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PERGAMON PRESS LTD. · LONDON · NEW YORK · PARIS

Reprinted from "Progress in Nuclear Energy"

Volume 1, Series V (1956)

with the original pagination

Printed in Northern Ireland at The Universities Press by Sir Isaac Pitman & Sons Ltd.

CHAPTER 4

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A REVIEW OF THE PHYSICAL METALLURGY OF PLUTONIUM

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Abstract—The historical development of plutonium metallurgy, in so far as it is known to the authors, has been traced up to the point at which detailed publication of results became possible through declassification changes. The precautions found to be necessary for the safe handling of plutonium are summarised and the means of giving effect to these in different laboratories are discussed. The available data on the physical properties and intermetallic compounds of plutonium are reviewed, with the inclusion of some recent unpublished information.

An attempt has been made to cover effectively the work on plutonium metallurgy in America, Britain and Canada, but knowledge of Russian achievements is limited to that disclosed in a single article by KONOBEVSKY. There are, of necessity, some fields of work by American and British laboratories which remain unpublishable and represent a gap in the scope of this paper.

1. HISTORICAL INTRODUCTION

THE earliest history of plutonium metallurgy is the story of the American pioneer work that was done in this field during World War II. Brief accounts⁽¹⁾ of some portions of this work have been written as parts of papers by two different authors, CYRIL STANLEY SMITH (1954) and ERIC R. JETTE (1955a), both of whom are eminently qualified to discuss the subject by virtue of the prominent roles they played in the metallurgical activities of the Los Alamos project in the period from 1943 to 1945. During this period both scientists served in supervisory capacities in which they were closely associated with research done on the extractive and physical metallurgy of plutonium. Since that time JETTE, as Division Leader for Chemistry and Metallurgy, has remained at the Los Alamos Scientific Laboratory, New Mexico, where a very major portion of all research on plutonium metallurgy in the United States has continued to be performed. It is probable that a more complete and detailed story than has been recorded by either SMITH or JETTE could be found by searching through early reports and notebooks that are still classified, but the task would

⁽¹⁾ In relating the accomplishments that constitute milestones along the road of progress in plutonium metallurgy, the present authors have attempted, insofar as the facts are known to them, to report the names of those who have been responsible for major achievements. In so doing, very few references have been given, however, because in only a few instances have the records of early work in plutonium metallurgy been declassified, and only a few papers reporting the results of more recent investigations of the properties of plutonium have as yet appeared in the unclassified literature.

be a difficult and time-consuming one, and the present authors have elected not to undertake it. Their account of the early American work will do no more than repeat a portion of what has already been written, but because no comparable record of the earliest British work has previously been presented, a short account will be given of the beginnings of research on plutonium metallurgy in the United Kingdom and in Canada.

The very first reductions of plutonium to metal were not made at Los Alamos. This brilliant accomplishment of micrometallurgy was realized by scientists of the "Metallurgical Project" at the University of Chicago, a group led originally by PAUL F. KIRK and later by HARLAN L. BAUMBACH. In 1943, minute beads of metal were produced first by BAUMBACH, and shortly thereafter by SHERMAN FRIED. Although the tiny spheres of plutonium that were obtained weighed less than 50 micrograms, they were large enough to enable FRIED to make the first measurement of their density, using a capillary method developed by KIRK, and to permit Z. V. JASAITIS to investigate their melting temperature. R. S. ROSENFELS developed a technique for mounting the microgram quantities of metal in Perspex, which enabled metallographic examinations to be made. R. C. L. MOONEY and W. H. ZACHARIASEN established the presence of a face-centred-cubic crystal structure. Some of the beads that were found to be malleable had a density of about 16 g/cm^3 , but others that were brittle gave values closer to 20. The work at Chicago was carried on for only a limited time, because as soon as gram quantities of plutonium became available at Los Alamos, the major research on the metallurgy of that element was transferred to the New Mexico site.

When it was found that, in agreement with the Chicago results, measurements made at Los Alamos gave equally good evidence for densities of about 16 and about 20, it was suspected that plutonium had more than one allotropic form. The existence of at least two modifications was confirmed when F. J. SCHNETTLER ran a specimen in an oil-filled volumetric dilatometer; a transition was observed at about 120°C . An intimation that plutonium might, however, have many allotropic forms was obtained in early June of 1944 when a thermal analysis curve was run with a one-gram sample. On heating, arrests occurred at 130° , 222° , 324° , 480° , and 630°C , but on cooling they were obtained only at 621° and 460°C . The 630° and 621°C arrests were identified with melting and freezing, respectively, and it appeared obvious that the 480° and 460°C arrests pertained to a solid-state transformation. But why the heating arrests at 130° , 222° and 324° were not repeated on cooling was difficult to understand, and it seemed almost unbelievable that an element could have as many as five different solid-state forms, especially between room temperature and a melting point no higher than 630°C .

When enough metal had been obtained to provide a dilatometer specimen 0.4 in. long, a curve of linear dilation versus temperature (Fig. 1) was run. Although the transformations obviously occurred in a manner more characteristic of an alloy than a pure metal, it seemed unmistakable from this curve that phase changes had begun on heating at about 135° , 220° , 325° and 465°C , but that only the last of these transitions was clearly reproduced in the reverse direction on cooling. In any case, the existence of four different phase transformations involving five different allotropic forms of plutonium appeared to

have been established, but an even more surprising feature of the curve was its revelation that throughout a considerable range of temperature plutonium does not expand on heating but contracts at an appreciable rate. This behaviour is unique among pure isotropic substances.

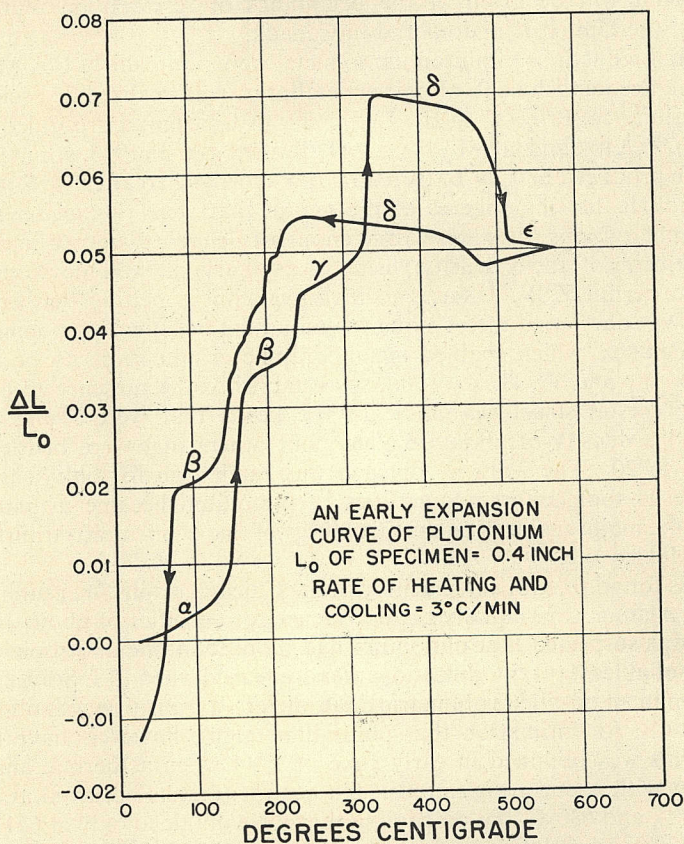


Fig. 1. An early expansion curve of plutonium. (Los Alamos).

The five allotropic forms of plutonium were designated alpha to epsilon in accordance with conventional practice, and their existence was confirmed by measurements of electrical resistivity as a function of temperature. It was learned that whereas alpha plutonium has an unusually large positive coefficient of expansion and a negative coefficient of resistivity, the delta phase has a negative coefficient of expansion and a positive coefficient of resistivity. The resistivity of all the phases was found to be high and of a character more suggestive of a semiconductor than a metal.

SCHNETTLER obtained powder patterns of all five phases in a high-temperature X-ray diffraction camera. Very complex patterns were found for the alpha, beta and gamma phases; it was discovered that the face-centred-cubic structure determined by MOONEY and ZACHARIASEN was that of the delta phase; and epsilon proved to be body-centred cubic. By this time it had become fairly

clear why the first specimens of metal reduced at Chicago and at Los Alamos gave conflicting answers regarding density and deformability. The purest metal obtained was obviously the alpha phase which, having a complex crystal structure, was brittle. In the presence of some type of impurity, however, it appeared that the face-centred-cubic delta phase was retained and that this modification manifested much more metallic behaviour, at least with regard to malleability.

A few other accomplishments in the early work at Los Alamos are worthy of mention. The first sample of clean metal (delta phase) was produced by T. T. MAGEL and N. S. DALLAS by carrying out the reduction in a 900-r.p.m. centrifuge. Shortly thereafter, a technique for producing satisfactory buttons in stationary bombs was perfected by R. D. BAKER. Also, MORRIS KOLODNEY developed a method for obtaining plutonium by electrolysis in a fused salt bath. When the metal was observed to deposit as drops of liquid it was realized that the melting temperature of plutonium must be relatively low. Early in 1944 tensile and compression tests were made on one-gram samples using a Chevenard microtesting machine borrowed from Canada.

Throughout a nine-year period following 1944 plutonium metallurgists at Los Alamos continued to work with metal that was of quite good purity by ordinary standards, and they did so feeling that five solid modifications of any element constituted a truly remarkable number. It was with a sense of surprise reminiscent of the war-time work that in 1953 a sixth form was discovered. The finding of this new phase, designated delta-prime, was a consequence of dilatometer runs made by E. M. CRAMER, W. N. MINER, F. W. SCHONFELD and L. L. HAWES with metal of a new high purity. A further innovation made in these dilatometer runs contributed to revealing the existence of the new phase. The conditions of the experiment were changed so as to let the temperature of the specimen be raised only by the heat generated within it as a consequence of the radioactivity of plutonium. In this way temperature gradients within the metal that were responsible for an alloy-like form of earlier dilatometer curves (Fig. 1) were eliminated, and because the specimen was now heated more uniformly throughout its entire volume, a curve more accurately representative of the transformation behaviour of a pure metal was obtained (Fig. 2). It is readily apparent from a comparison of Figs. 1 and 2 that only through a sharpening of the dilatometer trace at critical temperatures could the negative expansion behaviour of the delta-prime phase have been clearly distinguished from that of delta.

The discovery of delta-prime was not announced, however, until after F. H. ELLINGER had confirmed its existence by seeking and finding a new crystal structure in the high-purity metal. Although this structure is properly described in the best crystallographic tradition as body-centred tetragonal, it is more commonly referred to as face-centred tetragonal because it may be regarded as a slightly distorted form ($c/a \sim 0.95$) of the face-centred-cubic delta phase. This close similarity of structures was thought to justify calling the new phase "delta-prime" in lieu of assigning to it a new letter⁽²⁾ of the Greek alphabet.

⁽²⁾ The Russian workers have named the delta-prime phase "eta," but by now "delta-prime" seems to have become too well established in American and British usage to be supplanted.

During the period when the early research on plutonium metallurgy was being done as part of the American war-time programme for development of an atomic bomb, British contributions to the advancement of nuclear science were being made chiefly by those sent to North America from the United Kingdom to participate in the American and Canadian projects. With the war's end it became possible within the United Kingdom to create organizations

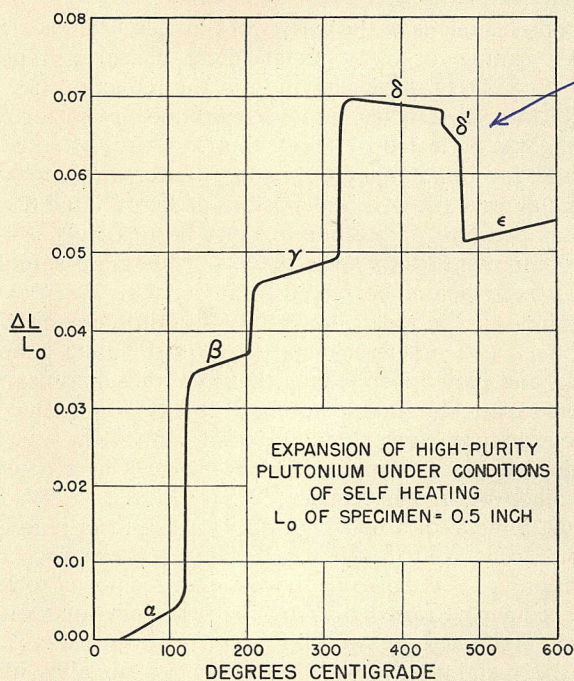


Fig. 2. Expansion curve for high-purity plutonium under conditions of self-heating. (Los Alamos).

for research in all branches of nuclear science comparable to the national laboratories that had already come into existence in the United States. The first of these new research centres, the Atomic Energy Research Establishment, was founded at Harwell, Berkshire, in 1946, and shortly thereafter plans were laid for the building of production centres, such as the plutonium piles to be located at Windscale in Cumberland. Meanwhile an atomic weapon development programme had been initiated within the Armament Research Establishment at Woolwich and in associated establishments. In 1951, this work was transferred to the newly constructed Atomic Weapons Research Establishment at Aldermaston, Berkshire.

But because plutonium had not yet been produced in Britain, it was planned that the first investigations to be undertaken with this metal would be performed at the Chalk River Project in Canada, where a joint U.K.-Canadian programme on plutonium metallurgy was originated in early 1947. J. MILSTED was selected by the British authorities to remain at Chalk River to devise means for

reductions to metal on a microgram scale in anticipation of the first supply of plutonium that would be extracted from the uranium fuel of the N.R.X. reactor. By means of a vapour reduction technique similar to that employed by FRIED & DAVIDSON (1948) for neptunium, the first clean metal beads were produced on a 20 to 500 microgram scale in June of 1949 (CARTER *et al.*, unpublished). Like the early reductions made at Chicago and at Los Alamos, these first beads were bright and malleable and gave the X-ray diffraction pattern of a face-centred-cubic structure having a lattice parameter of 4.61 Å. Again, because of the presence of impurities, the delta phase was retained. The American experience was duplicated further when, as later reductions yielded metal of higher purity, the samples proved to be hard and brittle and gave the diffraction pattern of alpha plutonium. Work with these very small samples was limited to measurements of room-temperature density, the obtaining of X-ray diffraction patterns, and determinations of melting point. Densities as high as 18.3 g/cm³ were achieved and melting points around 620°C were recorded.

At this stage the development of plutonium metallurgy was divided into two independent efforts, one being a continuation of the work at Chalk River, and the other constituting the initiation of plutonium metallurgical research at Harwell. Studies of plutonium in the form of pure metal were eventually continued at Harwell, but the further investigations at Chalk River were concerned chiefly with plutonium alloys. Through modifications of the method of reducing plutonium trifluoride to metal, O. J. C. RUNNALLS (1956) succeeded in producing a considerable number and variety of alloys and intermetallic compounds. In some cases direct reduction with an excess of the alloying element was found to be an effective means for obtaining a desired alloy composition; in other instances an alloy addition in the form of metal powder was made to a lithium-vapour reduction. RUNNALLS has investigated the crystal structures of a number of intermetallic compounds of plutonium and his results are reported in a later section.

Meanwhile, the first task to be performed in plutonium metallurgy at Harwell became the joint enterprise of R. H. MYERS and H. J. HEDGER, who were metallurgists, and R. HURST, a chemist. The requirement was to set up a facility for larger-scale reductions of plutonium as a preliminary development to the full-scale production line that would be built at Windscale. While this work was in progress, facilities for handling plutonium and for performing a variety of metallurgical experiments with it were devised and installed under the direction of J. G. BALL at A.E.R.E.

Several members of the A.W.R.E. staff, including G. L. HOPKIN and W. B. H. LORD, co-operated with the Harwell metallurgists in commissioning these facilities and were the first to make use of them in some initial experiments on the density and dilatometry of plutonium, the results of which have been published (LORD, 1954). Some experiments on process metallurgy were also conducted by R. WILLOWS and A. KNIGHT. At this stage, the A.W.R.E. effort was transferred to their own laboratories at Aldermaston. The work on plutonium metallurgy at Harwell by BALL and his associates has been continued until the present time with progressive increases in scope and rate of accomplishment.

The publication of papers presented in Moscow, in July of 1955, at the

Session of the Academy of Science of the U.S.S.R. (KONOBEEVSKY, 1955) on the Peaceful Uses of Atomic Energy, gave the Western World its first glimpse of the extent to which research in plutonium physical metallurgy has been advanced within the Union of Soviet Socialist Republics, and established that the Russian work has been both extensive and of good quality, but nothing was indicated regarding where, or within what organizational framework, the work was performed.

