The Crystal Structure and the Equation of State of Thorium Nitride for Pressures up to 47 GPa

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Abstract
Experimental high-pressure X-ray diffraction studies have been performed on ThN powder for pressures up to 47 GPa using synchrotron radiation and a diamond anvil cell. The bulk modulus $B_0$ and its pressure derivative $B'_0$ have been determined: $B_0 = 175(15)$ GPa and $B'_0 = 4.0(4)$. No structural phase transition has been found in contrast to UN studied previously.

1. Introduction
Thorium nitride (ThN) belongs to the actinide pnictide compounds with the rock-salt structure (space group $Fm\bar{3}m$). In a previous paper (Olsen, Gerward & Benedict, 1985), high pressure X-ray diffraction studies were performed on the chemically and structurally related compound UN. The latter was found to transform into a rhombohedral structure at 29 GPa (space group $R\bar{3}m$), indicating a change of behaviour of the $5f$ electrons. The unit cell of the high-pressure phase of UN can be described as a slight distortion of the face-centred cubic unit cell of the low-pressure phase.

The present work describes the results of a high-pressure structural study of ThN up to 47 GPa with the aim of determining the equation of state and looking for a structural phase transition similar to that of UN. The neutral thorium atom has no $5f$ electrons in contrast to uranium. A comparison between the high-pressure behaviour of ThN and UN may therefore give information about the influence of the $5f$ electrons in structural transitions.

2. Experimental
X-ray diffraction experiments were performed at room temperature on powdered samples in a diamond anvil high-pressure cell using synchrotron radiation (HASYLAB, Hamburg; electron energy 3.7 GeV). The diffracted X-rays were recorded with the aid of the white-beam energy-dispersive method. Experimental details have been described elsewhere (Olsen, Buras, Gerward & Steenstrup 1981).

The pressure was determined from the pressure-induced wavelength shift of the fluorescence lines of a small ruby added to the powdered sample. The wavelength shift is generally assumed to be a linear function of the pressure. However, above 20 GPa a correction to the linear scale is necessary. Mao, Bell, Shaner & Steinberg (1978) have proposed the following relation

$$P = 380.8\left[ (1 + \Delta \lambda / \lambda_0)^5 - 1 \right],$$

(1)

where $P$ is the pressure in units of GPa, $\Delta \lambda$ the wavelength shift and $\lambda_0 = 6942.4$ Å.

Expanding (1) and using terms up to $(\Delta \lambda / \lambda_0)^3$ one can show that the pressure is given by

$$P'(\text{GPa}) = P'\{1 + (P' / 952)[1 + (P' / 1904)]\},$$

(2)

where

$$P'(\text{GPa}) = 1904 \Delta \lambda / \lambda_0 = 0.2743 \Delta \lambda (\text{Å}).$$

(3)

$P'$ in (3) is the corresponding pressure in the linear approximation of (1). The correction to the linear scale amounts to 2% at 20 GPa and 4% at 40 GPa.

The ThN powder was prepared at the European Institute for Transuranium Elements in Karlsruhe. The lattice parameter of ThN at atmospheric pressure was determined by the Debye–Scherrer method. It was subsequently checked in the high-pressure cell using NaCl as a reference material.

3. Results and discussion
The lattice constant of ThN at atmospheric pressure determined in the present work is 5.1666(4) Å. Very
few measurements have been found in the literature. Chiotii (1952) gives the value 5·21 Å. Holleck & Smailos (1980) have studied the lattice constant of mixtures of ThN and rare-earth nitrides. Their results are in graphical form only. For pure ThN we read 5·16(1) from their diagrams. This value is in agreement with our result quoted above.

All high-pressure diffraction spectra could be indexed according to the f.c.c. unit cell of the rock-salt structure. Table 1 shows the lattice constant as a function of pressure for an experimental run to 42 GPa. The variation of the lattice constant with pressure has been fitted to the Murnaghan and the Birch first-order equations of state (see, for example, Anderson, 1966) using the method of non-linear least squares.

The Murnaghan equation for a cubic crystal structure is

$$P = \left(\frac{B_0}{B'_0}\right)\left[\left(a_0/a\right)^{3B_0} - 1\right]$$

(4)

and the Birch equation is

$$P = \frac{3}{4}B_0\left[\left(a_0/a\right)^7 - (a_0/a)^5 \right]$$

$$\times \{1 + \frac{3}{4}(B'_0 - 4)\left[(a_0/a)^2 - 1\right]\},$$

(5)

where $a$ is the lattice constant at pressure $P$, $B_0$ the isothermal bulk modulus and $B'_0$ its pressure derivative, both at ambient pressure.

For the present data there is no significant difference between the Murnaghan and the Birch equations and the choice between them is a matter of taste. As a final result we quote $B_0 = 175(15)$ GPa and $B'_0 = 40(4)$, where the uncertainties are the standard errors of the fit. To the best knowledge of the authors there are no other experimental data to compare with in the literature.

The experimental results for ThN in this work and

<table>
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<th>$P$ (GPa)</th>
<th>$a$ (Å)</th>
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<tr>
<td>0</td>
<td>5·1666(4)</td>
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<tr>
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<tr>
<td>1·45</td>
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<td>35·88</td>
<td>4·913(15)</td>
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<tr>
<td>39·55</td>
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<tr>
<td>41·72</td>
<td>4·883(18)</td>
</tr>
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</table>

for UN in the previous work (Olsen et al., 1985) can be compared with the results of self-consistent energy-band calculations, performed for the actinide nitride series by Brooks, Johansson & Skriver (1984). The bulk modulus of UN shows a very good agreement, the experimental value being 203(6) GPa and the theoretical value 214 GPa. For ThN our measured value 175(15) GPa is about 20% lower than the calculated value 217 GPa.

The experimental bulk moduli of UN and ThN are consistent, however, with a remark by Brooks et al. (1984) that small lattice parameters generally lead to high bulk moduli for a given type of system. In the present case it is noticed that the lattice constant of UN, 4·8887(3) Å (Olsen et al., 1985), is smaller than that of ThN, 5·1666(4) Å (Table 1). It has been shown (Brooks et al., 1984) that the lattice parameters of the actinide series from ThN to AmN have a minimum at UN. Correspondingly, it may be reasonable to expect that the bulk moduli have a maximum at UN.

Unlike the case of UN, no phase transition has been observed for ThN and the rock-salt structure of ThN has been found to be stable at least up to 47 GPa, which is the highest pressure achieved in this work.

An important theoretical problem is to explain why a phase transition to a low-symmetry structure is observed for UN but not for ThN. A possible explanation could be that the actinide atoms do not have the same shape in the two compounds. The electronic configuration of the neutral atoms contains 5f electrons in uranium but not in thorium. The experimental results emphasize the call for the study of the role of the 5f electrons in structural phase transitions.

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References
