

Volume and structural behavior of UP and USb up to 25 GPa

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X-ray powder diffraction patterns for UP and USb have been obtained up to 25 GPa in a diamond-anvil cell. An account of the uniaxial stress components is revealed to be essential for UP to determine reliable volume variations. UP maintains its NaCl-type structure while USb undergoes a phase transformation at 8 GPa towards a cubic CsCl-type structure. The experimental bulk moduli at normal pressure of UP and USb are, respectively, equal to 102 and 72.7 GPa, and their first pressure derivatives are equal to 4.7 and 2. For uranium mononictides the initial bulk modulus is directly proportional to the $-\frac{5}{3}$ power of the volume.

I. INTRODUCTION

The lattice parameters of the actinide mononictides decrease as a function of the atomic number of the cation, but not as smoothly as observed in the corresponding rare-earth compounds, except for CeN, which is a well-known intermediate-valence compound. From linear muffin-tin orbital (LMTO) calculations,¹ it was shown that the variations of the covalent and metallic parts of the bond lead to a minimum of the lattice parameter at the beginning of the actinide series, as is often observed for uranium compounds.

In the uranium mononictides the increase of the anion size leads to a decrease of the $5f$ hybridization and so yields a lower covalent part of the bond. This is well illustrated by a smaller decrease of the unit-cell parameter from thorium to uranium antimonides than from thorium to uranium phosphides.

In order to probe the difference in bonding between UP and USb and the accuracy of LMTO calculations of the bulk moduli,¹ we have undertaken measurements of the unit-cell parameters of UP and USb as a function of pressure.

II. EXPERIMENTS

The lattice parameters of UP and USb, which have cubic NaCl-type structure, have been determined by x-ray powder diffraction. The high-pressure x-ray patterns were obtained by using a diamond-anvil cell in conjunc-

tion with a flat film camera.² The incident beam of the zirconium-filtered molybdenum radiation was collimated to 0.1 mm by crossed slits and the angular aperture for the diffracted beam was $4\theta = 80^\circ$. The films were placed at 25 mm from the samples and were analyzed with a low-power microscope. Exposure times of 24 h were required to obtain good quality patterns.

The samples were obtained by crushing small single crystals and mixing them with a pressure marker used to determine the pressure by measuring its lattice parameter and using an equation of state. The pressure marker was chosen to avoid any overlapping between diffraction lines; for experiments with UP, gold, silver metal, or cesium chloride were successively used, whereas for USb only silver metal was employed.

The sample and the pressure marker were embedded in the pressure-transmitting medium, which was generally silicon grease because it protects efficiently the samples against moisture. The usual 4:1 methanol-ethanol mixture was used, however, in the case of UP because the pressure remains truly hydrostatic up to 12–15 GPa and so does not introduce uniaxial stresses in this pressure range.

Actually uniaxial-stress components act on the samples when the pressure-transmitting medium is solid; for a liquid medium they are also present above the freezing point, at large enough pressures; then the effects of uniaxial components must be taken into account. This has been done carefully for UP because our experiments have revealed that this compound is extremely sensitive to anisotropic stresses, whereas the uniaxial-stress effects for USb

were found to be negligible and well within the experimental uncertainties.

III. RESULTS

A. Uranium phosphide

X-ray diffraction patterns do not show relative intensity variations over the investigated pressure range. However, using different diffraction lines (hkl) to calculate the unit-cell parameter a_{hkl} we obtained different values well outside the experimental uncertainties. This effect is particularly large for UP; actually among the numerous compounds we have investigated so far,^{2,3} we have never observed such a large effect even though the experimental conditions were identical and in particular we used the same pressure-transmitting medium. We attribute this variation of the unit-cell parameter to the effects of the anisotropic stresses. This was clearly demonstrated by the experiments performed in a truly hydrostatic medium where no such effects could be observed.

Therefore, the data obtained in the solid medium were interpreted by calculating the volume from the (200) line only because the effects of the anisotropic stress components on the interplanar distances $d(hkl)$ are proportional to the function $\Gamma(hkl)$,

$$\Gamma(hkl) = h^2k^2 + k^2l^2 + l^2h^2 / (h^2 + k^2 + l^2)^2,$$

which is zero for ($h00$) lines and maximum for (hhh) lines (Refs. 4–6). Actually the cell parameter a_{200} observed in the solid pressure-transmitting medium agrees quite closely with the mean value of a_{hkl} deduced from eight diffraction lines in the liquid medium (see Fig. 1).