In the United States, the United Kingdom and France, additional facilities for research in plutonium physical metallurgy are currently at the stage of being either quite recently completed, under construction, or in design planning. Since early in 1954 a relatively small but compact and versatile facility for research in plutonium metallurgy has been in operation at the Argonne National Laboratory at Lemont, Illinois, but the work done to date has consisted primarily of applying information obtained elsewhere to research having pertinence to reactors, and has not yet led to sufficient new knowledge of a fundamental character to warrant its publication. A much larger laboratory that will provide for plutonium metallurgy research along more basic lines is being planned at the Argonne Laboratory, and a facility for the fabrication of plutonium fuel is now under construction there.

It is intended that plutonium research at Harwell shall be as fundamental in character as possible, and not be directly concerned with development problems relating to specific applications. Already in operation at the Atomic Weapons Research Establishment in Aldermaston is a group of physical metallurgists (including most of those who did the first plutonium experiments at Harwell) who have the responsibility for fundamental research aimed at solving problems connected with both military and certain peaceful applications of plutonium. Also, now under construction at Dounreay, in the north of Scotland, is a laboratory in which the plutonium metallurgy problems of the Dounreay fast-reactor project will be investigated. The French have just reported (ANSELIN *et al.*, 1956) their first preparation of plutonium metal on the gramme scale and they are believed to be well advanced toward completion of facilities providing for an extensive and aggressive programme in this field at the Laboratoires du Fort de Chatillon of the Commissariat à l'énergie atomique at Fontenay-aux-Roses (connected with the Centre d'études nucléaire at Saclay, Seine-et Oise).

2. THE HANDLING OF PLUTONIUM

2.1 General Principles

Before undertaking consideration of the results of experimental work that has been done on the physical metallurgy of plutonium, it is appropriate to discuss some of the precautions that must be observed in handling the metal and its alloys. These precautions are of two general types and are required as a consequence of two important nuclear properties of plutonium: it is a fissionable material and it is an alpha-emitter.

Because it is fissionable, plutonium has a critical mass with respect to neutron multiplication, and in the case of this element the critical mass tends to be appreciably smaller than it is for most other fissionable materials, of the order

of a very few pounds, although the exact value in a given instance depends on many conditions. So far as experimental work on the physical metallurgy of plutonium is concerned, critical mass considerations are not a serious problem because of the small size of samples ordinarily used. But attention does have to be paid to the quantities of metal assembled in storage, and to the size of pieces worked with in the operations of metallurgical fabrication. Plans for any type of plutonium-handling facility must be carefully reviewed by a competent nuclear physicist, who can prescribe rules for sizes of pieces and ways in which metal or alloys must be treated from the criticality standpoint. JETTE (1955b), in a paper on plutonium metal, has discussed briefly the philosophy of dealing with the criticality problem in handling plutonium.

A problem of much more constant concern to all who do research with plutonium is the health hazard (JETTE & COFFINBERRY, 1955; DUNSTER & BENNELICK, 1955) created by its radioactivity. Ordinarily this problem is a consequence of alpha emission only, as plutonium-239 (the isotope it contains in very major proportion) is neither beta active nor strongly gamma active. Also, the alpha particles of plutonium-239 have very little penetrating power, 3.68 cm in air and about 45 microns in body tissue. They do, however, cause severe biological damage to tissue immediately surrounding any point at which a particle of plutonium in any chemical form may be deposited; hence the important consideration is to avoid entry of plutonium into the body. The toxic effect is such that the maximum total body-burden permissible has been set at approximately 0.6 microgram. Although it is estimated that for normal sub-tolerance intakes of plutonium only a tenth of the quantity inhaled is retained, or only one ten-thousandth of the intake by ingestion, the levels set for permissible airborne and surface contamination are so low that it is difficult to envisage the amounts involved. This stringency is a consequence of the way plutonium entering the body settles largely in the bones and is excreted very slowly.

Under some circumstances there may also be a radiation hazard associated with the handling of plutonium or certain plutonium alloys. Depending on the history of the metal, isotopes that strongly emit gamma rays or high-energy X-rays may be present in significant amounts, or if the alpha-emitting plutonium-239 is alloyed with a light element such as beryllium, neutrons may be produced. In these cases, care must be exercised to make sure that the dosages of penetrating radiation received by the body, particularly the hands and fingers, do not exceed the tolerance amounts. Remote manipulation may be required.

The chemical properties of plutonium contribute to the difficulties involved in the problem of its health hazard. It oxidizes rapidly in ordinary air, especially if moisture is present. Although the initial oxide layer is usually adherent and protective, nonadherent oxide forms eventually, quite soon if humidity is high. Because the nonadherent oxide consists of extremely fine particles having remarkable penetrating power, a high level of alpha activity may be built up rapidly in the surrounding atmosphere. Plutonium metal in finely divided form is pyrophoric, and when spontaneous ignition and burning occur, an especially serious spreading of contamination results. Plutonium hydride is also pyrophoric, and certain plutonium alloys appear to be more pyrophoric than the pure metal, particularly after they have undergone partial oxidation. In

the most complete account⁽³⁾ that has yet been written regarding the plutonium health hazard and equipment for handling the metal, KELMAN, WILKINSON, SHUCK, & GOERTZ (1956) have emphasized the greater magnitude of the difficulties involved in working with plutonium in finely divided or other pyrophoric form.

Plutonium-handling practices at the different laboratories differ in detail, but they are all based on similar principles. In general, equipment is housed in glove boxes which are airtight and maintained at a slightly negative pressure, so that any leakage is not into the laboratory. Once a box is made active, it is normally kept at less than atmospheric pressure day and night, and the extracts from such boxes are connected to a suitably filtering extract system. Operations within the boxes may be conducted by remote control, but are more commonly performed through gloveports in the side of the box into which long-sleeved rubber gloves are sealed. Procedures that may involve the formation of fine particles of metal, such as machining, grinding or the operations of powder metallurgy, are preferably performed in an inert atmosphere, which is usually argon or helium of high purity. Low water content is the most important consideration. Operations in which plutonium is heated, such as melting, thermal analysis, etc., may be carried out in an inert atmosphere of adequate purity, but more frequently they are performed in the best vacuum attainable.

In addition to these special methods used in working with plutonium, care is continually exercised to prevent the spread of alpha activity to personnel, or to the surfaces of laboratory furniture and fittings from which it might be picked up by personnel or become airborne. Frequent surveys for surface contamination are made with alpha counters by health-physics monitors. Similarly, to reduce the risk of personal contamination, all operators wear changes of specially provided clothing. Other forms of health-physics monitoring ensure that personnel do not exceed a safe level of exposure to plutonium toxicity on a weekly or longer term basis. These measures include continuous air sampling, urine sampling, and frequent checking at hand and clothing counters. These routines are supplemented at some laboratories by such further checks as "nose-counts" (checking the nostrils for alpha-activity), regular blood counts, chest radiographs and full medical inspections.

2.2 Procedures at Los Alamos

The first work with plutonium in gram-size or larger amounts was done at Los Alamos during the war years when, partly because of ignorance and partly because of the stress of war-time conditions, less elaborate protective measures were exercised with respect to the health hazard than have been in force since then. No known injury to personnel ever resulted, however, and some things were learned regarding what can and cannot safely be done with plutonium that might not otherwise have been discovered until much later. As a consequence of this background of experience, supplemented by additional facts learned since the war-time period, the philosophy of handling plutonium in physical metallurgy research at Los Alamos is somewhat different from that at ANL and at the British laboratories.

⁽³⁾ Shorter discussions of the plutonium health hazard, including rules of procedure for working with plutonium, are given in JETTE & COFFINBERRY (1955), and in DUNSTER & BENNELICK (1955).

Although the Los Alamos gloveboxes are tight in a practical sense, no effort has been made to achieve the consistent tightness that the Argonne and British laboratories find necessary to avoid leakage of air into their inert atmospheres. Because only a few operations at Los Alamos are carried out in an inert atmosphere, experience there has indicated that complete gas-tightness of enclosures is not essential for adequate health protection. It has been found that clean, massive plutonium metal is not corroded by ordinary air nearly so readily as has been believed by some to be the case, so that many operations may be performed safely in gloveboxes containing only laboratory air at slightly less than atmospheric pressure, which ensures that any small leakage moves air into the boxes and not out of them. Even though an inert atmosphere is used in working with finely divided metal or plutonium hydride (both of which are highly pyrophoric), or in performing certain cutting operations (machining, filing, etc.) which produce material that burns spontaneously in air, the objective is not so much to avoid corrosion as simply to ensure that oxygen will be present in too low a concentration to support combustion.

At Los Alamos much reliance is placed on the experience that has been gained since 1943, and on procedures that have been developed as a result of this experience. The personnel who work with plutonium have the greatest respect for its danger, yet they operate with great confidence in the protective measures that have been devised. Whenever any type of operation is to be done that seems to involve a chance of spreading contamination, the plutonium scientist is authorized to call upon the Health Division of the Los Alamos Laboratory to conduct a "special air count." This request sets in motion a series of steps that are less elaborate for familiar and well understood operations, but which are best exemplified by the measures exercised in the case of a new type of operation that is being undertaken for the first time. In this case the steps include (1) discussion of the possible hazards with Health Division personnel, (2) a decision as to what types of protective clothing and respirators or air masks should be worn, (3) the assignment of health-monitoring personnel and equipment to the site of the operation, (4) surveillance of the operation from start to finish by the monitoring personnel and other Health Division people, and (5) special medical checks for possible intake of contamination made on those who performed the operation. The effectiveness of these procedures, employed in combination with routine health checks, has been such that throughout the period of more than twelve years since the end of the war no employee of the Los Alamos Scientific Laboratory has accumulated plutonium within his system in excess of the tolerance body-burden (0.6 microgram).

At the Argonne Laboratory, all of the gloveboxes, whether separate or interconnected, are housed in one laboratory room, at the British establishments, the practice varies according to the nature of the work. In the building at Los Alamos in which research on plutonium physical metallurgy is done, separate rooms are provided for each of the various usual operations of physical metallurgy research. Thus, melting and alloying are done in one room, metallography in another, mechanical fabrication in a third, etc. This arrangement has the advantage that if an overtolerance air count should develop in one of

the rooms, that laboratory can be closed off and work may be continued in the others.

Most of the gloveboxes used at Los Alamos are interconnected into trains, or suites, in such a way that a series of related operations can be performed on materials without taking it out of the enclosures. Fig. 3 shows such a glovebox train in which mechanical working of metal is done. In designing the arrangement of the train, provision is made to keep as many of the equipment units as possible outside the enclosures, so that access to them for servicing will be more convenient. The electric motor shown in the foreground of Fig. 3, and the resistance heating units shown at the left side, are examples of this. Fig. 4 shows a vacuum pump located outside a "furnace housing" that contains two dilatometers.

Plutonium materials are usually introduced into a train of gloveboxes through an airlock at one end of the train. A desirable arrangement of the train is to provide for the "hottest" operations (i.e. those most likely to create and spread plutonium-oxide dust) to be performed in the boxes furthest removed from the airlock, the doors between boxes being kept closed except when material is moved through them. This provision for a contamination gradient along the train from the hottest box at one end to the airlock at the other is very effective in avoiding escape of contamination into the room when plutonium materials (usually contained in sealed plastic jars) are transferred into and out of the boxes through the air-lock. Fig. 5 shows airlocks on both sides of a single glovebox in which weighing, a relatively "cold" operation, is done. JETTE (1955b) has discussed the ways in which equipment of the type shown in the figures is put to use.

It has been mentioned above that plutonium handling practices at Los Alamos vary from one operation to another depending on the character and extent of the hazard involved. The nature of the hazard depends in turn on the form of the plutonium and on the operation that is performed with it. Plutonium metal in massive form is relatively safe to handle in any reasonably dry atmosphere, especially if its surface is polished or generally smooth. Alloys dilute in plutonium are at least as safe and may be made even safer by pickling to dissolve away particles of plutonium intermetallic compound at the surface if these are imbedded in a plutonium-free matrix phase (i.e., one in which there is no solid solubility of plutonium). Intermediate alloy compositions are more tricky. Some intermetallic compounds, such as PuAl_4 , have quite good corrosion resistance and may therefore be handled with less drastic restrictions. But other intermediate phases, like PuBi_2 and Pu_3Pb , may oxidize very rapidly or even be pyrophoric; preferably these alloys should be handled in an inert atmosphere. The dangerous operations are the ones that produce metal in finely divided form or in thin sections, such as machine turnings. As long as the metal or alloy remains massive, has clean smooth surfaces, and is not an alloy composition of the more reactive type, it normally will not oxidize too rapidly to be handled safely for a *short period of time* in a fume hood, or even in the open room, if ventilation is adequate.

The first preparations of new alloy compositions are made at Los Alamos by melting in either vacuum or inert atmosphere, and after being prepared the ingots are under observation in ordinary air inside a tight glovebox long

enough to establish how chemically stable they are. Thus the type of handling they require is known by the time they become available for the further work that is to be done with them.

The possibility of handling plutonium in reasonably dry air instead of (or possibly in preference to) an inert gas seems to be a result of the formation of an oxide film on the surface of the metal or alloy that is adherent (and therefore protective) for a certain length of time. Although nonadherent powdery oxide will form eventually, how soon it does so depends in a sensitive way on the moisture content of the atmosphere, whether air or inert gas.

Evidence obtained at Los Alamos has indicated that if water is present in only trace amounts, the formation of powdery, green, nonadherent PuO_2 begins sooner and progresses more rapidly in atmospheres of helium or argon than it does in air or oxygen having the same water content. Thus oxygen appears to inhibit formation of the nonadherent oxide by promoting formation of an oxide layer that is adherent and protective. Also, it seems to be water, rather than oxygen, that causes plutonium to oxidise in the most undesirable way and at the fastest rate, by formation of the nonadherent PuO_2 dust.

Because of the facts stated above there has been a tendency to believe that plutonium could be handled in the manner practised at Los Alamos only because of the dry climate that prevails in New Mexico. More recent experience in an air-conditioned building has demonstrated, however, that although the normally low humidity characteristic of the southwestern part of the United States is definitely advantageous, the same general plutonium-handling methods can be employed about as safely and almost as conveniently with humidities as high as those ordinarily prescribed for human comfort (i.e. relative humidities in the vicinity of 50%).

Thus microscopic examinations, photomicrography and microhardness testing are done on metallographic specimens in the open laboratory, and the same specimens are merely covered with a piece of transparent tape for X-ray diffractometry. These specimens are mounted in plastic, however, and have only a single highly polished surface exposed—a surface that may have been given its final polishing treatment electrolytically.⁽⁴⁾ The room is well ventilated by air flow at a high rate (about 40 air changes per hour), and the laboratory atmosphere is continuously monitored with an air sampler. The operator wears protective clothing, and unless both the operation and the specimen have been amply demonstrated to be completely safe, the operator wears a respirator. Finally, the work is done rapidly, so that specimens may be returned to their sealed containers before oxidation progresses beyond a slight discoloration of the bright surface of the metal.

It has been found that such diverse operations as electropolishing, the

⁽⁴⁾If the proper electrolyte is used, electropolishing appears to be an especially effective means of forming an oxide film of the protective type. Also if the low-temperature phase transformations of plutonium are eliminated by a suitable alloy addition, "temper colours" may be formed on the metal in about the same manner as they are formed on steel—by heating in air to moderate temperatures. The range of colours is much the same, from straw to blue, and the oxide film on plutonium seems to be protective in about the same way as that formed on steel, i.e. it appears to inhibit formation of nonadherent oxide unless moisture is present in appreciable amount.

evacuation and sealing off of silica capillaries for Debye specimens, the blanking out of sheet metal with a punch press, and the handling of aqueous solutions containing plutonium may safely be performed in fume hoods if the air velocity through the open face of the hood is not less than 100 feet per minute. In any type of metal-cutting operation care must be exercised, however, to avoid the formation and spreading of thin splinters of metal. Ordinary mineral oil can be used quite effectively as a medium in which to catch fine particles, or to hold them, in cleanup operations that are performed either inside or outside of enclosures. "Furnace housings," such as the one shown in Fig. 4, are boxes having their entire front in the form of a hinged door that may be opened to give easy access to the interior, but again only with air being drawn through the opening at not less than 100 feet per minute. These enclosures are used to house operations in which plutonium is heated in vacuum or inert atmosphere (usually within a smaller enclosure called a "vac can") so that very little formation of oxide results.

The atmosphere used in gloveboxes at Los Alamos is in almost all cases ordinary laboratory air kept at slightly less than atmospheric pressure while being continuously extracted at a slow rate. If pyrophoric materials are handled in these boxes, the size of the samples is kept small. On the few occasions when fires have occurred, all the oxide smoke has been caught in the exhaust filters. Inert atmospheres are preferable for the handling of pyrophoric materials, however, and for such operations as machining, the preparation of filings, powder metallurgy work, or any procedure giving rise to plutonium in finely divided form, tight boxes containing an inert atmosphere are mandatory. Thus the arrangements for any given job to be done with plutonium are tailored to meet the specific requirements imposed by the character of the work and the nature of the material being handled. Simplicity and freedom of operation are retained, however, insofar as safety permits.

