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X-ray diffraction study of pure plutonium under pressure

Ph. Faure *, C. Genestier

CEA, Valduc, F-21120 Is-sur-Tille, France

ABSTRACT

Atomic volume and bulk modulus represent basic cohesion properties of a material and are therefore linked to many other physical properties. However, large discrepancies are found in the literature regarding values for the bulk modulus of pure plutonium (α-phase). New X-ray diffraction measurements of plutonium in diamond anvil cell are presented and the isothermal bulk modulus is extracted.

1. Introduction

Plutonium exhibits six allotropic solid phases at ambient pressure under temperature and is known to be particularly unstable with pressure, temperature, chemical addition and time (mainly due to self-irradiation effects) [1]. The low-temperature α-phase of Pu is highly unusual because it has an open low-symmetry structure (16 atoms per unit-cell, monoclinic $P2_1/m$). It is also the densest form of Pu, mechanically hard and brittle although it is vibrationally soft with a Debye temperature of 205 K [2]. Along with the binding energy, atomic volume and bulk modulus represent the basic cohesion properties of a material. It is important to determine their value with accuracy as they are linked to so many other physical properties and they are used to test theorist calculations. Large discrepancies are to be noticed in the literature regarding the α-phase bulk modulus, but recent resonant-ultrasound spectroscopy measurements would indicate that the most accurate value for the adiabatic bulk modulus B_s would be 54.4 GPa [2]. Isothermal bulk modulus B_T is usually derived by fitting an equation of state (EOS) on atomic volumes measured as a function of pressure. The volume/pressure accuracy (together with hydrostaticity conditions), the pressure range investigated and the number of measurements influence greatly such a fit and therefore the value of B_T [3]. This could explain part of the discrepancies observed in the few studies released in literature. We report here new low pressure *in situ* X-ray diffraction results on pure plutonium (α-phase) under better hydrostatic conditions than previous studies. Measurements presented here are restricted to low pressure (<2 GPa) as the main objective of the present work is to provide a good experimental description of plutonium room temperature compressibility near ambient pressure and therefore derive a good estimate for B_T.

2. Experimental

A piece of plutonium, arc melted 2 years before the experiment, was scraped in glove boxes under argon atmosphere to remove surface oxides. Then, three samples of about 100 μm edge and about 10–20 μm thickness were obtained by cutting with a scalpel. Each sample was loaded in a DAC equipped with a boron seat (that ensures an 80° X-ray aperture in 4θ) and with a gas membrane for fine pressure tuning. Five hundred and twenty micro meters culet diamonds together with a 250 μm thickness rhenium gasket preindented to 90 μm and drilled with a 270 μm diameter hole were used. A high pressure gas-loading system was employed for the loading of argon, the pressure transmitting medium, at room temperature, and at a pressure ranging from 50 bar to 200 MPa depending on the desired set-up. Pressure was determined by the fluorescence method using the ruby (Al_2O_3:Cr^{3+}) quasi-hydrostatic law [4]. Fluorescence of each of the four ruby spheres close to the sample was measured, after excitation with a Nd:YAG laser (532 nm), using a 1800 lines/mm spectrometer (Jobyn Yvon HR320) coupled with a 64 × 1024 pixels CCD captor (C5809 Hamamatsu). Neon light was used for calibration purposes. The temperature was monitored with ±1 K by using a thermocouple on one of the diamond, so that temperature dependence of the ruby fluorescence was taken into account in the pressure calculation [5]. Variation of pressure (differences between each of the ruby chips and differences between measurement before and after X-ray exposure) was thus observed to be less than 2%. Note that the absolute error on the pressure is higher as it must also include the ruby scale uncertainty. Comparison of the accurate calibration of the ruby R lines made by Grasset [6] in the pressure range [0–1 GPa] with the ruby quasi-hydrostatic law [4] reveals an agreement within ±10 MPa in this pressure range. Furthermore, Grasset has shown that the pressure can be measured with the ruby fluorescence technique with a standard deviation as low as 10 MPa if the temperature is known at 0.5 K.

