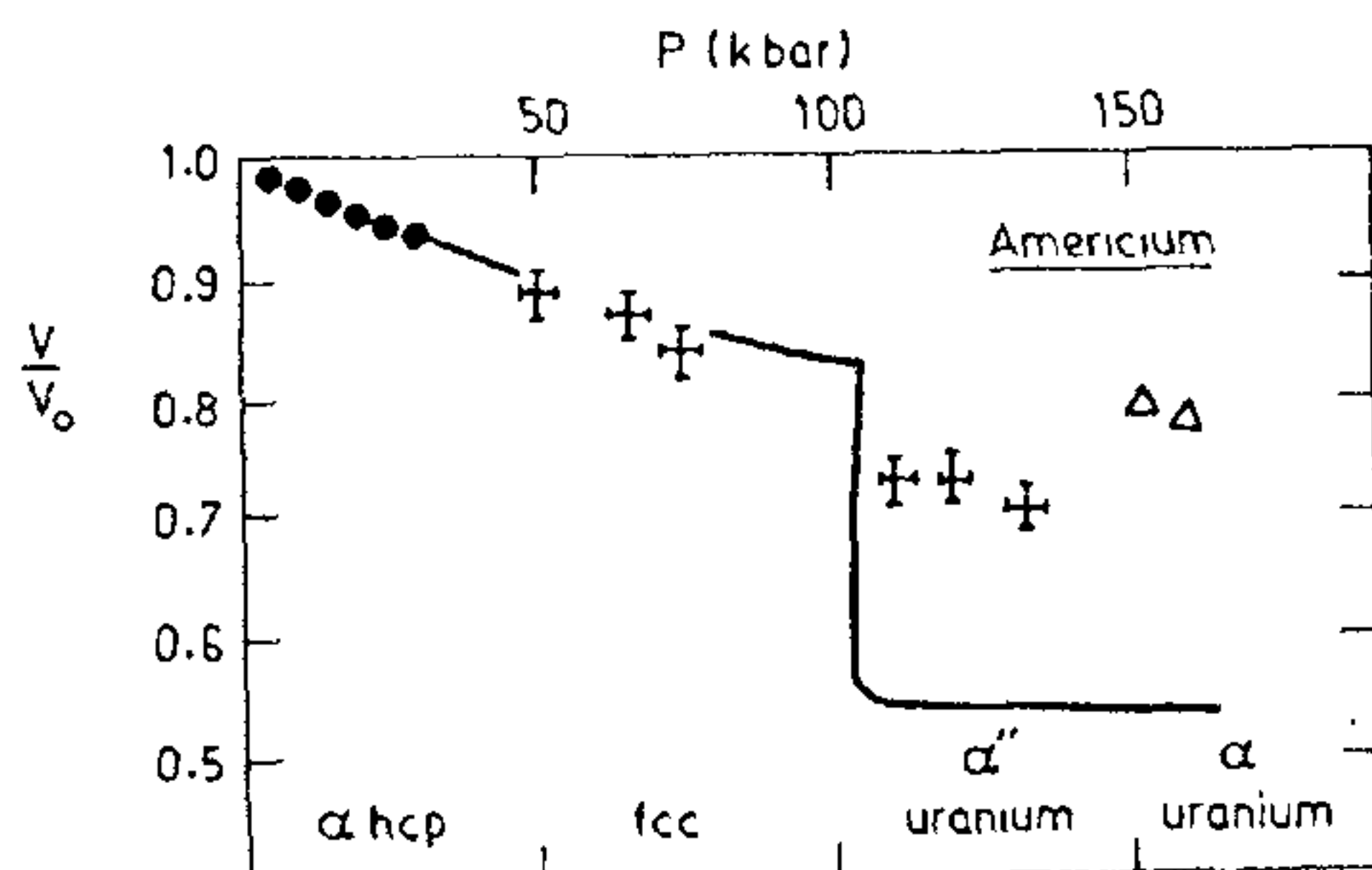


Figure 13. The decrease of volume of Am with pressure. V_0 is the equilibrium volume⁶.