An important factor in the success of this type of approach to handling plutonium is the matter of housekeeping in general. Not only must all laboratory areas exterior to enclosures be kept meticulously free from any form of plutonium contamination, but the accumulation of contamination inside boxes should be minimized in every possible way. Experience has shown that the difficulty of preventing spread of contamination increases in about geometric proportion as the amount of accumulated oxide, or other form of scrap, increases. For this reason, enclosures at Los Alamos are kept as small as possible and have the simplest possible structural features within them in order that cleanup operations may be performed with maximum ease.

A final word of explanation should be given regarding the extent to which these plutonium-handling methods are used at Los Alamos. In the form described above, they are employed only in research on the physical metallurgy of plutonium. The personnel who use them are primarily staff scientists who have a clear understanding of the behaviour to be expected of plutonium and a proper respect for the risks that attend its behaviour under various circumstances. Their training in laboratory arts and their skill in laboratory manipulations are important factors in making these methods adequately safe. The few technicians who use these methods must possess similar attributes of judgment and dexterity, which in their case have to be acquired through experience and through guidance received from their associates.

For production-type operations at Los Alamos a considerably different philosophy is followed in handling plutonium. Although the simplicity, freedom and flexibility made possible by not having to work entirely within tight boxes are highly advantageous in experimental work, they are less important for procedures that are routine and repetitive. With operations of the latter type methods can usually be developed for performing them remotely, but manipulation by remote means may not necessarily be the best answer in all cases. At Los Alamos it has been found that remote handling devices used in conjunction with the manual operating features afforded by gloves in gloveports constitute the simplest, safest and most effective type of design to be employed in developing the facilities incorporated into a plutonium production line. All production operations are performed in tight boxes, but the atmosphere inside the enclosures is more frequently air than it is inert gas, the latter always being used where machining is done.

2.3 Procedures at other Laboratories

At the Argonne National Laboratory and at the British establishments very similar practices are followed with respect to the enclosing of equipment and the control of atmospheres within the enclosures. Rigid specifications for the construction of gloveboxes are laid down, aiming at complete tightness. The objective is always to avoid exposure of personnel to plutonium in any concentration, however slight. Purified inert atmospheres are provided for all operations, helium at ANL, and argon at A.W.R.E. and, with a few exceptions, at A.E.R.E. Vacuum systems are housed in special enclosures sealed from the laboratory. Both American and British laboratories have evolved similar gloveports and transfer ports of a snout type onto which beaded gloves or vinyl bags are sealed by clamping the open ends into grooves. Objects are transferred from one box to another by sealing them diathermally into sections of the vinyl bags attached to each box.

The principal difference between the Argonne and British practices arises in the arrangement of the boxes used for research. At ANL the boxes are all interconnected into a single closed system as shown in Fig. 6, so that a specimen once introduced into this train of boxes can be taken anywhere within the boxes without removal into the laboratory. KELMAN, WILKINSON, SHUCK & GOERTZ (1956) have described the design, construction and operation of a plutonium research facility that has been functioning at ANL since 1954. The design of a fabrication facility for plutonium fuel elements is also described.

The ANL gloveboxes are designed with special gasket-flanges for windows and interbox connections which meet a helium-sensitive mass spectrometer test. Groups of boxes can be isolated so that leaks in one part of the system need not cause a complete shutdown. Auxiliary equipment, such as vacuum systems, which may become contaminated, are housed in subsidiary gloveboxes or hood enclosures, made to a less rigorous specification, to make possible maintenance operations without spread of activity. The tendency is to keep the box size smaller than elsewhere because easy glovehand access to all parts of the box is considered of great importance; this also gives greater rigidity of box-construction and reduces the strain on the purification system used for the inert gas atmosphere, but it is admitted that storage space is seriously

restricted as a consequence. It has proved possible to use combinations of three standard modules for 85% of the enclosure requirements of their fuel fabrication facility.

At both A.W.R.E. (LORD, to be published) and A.E.R.E., glovebox design has developed along similar lines. Initially equipment was set up in cells backing on to a frogsuit room or corridor from which access can be obtained by removable panels. In these, the equipment is normally operated from the front face only, through gloves let into perspex windows. The frogsuit area is normally entered through a series of airlocks by operators wearing heavy rubber suits with hose connections for a fresh air supply. More recently, at A.E.R.E. particularly, advantage has been taken of the ease with which samples can be transferred between any two boxes by using vinyl bags, to have completely mobile freestanding gloveboxes generally receiving their supplies of power, gases, etc. from overhead trunking through quickly detachable couplings. These boxes can be operated through gloveports in any of the four faces and can be moved out of the way when not in use. With such a system, it is more economical of space and effort and in some ways more safe to have a large number of boxes in the same open area. However, some suites, for operations which are more hazardous, are housed in a smaller laboratory which could be sealed in an emergency to limit the spread of activity.

These boxes are also used in conjunction with frog-suiting facilities which allow access to the contaminated interiors of gloveboxes in order to clean them, or to work on the equipment they contain. In order to avoid contamination of the exteriors of the boxes, one side is clamped against a covered aperture in the wall of the frog suit room, and after removal of the cover, together with the side of the box, the operators have access to the interior of the box without its having to be brought into the frogsuit room. Fig. 7 shows a typical Harwell glovebox in the laboratory area, and Fig. 8 shows a similar box connected to the frogsuit area.

The detailed design of the box is dependent on the equipment it contains, but there are usually two compartments; the upper contains the experimental equipment and is argon filled, the lower contains auxiliary equipment including vacuum systems and is nitrogen filled to minimize fire risks from electrical causes.

Where boxes are intended to operate as a suite, they may have interconnecting ports through which specimens can be transferred directly. The vinyl sleeve joining the two ports is heat sealed and severed along the seal if it is necessary to separate the boxes comprising the suite.

Whilst the freestanding dry boxes have been developed as the principal technique at A.E.R.E., A.W.R.E. have developed a different modification known as "island cells," as well as using very similar freestanding boxes. These island cells are arranged as branches from a frog suit facility, each containing two or three pieces of equipment side by side, so that access can be obtained through gloveports from two opposite faces and from the third face of the end compartment of the island cell. This design has advantages for heavy equipment, where the loading would be too great for mobile glove boxes. With this arrangement, frogsuit access may involve disturbing other pieces of equipment in the same island cell.

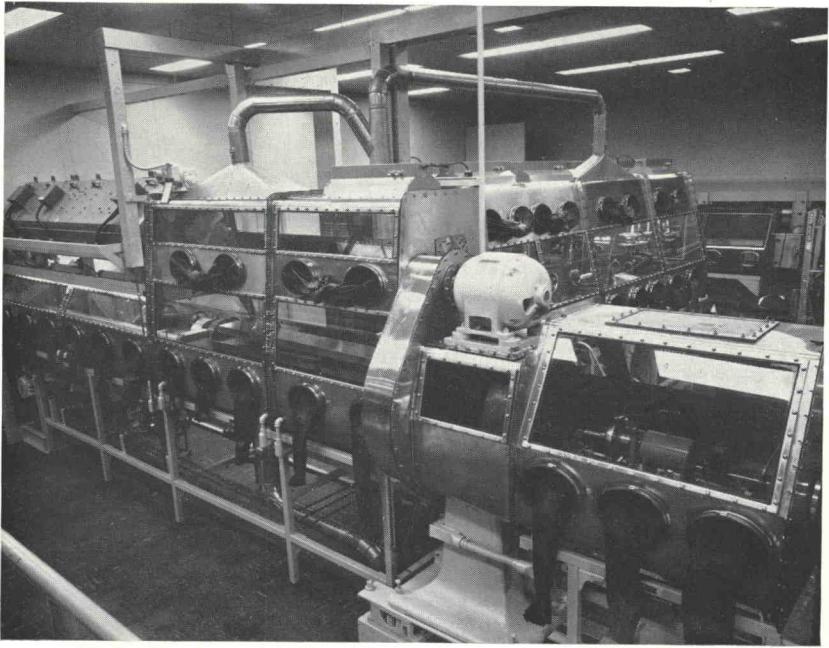


Fig. 3. Los Alamos gloveboxes for mechanical working.

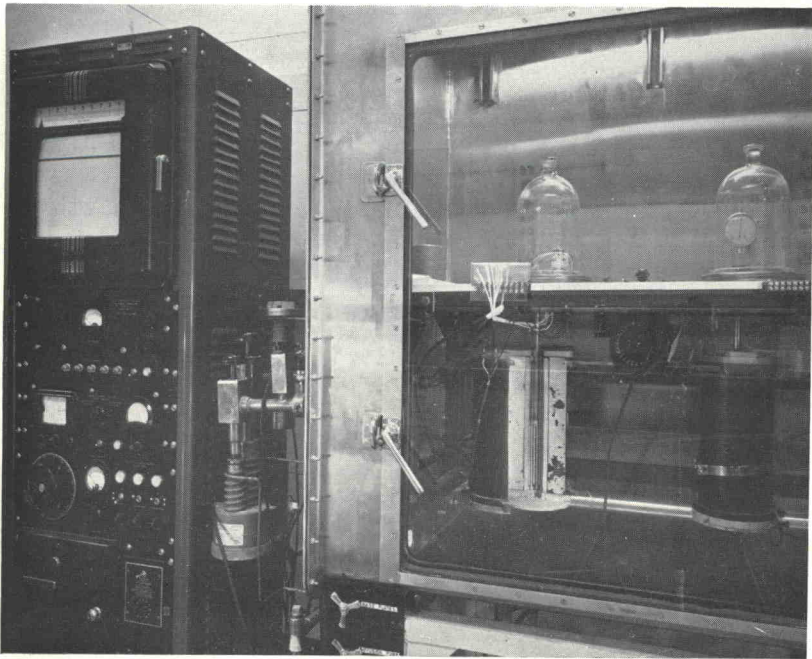


Fig. 4. Los Alamos housing for vacuum furnaces with external vacuum pumps visible.

To face page 368

stated that "despite its fusibility, the handling of molten plutonium is very difficult because of its extreme reactivity. No ordinary refractory was found to be satisfactory for crucibles in which to melt and cast very small pieces of the metal. . . . As larger amounts of the metal were melted at one time with relatively smaller areas of contact with the crucible, the refractory problem became somewhat simpler."

It is now known that a wide variety of refractory materials may be used for the melting and casting of plutonium and its alloys, although because of the strong affinity of plutonium for oxygen, carbon, nitrogen, etc., only the more stable compounds of the oxide, carbide, nitride, boride and silicide types constitute suitable container materials for the molten metal. Graphite may be used for moulds in which to cast plutonium experimentally. The applicability of graphite for crucibles in which to do melting is preferably limited to dilute alloys unless it is coated with some other refractory material, but it may be used where a slight carbon pickup is permissible. Certain sulphides and fluorides have been found useful as refractory materials, but they are subject to limitations imposed by their own properties, such as a low melting temperature. Some of the refractory metals have shown good promise as container materials for plutonium in liquid form. In reporting their work on the vapour pressure of liquid plutonium, PHIPPS, SEARS, SEIFERT & SIMPSON (1955) have indicated that tantalum does not have a "significant" solubility in liquid plutonium under the condition of their experiments, heating to about 1500°C. However, their observations were made on tantalum and molten plutonium in the presence of an oxide phase, which may have acted as a solution barrier.

Finally, it should be noted that many of the refractory materials which appear to have good compatibility with the pure metal may be strongly attacked by certain plutonium alloys when the latter are melted in them.

3. THE PHYSICAL PROPERTIES OF PLUTONIUM METAL

3.1

As shown in Fig. 2, the six allotropic modifications of plutonium have been designated, in order of increasing temperature of stability, alpha, beta, gamma, delta, delta-prime⁽⁵⁾ and epsilon. Fig. 2 also shows that the temperatures of the corresponding five phase-transitions on heating, are quite roughly 120°, 220°, 320°, 450° and 475°C.

3.2 *Metal Purity*

It is apparent from the conflicting and mystifying results that were encountered in all of the earlier studies of plutonium, and from the long period during which the delta-prime phase escaped detection, that the transformation behaviour of this metal is strongly influenced by the presence of impurities in amounts which may be quite small. There has been a tendency on the part of some who have studied plutonium to attribute to impurities many of its more unusual properties, as well as the variability of results obtained in experiments performed with the metal. It remains to be determined, however, to just what

⁽⁵⁾ See footnote on page 357.

extent purity is significant in each of these respects. But because plutonium is so very unusual in its behaviour, particular importance must be attached to ensuring that the purity of all samples on which physical-property measurements are made shall be of the highest purity attainable. Table 1 shows some typical values for the total plutonium content of samples that have been studied at Los Alamos.

The purity of plutonium which has been used in Britain for the published investigation is roughly comparable to the best material that was available at Los Alamos before 1953 (see, for example, J. K. DAWSON, 1954). In metal of this "inferior" quality, neither the American nor the British workers have succeeded in obtaining the X-ray diffraction pattern of the delta-prime phase; the Soviet workers have reported that the heat effect (Fig. 11), accompanying the delta/delta-prime (delta-to-eta) transformation is "usually hardly noticeable and it vanishes on slight additions of a second component." ELLINGER (at Los Alamos) has been able to obtain the delta-prime pattern only if the metal was as pure as the two best samples listed in Table 1, and it was material of this

Table 1. Typical Purities of Plutonium Samples Studied at Los Alamos

	Total plutonium	
	Weight per cent	Atomic per cent
Metal available before 1953	99.87	99.01
High purity sample No. 1	99.97	99.82
High purity sample No. 2	99.95	99.75

quality that gave the dilatometer curve (Fig. 2) which first revealed the existence of a delta-prime phase to the Los Alamos investigators. It is interesting that the British workers, with their less pure metal, obtained a clear indication of delta-prime in both dilatometer (W. B. H. LORD, unpublished work, 1951-52; J. A. LEE, unpublished work) and thermal-analysis traces (J. NORTH, private communication) before it was noted at Los Alamos. Investigation of these anomalies by X-rays yield only delta, (delta + epsilon), and epsilon diffraction patterns in the appropriate temperature range so that the British workers were unable to understand the significance of the effects.

It appears that small additions of a second element will in general cause all evidence for the existence of delta-prime plutonium to vanish, but the Russians have indicated in their plutonium-vanadium phase diagram (Fig. 17), that throughout this system delta-prime persists in a two-phase field with pure vanadium. Also, R. O. ELLIOTT (private communication, Los Alamos) has quite recently found that a plutonium alloy containing 10 atomic per cent titanium gave only the delta-prime pattern on a film taken in the delta-prime temperature range with a high-temperature X-ray camera.

3.3 Transformation Temperatures

The transformation temperatures of the plutonium allotropes have been determined by thermal analysis and dilatometry, and by measurements of electrical resistivity and magnetic susceptibility, but only thermal analysis and dilatometric results have been reported in every case for work done in the U.S., U.K. and U.S.S.R. Representative results, together with data for the melting temperature, are compared in Table 2. The Los Alamos values have been

Table 2. Phase Transformation Temperatures of Plutonium on Heating
(in °C)

Transition	JETTE (1955a, b)		BALL <i>et al.</i> (1954)		KONOBEEVSKY (1955)
	Dilatometry	Thermal analysis	Dilatometry	Thermal analysis	Dilatometry and thermal analysis
α to β	122 ± 2	122	135	125 ^(a)	119
β to γ	206 ± 3	203	225	235	218
γ to δ	319 ± 5	317	315	325	310
δ to δ'	451 ± 4	453	450 ^(b)	450 ^(b)	450
δ' to ϵ	480 ± 7	478	480	475	472
ϵ to liquid		639.5 ± 2		640	640

^(a) Revised value.

^(b) Evidence for the delta/delta-prime transition was present on BALL's original curves (both dilatometric and thermal analysis) but its significance was not understood, (see text, page 372).

reported previously in two different papers⁽⁶⁾ by E. R. JETTE (1955a, b), the Harwell results by J. G. BALL and associates (1954), and the Soviet values are taken from the Moscow report of S. T. KONOBEEVSKY (1955). His values are presumably representative of Russian results obtained by both thermal-analysis and dilatometric methods. The Los Alamos figures given for dilatometry are averages for seven runs, but the thermal analysis results (except melting temperature) represent only two runs. All of the Los Alamos specimens were metal of the high-purity type (Table 1). Other values are given in SMITH (1954) and LORD (1954).

These transformation temperatures are reported only for the transitions as they have been observed to occur on heating at a slow rate. As indicated by the shape of the cooling trace in Fig. 1, appreciable hysteresis effects occur on cooling and render meaningless any attempt to take account of cooling behaviour in fixing the transition temperatures. Recent work done at Los Alamos has indicated that the equilibrium temperatures for the phase transitions differ by not more than a few degrees from the arrest temperatures observed on heating.⁽⁷⁾

⁽⁶⁾ In the first of his papers JETTE reported Los Alamos data as of July, 1954. In the second paper revisions were made to take account of new results obtained previous to May, 1955.