After loading the sample in the DAC and checking non-contamination of surfaces, the DAC is operated out of glove box, to perform

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* Corresponding author. Tel.: +33 03 80 23 44 73; fax: +33 03 80 23 52 17.
E-mail address: philippe.faure@cea.fr (Ph. Faure).

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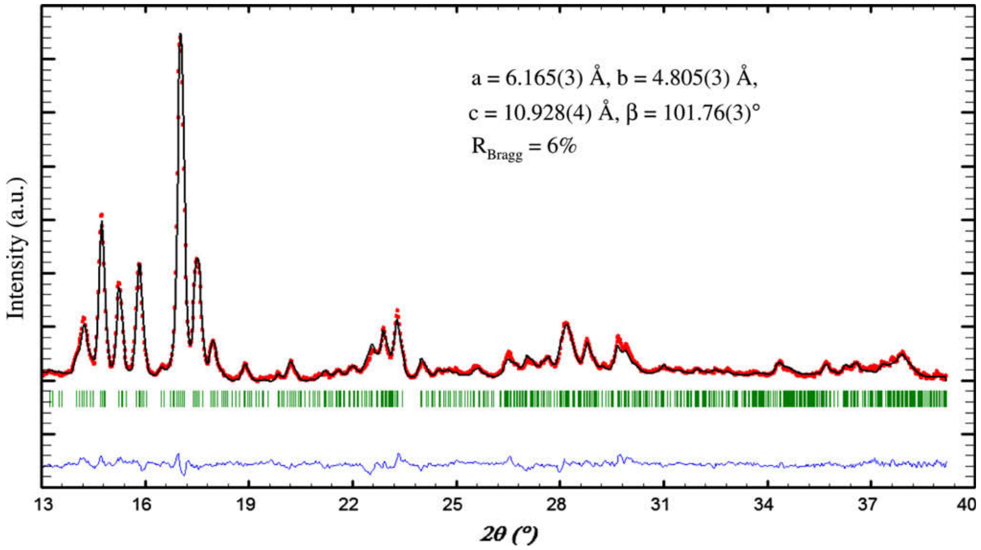

Fig. 1. Rietveld refinement of α-phase pure plutonium at 0.54(2) GPa. Vertical lines indicate the calculated hkl positions, points are the experimental data, the top continuous line is the calculated patterns and the lower continuous line is the difference profile.

XRD measurements for instance. All XRD experiments were carried out in transmission angular-dispersive mode with a rotating anode X-ray diffractometer (Nonius FR591 with molybdenum; $\lambda_{K\alpha_1} = 0.7093$ Å and $\lambda_{K\alpha_2} = 0.71359$ Å intensity ratio $I(K\alpha_2)/I(K\alpha_1) = 0.37$) equipped with a graphite monochromator and an image plate. During exposures, ranging from 2 to 16 h, and to ensure good statistics the sample was oscillated by ±4° around two rotation axes of the goniometer perpendicular to the 100 μm diameter collimated incoming X-ray beam. The sample to detector distance (~200 mm) was determined from the diffraction pattern of a NIST standard, LaB_6 (SRM660), positioned at the centre of the goniometer as for the sample. Uncertainty in the positioning was less than 5 μm. Complete Debye rings out to 1.1 Å could be collected with this geometry and relative uncertainty obtained for the cell parameter was $\Delta a/a \sim 1 \times 10^{-4}$.

Sample diffraction patterns were integrated with the FIT2D software [7] after removal of parasitic regions containing for example diamond Bragg spots. The resulting data, equivalent to 2θ-scans, were then analysed using the Fullprof program [8] with the Rietveld structural refinement method (Fig. 1). Pseudo-Voigt functions were used to describe peak shapes. An X-ray diffraction pattern of the sample is collected before argon was loaded to have a reference at ambient conditions.

We present, in the following, XRD results established up to 2 GPa by performing small pressure steps (50–100 MPa) once to twice a day on three pure plutonium samples referred as p1, p2 and p3.

