*Journal of Alloys and Compounds, 189* (1992) 205–208
*JALCOM 368*



# Compression study of uranium borides $UB_2$, $UB_4$ and $UB_{12}$ by synchrotron X-ray diffraction

J.-P. Dancausse, E. Gering, S. Heathman and U. Benedict
*Commission of the European Communities, Joint Research Centre, Institute for Transuranium Elements, Postfach 2340, D-7500 Karlsruhe (Germany)*

L. Gerward
*Laboratory of Applied Physics, Technical University of Denmark, Building 307, DK-2800 Lyngby (Denmark)*

S. Staun Olsen
*Physics Laboratory, University of Copenhagen, Universitetsparken 5, DK-2100 Copenhagen (Denmark)*

F. Hulliger
*Laboratorium für Festkörperphysik, ETH Zürich, CH-8093 Zürich (Switzerland)*

(Received May 23, 1992)

**Abstract**

X-ray diffraction analysis was performed on uranium borides under pressure to study their stability *vs.* compression as well as to obtain their ambient pressure bulk moduli $B_0$. Their crystalline structures remain stable up to 50 GPa and the mean values of $B_0$ and $B_0'$ are 225 GPa and 2.6 for $UB_2$, 181 GPa and 4.8 for $UB_4$, 249 GPa and 3.4 for $UB_{12}$ respectively.

## 1. Introduction

Uranium borides can be described in terms of bidimensional networks of boron for $UB_2$ and of tridimensional networks of boron for $UB_4$ and $UB_{12}$ [1]. In these systems the boron atoms are strongly bonded together, providing their high stability. These compounds have, to our knowledge, never been examined under pressure. Obtaining information about their stability under pressure, their compressibility and possible pressure induced phase transitions was the object of this study.

## 2. Experimental details

Well crystallized uranium boride samples were prepared by arc melting boron and uranium in stoichiometric amounts. Their lattice parameters at ambient pressure (Table 1) were in good agreement with literature values [2]. Finely powdered samples were loaded into the central hole of an Inconel gasket together with a ruby chip, used for *in situ* pressure measurement by ruby fluorescence [3], and silicone oil, used as a pressure transmitter. The device for generating high pressure is a diamond anvil cell of Syassen-Holzapfel type. Energy-dispersive X-ray diffraction experiments at ambient temperature were performed at the EDS facility of storage ring DORIS II of Hasylab, DESY, Hamburg. The exact value of the Bragg angle was calculated from the diffraction pattern of an NaCl reference sample. For each pressure step, the lattice parameters and the relative volume $V/V_0$ were calculated. The $V(p)$ data were fitted to several equations of state [4] to obtain the bulk modulus $B_0$ and its pressure derivative $B_0'$ (the subscript zero indicates ambient pressure).

## 3. Results and discussion

### 3.1. $UB_2$

$UB_2$ was studied up to 50.3 GPa in 15 steps without any structural change observed. The variation of lattice parameters and of relative volume with pressure are plotted in Figs. 1 and 2. The relative contractions of lattice parameters $\Delta a/a_0$ and $\Delta c/c_0$ between ambient and the highest pressure are 6.5% and 3.9% respectively. $B_0$ and $B_0'$ were calculated fitting the experimental curve $V/V_0 = f(p)$ to several equations of state [4] (Table 2).

TABLE 1. Crystal data of uranium borides at ambient pressure ($Z$ is the number of molecules per unit cell); lattice parameters were determined on a powder diffractometer (Cu $K\alpha_1$ monochromatic X-ray beam)

| Compound | Structure (type) | Space group | $Z$ | Lattice parameters (pm) |
|---|---|---|---|---|
| $UB_2$ | Hexagonal ($AlB_2$) | *P6/mmm* (n. 191) | 1 | $a=313.02(3)$<br>$c=398.78(3)$ |
| $UB_4$ | Tetragonal ($ThB_4$) | *P4/mbm* (n. 127) | 4 | $a=705.73(5)$<br>$c=390.08(5)$ |
| $UB_{12}$ | Cubic | *Fm3m* (n. 225) | 4 | $a=747.50(5)$ |