⁽⁷⁾ This has not yet been established for the α/β transformation.

The high-temperature X-ray work of ZACHARIASEN and ELLINGER (1955) on the gamma phase, and of ELLINGER (1956) on the delta, delta-prime and epsilon phases has indicated good agreement between the stability ranges observed with the high-temperature camera and JETTE's transformation temperatures given in Table 2, except in the range of the transitions from delta through delta-prime to epsilon. ELLINGER has found that in his Debye specimens transformation of delta to epsilon (rather than delta-prime) begins at 450°C, and delta-prime does not appear below about 465°C. At this temperature the metal transforms largely to delta-prime, but small amounts of both delta and epsilon coexist with the delta-prime phase up to about 485°C, where transformation to epsilon is completed. This alloy-like behaviour he attributes to the presence of very small amounts of impurity (possibly picked up from the silica capillary of his Debye specimen) even though his samples are the Los Alamos high-purity metal.

3.4 Crystal Structures

The crystal structures of the delta and epsilon phases of plutonium were reported in the classified literature by SCHNETTLER and JETTE during the war years, ZACHARIASEN and ELLINGER (1955) have since established the structure of the gamma phase, and ELLINGER⁽⁸⁾ has more recently determined the atomic

Table 3. Crystal Structure Data for the Plutonium Phases

Phase	Crystal lattice	Unit cell dimensions, <i>A</i>	Number of atoms in unit cell	Calculated density (g/cm ³)
Alpha	Monoclinic ^(a)	At 21°C $a = 6.1835 \pm 0.0005$ $b = 4.8244 \pm 0.0005$ $c = 10.973 \pm 0.001$ $\beta = 101.81^\circ \pm 0.02^\circ$	16	19.816 $\pm$ 0.006
Beta	Crystal structure unknown			
Gamma	Face-centred orthorhombic ^(b)	At 235°C: $a = 3.1587 \pm 0.0004$ $b = 5.7682 \pm 0.0004$ $c = 10.162 \pm 0.002$	8	17.14 $\pm$ 0.01
Delta	Face-centred cubic ^{(c)(d)(e)}	At 320°C: $a = 4.6371 \pm 0.0004$	4	15.92
Delta-prime	Body-centred tetragonal ^{(c)(d)(e)}	At 465°C: $a = 3.327 \pm 0.003$ $c = 4.482 \pm 0.007$	2	16.00
Epsilon	Body-centred cubic ^{(c)(d)(e)}	At 490°C: $a = 3.6361 \pm 0.0004$	2	16.51

(a, b, c, d, e) See Table 4.

(8) Reported in a paper submitted for publication to the *Journal of Metals*.

arrangement in delta-prime. The results of these determinations are given in Table 3. The crystal structure of the beta phase has not been solved, and the structure determination for alpha has not yet been completed. But in a brilliant achievement that could only have been realized by one possessing his remarkable skill for interpreting powder patterns, ZACHARIASEN (private communication) has recently succeeded in indexing the Debye pattern of alpha plutonium. The unit cell that he has found is monoclinic and contains 16 atoms; the calculated density at room temperature is $19.816 \pm 0.006 \text{ g/cm}^3$. The working out of a complete solution for the atomic arrangement is now in progress, and so far as the present authors are aware, this will be the only instance of a monoclinic metallic structure having been solved from powder data alone.⁽⁹⁾

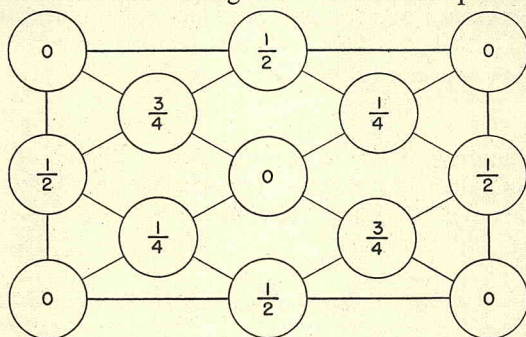


Fig. 10. Atomic positions in the gamma-plutonium structure projected onto the (001) face.

The crystal structure of the gamma phase is interesting; the plutonium atoms have a co-ordination number of 10 and yet are quite closely packed. The structure approaches triangular close packing in layers perpendicular to the *c*-axis, with the stacking of these layers in the direction of the *c*-axis somewhat less close than is the case for hexagonal close packing. These relationships are illustrated in Fig. 9. Fig. 10 shows the atomic positions projected onto a (001) face. Expressed as fractional parts of the unit-cell dimensions, the co-ordinates of these atomic positions are the same as those in the diamond structure. The space group is Fddd.

It has been mentioned in the introductory section of this chapter that the body-centred tetragonal structure of the delta-prime phase may alternatively be regarded as face-centred tetragonal. If this is done, the unit-cell dimensions at 465°C become $a = 4.704 \text{ \AA}$, $c = 4.482 \text{ \AA}$, $c/a = 0.953$. A comparison of these values with $a = 4.6323$, the lattice constant of the face-centred-cubic delta phase at 440°C , indicates the close structural relationship of delta-prime to delta.

3.5 Coefficients of Expansion

ZACHARIASEN & ELLINGER (1955) have determined the coefficients of thermal expansion of gamma plutonium with a high-temperature X-ray camera, and

⁽⁹⁾ Our attention has been drawn to a study of triclinic mineral kaolinite reported by G. W. BRINDLEY and K. ROBINSON in the *Journal of the Mineralogical Society* (1946) 27, 194, 242. This study was apparently assisted by predicted structural relationships.

ELLINGER has performed similar measurements on the delta, delta-prime and epsilon phases. The results of these determinations are shown in Table 4,

Table 4. Coefficients of Thermal Expansion of the Plutonium Phases

Phase	Temperature range (°C)	Coefficient of linear expansion ($t = ^\circ\text{C}$)	Ref.
Alpha	-186 to 100	$10^6\bar{\alpha} = [(46.85 \pm 0.05) + (0.0559 \pm 0.0004)t]/^\circ\text{C}$	(f)
Beta	133 to 197	$10^6\bar{\alpha} = (33.86 \pm 0.11)/^\circ\text{C}$	(f)
Gamma	210 to 310	$10^6\bar{\alpha}_a = (-19.7 \pm 1.0)/^\circ\text{C}$ $10^6\bar{\alpha}_b = (39.5 \pm 0.6)/^\circ\text{C}$ $10^6\bar{\alpha}_c = (84.3 \pm 1.6)/^\circ\text{C}$ $10^6\bar{\alpha}_p = (34.7 \pm 0.7)/^\circ\text{C}$	(b)
Delta	320 to 440	$10^6\alpha = (-8.6 \pm 0.3)/^\circ\text{C}$	(e)
Delta-prime	465 to 485	$10^6\bar{\alpha}_a = (305 \pm 35)/^\circ\text{C}$ $10^6\bar{\alpha}_c = (-659 \pm 67)/^\circ\text{C}$ $10^6\bar{\alpha}_p = (-16 \pm 28)/^\circ\text{C}$	(e)
Epsilon	490 to 550	$10^6\bar{\alpha} = (36.5 \pm 1.1)/^\circ\text{C}$	(e)
Liquid	at 665	Volume coefficient = $(50 \pm 25) \times 10^{-6}/^\circ\text{C}$	(g)

(a) W. H. ZACHARIASEN, private communication.

(b) W. H. ZACHARIASEN & F. H. ELLINGER, *Acta Cryst.* **8** (7), 431 (1955).

(c) E. R. JETTE, *J. Chem. Phys.* **23**(2), 365-368 (Feb. 1955).

(d) E. R. JETTE, Symp. on Nuclear Metallurgy, Inst. of Metals Div. Report Series No. 1, A.I.M.M.E., p. 29 (1955).

(e) F. H. ELLINGER, Paper submitted for publication in *J. Metals*.

(f) E. M. CRAMER, L. L. HAWES, & F. W. SCHONFELD, unpublished data.

(g) A. A. COMSTOCK and R. B. GIBNEY, USAEC report LA. 1348.

together with expressions for the thermal expansion behaviour of the alpha and beta phases as measured in a linear dilatometer. The dilatometer specimens were polycrystalline material believed to be free from preferred orientation, so that the values obtained should be averages for randomly oriented grains of the anisotropic expansion behaviours that it may be assumed are characteristic of single crystals of alpha and beta. Thin-walled tubular specimens were used to minimize thermal gradients within the specimens, which were of high purity metal.

The temperature ranges listed in Table 4 are the ranges in which the experimental measurements of expansion were made. The coefficients tabulated for all except the alpha phase are average figures for the temperature ranges indicated. Values designated $\bar{\alpha}_p$ are for polycrystalline material having randomly oriented grains. They have been calculated from the single-crystal coefficients;

thus for gamma $\bar{\alpha}_p$ $(\bar{\alpha}_a + \bar{\alpha}_b + \bar{\alpha}_c)/3$, and for delta-prime, $\bar{\alpha}_p = (2\bar{\alpha}_a + \bar{\alpha}_c)/3$. The volume coefficient for the thermal expansion of liquid plutonium at 665°C was measured by A. A. COMSTOCK and R. B. GIBNEY (1952) using a radiographic method.

Considerable interest has attached to the negative coefficients of expansion of the pure metal in the face-centred cubic delta-phase and in the tetragonal delta-prime phase. This behaviour is unique among pure metals having isotropic crystal structures and in the early days was attributed to the possible

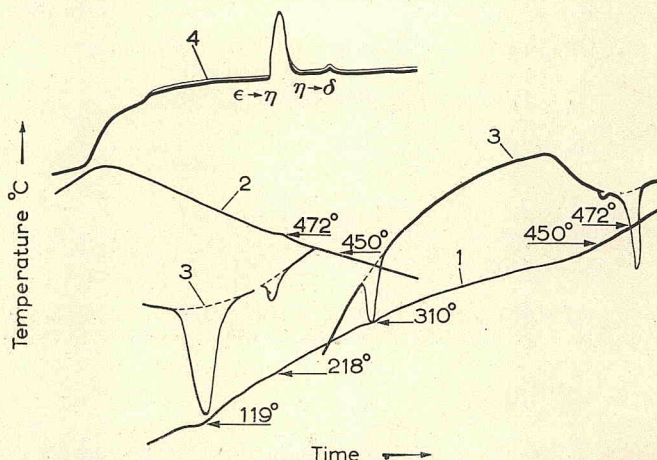


Fig. 11. Thermal analysis curve for plutonium made with a 48 milligram sample. (U.S.S.R.).

- (1) Record of an ordinary thermo-couple during heating.
 - (2) Record of an ordinary thermo-couple during cooling.
 - (3) and (4) Records of a differential thermo-couple.
- (Abscissa—time; ordinate—temperature °C.).

influence of impurities. This viewpoint is rendered highly improbable by virtue of the fact that the use of the purest material has fully confirmed the negative coefficient, especially in the face-centred-cubic structure. The careful crystallographic measurements of ELLINGER has also strengthened the case for a negative coefficient of expansion of delta-prime, although the nonequilibrium structures reported by him must leave some uncertainty as to the validity of the figures quoted.

Attempts by both American and British workers to understand this effect have followed two lines of reasoning. On the one hand, some factor has been sought which might suitably affect the form of the curve of potential energy as a function of the distance between atomic centres. Alternatively, factors which cause a diminution of the electronic or Fermi energy with increase in temperature have been proposed. Attempts to derive a potential energy relationship with a suitable asymmetry about the point of minimum energy have not seemed promising.

Two ways have been proposed in which a suitable temperature dependence of the Fermi energy may result, however. In an entirely qualitative manner it

has been suggested that a continuous change of electrons from essentially 6d to 5f states would result in the appropriate kind of change in interatomic spacing. A further development has been to imagine atoms of two electronic structures tending to exist simultaneously in proportions which vary with temperature and to relate this to the formation of the tetragonal delta-prime structure, which is reminiscent of the ordered AuCu phase. Although the interatomic distances in the delta, delta-prime and epsilon phases support this approach, it is subject to criticism on at least two counts. Firstly, the entropy change from delta to delta-prime would appear to be in the wrong direction for a rise in temperature, secondly, it is difficult to understand why atoms of the same metal should order on crystallographically equivalent sites.

More recently, VARLEY⁽¹⁰⁾ at A.E.R.E. has treated theoretically the factors controlling the thermal expansion, and by introducing certain simplifying assumptions has shown that a negative coefficient of volume expansion is possible in a system in which the potential energy relationships and electronic configurations remain unchanged. He has shown that if the Fermi energy of the electrons has a value for which the density of states of the electrons increases sufficiently sharply with energy, this condition may arise, particularly if it is associated with the existence of a large number of partially filled, overlapping electron bands. A high electronic specific heat would be associated with such a system.

He proposes that suitable alloying should eliminate the negative coefficient of delta plutonium, or conversely, that other critical compositions of alloys of the heavy elements may show low, or negative, expansion coefficients. It seems possible that similar theoretical treatments may explain on such a basis some of the other anomalous properties of the plutonium phases.

It is, however, tempting to seek a common explanation for three features which appear at first sight as though they might be related. These are firstly, the negative coefficient of expansion, already considered; secondly, the reduction in volume on transforming from the "close-packed" face-centred-cubic delta structure through tetragonal delta-prime structure to the body-centred-cubic epsilon structure; thirdly, the difference that has been observed in the volume changes and expansion coefficients on going through the delta and delta-prime phases on heating and cooling. VARLEY's treatment would appear to be only relevant to the first topic, whereas a treatment on the basis of changing electronic configuration may also explain the second feature.

The differences observed in the volume changes and expansion coefficients on heating and cooling may well be a totally distinct phenomenon, and they will be discussed further in connection with the cycling behaviour of plutonium.

At both Harwell and Los Alamos thermal expansion coefficients determined by the X-ray method are regarded as having greater validity than values indicated by dilatometry. Among the reasons for this is the poorer reproducibility of the dilatometric results, together with the failure of the dilatometer specimens to return to their original shape, dimensions and density after a heating and cooling cycle. It is of interest, however, to compare values yielded by the two methods. Typical Los Alamos dilatometric values for alpha and beta, together

⁽¹⁰⁾ Paper submitted for publication.

All these observations suggest that there is a structure-sensitive phenomenon involved which is additional to and possibly quite distinct in origin from, the negative expansion coefficients of delta and delta-prime shown by crystallographic measurements. An explanation⁽¹¹⁾ which appears to the authors to be consistent with these observations is put forward as a basis for discussion.

It is proposed that all dilatometer specimens as cast, and after going through the transformations on cooling to room temperature, contain micro-voids, as well as retained phases which further decrease their density. The micro-voids apparently are established chiefly in the gamma-to-beta transformation on cooling, this being the first transformation on cooling between two complex lattices. On reheating the micro-voids may be enlarged by the gamma-to-delta transformation, since the dilatometric expansion seems to be generally greater than would be expected from the crystallographic measurements. At the delta—delta-prime—epsilon changes, relatively simple lattices are involved which may favour the elimination of microvoids, further assisted by “sintering” which might be expected at the relatively high temperatures involved. Some indication of this is found in dilatometer curves, since the slope on first heating in the epsilon phase is much lower than the slope on cooling. However the cooling slope is comparable with the X-ray expansion coefficient and is retraced on repeatedly cycling through the delta-epsilon change on both heating and cooling.

If the voids are substantially eliminated in the epsilon phase, it is then understandable that cooling from the epsilon phase follows reversibly a trace which lies near the crystallographic values until the gamma-to-beta phase change is involved.

Consistently with these ideas, the expansion behaviour on heating varies markedly from one sample to another and for different runs with the same specimen, which would be expected as a consequence of variations in grain structure and of impurity effects; the cooling behaviour is more uniform, although still affected by the persistent surface deformation effects alluded to earlier.

The true contraction of the delta-phase on heating may help the tendency of the microvoids opened up by the gamma-to-delta transformation to heal, thus apparently increasing the negative coefficient of expansion.

3.7 Density Measurements and Volume Changes

In view of the effects on density of passage through the transformations which have just been discussed, a detailed comparison of all the published values for the densities of the various phases in plutonium does not seem justified. However, the most recently reported Los Alamos results are tabulated in Table 6 together with Harwell values deduced from dilatometric measurements on specimens of known initial density, so that some comparison can be made. The most recent value for the beta density reported from Los Alamos differs from the previous value of 17.65 (JETTE, 1955a) because a revised value for the expansion coefficient has been used to correct to 150°C the result obtained by SCHNETTLER in an oil dilatometer.

⁽¹¹⁾ Discussions with J. G. BALL, J. A. L. ROBERTSON and J. A. LEE have led to an essentially similar concept being put forward previously in a British classified report.