Apparently, this structure is commonly found in certain quenched uranium alloys, such U + 10 at% Mo. But, for the α'' phase of Am the experimental volume change is much smaller than the calculated value. Above 160 kbar, the α'' structure goes over to the α -U (orthorhombic) structure. There is, at present, considerable scatter in the findings between the various experimentalists. Despite this the significant conclusion is that $5f$ delocalization takes place in Am. In this connection, it is quite significant to note that Ce in its α' phase (after the γ - α transition) has the α -U structure, which is characteristic of the itinerant $4f$ band in this metal. The high pressure transition in Praseodymium (around 200 kbar) also is suspected to be of the same origin and one can expect the higher actinide-type structures even for Pr at higher pressures.

Judging from the encouraging results obtained so far, it will be worthwhile carrying out Mössbauer experiments to high pressures. Also useful will be the low temperature investigations, including the measurement of the superconducting transition temperature. We may note that the six $5f$ electrons in Am are more effective in deciding the solid state behaviour than the one $4f$ electron in Ce. The phase diagram of Am at elevated temperatures is shown in figure 14.

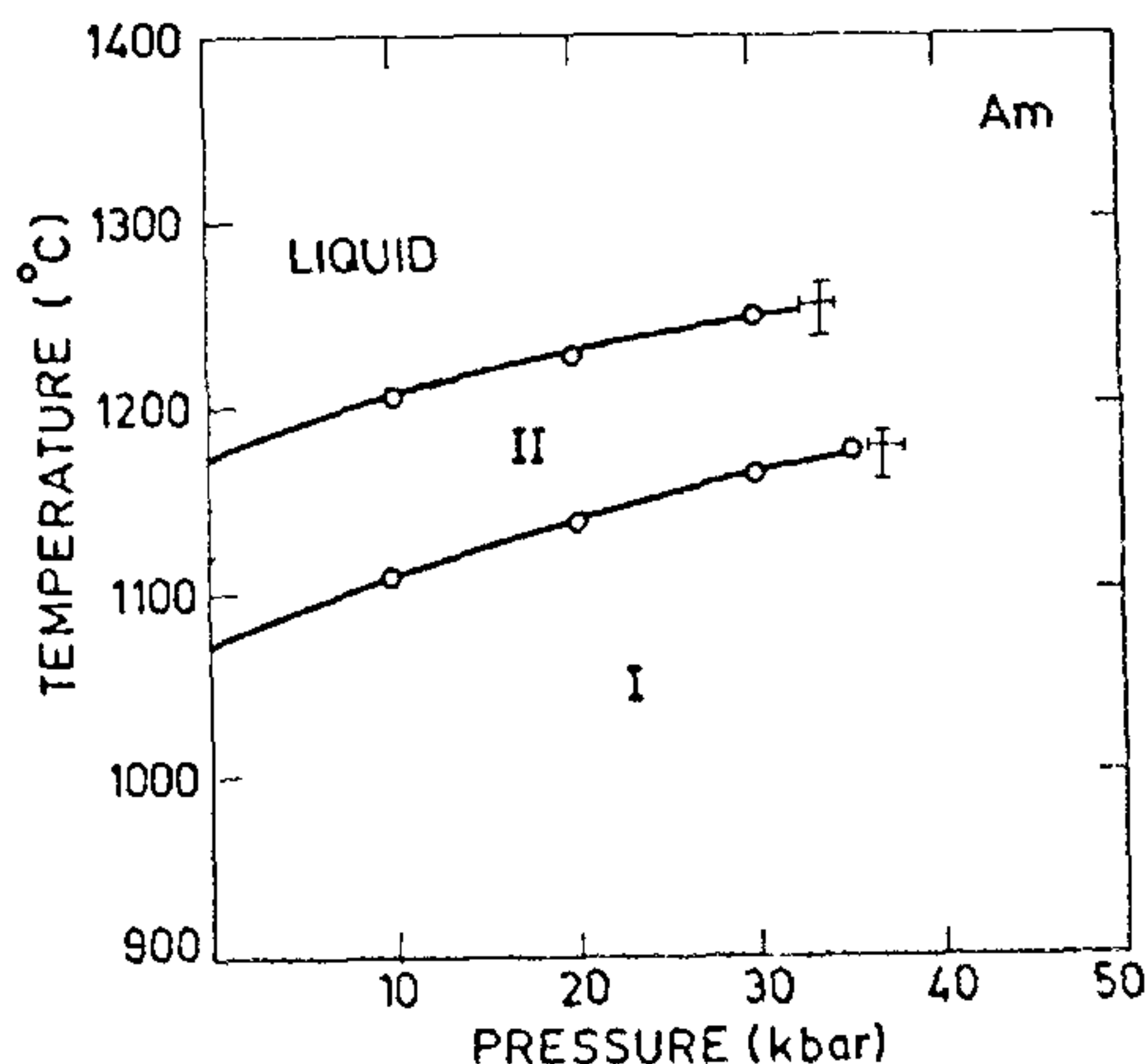


Figure 14. Phase diagram of Americium to 40 kbar.

Curium (Z = 96)

The crystal structure of Cm at normal pressure is dhcp (α -phase). At higher temperatures (at atm. pr) there is a structural transition to the fcc (β) phase. Compressing cerium at room temperature produces two phase transitions. The first one occurs at 120 kbar and is from the dhcp phase to the hcp phase. The second phase transition takes place at about 185 kbar, but the resulting structure is not yet determined. The first phase transition to the hcp phase is unwelcome news to us because we expect a transition rather to the fcc phase. This is so, as we expect from Am onwards *more and more rare earth like behaviour*. It is well known that La, Pr and Nd all undergo the dhcp to fcc transition under pressure. The observed phase change in Am at 50 kbar to fcc provided much faith in this picture. We can at this stage only say that the result on curium has to be independently confirmed. As of now, the above mentioned high pressure result on curium is due to the efforts of a single group.

Berkelium (Z = 97)

The normal pressure crystal structure of Bk is dhcp, and like curium, it is also known to undergo a structural transition at high temperature to the fcc phase. No high pressure data has been published to date.

Californium (Z = 98)