3. Results and discussion

Ambient pressure unit-cell parameters obtained in this work (Table 1) are in good agreement with the ones published by Roof [9] but are slightly higher than Zachariasen's and Dabos' measurements [10,11]. Plutonium atomic positions, derived from Rietveld refinement, are found to be in overall good agreement (Fig. 2) with the ones published by Zachariasen [10] and no significant change is observed with pressure. Good reproducibility, within error bars, of atomic volumes measurements as a function of pressure is observed (Fig. 3). These data are also compared to the scarce data available in literature within this low pressure range. An excellent agreement is found with Roof's DAC XRD measurements [9] but

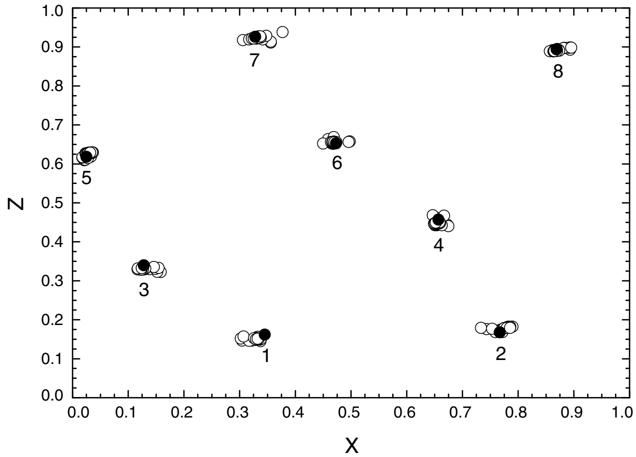

Fig. 2. (X, Z) fractional coordinates of plutonium atom positions within the α-phase unit-cell (with $Y = 0.25$). Circles correspond to the whole set of data refined in the present work (all samples and all pressures) with the Rietveld method. Filled circles correspond to Zachariasen values. Numbers correspond to atomic position labels following Zachariasen nomenclature [10].

Table 1
Unit-cell parameters for α-phase pure plutonium. Numbers between brackets correspond to errors.

	a (Å^3)	b (Å^3)	c (Å^3)	β (°)	V_0 (Å^3/at.)
Present work (average values over three samples)	6.194 (6)	4.829 (5)	10.973 (9)	101.77 (5)	20.08 (2)
Roof [9]	6.185 (6)	4.828 (5)	10.980 (10)	101.81 (9)	20.06 (6)
Zachariasen and Ellinger [10]	6.183 (1)	4.822 (1)	10.963 (1)	101.79 (1)	20.00 (1)
Dabos-Seignon et al. [11]	6.179	4.806	10.94	101.74	19.88

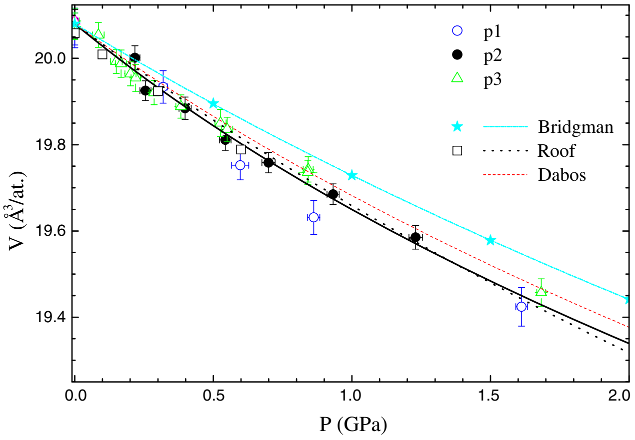

Fig. 3. Room temperature atomic volumes measured when increasing pressure for pure plutonium. Solid line is a fit with Vinet equation of state of the present work data (Table 2). Brigman's, Roof's and Dabos' isotherm (are normalized here, for comparison purposes, to the ambient pressure atomic volume $V_0 = 20.08$ Å^3/at.

not with Bridgman's early volumetric measurements [12], the latter giving higher volumes (i.e. a lower compressibility).