The dilatometric values are seen to be generally lower than the X-ray values, where these are known. This may be partially attributed to the retention of high temperature phases and, if the ideas mentioned previously are correct, to the microvoids formed by the lower temperature transformations. Closer

Table 6. Comparison of Density Measurements (g/cc)

	Los Alamos X-ray data ^(m)	Harwell dilatometric data ^(h)
α	19.737 ⁽ⁱ⁾ (25°C) 19.816	As cast density 19.4
β	17.77 ^(j) (150°C)	17.07-17.46
γ	17.14 (235°C)	16.64-16.78
δ	15.92 (320°C)	15.52-15.69
δ'	16.01 (477°C)	15.82-15.87
ϵ	16.48 (510°C)	16.13-16.46 ^(k)
liquid	16.50 $\pm$ 0.08 ^(e) (665°C)	—

^(h) J. A. LEE, unpublished work.

⁽ⁱ⁾ Measured on specimen pressed at 50,000 psi at 300°C and cooled under pressure.

^(j) Measured by an oil volume dilatometer.

^(k) Value on initial cooling cycle.

^(l) Measured by radiography of a meniscus.

^(m) References are given in Tables 3 and 4.

agreement between X-ray and dilatometric density values is found for delta-prime (on cooling) and epsilon than in the other phases, consistent with the removal of these defects at the highest temperatures, as already suggested.

The volume changes at each phase transition have been estimated by JETTE (1955a, b), mainly from X-ray data, and by J. A. LEE (unpublished) from his

Table 7. Comparison of Volume Changes $\frac{(V_1 - V_2)}{V_1} \times 100$

	JETTE (1955a, b)	LEE (unpublished)
$\alpha-\beta$	8.9 (11.03)*	8.30 to 8.95
$\beta-\gamma$	2.4 (2.77)*	2.30 to 2.45
$\gamma-\delta'$	6.8	4.4 to 7.8
$\delta-\delta'$	-0.1	-0.45 to -0.96
$\delta'-\epsilon$	-3.0	-1.72 to -3.71 heating +1.72 to +1.81 cooling

* The figures in brackets are recalculated from more recent American data than that reported by JETTE.

dilatometric measurements. Table 7 summarizes these values, with revised figures (calculated by the authors) for the alpha-to-beta and beta-to-gamma volume changes added in brackets. JETTE's values were based on SCHNETTLER's dilatometric work already mentioned, coupled with the X-ray value for γ . The revised values are based upon the crystallographic density for alpha, the most recent values of the coefficients of expansion in the alpha and beta phases, the quoted beta density, and the X-ray density of the gamma phase.

It is to be noted that the alpha-to-beta and beta-to-gamma volume changes observed dilatometrically are, severally or together, appreciably lower than those deduced from the X-ray studies. This is consistent with JETTE's remark (1955a) that X-ray diffraction will almost always show some beta phase (retained in α) unless special precautions are taken. The diffraction pattern for gamma has not been reported but this phase may also be present in appreciable amounts in a strained condition without detection. It is also a notable feature of the cycling experiments, mentioned earlier, that the progressive decrease in density room temperature after successive cycles has no consistent effect on the magnitude of the alpha-to-beta, or other, volume changes. This is strong evidence for a progressive development of internal flaws or voids on cycling, rather than progressive retention of high temperature phases.

The remarkable variation in the gamma-to-delta volume change, in some cases larger than the theoretical value, emphasises the anomalous character of this transformation. The value for the delta-to-delta-prime transition are in close agreement considering the uncertainty attaching to the detection of the delta-prime range. The low dilatometric values for the delta-to-epsilon volume change, on cooling especially, seem difficult to understand in view of the reproducibility of the dilatometric curve on cooling. This suggests that the explanation of the cycling results which has been given may not be complete.⁽¹²⁾

3.8 Other Physical Properties

Among these mechanical properties that are conventionally of interest to metallurgists, the only declassifiable information available to the authors relates to the elastic modulus of the α -phase of plutonium. This has been determined at A.W.R.E., Aldermaston (W. B. H. LORD, private communication, by derivation from tensile stress-strain curves, as 8.2×10^{11} dynes/cm² (11.9×10^6 lb./in.²). A dynamic method was used at A.E.R.E., Harwell (J. A. LEE & N. H. HANCOCK, private communication), which gave a value of 8.6×10^{11} dynes/cm² (12.5×10^6 lb./in.²). These results are in reasonable agreement, when one considers the latitude possible in the measurement of elastic modulus from stress-strain curves.

F. W. SCHONFELD & W. C. SPINDLER (unpublished data, 1947) in compression experiments at Los Alamos found the elastic modulus of alpha plutonium to lie in the range of 13 to 16×10^6 lb/in.² SCHONFELD (private communication, 1955) in later tensile tests narrowed this range to 14.0 to 15.5×10^6 lb/in.²

H. L. LAQUER (unpublished data, Los Alamos, 1949-53) studied 17 samples of the alpha phase by sound-velocity methods, using both the resonance and pulse techniques. His results were very sensitive to variations in the densities of his specimens, and varied in such a way as to suggest the existence of some type of inhomogeneity or discontinuity within specimens of low density.

This is pertinent to the deductions made by the authors regarding the expansion behaviour of plutonium on thermal cycling, as also are two further observations made by LAQUER when using the resonance technique, namely, (1) that specimens of alpha plutonium prepared by extrusion in the gamma temperature range behaved as though they contained fewer and/or smaller microvoids than the cast metal, and (2) that specimens composed of delta

⁽¹²⁾ E.g. the effects of possible preferred orientations have not been considered.

plutonium, stabilized against transformation to lower-temperature forms, behaved as though almost no discontinuities existed within them. Finally, specimens of high-density alpha phase, formed by pressing the plutonium at 50,000 lb/in.² and 300°C, and cooling to room temperature under load, when measured by the pulse technique gave results which indicated that microvoids had been removed by the hot-pressing. These hot-pressed, high-density specimens studied by LAQUER being cylinders 0.75 in. in diameter and 1.0 in. long, could be investigated by the pulse technique only. In Table 8 are listed values determined for the elastic properties of a "high-purity" metal specimen, together with sound-velocity data from which they are derived. The density of this specimen was 19.722 ± 0.005 g/cm³ at 30°C (19.737 g/cm³ at 25°C). Cast specimens of lower density (19.50 to 19.62 g/cm³ at 30°C) and lower purity (Table 1) were used to obtain the pressure and temperature coefficients listed in Table 8. The pulse technique was employed in measuring the pressure

Table 8. Elastic Properties and Sound Velocities of Alpha Plutonium at 30°C (LAQUER)

Property	Value ^(a)	Pressure coefficient ^(b) ($\times 10^{-6}$ /bar)	Temperature coefficient ^(c) ($\times 10^{-5}$ /°C)
YOUNG's modulus	$(9.93 \pm 0.03) \times 10^{11}$ dynes/cm ² $(14.40 \pm 0.04) \times 10^6$ lb/in. ²	$+18 \pm 1$	-127 ± 8
Shear modulus	$(4.34 \pm 0.01) \times 10^{11}$ dynes/cm ² $(6.29 \pm 0.01) \times 10^6$ lb/in. ²	$+14 \pm 1$	-145 ± 10
POISSON's ratio	0.15 ± 0.01	$+27 \pm 7$	$+138 \pm 71$
Compressibility	$(2.14 \pm 0.02) \times 10^{-6}$ /bar	-28.5 ± 3	$+68 \pm 32$
Rod velocity (v_0)	$(2.244 \pm 0.004) \times 10^5$ cm/sec	$+7.8 \pm 0.6$	-56 ± 4
Shear velocity (v_T)	$(1.483 \pm 0.002) \times 10^5$ cm/sec	$+6.1 \pm 0.7$	-65 ± 5
Infinite medium velocity (v_L)	$(2.301 \pm 0.003) \times 10^5$ cm/sec	$+9.2 \pm 0.4$	-48 ± 6

^(a) Measurements by pulse technique on sample having $\rho = 19.722 \pm 0.005$ at 30°C.

^(b) Measurements by pulse technique on sample having $\rho = 19.62$ at 30°C.

^(c) Measurements by resonance technique on two different samples ($\rho = 19.5$ and 19.6).

coefficients, and pressure was varied from atmospheric to 30,000 lb/in.². The temperature coefficients were measured by the resonance technique with specimen temperatures varying from 10 to 30°C. The values reported for the temperature coefficients should be regarded as questionable because they were determined "on the run," and the hot-pressing operation, including transformation under uniaxial stress, may well have introduced some degree of preferred orientation.

The earliest measurements of the compressibility of plutonium were made by P. W. BRIDGMAN (unpublished data) in 1945 in collaboration with Los

Alamos, at the request of CYRIL SMITH. BRIDGMAN reported his results in the form $\Delta V/V_0$ for successively higher steps in pressure up to 100,000 kg/cm² (1.42×10^6 lb/in.²). LAQUER, for easier comparison with his own results, has recomputed BRIDGMAN's data into the form of "instantaneous" compressibilities, $\Delta V/V_p \Delta P$, where the pressure increments (ΔP) vary from 1000 to 10,000 kg/cm². A plot of these instantaneous compressibilities as a function of pressure gives a curve which for the lower pressures investigated by LAQUER agrees reasonably well with his values of both compressibility and pressure coefficient of compressibility, but BRIDGMAN's results extend to much higher pressures. An extrapolation of BRIDGMAN's data gives a value of about 2.0×10^{-6} /bar for the instantaneous compressibility at atmospheric pressure.

SCHONFELD & SPINDLER obtained values at lower pressures (0 to 25,000 lb/in.², ~ 2000 bars) for the compressibilities of both the alpha and beta phases, namely, $(2.5 \pm 0.5) \times 10^{-6}$ /bar for alpha plutonium at 150°C, and $(2.3 \pm 1.0) \times 10^{-6}$ /bar for beta plutonium at 200°C. Some uncertainty exists regarding an approximate correction for the compression of their steel dies, so that the reported values may be too high. The metal they used had a density of 19.83 ± 0.05 at 25°C, but was not "high-purity" plutonium (Table 1).

Thermodynamic Data. BRIDGMAN measured the increase in temperature of the alpha-to-beta transformation with increasing pressure. For pressures up to 7000 bars he obtained a linear relationship having a slope of 0.00105°C/bar. SCHONFELD & SPINDLER obtained the values 0.00073°C/bar at 1000 bars and 0.00102°C/bar at 5000 bars.

From selected values of the pressure coefficient and the volume change, the latent heat (ΔH) of the alpha-to-beta transformation may be calculated from the Clapeyron-Clausius relation. SCHONFELD has computed $\Delta H = 985$ cal/gram-atom, in reasonable agreement with a calorimetric determination, 925 cal/gram-atom, made by T. A. SANDENAW & R. B. GIBNEY (unpublished data). The latter workers also made preliminary measurements of the heat capacities of the alpha and beta phases, obtaining for alpha, $C_p = 8.0$ cal/gram-atom at 25°C, and for beta, $C_p = 9.3$ cal/gram-atom at 160°C. From these values and data for the compressibilities and coefficients of expansion, the following derived values have been calculated:

$$C_v = 7.3 \text{ cal/gram-atom at } 25^\circ\text{C (alpha).}$$

$$C_v = 8.7 \text{ cal/gram-atom at } 160^\circ\text{C (beta).}$$

The vapour pressure of liquid plutonium was reported by PHIPPS, SEARS, SEIFERT & SIMPSON (1955) at the Geneva Conference. This work, which was done in 1944, gave values in the range 1100° to 1500°C, obtained with apparatus of the Knudsen type. Results with two different pieces of equipment are reported and these agree fairly closely. The more accurate results fit the relationship $\log_{10} P_{MM} = -(17587 \pm 73)/T + 7.895 \pm 0.047$ and the authors ascribe an overall error of approximately 5% to values obtained from this equation. The average heat of vaporization of liquid plutonium in the temperature range 1400 to 1800°K is calculated to be 80.46 ± 0.34 kcal/gram atom. Effusion methods are very sensitive to impurities, and to gaseous contaminants in particular, when used with reactive metals, so that revision of these values

may result from work on purer materials. Experience with uranium (SULLY, 1953) has shown that different geometrical arrangements of the effusion cell apparently lead to discrepancies between the results obtained, through surface diffusion and bulk diffusion of the metal under examination through the edges of the orifice. It is not possible to say whether errors of this kind have affected the accuracy of the measurements of these workers.

Extrapolation of the vapour pressure measurements indicates a boiling point at 3500°K . This value would indicate an exceptionally wide range of liquid stability. FROST (1954) has reviewed the available information on liquid metals and has tabulated values of the expression $(\theta_v - \theta_f)/\theta_v$ where θ_v = the boiling point and θ_f = melting point in degrees absolute. Values range from 0.868 for gallium to 0.331 for magnesium, while the corresponding figure for plutonium is 0.740.

An early approximate determination of the surface tension of plutonium has been reported by COMSTOCK & GIBNEY, (1952) in which a value of 100 dynes/cm was deduced from radiographs of a plutonium meniscus. Predictions of the surface tension from known physical constants have been made at A.E.R.E. by J. W. TAYLOR (private communication) which lie in the range 490–580 dynes/cm. Because the experimental method used would be very liable to inaccuracies arising from surface oxidation and contamination of the melt, the discrepancy between the observed and predicted values calls for a fresh experimental determination by an improved technique.

Measurements of the magnetic susceptibility of plutonium have been made in Russia (KONOBEEVSKY, 1955), Britain (DAWSON, 1954), and the United States (JETTE, 1955a) which show widely differing absolute values and notable differences in the temperature dependence of susceptibility. Typical figures from American work carried out by COMSTOCK and reported by JETTE and from British results are tabulated in Table 9, together with values read from the reported Russian curve which is reproduced in Fig. 12.

The discrepancy in absolute values is possibly a function of either the calibration of the various pieces of equipment used, or the presence of insoluble impurities which may differ from sample to sample, since the ratios of the susceptibilities for a given pair of phases are in fairly close agreement in the three sets of results reported. The differing temperature dependence of the phases seems to indicate an extreme sensitivity to dissolved impurities, which is more marked in this case than in any other reported physical property. It has in fact been both American and British experience that measurements vary considerably from one sample to another, or even among different runs of the same sample.

The American values refer to their material of so-called normal purity, which is in general comparable with the British metal, although specific impurities may vary considerably. There is no information available on the purity of the Russian plutonium.

It is unfortunate that there are such differences in the temperature dependence of the magnetic susceptibility, since this might well help to provide some understanding of the electronic configuration of plutonium in its various phases. Thus DAWSON has pointed out that a susceptibility which is independent of temperature, as is also found for uranium, may be associated with free electrons

Table 9. *Magnetic Susceptibility Values*
(Calculated as $\chi_m \times 10^6$ from published data)

JETTE (1955a)			KONOBEEVSKY (1955)	DAWSON (1954)	
	Temperature dependence	Value for mid-range		Sample A*	Sample C*
α	nil	532 (25°)	565 (25°) 575 (120°)	638 (27°) 623 (110°)	600 (20°) 593 (115°)
β	markedly negative	553	603 (140°) 590 (210°)	641 (140°) 641 (200°)	622 (140°) 617 (200°)
γ	negative	531	577 (230°) 573 (300°)	633 (210°) 610 (280°)	600 (216°) 600 (280°)
δ	negative	515	562 (330°) 557 (430°)	598 (327°) (no obvious dependence)	— — —
δ'	positive†	—	560 (450°)	—	—
ϵ	negative	522	577 (480°) 560 (580°)	— —	— —

* Sample B is now known not to be representative of normal material.

† Value computed from COMSTOCK's original data.

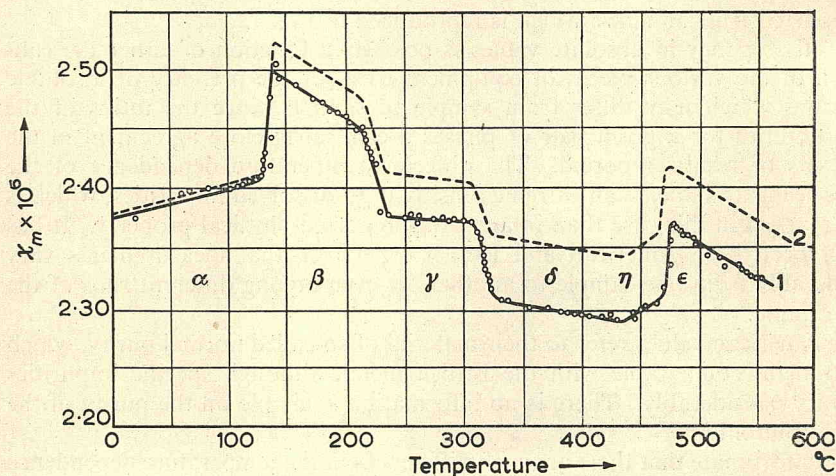


Fig. 12. Magnetic susceptibility curve for plutonium made with a 48 milligram sample. (U.S.S.R.).

(1) Weight of specimen in the magnetic field.
(2) Paramagnetic susceptibility.

in "d"-energy levels. He similarly connects a decrease of susceptibility with temperature with lanthanide behaviour involving electrons in the "f" energy levels. It would seem however that interpretations on these lines must await more consistent results, obtained with metal of the highest purity.