If nothing were known about the true experimental conditions, it would be possible, however, to determine correctly the volume of the unit cell provided that all the interplanar distances were accounted for. To do this a small deformation of the unit cell must be introduced; in the case of a cubic lattice, the simplest is a rhombohedral deformation.

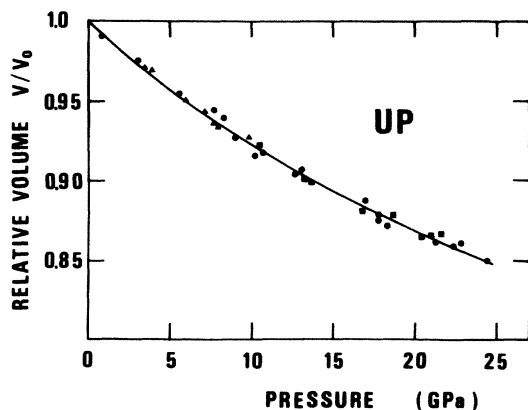


FIG. 1. Relative volume of UP as a function of pressure. Experiments have been performed in a solid pressure-transmitting medium: ●, increasing, or ■, decreasing pressure, and in a liquid pressure-transmitting medium: ▲, increasing and decreasing pressure.

If β is the small shift from the right angle of the unit-cell axes, one obtains for the interplanar distances d_{hkl}

$$d(hkl) = \frac{a}{(h^2 + k^2 + l^2)^{1/2}} \{1 + \beta\phi(hkl) - \beta^2[1 + \phi(hkl)]\},$$

with

$$\phi(hkl) = \frac{hk + kl + lh}{h^2 + k^2 + l^2}.$$

Then the volume is given by

$$V = a^3(1 - \frac{3}{2}\beta^2).$$

These results show that the interplanar distances are equal, to second order in β , to those given by a cubic lattice only if $\phi(hkl)$ is zero, which is verified for ($h00$) lines. In this case the volume of the unit cell is equal to the volume of the cube to second order in β . Otherwise, if $\phi(hkl)$ is nonzero, the interplanar distances depend to first order on the deformation and the volume must be calculated accordingly. For example, one obtains the following results from the (111) and (200) lines:

$$d_{200} = \frac{a}{2}(1 - \beta^2), \quad V_{200} = V_{\text{cub}}(1 + \frac{3}{2}\beta^2),$$

$$d_{111} = \frac{a}{3^{1/2}}(1 + \beta - 2\beta^2), \quad V_{111} = V_{\text{cub}}(1 - 3\beta + \frac{9}{2}\beta^2),$$

where V_{cub} is the volume of the cubic unit cell of length a . It follows that the deformation β must be taken into account when the volume is calculated from the (111) line.

The functions $\Gamma(hkl)$ and $\phi(hkl)$ have both a zero value for ($h00$) lines and take a maximum value for (hhh) lines, so they give very similar results. For example, the volume of UP calculated in the solid pressure-transmitting medium by taking into account the anisotropic components is the same as the volume obtained from a rhombohedral unit cell, the β angle being then equal to about 1° at 20 GPa.

Once the uniaxial-stress components have been taken into account, the pressure-volume relation of UP can be represented by a Birch equation of state, and a least-squares fit to the data yields the following values for the bulk modulus B_0 and its first pressure derivative B'_0 at ambient pressure:

$$B_0 = 102 \pm 3 \text{ GPa}, \quad B'_0 = 4.7 \pm 0.5.$$

The volume variation we determined under pressure is in rough agreement with previously reported results up to 15 GPa (Ref. 7), but the deduced values for B_0 and B'_0 are quite different. This discrepancy comes from the anisotropic stresses which were previously neglected and then led to an apparent increase of B_0 and a decrease of B'_0 (Ref. 7).