Knowing that, when fitting an EOS, strong correlations are often observed between B_T and its pressure derivative B'_T, especially when the pressure range of compression data is limited or experimental errors are high, care was taken when deriving these parameters. Predicted uncertainties on B_T and B'_T [3] are, respectively, for

Table 2

Equation of state parameters for α-phase pure plutonium. B_T is the isothermal bulk modulus at ambient conditions and B'_T is the first derivative of B_T versus pressure. The present work parameters are derived from a Vinet fit over all compression data in the 0–2 GPa pressure range using $V_0 = 20.08$ Å^3/at. γ and γ_S are estimates for the Grüneisen parameter (see text). γ was calculated, at $T = 295$ K, using Ledbetter's value for the adiabatic bulk modulus [2] and the mean volumetric thermal expansion coefficient $\beta = 1.6 \times 10^{-4}$ K^{-1} calculated from the linear coefficients of thermal expansion [10]. Numbers between brackets correspond to errors.

	B_T (GPa)	B'_T	γ	γ_S
Present work	37 (2)	19 (5)	9.7 (2.0)	9.3 (3.0)
Bridgman [12]	51.0 (2)	12.1 (2)	1.4	5.9
Roof [9]	42.2 (7)	10.5 (2)	6.0	5.1
Dabos-Seignon et al. [11]	43 (2)	15 (2)	5.5	7.3

the present case (EOS parameters for pure plutonium, number of data points, pressure range, experimental uncertainties for P and V of 0.03 GPa and 0.03 Å^3/at, respectively) 2.5 GPa and 5. Vinet fits of B_T [13] were performed over the very low pressure data points (11 points between ambient pressure and 0.4 GPa), fixing the ambient pressure atomic volume to the average value 20.08 Å^3/at (Table 1) and fixing B'_T to arbitrary extreme values (between 1 and 20). The resulting values ranged between 38.4(1.5) GPa and 35.7(1.5) GPa. A Vinet fit was then performed over all compression data in order to derive altogether values for B_T and B'_T (Table 2). The fact that, (i) the value derived for B_T, 37(2) GPa, lies in the domain of variation determined before 'whatever B'_T is' and (ii) resulting errors are in good agreement with predicted ones, gives confidence in the fitted parameters.