Electrical resistivity measurements—There is very satisfactory agreement between the various measurements of electrical resistivity, which are summarized in Table 10. The values published by BALL *et al.* (1954) are replaced by a more recent set of results based on the same experimental measurements. These results and the measurements reported by JETTE, which were carried out by T. A. SANDENAW and R. B. GIBNEY, are corrected for volume changes; this procedure apparently was not adopted by SMITH.

The agreement in the results suggests that the high resistance values and the signs of the coefficients of resistivity are representative of pure plutonium, rather than due to impurities. The alpha phase appears to behave qualitatively as a semi-conductor but the observed results do not follow the normal resistance temperatures relationship of an intrinsic semiconductor.

The high resistivity and low positive coefficient of the delta phase, in keeping with other physical properties, are abnormal for a face-centred cubic metal, but the resistivity is not so high as it at first appears, when compared with other

Table 10. Resistivity Data

Resistivity $\rho \times 10^6$ (ohm-cm)				Coefficient $1/\rho \, d\rho/dt \times 10^5$		
	SMITH (1954)	JETTE (1955b)	BALL <i>et al.</i> (to be published)	SMITH (1954)	JETTE (1955a)	BALL <i>et al.</i> * (to be published)
α	150 (25°)	145 (25°)	150 to 156	-29.7	-21	-22 to -40
β	110 (200°)	108 (150°)	115 to 119	0	-6	-4.8 to -17.7
γ	110 (300°)	107.5 (235°)	114 to 118	0	-5	-3.6 to -8
δ	102 (400°)	100 (370°)	108 to 112	+1.5	+7	+8 to +18
δ'	—	103 (475°)	—	0	+45	0
ϵ	120 (500°)	111 (510°)	124	0	-7	0

* Low temperature end of each range.

metals showing the same crystal structure (BALL *et al.*, to be published). MOTT & JONES (1936) have shown that elements belonging to the same group of the periodic table tend to have similar values of the function $\sigma/M\theta^2$ where σM = atomic weight and θ = Debye temperature. The noble metals and alkali metals give values in the region of $10 - 20 \times 10^{-2}$, the transition metals in the region $0.5 - 1.5 \times 10^{-2}$, and the rare earths approximately 0.5×10^{-2} . Assuming $\theta = 130^\circ\text{K}$ for plutonium, $\rho/M\theta^2 = 0.17 \times 10^{-2}$; for thorium and uranium values of 1.17×10^{-2} and 0.68×10^{-2} are obtained. These values suggest a progressive change in behaviour rather than extreme abnormality on the part of plutonium.

4. THE INTERMETALLIC COMPOUNDS OF PLUTONIUM

4.1

The intermetallic compounds of plutonium have been discussed by COFFINBERRY & ELLINGER (1955) in a report written for the International Conference on the Peaceful Uses of Atomic Energy. Their paper consists primarily of a listing of crystal structures that have been determined for various intermediate phases in plutonium alloy systems studied at the Los Alamos Scientific Laboratory. These authors also reported the results of crystal structure determinations made by O. J. C. RUNNALLS at the Chalk River Project. RUNNALLS has since published his data in two papers, one on β -PuSi₂ (RUNNALLS & BOUCHER, 1955a) and another dealing with eleven other binary intermetallic compounds of plutonium (RUNNALLS, 1956). Meanwhile, a number of the metallic compounds of plutonium have been prepared and studied at Harwell (MARDON *et al.*, private communication), and the publication by S. T. KONOBEVSKY (1955) of Russian phase-diagram work has further augmented the number of such compounds for which crystal-structure data may now be tabulated.

Table 11 is essentially the Los Alamos table with Chalk River, Harwell and Moscow values added. A few minor changes have been made in the Los Alamos data, and results for three new cobalt compounds have been added. Los Alamos values for carbides, hydrides, oxides and α -PuSi₂ have been left in the table because these compounds are of importance to metallurgists, but the reader should understand that other data for these compounds exist and that the values listed are not necessarily better than any of the others. Also, it should be understood that many alloy systems have been studied only in part, so that the compounds listed may not be all that exist in a particular binary system. A question mark following the formula of a compound means only that the composition indicated by the formula is in doubt, there being no intention to imply uncertainty regarding the existence of the compound.

4.2

PuAg₃—The crystal system and unit-cell dimensions of this compound were established by RUNNALLS from rotation patterns, but the atomic positions in the crystal structure have not been determined. From the absence of 00.L reflections having L odd, RUNNALLS concluded that the space group is P6₃, P6₃/m or P6₃22.

4.3

Pu₃Al—This compound was considered by COFFINBERRY and ELLINGER to be a tetragonal distortion of the cubic AuCu₃ structure with axial ratio greater than one and with the two kinds of atoms only partially ordered, thus making it a partially ordered form of the SrPb₃ structure. The Harwell workers have obtained substantially the same lattice-constant values as those found at Los Alamos, but on the basis of their observed intensities, have interchanged the *a* and *c* axes, making the axial ratio less than one. See also the discussion of Pu₃In.

4.4

PuAl—The composition range between Pu_3Al and PuAl_2 has been studied at Los Alamos, Chalk River and Harwell, but to only a limited extent at any of the three laboratories. Because the investigational approaches have been rather different, the conflicting results obtained are difficult to reconcile at present. It may be stated, however, that several different X-ray diffraction patterns have been found for compositions in the vicinity of PuAl, and that Los Alamos workers are of the opinion that a range of solid solubility exists in this region of the phase diagram. Although the phase relationships have not yet been explained by the X-ray patterns, they indicate that the crystal structures involved are probably rather simple, one or more forms of a distorted CsCl structure appearing to be the most likely possibility indicated by the Chalk River and Los Alamos work.

4.5

PuAl₂—Los Alamos, Chalk River and Harwell values for the size of the cubic unit cell are compared in the table. It is perhaps worth noting that the unit-cell size is smaller when this phase contains a larger proportion of the larger plutonium atoms. To explain a similar situation for NiAl, BRADLEY & TAYLOR (1937) have proposed that the increase in the proportion of larger atoms (aluminium in NiAl) is accompanied by an increase in vacant atom sites, so that the over-all result is a decrease in the size of the unit cell.

4.6

PuAl₃—RUNNALLS has published the description of an approximate solution for the crystal structure of this compound. It is the same result that was obtained when study of the compound was first undertaken at Los Alamos, and except for reflections of low intensity it satisfactorily accounts for the observed powder and single-crystal patterns. When C. K. STAMBAUGH working at Los Alamos discovered the weak reflections, he realized that the true structure was somewhat less simple than it had at first appeared to be, but the weak spots he obtained in Weissenberg photographs taken with copper *K*-alpha radiation were too few in number to give an unambiguous indication of all details of the correct solution. Further work on PuAl_3 has recently been done at Los Alamos using molybdenum *K*-alpha radiation, and from the larger number of reflections obtained the structure has been completely solved. Following STAMBAUGH's leads LARSON and CROMER⁽¹³⁾ have found the following to be the correct description of the equivalent positions in space group $\text{P6}_3/\text{mmc}$ that are occupied by plutonium and aluminium atoms:

2 Pu in 2b: $\pm(0, 0, \frac{1}{2})$

4 Pu in 4f: $\pm(\frac{1}{3}, \frac{2}{3}, z_1; \frac{2}{3}, \frac{1}{3}, \frac{1}{2} + z_1)$ with $z_1 = 0.0892 \pm 0.0001$

6 Al in 6h: $\pm(x_1, 2x_1, \frac{1}{4}; 2x_1, x_1, \frac{1}{4}; x_1, x_1, \frac{1}{4})$ with $x_1 = 0.5160 \pm 0.0030$.

12 Al in 12k: $\pm(x_2, 2x_2, z_2; 2\bar{x}_2, \bar{x}_2, z_2; x_2^2, \bar{x}_2, z_2; \bar{x}_2, 2\bar{x}_2, z_2 + \frac{1}{2}; 2x_2, x_2, z_2 + \frac{1}{2}; \bar{x}_2, x_2, z_2 + \frac{1}{2})$ with $x_2 = 0.8336 \pm 0.0040$ and $z_2 = 0.0815 \pm 0.0006$.

⁽¹³⁾ A. C. LARSON, D. T. CROMER and S. K. STAMBAUGH, Paper submitted to *Acta Cryst*

Table 11. *X-ray Diffraction and Crystal Structure Data for Some Binary Compounds of Plutonium*

s.c. = Simple cubic. CR = Chalk River
 b.c.c. = Body-centred cubic. H = Harwell
 f.c.c. = Face-centred cubic. M = Moscow
 s.t. = Simple tetragonal. LA = Los Alamos

b.c.t. = Body-centred tetragonal.
 Tetr. = Tetragonal.
 Hex. = Hexagonal.
 Orth. = Orthorhombic.

Where no letter symbols are used, data are from Los Alamos.

Compound	Structure type	Crystal lattice	Unit cell dimensions (Å)	Formula units in unit cell	Space group	Calculated density, (g/cm ³)
PuAg ₃	Chalk River data; see discussion	Hex.	CR: $a = 12.730 \pm 0.003$ $c = 9.402 \pm 0.005$	16	P6 ₃ , P6 ₃ /m or P6 ₃ 22	11.33
Pu ₃ Al		Tetr.	$a = 4.499 \pm 0.002$ $c = 4.538 \pm 0.002$ H: $a = 4.530$ $c = 4.475$	1		13.45
PuAl(?)	Unsolved powder patterns, LA, CR and H; see discussion.					
PuAl ₂	Cu ₂ Mg	f.c.c.	Pu-rich: $a = 7.838 \pm 0.001$ Al-rich: $a = 7.848 \pm 0.001$ CR: $a = 7.831 \pm 0.005$ H: $a = 7.832$	8	Fd3m	8.06
PuAl ₃	PuAl ₃ See discussion	Hex.	$a = 6.10 \pm 0.02$ $c = 14.47 \pm 0.02$ CR: $a = 6.08 \pm 0.01$ $c = 14.40 \pm 0.03$	6	P6 ₃ /mmc	6.67

PuAl ₄	UAl ₄	Orth.		4	Imma	6·02
			$a = 4·41$ $b = 6·29$ $c = 13·79$ CR: $a = 4·42 \pm 0·02$ $b = 6·26 \pm 0·02$ $c = 13·66 \pm 0·03$			
PuAs	NaCl	f.c.c.		4	Fm3m	10·39
PuBe ₁₃	NaZn ₁₃ See discussion	f.c.c.	Be-rich: $a = 10·282 \pm 0·001$ CR: Pu-rich: $a = 10·278 \pm 0·001$ Be-rich: $a = 10·284 \pm 0·001$ M: $a = 10·274 \pm 0·002$	8	Fm3c	4·35
PuBi	NaCl	f.c.c.	$a = 6·350 \pm 0·001$	4	Fm3m	11·62
PuBi ₂	Metallographic evidence only; see discussion					
PuC	NaCl See discussion	f.c.c.	$a = 4·97 \pm 0·01$	4	Fm3m	13·6
Pu ₂ C ₃	Pu ₂ C ₃ See discussion	b.c.c.	$a = 8·129 \pm 0·001$	8	I43d	12·70
Pu ₆ Co	U ₆ Mn See discussion of Pu ₆ Fe	b.c.t.	$a = 10·46 \pm 0·02$ $c = 5·33 \pm 0·01$	4	I4/mcm	17·00
Pu ₃ Co(?)	Unsolved powder pattern; see discussion					
Pu ₂ Co	Fe ₂ P Tentative; see discussion	Hex.	Pu-rich: $a = 7·902 \pm 0·004$ $c = 3·549 \pm 0·002$ Co-rich: $a = 7·762 \pm 0·003$ $c = 3·649 \pm 0·002$	3	P321	14·0

Table 11 (continued)

Compound	Structure type	Crystal lattice	Unit cell dimensions (Å)	Formula units in unit cell	Space group	Calculated density, (g/cm ³)
PuCo ₂	Cu ₂ Mg PuNi ₃ Unsolved powder pattern; see discussion	f.c.c.	Pu-rich $a = 7.081 \pm 0.001$ C.R. $a = 7.075 \pm 0.005$	8	Fd3m	13.35
PuCo ₃						
Pu ₂ Co ₁₇	Th ₂ Ni ₁₇	Hex. See discussion	$a = 8.325 \pm 0.002$ $c = 8.104 \pm 0.003$	2	P6 ₃ /mmc	10.10
PuCu(?)	Unsolved powder pattern; see discussion	b.c.t.	$a = 10.41 \pm 0.01$ $c = 5.359 \pm 0.004$ H: $a = 10.40 \pm 0.02$ $c = 5.345 \pm 0.005$ M: $a = 10.403$ $c = 5.348$	4	I4/mcm	17.04
PuCu ₃ (?)	Unsolved powder pattern; see discussion					
PuCu ₇ (?)	Unsolved powder pattern; see discussion					
Pu ₆ Fe	U ₆ Mn See discussion					
PuFe ₂	Cu ₂ Mg	f.c.c.	Pu-rich: $a = 7.191 \pm 0.001$ CR, (a): $a = 7.150 \pm 0.005$ (b): $a = 7.190 \pm 0.005$ H, Pu-rich: $a = 7.18 \pm 0.01$ M: $a = 7.178$	8	Fd3m	12.53

Pu_2Ge_3	Pseudo- AlB_2 (Hex.) See discussion	b.c.t.	Pseudo-unit: $a = 3.876 \pm 0.002$ $c = 4.090 \pm 0.002$	4	14/amd	10.98
PuGe_2	ThSi_3 See discussion		Ge-rich: $a = 4.102 \pm 0.002$			
PuGe_3	Ordered AuCu_3 See discussion	s.c.	$a = 4.223 \pm 0.001$	1	$\text{Pm}3\text{m}$	10.07
$\text{PuH}_{2.0}$	See discussion CaF_2	f.c.c.	$\text{PuH}_{2.0}$: $a = 5.359 \pm 0.001$	4	$\text{Fm}3\text{m}$	10.40
$\text{PuH}_{2.7}$			$\text{PuH}_{2.3}$: $a = 5.34 \pm 0.001$			
PuH_3	PuH_3	Hex.	$a = 3.78 \pm 0.01$ $c = 6.76 \pm 0.01$	2	$\text{P}6_3/\text{mmc}$	9.61
PuHg_3	UHg_3 See discussion	Hex.		1/2	$\text{P}6_3/\text{mmc}$	
PuHg_4	UHg_4 See discussion	Pseudo-b.c.c.		2 in pseudo-unit		
Pu_3In	Partially ordered AuCu_3 See discussion of PuXe_3	Cubic	$a = 4.703 \pm 0.002$	1		13.3
$\text{Pu}_2\text{Mg}(?)$	Probably CaF_2 See discussion	f.c.c.	$a = 7.34 \pm 0.01$	4(?)		
$\text{PuMg}_2(?)$	See discussion	Hex.	$a = 13.8 \pm 0.1$ $c = 9.7 \pm 0.1$			
PuMn_2	Cu_2Mg	f.c.c.	$\text{Pu-rich: } a = 7.292 \pm 0.001$ $\text{CR: } a = 7.290 \pm 0.005$ $\text{M: Pu-rich: } a = 7.29$ $\text{Mn-rich: } a = 7.26$	8	$\text{Fd}3\text{m}$	11.95

Table 11 (continued)

Compound	Structure type	Crystal lattice	Unit cell dimensions (Å)	Formula units in unit cell	Space group	Calculated density, (g/cm ³)
PuNi	Unsolved powder patterns, LA and M					
PuNi ₂	Cu ₂ Mg	f.c.c.	Pu-rich: $a = 7.141 \pm 0.001$ Ni-rich: $a = 7.115 \pm 0.001$ CR: $a = 7.16 \pm 0.01$ M: $a = 7.14$	8	Fd3m	13.1
PuNi ₃	Unsolved powder pattern; see discussion of PuCo ₃					
PuNi ₄	Unsolved powder pattern					
PuNi ₅	CaZn ₅	Hex.	Pu-rich: $a = 4.872 \pm 0.002$ $c = 3.980 \pm 0.001$ Ni-rich: $a = 4.861 \pm 0.002$ $c = 3.982 \pm 0.001$ CR: $a = 4.875 \pm 0.005$ $c = 3.970 \pm 0.005$	1	P6 ₃ /mmm	10.8
Pu ₂ Ni ₁₇	Th ₂ Ni ₁₇ See discussion of Pu ₂ Co ₁₇	Hex.	$a = 8.29 \pm 0.02$ $c = 8.01 \pm 0.02$ CR: $a = 8.30 \pm 0.01$ $c = 8.00 \pm 0.01$	2	P6 ₃ /mmc	10.3
PuO	NaCl	f.c.c.	$a = 4.96 \pm 0.01$	4	Fm3m	13.9
Pu ₂ O ₃	La ₂ O ₃	Hex.	$a = 3.841 \pm 0.006$ $c = 5.958 \pm 0.005$	1	P3ml	11.47
Pu ₂ O ₃ to Pu ₄ O ₇	Mn ₂ O ₃	b.c.c.	Pu ₂ O ₃ : $a = 11.04 \pm 0.02$	16	Ia3	10.2