Californium crystallizes in the dhcp structure at atmospheric pressure. Four laboratories collaborated on the only high pressure investigation reported so far (two from USA and two from FRG). ^{249}Cf prepared at ORNL, USA, was studied by the diamond anvil cell technique with ruby-fluorescence pressure calibration. The dhcp Cf transformed sluggishly to fcc allotrope around 100 kbar. The relative volume of fcc Cf at 162 kbar was $V/V_0 = 0.76$. There is no large volume change at the dhcp-fcc transition. On pressure release, hysteresis to transition was observed; the sample was predominantly fcc at 100 kbar. The lattice parameter of the fcc allotrope was 4.7 Å at 1 bar (metastable) and decreased to 4.3 Å at

160 kbar. After Am, Cf is the second actinide for which the dhcp-fcc transition is observed under pressure. This and the value of the bulk modulus $B_0 = 50$ GPa (low compared to lighter actinides) indicate similarity with the lanthanides.

FUTURE PROSPECTS

It is probably by now clear that the most fascinating aspect of the actinides is the dual role played by the 5f electrons, in the beginning of the series they are *itinerant (band) electrons*, while for the later actinides they form localized (non-bonding), magnetic states. Subjecting Am to high pressure demonstrated the delocalization process. Evidently, this remarkable behaviour occurring at a relatively low pressure must be examined in greater detail. Also, a study of the low temperature behaviour of Am, including the pressure dependence of superconducting transition temperature would be quite interesting. For curium and berkelium the pressure for delocalization would be expected to be much higher. Also in Bk, there might be isostructural valence transition from +3 to +4 occurring at reasonably low pressures. If the analogy with the rare earths is pushed further, then one can expect the unique Sm-type crystal structure in einsteinium. Here a remarkable deviation is predicted. Going back to figure 2, it can be seen that starting with Cf, the metallic radii undergo a change in trend. The prediction is that from Cf onwards to lawrencium, all the actinides will possess the trivalent state in the metal at NTP. Thus it is unlikely that Es will display the Sm-like structure, but Es at high pressure may display this structure. The sensational feature of the prediction on the existence of +3 valence state in the actinides is that while in the case of rare earths there are only two exceptional cases, *viz*, Eu and Yb with +2 valence state (the rest are in the +3 state), there is a bunch of nearly half-a-dozen elements in the actinides crystallizing in the +3 state. Thus, a richer variety of pressure-induced valence transitions induced by pressure is anticipated with the actinides.