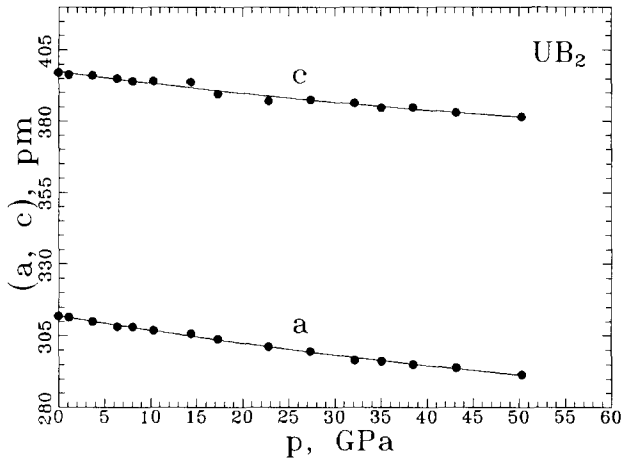


Fig. 1. Variation of lattice parameters of $UB_2$ *vs.* pressure.

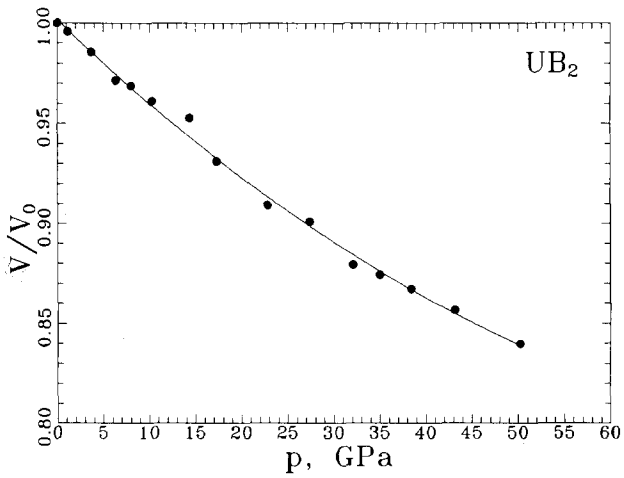


Fig. 2. Relative volume of $UB_2$ *vs.* pressure.

TABLE 2. Isothermal bulk modulus of $UB_2$ and its pressure derivative determined from several equations of state described by Holzapfel [4]; average uncertainty is equal to 12 GPa for $B_0$ and 0.1 for $B_0'$

| Equation | $B_0$ (GPa) | $B_0'$ |
|---|---|---|
| Murnaghan | 225 | 2.5 |
| Birch | 222 | 2.9 |
| Rose | 224 | 2.7 |
| General MVL | 225 | 2.6 |
| Holzapfel 0–1 | 224 | 2.6 |
| Holzapfel 1–1 | 227 | 2.2 |
| Mean | 225 | 2.6 |

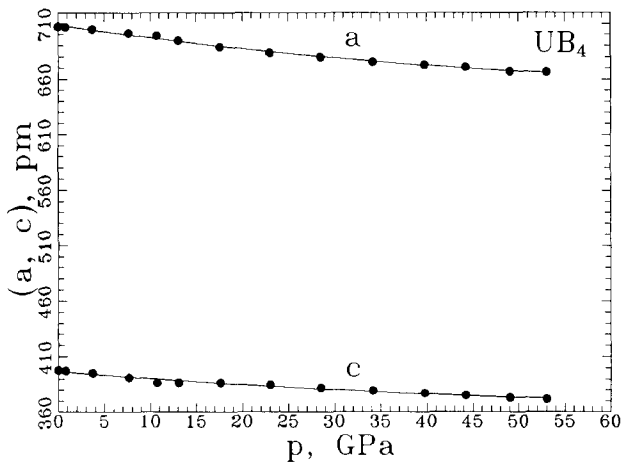


Fig. 3. Variation of lattice parameters of $UB_4$ *vs.* pressure.