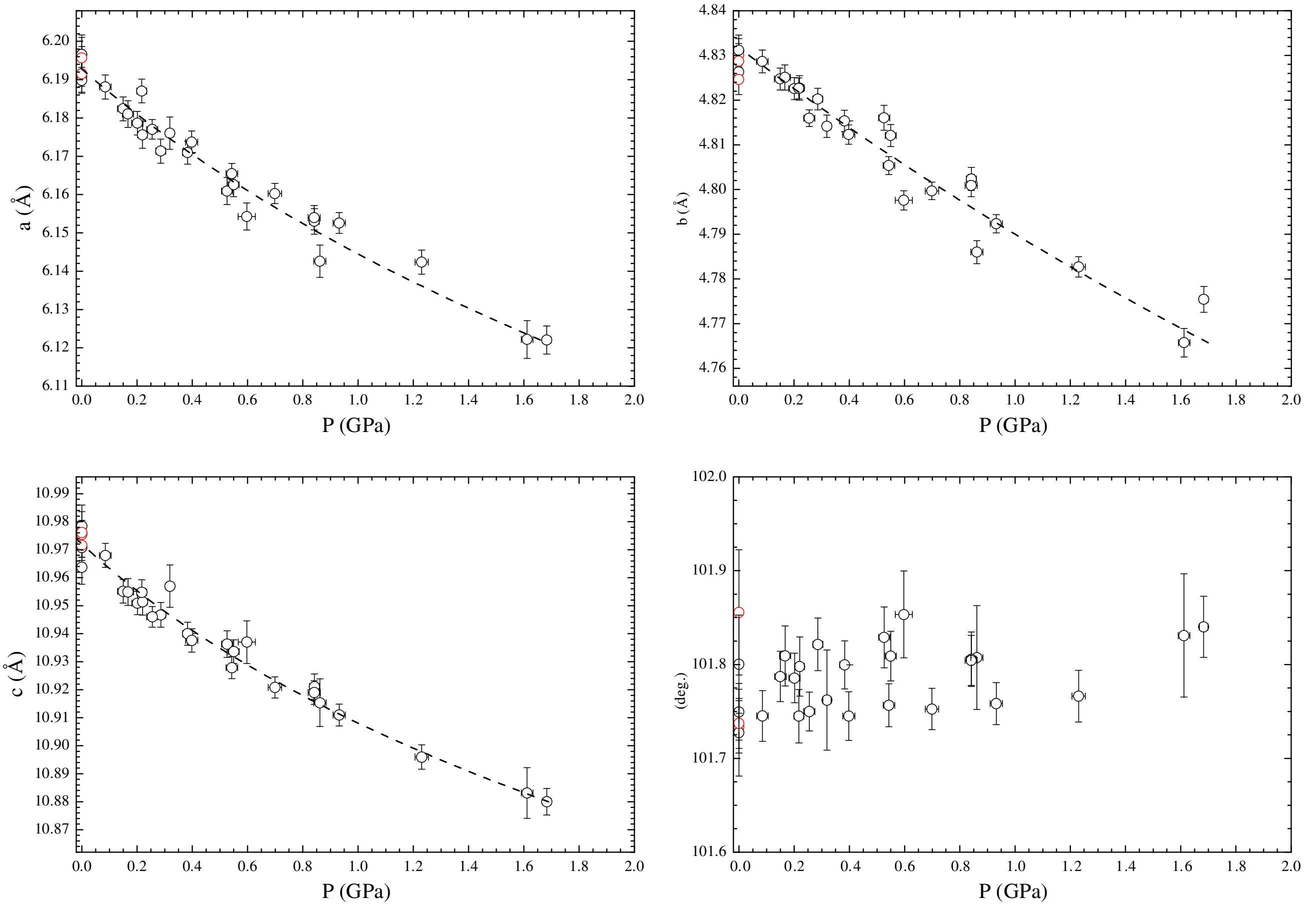

Fig. 4. Room temperature unit-cell parameters measured when increasing pressure for α-phase pure plutonium. Dashed lines represent Vinet fit (see text). Data after decompression are in red. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3
Equation of state parameters derived from a Vinet fit over unit-cell parameters for pure plutonium (in the 0–2 GPa pressure range). B_T is the isothermal bulk modulus at ambient conditions and B'_T is the first derivative of B_T versus pressure. Numbers between brackets correspond to errors.

	Unit-cell parameter at ambient pressure (Å)	B_T (GPa)	B'_T
a axis	6.193 (2)	33 (5)	22 (8)
b axis	4.832 (2)	34 (6)	9 (9)
c axis	10.972 (2)	40 (5)	41 (9)

These values are compared in Table 2 to other experimentally derived parameters available in literature and the corresponding isotherm curves are plot on Fig. 3. There is an overall good agreement between literature and the present work (with the exception of Bridgman's work), values for B'_T being always very high (>10). The set of parameters, proposed in this work describes accurately pure plutonium low pressure compressibility as measured under very good hydrostatic conditions, but it must be noted that it may not give a good description of plutonium compressibility at high pressure. This is not the scope of this paper.

What is the relevance of such a high value (19) for B'_T? The Grüneisen parameter has been calculated (Table 2), for each set of parameters, according to the relation linking the adiabatic and the isothermal bulk moduli, $\gamma = \frac{\frac{B_S}{B_T}-1}{\beta.T}$, and according to the Slater's approximation [14], $\gamma_S = \frac{B'_T}{2} - \frac{1}{6}$.

All values (except for Bridgman) are high (>6). The ones obtained with the parameters of the present work are the highest but appear to be very consistent. This could be regarded as another indication of the reliability of these parameters. However, the present work γ is higher than the one (5.1) derived from the measurement of the high-temperature slope dB_S/dT [2]. Knowing existing discrepancies between authors regarding cell parameters at ambient conditions, bulk moduli and thermal expansion coefficients, and knowing the α-structure anisotropy and its complex electronic structure, it is not surprising to obtain discrepancies when deriving the Grüneisen parameter. It would be valuable to carry out in the future *in situ* XRD under pressure and temperature from a same sample batch in order to derive a coherent α-phase equation of state in which anisotropy could be taken into account. In order to illustrate this point, Vinet fit were also performed over unit-cell parameters (Fig. 4 and Table 3). Crystallographic axis *c* is characterized by higher B_T and B'_T than for crystallographic axis *a* and *b*, which means stiffness is higher in the former direction. This is also the axis presenting the minimal thermal expansion [10].

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