PuO ₂	CaF ₂	f.c.c.	$a = 5.3960 \pm 0.0003$	4	Fm3m	11.46
Eta Pu-Os (~Pu ₁₁ Os)	Moscow data; see discussion					
Theta Pu-Os (Pu ₂ Os)	Moscow data; see discussion					
Pu ₅ Os	Moscow data; presumably an unsolved powder pattern					
PuOs ₂	MgZn ₂	Hex.	M: $a = 5.337$ $c = 8.683$	4	P6 ₃ /mmc	19.2
PuP	NaCl	f.c.c.	$a = 5.664 \pm 0.004$	4	Fm3m	9.87
PuPb ₃	Disordered AuCu ₃ See discussion of PuGe ₃	f.c.c.	$a = 4.808 \pm 0.001$ M: $a = 4.81$	1	Fm3m	12.86
Pu ₂ Si ₃ (?)	Unsolved powder pattern					
Pu ₃ Si ₂ (?)	Unsolved powder pattern					
PuSi	FeB	Orth.	$a = 5.727 \pm 0.005$ $b = 7.933 \pm 0.003$ $c = 3.847 \pm 0.001$	4	Pbnm	10.15
Pu ₂ Si ₃ or β -PuSi ₂	See discussion					
Los Alamos data for Pu ₂ Si ₃ : Pseudo-AlB ₂			Pseudo-unit: $a = 3.975 \pm 0.002$ $c = 4.198 \pm 0.002$			

Table 11 (continued)

Compound	Structure type	Crystal lattice	Unit cell dimensions (Å)	Formula units in unit cell	Space group	Calculated density, (g/cm ³)
	Chalk River data for β -PuSi ₃ : AlB ₃	Hex.	$a = 3.884 \pm 0.003$ $c = 4.082 \pm 0.003$	1	P6/mmm	9.18
α -PuSi ₂	ThSi ₂ See discussion of PuGe ₂	b.c.t.	Si-rich: $a = 3.967 \pm 0.001$ $c = 13.72 \pm 0.03$	4	14/land	9.08
PuSn ₃	Ordered AuCu ₃ See discussion of PuGe ₃	s.c.	$a = 4.630 \pm 0.001$	1	Pm3m	9.96
PuTe	NaCl	f.c.c.	$a = 6.183 \pm 0.004$	4	Fm3m	10.33
Pu ₂ Th	Harwell data					
Eta Pu-U (2-70%U)	See discussion	Apparently s.t.	Pu ₃ U: $a = 10.57 \pm 0.05$ $c = 10.76 \pm 0.05$	52 atoms		17.15
Zeta Pu-U (25 to 74% U)	See discussion	Apparently s.c. at room temperature	PuU: $a = 10.664 \pm 0.005$ See discussion	58 atoms		18.95
Pu _x Zr ($x > 3$)	Unsolved powder patterns, LA and H; see discussion					

RUNNALL's approximate solution is described by the above coordinates if the following values are assigned to the atomic parameters:

$$z_1 = 0.0833$$

$$x_1 = 0.5000$$

$$x_2 = 0.8333$$

$$z_2 = 0.0833$$

Thus it is seen that the true structure is a distortion of the more ideal configuration represented by the approximate solution, illustrated in Fig. 13.

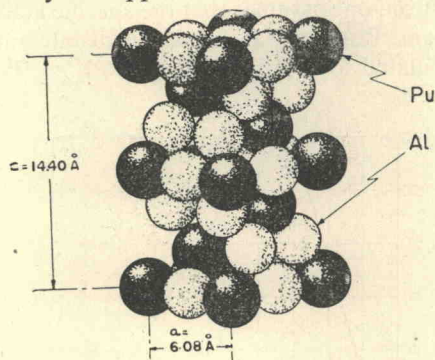


Fig. 13. Perspective model of the PuAl_3 unit cell.

4.7

PuBe_{13} —It has been found at both Chalk River and Los Alamos that this phase has a measurable range of homogeneity. As is also the case for PuAl_2 , the unit cell is smaller for the higher concentration of larger atoms.

Because plutonium emits alpha particles and beryllium has a strong (α, n) reaction, PuBe_{13} makes a very satisfactory neutron source. Although its total yield of neutrons per second per cubic centimetre is less than that of mechanical mixtures of Po-Be or Ra-Be, it possesses a number of advantages over the stronger sources. Chief among these is its greater stability, which derives from the fact that the half-life of Pu^{239} is 24,300 years. Another important characteristic of PuBe_{13} is that it is the only commonly employed neutron source for which a specified weight of source material has a known and predictable neutron yield. STEWART (1955) has pointed out that, Po-Be and Ra-Be being mixtures, the total yield and the neutron spectrum of these sources vary with the particle size of their constituents and with the character of mixing.

STEWART determined the neutron spectrum of PuBe_{13} , and by the integration of the energy distribution she obtained 6.1×10^4 neutrons per second per gram of PuBe_{13} for the total yield. In view of the possibilities for error in her method, this result appears to be in reasonably good agreement with an average value, 6.8×10^4 n/sec/g, obtained by comparing several specimens of PuBe_{13} with Los Alamos secondary standards. KONOBEVSKY has reported 6.7×10^4 neutrons per second per gram for the total yield of PuBe_{13} and has stated that this is the maximum yield per gram of alloy in the Pu-Be system (Fig. 14). Measurements made at Los Alamos have indicated that higher yields per gram of alloy are obtainable from alloys of lower beryllium content, which consist

of PuBe_{13} particles in a matrix of alpha plutonium. In this case, however, the yield from a given composition varies with the size and shape of the PuBe_{13} particles. RUNNALLS & BOUCHER (1955b) have performed interesting experiments with americium-beryllium alloys that illustrate the manner in which the neutron yields of these alloys depend on their condition of aggregation. Sintering a powder compact at successively higher temperatures increased the neutron emission until a maximum was reached when melting occurred. In the same paper in which these results are reported, he also gives 38.7 ± 1.2 neutrons per 10^6 alpha particles as the neutron yield of PuBe_{13} . If, not knowing the isotopic composition, one assumes that the specific activity of the plutonium used by RUNNALLS and BUCHER was 1.4×10^8 disintegration per minute, this neutron yield is calculated to be approximately 6.1×10^4 neutrons per second per gram of PuBe_{13} .⁽¹⁴⁾

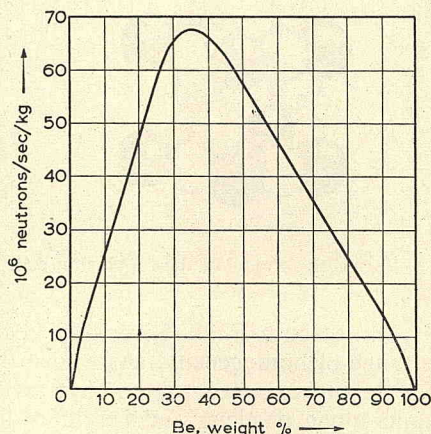


Fig. 14. Plot of neutron flux versus composition of plutonium-beryllium alloys. (U.S.S.R.).

4.8

PuBi and PuBi_2 —The plutonium-bismuth phases being very pyrophoric, it is extremely difficult to prepare X-ray diffraction specimens and obtain their patterns. The securing of an unequivocal powder pattern for PuBi was largely fortuitous, and although other Pu-Bi powder patterns were also found, none of these has indicated isostructuralism of PuBi_2 with UBi_2 . Metallographic and thermal-analysis evidence has appeared to indicate quite strongly, however, that a compound having the composition PuBi_2 exists.

4.9

PuC and Pu_2C_3 —Both of these carbides were studied by ZACHARIASEN (1949a)

⁽¹⁴⁾ In the first published version of the Geneva Conference paper by COFFINBERRY and ELLINGER (1955) it was stated that "the value 9.2×10^4 n/sec/g, obtained (for PuBe_{13}) at Chalk River, seems to be high . . .". This statement was based on an erroneous interpretation made in reading a Chalk River report and is completely misleading. No such high value of neutron yield was ever obtained in the Chalk River work on PuBe_{13} .—A. S. C.

during the war years. The NaCl structure of PuC he determined immediately. The structure solution for Pu₂C₃ he completed later (1952a).

4.10

Pu₃Co—A good powder pattern of this phase appears to have established its existence unequivocally. Although the composition has not yet been fixed, it appears to lie in the range, Pu₃Co to Pu₄Co.

4.11

Pu₂Co—The reason that the assignment of the Fe₂P structure-type to Pu₂Co is now regarded as "tentative" is that an intensity check has not yet been computed. When this is done, it is believed that Pu₂Co will be shown to have the Fe₂P structure.

4.12

PuCo₃ and **PuNi₃**—Although the crystal structure of these compounds is unknown, the close similarity of their powder patterns indicates that they are isostructural.

4.13

Pu₂Co₁₇ and **Pu₂Ni₁₇**—The type structure is Th₂Ni₁₇, described by FLORIO & RUNDLE (1952).

4.14

PuCu, **PuCu₃** and **PuCu₇**—According to metallographic and X-ray diffraction evidence obtained at Los Alamos, three compounds exist in the plutonium-copper system, but the compositions indicated are uncertain.

4.15

Pu₆Fe—The type structure, U₆Mn, was determined by BAENZIGER, RUNDLE, SNOW, & WILSON (1950). For this tetragonal compound the average coefficients of expansion between room temperature and 400°C have been determined by ELLINGER with a high-temperature X-ray diffraction camera. The results are:

$$\bar{\alpha}_a = (73 \pm 2) \times 10^{-6} \text{ per degree C.}$$

$$\bar{\alpha}_c = (-10 \pm 1) \times 10^{-6} \text{ per degree C.}$$

The Russian workers have found that Pu₆Fe has good ductility and lends itself to plastic deformation with the formation of a texture. When it was drawn at 350°C, the direction [001] became oriented parallel to the drawing axis.

4.16

Pu₂Ge₃—The crystal structure of this compound has been investigated at Los Alamos, where it has been found to be isostructural (or very nearly so) with Pu₂Si₃. The question of whether the latter compound should be designated Pu₂Si₃ or β-PuSi₂, and related crystal structure problems, appears to involve much the same considerations for both the germanium and silicon cases. See Pu₂Si₃ for further discussion.

4.17

PuGe₂ and **PuSi₂**—The type structure is ThSi₂ determined by BRAUER and MITIUS (1942). The unit-cell dimensions given in the table are for germanium-rich and silicon-rich limits of the respective homogeneity ranges. In the case

of the plutonium-rich solid solution in PuSi_2 , a splitting of the high-angle lines was observed, which appears to indicate a change of structure in this composition range. The same effect may exist for plutonium-rich PuGe_2 , but it has not yet been observed.

4.18

PuGe_3 , Pu_3In , PuPb_3 and PuSn_3 —These four compounds all have the face-centred-cubic "phase structure" of AuCu_3 . The true lattice of the two that appear to be fully ordered, PuGe_3 and PuSn_3 , is, of course, simple cubic. The powder patterns of these two were found to contain the simple-cubic superlattice lines having intensities (relative to the intensities of the "face-centred" lines) that are characteristic of complete ordering of the plutonium and group IV-B element atoms. Because PuGe_3 and PuSn_3 are not known to disorder at any temperature, they might best be described as simple cubic, without reference to ordering or a face-centred-cubic "phase-structure."

No superlattice lines could be found on the powder films of PuBb_3 , but because of the rather small difference in scattering powers of plutonium and lead atoms, the superlattice reflections may have been too weak to be detected. It seems likely, however, that in PuBb_3 at room temperature the plutonium and lead atoms are fully disordered, so that only the face-centred cubic pattern is obtained.

The powder pattern of Pu_3In showed superlattice lines, but with intensities uniformly lower than would be required if this phase were fully ordered, simple cubic. The reduced intensity of the superlattice lines has been interpreted, in accordance with the theory of BRAGG & WILLIAMS (1934, 1935), to mean that there is partial ordering of the atoms. A similar reduced intensity of superlattice lines in the powder pattern of Pu_3Al was also interpreted to indicate only partial ordering in this tetragonal phase.

4.19

$\text{PuH}_{2.0}$ – $\text{PuH}_{2.7}$ —This solid-solution phase formed by hydrogen with plutonium was the first to be discovered of a series of isostructural phases, the other members of which are formed by hydrogen with rare-earth elements. HOLLEY, MULFORD, ELLINGER, KOEHLER, & ZACHARIASEN (1955) have described the crystal structure of the latter, and MULFORD & STURDY (1955, and to be published) have reinvestigated the phase equilibria of plutonium and hydrogen.

The positions of the hydrogen atoms were determined for both ends of the homogeneity range, $\text{MH}_{2.0}$ to $\text{MH}_{2.7}$, by a neutron diffraction study of cerium deuteride. The composition MH_2 was found to have the CaF_2 structure. As additional hydrogen is taken into solid solution, the structure approaches that of a hypothetical face-centred cubic MH_3 having four H_{II} atoms per unit cell in the positions $\frac{1}{2}, 0, 0$; $0, \frac{1}{2}, 0$; $0, 0, \frac{1}{2}$; $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$; in addition to the eight H_{I} atoms in the fluorine positions and the four metal atoms in the calcium positions (0,0,0, etc.) of CaF_2 . In the case of plutonium hydride the H_{II} positions are never completely filled, because at about $\text{PuH}_{2.75}$ the structure begins to transform to hexagonal PuH_3 .

It is interesting to note that, throughout the entire solid-solution range,

the unit-cell size of both plutonium hydride and the rare-earth hydrides decreases as the hydrogen content increases.

4.20

PuH₃—This compound might be regarded as the hexagonal analogue of the hypothetical cubic PuH₃ described in the preceding section. In the true PuH₃ (GdH₃ and SmH₃ are isostructural with PuH₃) the metal atoms have hexagonal instead of cubic close packing, and as in the cubic "PuH₃", the hydrogen atoms occupy positions in two different sizes of interstices among the metal atoms. For hexagonal PuH₃, ZACHARIASEN (private communication) has suggested the following probable structure in space group P6₃/mmc:

$$2 \text{ Pu in } (c): \pm(\frac{1}{3}, \frac{2}{3}, \frac{1}{2})$$

$$2 \text{ H}_I \text{ in } (b): \pm(0, 0, \frac{1}{2})$$

$$4 \text{ H}_{II} \text{ in } (f): \pm(\frac{1}{3}, \frac{2}{3}, z; \frac{2}{3}, \frac{1}{3}, \frac{1}{2} + z) \text{ with } z = 0.607.$$

The correctness of this structure has not yet been proved by neutron-diffraction study of a rare-earth deuteride, but it may be noted that a similar prediction for the structure of cubic "PuH₃" was made before it was confirmed by neutron diffraction.

4.21

PuHg₃ and PuHg₄—Powder patterns have been obtained which establish the isostructuralism of these phases with UHg₃ and UHg₄, but the unit-cell dimensions have not been computed. It has not been determined whether plutonium forms PuHg₂, isostructural with UHg₂. The structures of UHg₂, UHg₃, and UHg₄ have been studied by RUNDLE & WILSON (1949).

4.22

Pu₂Mg and PuMg₂—These phases were formed under conditions such that knowledge of their compositions could be deduced only from their X-ray diffraction patterns. The apparent fluorite structure of Pu₂Mg seems to establish its composition rather firmly, but the composition of PuMg₂ must be regarded as questionable.

4.23

PuNi₅—The type structure is CaZn₅, determined by HAUCKE (1940). Both Los Alamos and Russian workers have found that a range of homogeneity exists for PuNi₅ (Fig. 20).

4.24

Oxides of plutonium—The crystal structures of PuO, PuO₂ and cubic Pu₂O₃ were determined by ZACHARIASEN (1949a,b). Only the structure of hexagonal Pu₂O₃ was established by others—by ELLINGER at Los Alamos in 1949, and independently by TEMPLETON & DAUBEN (1952) at the University of California Radiation Laboratory in 1952. The latter investigators obtained the unit-cell dimensions, $a = 3.840 \pm 0.004$ Å and $c = 5.957 \pm 0.006$ Å.

4.25

Eta Pu-Os—KONOBEEVSKY has reported the plutonium-osmium phase diagram from 0 to 66.7 atomic percent osmium as determined by the Russian

workers (Fig. 21). The most plutonium-rich phase in this system they designated "eta." It has an homogeneity range from about 3.5 to 7.5 at. % (2.7 to 6 wt. %) osmium and thus encompasses the composition Pu_{15}Os . The alloys in the solid solution range of composition are said to possess good plastic and mechanical properties. The density of an alloy containing 3 wt. % osmium was found to be 18.3 g/cm³. No crystal structure determination is reported for the eta phase.