### 3.2. $UB_4$

Uranium tetraboride was compressed up to 53 GPa in 14 steps without a phase transition observed. Figures 3 and 4 show the evolution of lattice parameters with pressure and relative volume. The relative contractions of lattice parameters $\Delta a/a_0$ and $\Delta c/c_0$ between ambient and highest pressure are 5.7% and 6.5% respectively. $B_0$ and $B_0'$ were calculated fitting the experimental curve $V/V_0=f(p)$ to several equations of state [4] (Table 3).

### 3.3. $UB_{12}$

The cubic structure of $UB_{12}$ remains stable up to 54.4 GPa, which pressure was reached in 19 steps. Figure 5 presents the $V(p)/V_0$ data from which $B_0$ was determined (Table 4).

From the previous results, assuming hydrostatic conditions, the linear compressibilities of $UB_2$ and $UB_4$ lattice parameters were calculated by fitting the experimental data with the following equation [5] (Table 5):

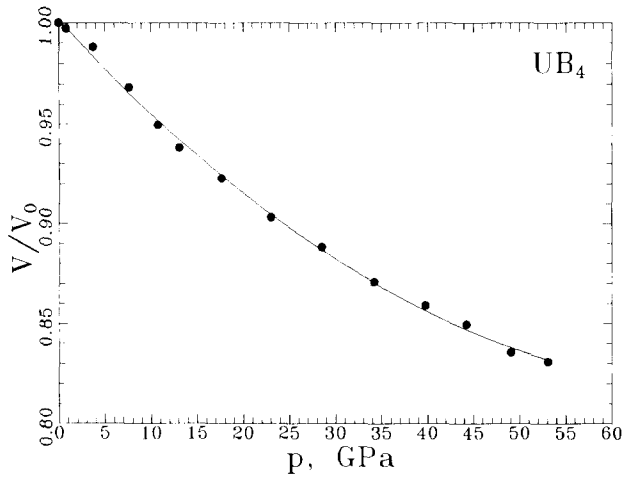


Fig. 4. Variation of relative volume of $UB_4$ *vs.* pressure.

TABLE 3. Isothermal bulk modulus of $UB_4$ and its pressure derivative determined from several equations of state described by Holzapfel [4]; average uncertainty is equal to 10 GPa for $B_0$ and 0.2 for $B_0'$

| Equation | $B_0$ (GPa) | $B_0'$ |
|---|---|---|
| Murnaghan | 182 | 4.4 |
| Birch | 180 | 4.8 |
| Rose | 180 | 4.9 |
| General MVL | 181 | 4.7 |
| Holzapfel 0–1 | 180 | 4.9 |
| Holzapfel 1–1 | 180 | 5.0 |
| Mean | 181 | 4.8 |

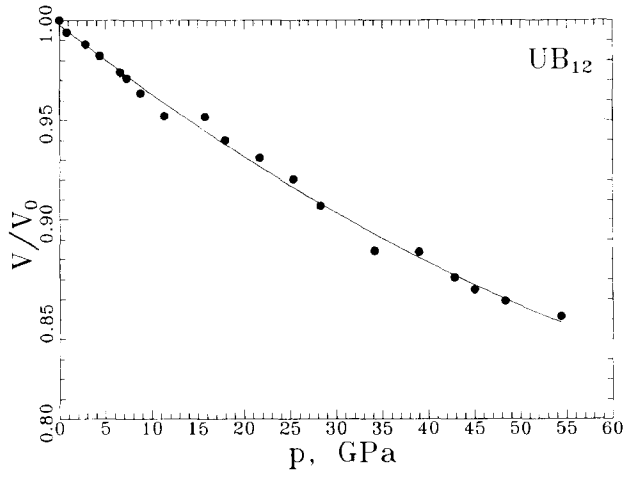


Fig. 5. Variation of relative volume of $UB_{12}$ *vs.* pressure.

$$g_i(p) = g_i(0) - \beta_i g_i(p)p + \delta_i g_i(0)p^2$$

where $g_i(p)$ is the $i$-axis lattice parameter at the pressure $p$, $\beta_i$ the linear compressibility in the $i$-axis direction and $\delta_i$ a constant that gives the $\beta_i$ pressure dependence.