It is also reported that a number of alloys are going to be investigated in the near future.

Examples are: Th-Ce, U-Ce, Am-Ce and Pu-Sc. In all these cases the second element expands the actinide lattice, and high pressure experiments naturally will give rise to exciting results. $Pu_{1-x}Am_x$ alloys can also be thought of and they should show a gradual change from the delocalized to the localized state.

ACKNOWLEDGEMENTS

The author thanks Dr G. Venkataraman for suggesting this topic for review, and for his continued interest. Thanks are due to Shri T. D. Sundarakshan and to Drawing Office for assistance.

3 August 1984

1. Moore, W. J., *Seven Solid States*, Benjamin, 1967.
2. McMohan, A. K. and Albers, R. C., *Phys. Rev. Lett.*, 1982, **49**, 1198.
3. Ashcroft, N. W., *Phys. Rev. Lett.*, 1968, **21**, 1748.
4. Bradley, C. C., *Solid state studies at high pressure*, Butterworths, 1968.
5. Freeman, A. J. and Darby, J. B. Jr., (eds) *The Actinides: Electronic structure and related properties*, Academic Press, 1974.
6. Johansson, B., Skriver, H. L. and Andersen, O.

- K., *Physics of solids under high pressure*, (eds) J. S. Schilling and R. N. Shelton, North-Holland, 1981, p. 245.
7. Johansson, B., *Philos. Mag.*, 1974, **30**, 469.
8. Jayaraman, A., *Rev. Mod. Phys.*, 1983, **55**, 65.
9. Govinda Rajan, K., Sankara Sastry, V. and Rita Khanna, *Rev. Sci. Instrum.*, 1981, **52**, 1734.
10. Mohammad Yusuf and Govinda Rajan, K., *Pramana*, 1982, **18**, 1.
11. Moser, J., Potzel, W., Dunlap, B. D., Kalvias, G. M., Gal, J., Wortman, G., Lam, D. J., Spirlet, J. C. and Nowik, I., In: *Schilling and Shelton*, 1981, p. 271.
12. Fertig, *Phys. Lett.*, 1972, **A38**, 517.
13. Schurber and Arko, *Phys. Rev.*, 1980, **B21**, 2175.
14. Sahu, P. Ch., Mohammad Yousuf and Govinda Rajan, K., Workshop on Actinides under pressure, Karlsruhe, 1983.
15. Govinda Rajan, K., Krishnan, R., Sequeira, A. and Venkataraman, G., *Nucl. Phys. Solid State Phys.*, (India), 1973, **C16**, 160.
16. Franse, J. J. M., Frings, P. H., de Boer, F. R. and Menovsky, A., In: *Schilling and Shelton*, 1981, p. 181.
17. Govinda Rajan, K., Rita Khanna, Sankara Sastry, V., Sundararajan, A. R. and Rafi Ahmed, A. G., *J. Nucl. Mater.*, 1981, **102**, 313.
18. Zankert, J., Potzel, W., Moser, J., Wunsch, M., Obenhuber, T., Kalvius, G. M. and Gal, J., Workshop on Actinides under pressure, Karlsruhe, 1983.

NEWS

INDIAN NATIONAL SCIENCE ACADEMY, NEW DELHI

Prof. C. N. R. Rao, Director, Indian Institute of Science, Bangalore, has been elected President of the Indian National Science Academy for the year 1985. Other office-bearers for the year will be Prof. R. R. Daniel and Dr S. Z. Qasim (Vice Presidents) Prof. P.

N. Srivastava (Treasurer) and Dr T. N. Khoshoo (Foreign Secretary).

Prime Minister Indira Gandhi and industrialist J. R. D. Tata are among the 30 people elected fellows of the Academy.

MEGHNAD SAHA MEDAL FOR 1984—INDIAN NATIONAL SCIENCE ACADEMY

Dr Raja Ramanna, Chairman, Atomic Energy Commission and Secretary, Department of Atomic Energy, Bombay, has been awarded the Meghnad

Saha medal for 1984 for his contributions in nuclear science. He is the tenth recipient of the award.