4.26

Theta Pu-Os—A solid-solution phase encompassing the composition Pu_2Os has been called "theta" by the Russians. Its homogeneity range extends from about 32.5 to 35.5 at. % osmium (18.5 to 20 wt. %). The theta phase has a high temperature modification (about 620°C) called "theta-prime." No crystal structures are reported.

4.27

Pu₃Pb—The form of the liquidus curve reported by KONOBEEVSKY for the plutonium-lead system indicates that an intermediate phase exists in the general vicinity of Pu_3Pb . The compound is apparently a difficult one to study because it is reported that "the first compound (in the plutonium-lead system), found in the concentration range of 30 to 50 at. % of lead, is readily oxidised and ignites in the air, being transformed into powdery oxides."

4.28

Pu₂Si₃—RUNNALLS and BOUCHER (1955a) have investigated the crystal structure of Pu-Si products having approximately the composition Pu_2Si_3 . These samples gave only the Debye lines of a single hexagonal phase which they found to be isostructural with ZACHARIASEN's $\beta\text{-USi}_2$, which is isostructural with AlB_2 . He labelled the new Pu-Si phase $\beta\text{-PuSi}_2$ to conform with ZACHARIASEN's terminology.

The composition Pu_2Si_3 has also been studied independently by ELLINGER, who observed a number of lines of low intensity in addition to the Debye lines that RUNNALLS obtained. On the strength of the extra lines and the knowledge that his samples were very close to the composition Pu_2Si_3 , ELLINGER concluded that a phase of composition Pu_2Si_3 has a crystal structure that is a distortion of the AlB_2 structure, and that a unit cell larger than that of AlB_2 is required to describe it. Accordingly, in their table COFFINBERRY and ELLINGER designated the structure type "pseudo- AlB_2 ." The discrepancy between ELLINGER's results and those of RUNNALLS has not been resolved. It seems likely that the answer is involved with the more general problem of phase relationships in this region of the plutonium-silicon system, and that similar questions are in need of careful investigation in the corresponding region of the uranium-silicon system.

4.29

Pu₂Th—The Harwell group have identified a phase in the region of Pu_2Th by both X-ray and metallographic techniques. A tentative indexing of the powder pattern suggests an orthorhombic unit cell with $a = 9.820\text{\AA}$, $b = 8.164\text{\AA}$ and $c = 6.681\text{\AA}$. The measured density of 14.0 g/cm³ corresponds roughly to 6 formula units in the unit cell.

4.30

Eta Pu-U—This phase has a homogeneity range that extends from about 2 to about 70 atomic percent uranium. Its field lies at higher temperatures in the plutonium-uranium diagram than does that of the zeta phase. The unit-cell dimensions given in the table were determined for a specimen having the composition Pu_3U . The crystal lattice is given as "apparently S.T." because it was not found possible to obtain a good powder pattern of this phase. Presumably, because of inhomogeneity of the specimen, the powder lines were broad and were not measurable beyond about $\sin^2 \theta = 0.36$. For this reason it is not certain that, if the broad Debye lines could be sharpened, a somewhat different structure might not be revealed.

4.31

Zeta Pu-U—The homogeneity range of this phase extends from about 25 to about 74 at. % uranium. It is the stable phase at room temperature, where the composition limits are somewhat narrower. The unit-cell dimension reported is for the composition PuU . Much better powder patterns have been obtained for this phase than for the eta phase, and the zeta unit cell appears to be a cube at room temperature. But it manifests the anomalous behaviour of expanding anisotropically when heated. The lines of its powder pattern split in exact accordance with tetragonal symmetry. For this reason it seems likely that the crystal structure of the zeta phase may be tetragonal with $c/a = 1.000$ at room temperature.

4.32

Pu_xZr —A compound near the high-plutonium end of the plutonium-zirconium phase diagrams forms by solid-state reaction. It was first detected through discovery of its Debye pattern on X-ray films taken at Los Alamos with heat-treated specimens. It has since been found to form under similar conditions at Harwell. Density measurements have indicated that it is unlikely to be a solid solution of zirconium in alpha plutonium. The Los Alamos workers have conservatively estimated that the value of x (in Pu_xZr) must be at least as great as 3 but is probably greater. Harwell opinion is that " x " is equal to or greater than 10.

5. THE SOVIET PHASE DIAGRAMS

At the time of present writing the binary phase diagrams of plutonium alloys (in so far as they have been determined) are not declassifiable in the United States, the United Kingdom or Canada, and therefore work from these three countries may not be published in this chapter. However, at a session of the Academy of Sciences of the U.S.S.R. on Peaceful Uses of Atomic Energy, held in Moscow in July of 1955, S. T. KONOBEVSKY reported the results of research in the Soviet Union on the physical metallurgy of plutonium, including the phase diagrams of eight binary alloy systems. Illustrations of the diagrams were presented for seven of the systems, those of plutonium with beryllium, lead, vanadium, manganese, iron, nickel and osmium, and it was indicated that the plutonium-chromium system is of the same type as plutonium-vanadium,

with a eutectic temperature of 615°C. The seven diagrams that were illustrated are reproduced here as Figs. 15 to 21.

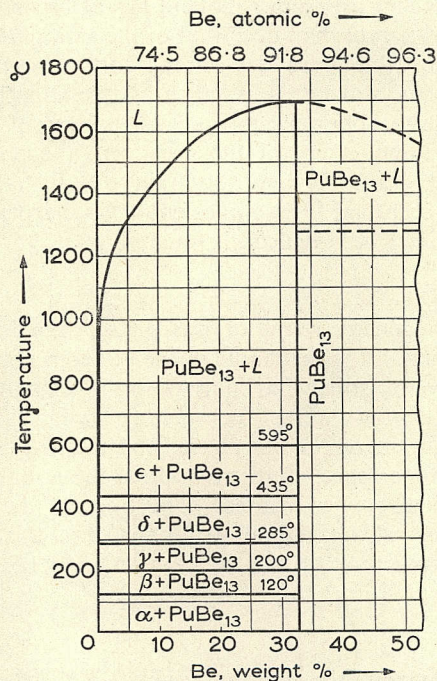


Fig. 15. Equilibrium diagram for plutonium-beryllium system, (upper scale—atomic per cent, lower scale—weight per cent).

In two cases, only a portion of the alloy system was investigated, but the other diagrams are fairly complete.

The diagram for the plutonium-nickel system is specifically said to require further study. It will be seen from Table 11 that compounds corresponding to

Table 12. Microhardness of Some Constituents of Plutonium Alloys

Microconstituent	Microhardness (kg/mm ²)
Alpha plutonium	233 to 250
PuBe ₁₃	947
Pu ₆ Fe	260
PuFe ₂	636
PuMn ₂	550 to 570
Eutectic at 2.5 wt.% iron	230
Eutectic at 2.3 wt.% manganese	280 to 330
Eutectic at 50 wt.% iron	473
Eutectic at 50 wt.% manganese	760 to 820

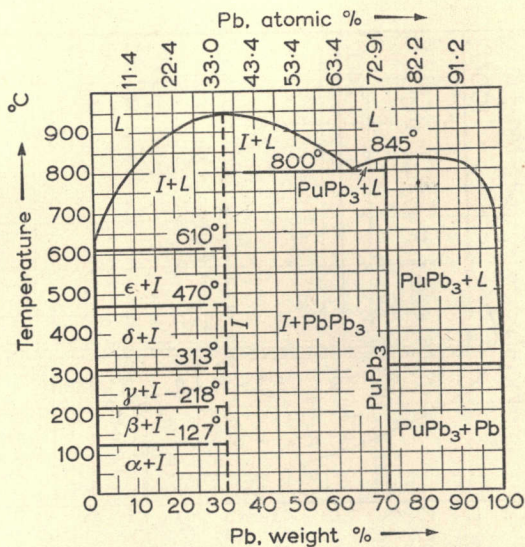


Fig. 16. Equilibrium diagram for plutonium-lead system.

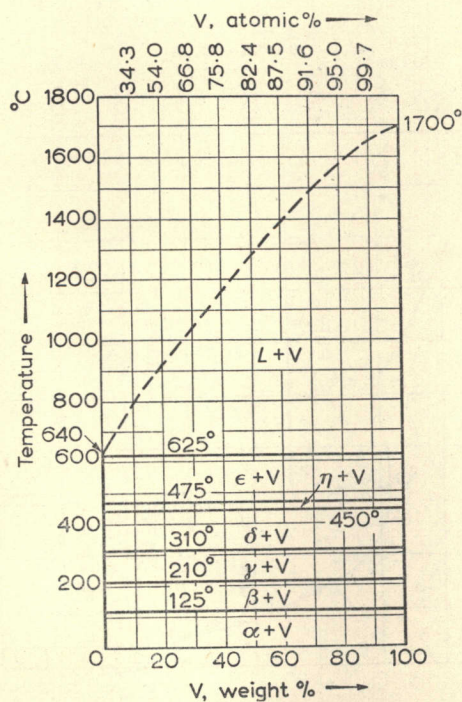
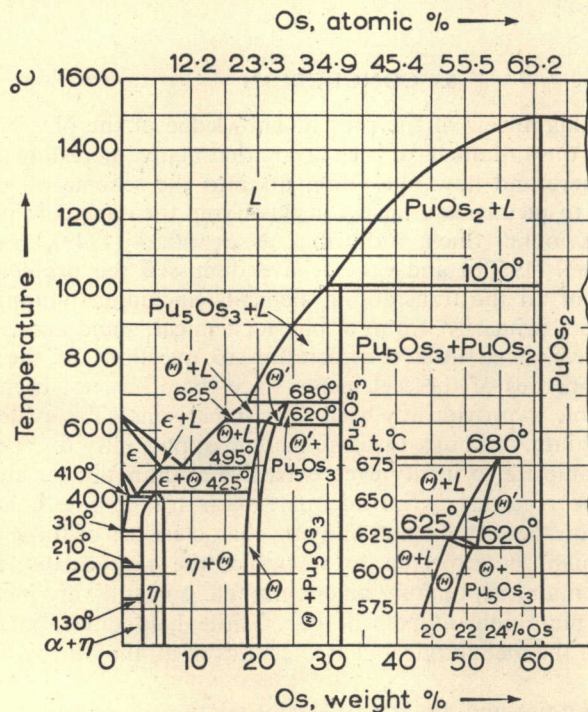
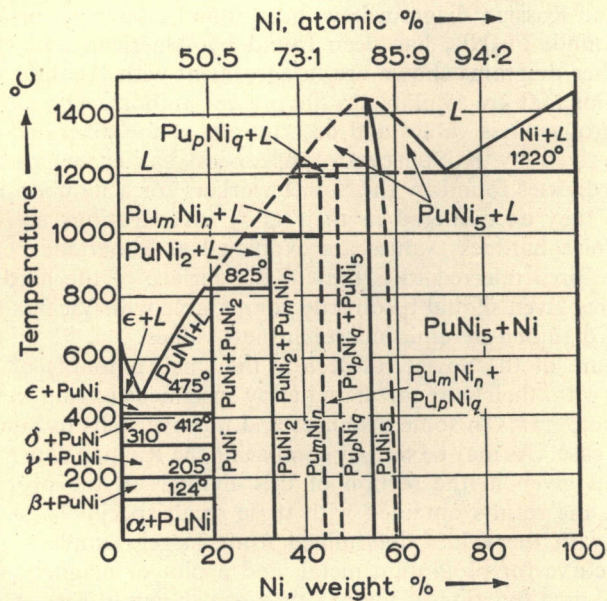


Fig. 17. Equilibrium diagram for plutonium-vanadium system.



those shown in the Russian diagram have been found elsewhere, and that an additional compound, $\text{Pu}_2\text{Ni}_{17}$ has been found by American and Canadian workers. The other diagrams shown are in agreement with the data on intermetallic compounds that are available to the present authors.

Except for microhardness values and descriptions of the diagrams, most of the information given by KONOBEEVSKY appears in earlier sections of this chapter. The hardnesses found by the Soviet workers for a number of microconstituents that they encountered in their alloy investigations are listed in Table 12. The microhardness values are expressed as kilograms per square millimetre. If the area referred to is that of the surface of the hardness impression, the figures given should be directly comparable with Vickers hardness numbers, or with diamond-pyramid microhardness values.

A notable feature of the Soviet research is the small amounts of material that they worked with, their pure metal and alloy specimens having weighed no more than ten micrograms in some instances and not over tens to hundreds of milligrams in any case. As may be seen by comparing the Russian with American and British values given in the section of this chapter on the properties of plutonium metal, the results obtained with these small specimens show quite good agreement with the values determined using larger samples. A Soviet thermal-analysis curve for plutonium metal, and a plot of magnetic susceptibility of the metal as a function of temperature, are shown in Figs. 11 and 12, to which reference has already been made in Sections 3.2 and 3.8

6. CONCLUSION

In undertaking this review of the present knowledge of the physical metallurgy of plutonium the authors have been aware that many interesting questions exist regarding where and how plutonium fits into the scheme of groupings ordinarily applied to metals as a basis for classifying their metallic properties and alloying behaviours. Such authorities as SEABORG (1949), HAISSINSKY (1949), ZACHARIASEN (1952b) and others have discussed the problem of the family affiliations of all the transradium elements, including plutonium, but they have done so primarily from a physiochemical standpoint. Understandably, they have given little consideration to questions of the metallic behaviour and properties of these elements since there has not been enough information available to provide any basis for comparisons. The evidence now available on plutonium, although furnishing some opportunity for speculation is still far too incomplete to justify even extensive examination or study, and certainly cannot be regarded as an adequate basis for definite conclusions. Also, information on the metallic and alloying characteristics of those elements that plutonium might be expected to resemble (the rare earths, thorium, uranium, protoactinium, neptunium, americium, etc.), is still very incomplete. Further study of plutonium alone will be of little help unless much more research is done on the metallurgical characteristics of all the other *f*-transition elements.

The low melting point and abnormal density relationships of plutonium, as well as many of the intermetallic compounds that it forms, suggest an affinity

to the lanthanide group, as though actinide⁽¹⁵⁾ behaviour is more characteristic of plutonium than it is of uranium. On the other hand, plutonium possesses many striking resemblances to the "thoride"⁽¹⁵⁾ series; the crystal structures of gamma plutonium for example, seem to belong to the class of complex pure-metal structures that characterize alpha and beta uranium, neptunium at room temperature and protoactinium, structures of a type that is not represented among the lanthanides.

Perhaps as much can be said is that with increasing atomic number beyond thorium the elements in the 5*f* transition series appear to become progressively less thoride-like, and increasingly actinide-like, until americium and curium in their chemical behaviours manifest pronounced actinide properties. Also, the crystal structure of americium has recently been found (GRAF *et al.*, 1956) to be the "double hexagonal" form of close packing discovered by ELLINGER in neodymium (ELLINGER, 1955). The position of plutonium in the 5*f* transition series appears to be the turning point between those elements that are more strongly of the thoride type and those that are more actinide in character, so that plutonium partakes of some of the characteristic properties of both in its alloying behaviour. For example, with nickel it forms the compounds PuNi, PuNi₂, PuNi₃, PuNi₄, and PuNi₅, which appear to be quite analogous to the series CeNi, CeNi₂, CeNi₃, CeNi₄, and CeNi₅. But plutonium also forms Pu₂Ni₁₇, isostructural with Th₂Ni₁₇; there is no Ce₂Ni₁₇ reported. With iron, plutonium forms PuFe₂, which has the CuMg₂ structure along with both CeFe₂ and UFe₂, but the M₆Fe type of compound is found only in the cases of Pu₆Fe and U₆Fe. Thus, with regard to alloying behaviour, plutonium might be said to be intermediate between uranium and the rare earths.

Rather than prolong such an immature discussion, it seems better to await the results of the gathering momentum of metallurgical research on plutonium and its alloys. It is to be hoped that contributions of the various laboratories whose existence is mentioned in this review, will gradually make clear what factors determine the detailed behaviour of this element plutonium, whose strange ways are only just now becoming manifest.

ACKNOWLEDGEMENTS

The authors have sought to include, either in the text or in references, some allusion to as many as possible of those who have contributed to the present knowledge of plutonium. There must, however, be many who have had part in the research projects touched upon in these pages, whose names are unintentionally omitted, probably because they are unknown to the present authors. Special thanks are offered to those who have made unpublished information available for inclusion in this review. The authors also acknowledge the encouragement and guidance of Dr. E. R. JETTE and Dr. H. M. FINNISTON in the preparation of this review, as well as the co-operation of their colleagues in both Britain and the United States.

⁽¹⁵⁾ The term Actinide is used to imply an analogy between two series involving filling of 4*f* and 5*f* electronic orbitals, commencing at lanthanum and actinium respectively. Thoride behaviour implies resemblance to thorium whose properties are more similar to the transitional elements rather than the rare earths. See for example SEABORG (1954).

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