B. Uranium antimonide

The relative volume of USB as a function of pressure is displayed in Fig. 2. With increasing pressure, a discontinuous transition is observed at about 8 GPa and a new phase appears which coexists with the low-pressure NaCl-type phase up to 11 GPa. The structure of this new

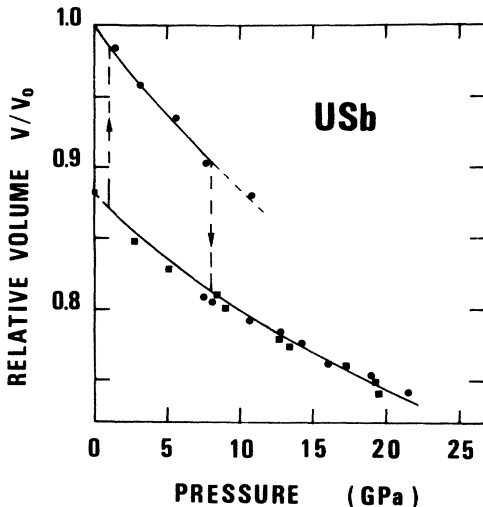


FIG. 2. Relative volume of USb as a function of pressure. The low pressure phase is of the NaCl type; the high-pressure phase is of the CsCl type. The experiments have been performed in a solid pressure-transmitting medium: ●, increasing pressure, and ■, decreasing pressure.

phase is cubic; the value of the lattice parameter and the intensities of the diffraction lines indicate a CsCl-type structure. Above $P = 11$ GPa, this CsCl phase is the only stable phase; with decreasing pressure, it remains stable down to very low pressures and some traces can even be found at ambient pressure.

The volume discontinuity $\Delta V/V_0$ at the NaCl-CsCl transition is equal to 9.2% at 8 GPa, but amounts to 11.8% at normal pressure, as observed when decreasing pressure. This large variation of $\Delta V/V_0$ is due to the lower value of the bulk modulus in the NaCl-type phase. A least-square fit of the experimental data to a Birch equation of state yields the following values at normal pressure for the bulk modulus B_0 and its first pressure derivative B'_0 for the two phases: for the low-pressure phase (NaCl-type)

$$B_0 = 72.7 \pm 5 \text{ GPa}, \quad B'_0 = 2 \pm 1,$$

and for the high-pressure phase (CsCl-type),

$$B_0 = 82.8 \pm 3 \text{ GPa}, \quad B'_0 = 4.1 \pm 0.5,$$

$$V_0(\text{CsCl})/V_0(\text{NaCl}) = 0.882 \pm 0.005.$$

IV. DISCUSSION

Uranium phosphide revealed a high sensitivity to anisotropic stress components. This proved to be the case for nonmetallic materials with high bulk moduli or unstable valence compounds. No change of the crystal structure is observed, at least up to 25 GPa. On the contrary, a NaCl-CsCl structure change takes place around 8 GPa in uranium antimonide, and the hysteresis field is so large that some traces of the high-pressure CsCl phase can still be found at normal pressure. Actually, USb is the first actinide compound among the monpnictides or chalcogenides reported to undergo this phase transformation,

which is frequently encountered in the similar lanthanide compounds (see, for example, CeAs or CeTe). However, LaSb or CeSb under pressure does not undergo this NaCl-CsCl transformation, but a rather unusual one: the structure changes from a cubic NaCl-type structure to a tetragonal one which is simply a largely distorted CsCl-type structure. This type of transition could not be attributed to a $4f$ effect since it has been observed for LaSb; therefore, an enhanced covalent bonding in rare-earth antimonides had to be assumed.

The sixfold-coordinated trivalent ionic radii of lanthanum and uranium are nearly equal,⁸ but in LaSb and USb the phase transformations under pressure are different; this may be due to a reduced covalent part in USb, as expected from the LMTO calculations.¹

The decrease of the volume of USb at the NaCl-CsCl transition is equal to 11.8% at normal pressure. Assuming that ionic radii are valid to describe this transformation where the coordination number increases from 6 to 8, then the calculated increase of the ionic radius of uranium amounts to 0.14 Å; this value is in good agreement with the value of 0.12 Å observed for lanthanides undergoing a similar phase transformation.⁸ At higher pressure, the volume jump at the NaCl-CsCl transition is reduced; this may indicate a growing size of the ion during the transition due to a reverse electronic transition induced by the larger U-Sb distance in the CsCl-type structure which comes from the increased coordination number. Similar phenomena were already observed in CeBi and CeTe.⁹ The experimental bulk moduli of UP and USb, 102 and 72.7 GPa, respectively, are in very good agreement with the theoretical values, 107 and 68 GPa, obtained from the self-consistent LMTO calculations.¹