Furthermore, for $UB_4$, supposing the atomic positions fixed in the experimental pressure range, it should be possible to observe a structural transition above 60 GPa on crossing the Hill limit [6].

TABLE 4. Isothermal bulk modulus of $UB_{12}$ and its pressure derivative determined from several equations of state described by Holzapfel [4]; average uncertainty is equal to 15 GPa for $B_0$ and 0.2 for $B_0'$

| Equation | $B_0$ (GPa) | $B_0'$ |
|---|---|---|
| Murnaghan | 249 | 3.2 |
| Birch | 248 | 3.4 |
| Rose | 249 | 3.4 |
| General MVL | 249 | 3.3 |
| Holzapfel 0–1 | 248 | 3.4 |
| Holzapfel 1–1 | 248 | 3.4 |
| Mean | 249 | 3.4 |

TABLE 5. Linear compressibilities of $UB_2$ and $UB_4$ lattice parameters

| | *a* | *c* |
|---|---|---|
| $UB_2$ | | |
| $\beta$ ($GPa^{-1}$) | $165(5)\times10^{-5}$ | $997(85)\times10^{-6}$ |
| $\delta$ ($GPa^{-2}$) | $68.5(13)\times10^{-7}$ | $41.8(22)\times10^{-7}$ |
| $UB_4$ | | |
| $\beta$ ($GPa^{-1}$) | $154(7)\times10^{-5}$ | $188(14)\times10^{-5}$ |
| $\delta$ ($GPa^{-2}$) | $82(17)\times10^{-7}$ | $132(32)\times10^{-7}$ |

The borides studied have similar compressibility to the element boron for which a bulk modulus $B_0 = 196$ GPa is reported [7]. The compressibility of these borides seems to be determined mainly by the boron networks.

## Acknowledgments

The authors wish to thank HASYLAB-DESY for permission to use the synchrotron radiation facility. Financial support from the Danish Natural Science Research Council (LG, JSO) is gratefully acknowledged.

## References

1 K. E. Spear, in A. M. Alper (ed.), *Phase Diagrams,* Materials Science and Technology, Vol. 4, New York, 1976, p. 105.
2 R. W. G. Wyckoff, *Crystal Structures,* Vols. 1 and 2, Interscience, New York, 1963 and 1965.
3 H. K. Mao, P. M. Bell, J. W. Shaner and D. J. Steinberg, *J. Appl. Phys., 49* (1978) 3276–3283.
4 W. B. Holzapfel, in R. Pucci and G. Piccitto (eds.), *Molecular Solids under Pressure,* North-Holland, Amsterdam, 1990, p. 61.

Also briefly described by J. P. Dancausse, S. Heathman, U. Benedict, L. Gerward, J. Staun Olsen and F. Hulliger, *J. Alloys Comp.*, in the press.

5 W. H. Fietz, H. A. Ludwig, B. P. Wagner, K. Grube, R. Benischke and H. Wühl, *Proc. NATO ARW on Frontiers of High Pressure Research, Pingree Park Campus, Colorado State University, July 15–18, 1991,* Plenum, New York, in the press.

6 H. H. Hill, in W. M. Miner (ed.), *Plutonium 1970 and other Actinides,* Met. Soc. AIME, New York, 1970.

7 D. Young, *Phase Diagrams of the Elements,* University of California Press, 1991.