In integral-valence rare-earth compounds it has been proposed¹⁰ that one express the bulk modulus at normal pressure of isostructural compounds by the relation

$$B_0 = \alpha Q / V_0$$

where α is a constant and Q the valence. This relation does not hold for uranium monpnictides. Actually in these compounds the bulk modulus varies, to the $-\frac{5}{3}$ power, with the unit-cell volume (Fig. 3), as expected for metallic or covalent bonding.¹¹ For USb the experimental value we obtained is slightly larger than the calculated one from this relationship but two remarks have to be made: the accuracy of B_0 for USb may be slightly lower than anticipated as the stability range of the NaCl phase is narrow, and a stronger ionic character of the bonding in USb could also lead to a different variation of the bulk modulus with the volume.

At normal pressure the resistivity behavior of USb was interpreted¹² by thermal activation of f electrons into the d band plus a Kondo effect which should bring a negative contribution to the bulk modulus.^{13,14} This lowering is not confirmed by the P - V relationship we measured, but the first pressure derivative of the bulk modulus appears to be rather low. This situation is very similar to what occurs in a typical, dense Kondo system such as CeAl₂ under high pressure.¹⁵ A small and continuous valence change is therefore possible in the cubic NaCl-type phase, although the small pressure range of its existence pre-

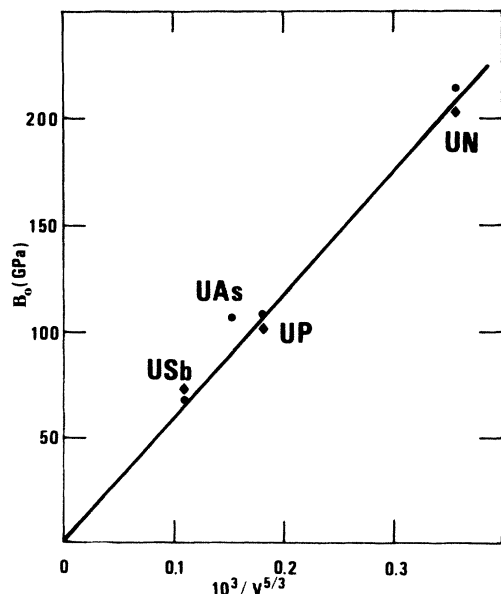


FIG. 3. Bulk modulus of uranium monopnictides as a function of the $-\frac{5}{3}$ power of the unit-cell volume. ●'s are theoretical values from Ref. 1, ◆'s are experimental values from Ref. 17 for UN and from this work for UP and USb.

cludes any definite conclusion.

At normal pressure the off-diagonal c_{12} elastic constant of USb is very low or even negative and was therefore taken as an indication of a possible intermediate-valence

state.¹⁶ This is possible but it must also be considered that a new crystallographic phase is stable down to very low pressures.

V. CONCLUSION

The volume variations of UP and USb have been determined by x-ray diffraction up to 25 GPa in a diamond-anvil cell. It has been shown that it is quite essential to account correctly for the uniaxial-stress components to obtain reliable variations of the volume with pressure.

The crystal structure of UP remains of cubic NaCl type, at least up to 25 GPa; the decrease of the volume with pressure is well represented by a Birch equation of state with an initial bulk modulus B_0 equal to 102 GPa and a first pressure derivative $B'_0 = 4.7$.

At 8 GPa, USb undergoes a crystallographic phase transformation from cubic NaCl to CsCl-type structure. This kind of phase change, although frequently encountered in rare-earth compounds, has not yet been reported for actinide monopnictides and it is generally thought to occur for rather ionic compounds.

The initial bulk modulus of the NaCl-type phase is not lowered by the presence of the Kondo effect found at normal pressure but the first pressure derivative is somewhat reduced: $B_0 = 72.7$ GPa, $B'_0 = 2$. In addition, the volume jump at the transition NaCl-CsCl under pressure is low. For uranium monopnictides the bulk modulus is inversely proportional to the $\frac{2}{3}$ power of the volume.

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