HIGH-PRESSURE X-RAY DIFFRACTION STUDIES ON ThS UP TO 40 GPa

USING SYNCHROTRON RADIATION

by

U. Benedict, J.C. Spirlet
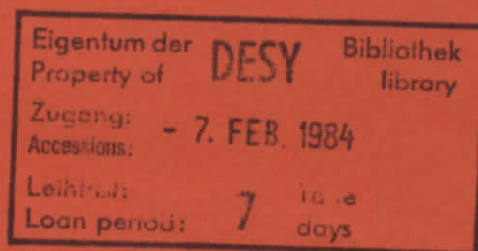
Commission of the European Communities, Joint Research Centre,
European Institute for Transuranium Elements, Karlsruhe

L. Gerward

Lab. of Applied Physics III, Technical Univ. of Denmark, Lyngby

J. Staun Olsen

Physics Lab. II, Univ. of Copenhagen, Copenhagen

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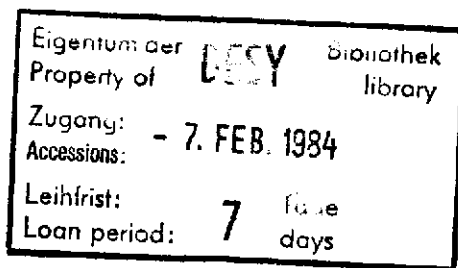synchrotron radiation.

U. Benedict, J.C. Spirlet
Commission of the European Communities, Joint Research Centre,
European Institute for Transuranium Elements, Postfach 2266,
D-7500 Karlsruhe, F.R.G.

L. Gerward
Laboratory of Applied Physics III, Technical University of
Denmark, DK-2800 Lyngby, Denmark.

J. Staun Olsen
Physics Laboratory II, University of Copenhagen,
Universitetsparken 5, DK-2100 Copenhagen, Denmark.

Abstract

High-pressure x-ray diffraction studies have been performed on
ThS up to 40 GPa using synchrotron radiation and a diamond anvil
cell. The measured value of the bulk modulus B_0= 145 GPa is in
disagreement with a previous measurement. The high-pressure behaviour
indicates a phase transformation to ThS II starting at 15 to 20
GPa. The transformation is of second order nature, the resulting
structure can be described as distorted fcc.

1. Introduction

Intermetallic compounds of the actinides represent an interesting area of research because of their complex structural, magnetic and electric properties. In a series of studies on these materials we have made high-pressure x-ray diffraction experiments using the synchrotron facilities at HASYLAB-DESY (Hamburger Synchrotron-strahlungslabor am Deutschen Elektronen-Synchrotron). It is inte-resting to compare the present results with those obtained for US in a similar study by J. Staun Olsen et al (1). Both ThS and US have rock-salt structure at room temperature and zero pressure. ThS is characterized as a material with a metallic lustre. The high pressure behaviour of ThS has only been mentioned in a short abstract by Govinda Rajan, Krishnan, Sequeira & Venkataraman (2). Th has in contrast to the other actinides no occupied 5f levels at normal pressure. Thus a comparative study of thorium compounds and uranium compounds may help to decide which effects can be ascribed to 5f electrons, and which ones are due to other factors. In this experiment we want to study the structure of ThS, and to see if any phase transformation happens at increasing pressure.

2. Experimental

The experiments were performed at the electron storage ring DORIS at HASYLAB-DESY   The measurements took place in a dedicated run with an electron energy of 3.7 GeV and an average electron current of 20-30 mA. The white beam energy-dis-persive diffractometer (3) was used for the experiments. The high pressure equipment consists of a diamond anvil cell of the Holz-apfel-Syassen type. A gasket of inconel with a hole 200 μm in diameter and thickness 80 μm enclosed the very fine ThS powder.

The material was prepared from the elements by two reaction steps at 500 and 1500 °C, at the European Institute for Transuranium Elements in Karlsruhe. No appreciable reaction with air was observed: The same lattice parameter was measured for powders crushed in air and in argon; a single phase was observed in both cases. The material in this type of experiments has to be a very fine powder or else a pronounced texture will be seen in the diffraction spectra. This is much more important when using synchrotron radiation instead of x-rays from a normal tube, because of the highly collimated synchrotron radiation. A 4:1 methanol-ethanol mixture and a ruby was added to the ThS powder to allow for hydrostatic pressure con-ditions and a proper pressure calibration, respectively. The maximum pressure was 40 GPa in the present work.

The uncertainty of the pressure determination is about 0.1 GPa for $p \lesssim 10$ GPa, where hydrostatic conditions can be maintained in the sample volume. For higher pressure the uncertainty is larger.

The synchrotron beam was defined by 100 μm x 100 μm slits, and the distance between sample and detector was 45 cm. This gives a good resolution (4) as compared with the case where an x-ray tube is used.

The spectrum of the scattered x-ray is measured by a pure germanium detector (FWHM = 150 eV at 5.9 keV) by Princeton Gamma Tech. The positions of the diffraction peaks were determined by the peak-search programme of the multichannel analyser.

3. Results

Fig. 1 shows a diffraction spectrum at normal pressure. The low-pressure spectra have been indexed according to the known rock-salt structure (Fm3m). The lattice parameter a = 568,51(3)pm was determined in an independent experiment on a powder diffractometer, in good agreement with literature data of Eastman, Brewer, Bromley, Gilles & Lofgren (5). The scattering angle 2θ has been determined from the zero-pressure spectrum and the known lattice constant. Because of the large distance between sample and detector a small shift in the sample position after applying pressure will have a negligible influence on the scattering angle. The uncertainty in the scattering angle determination is less than 0.01°. Unfortunately, the incident beam cross section could not be reduced to the size of the hole in the gasket. Therefore some diffraction lines from the gasket are seen in the diffraction spectra. All lines in the spectra could be identified as diffraction lines from ThS, fluorescene lines from Th, escape peaks or diffraction lines from the gasket.

The diffraction spectrum at 40 GPa shows broad peaks where the original fcc sharp peaks would be expected. In addition some new peaks are found.

The measured interplanar spacings d_{hkl} as functions of pressure are shown in Fig. 2. The filled circles denote increasing pressure, and the open circles decreasing pressure. Very little hysteresis has been observed for decreasing pressure. The spacing of the (111) planes is not shown for P > 15 GPa because the diffraction peak overlaps with Th fluorescence peaks.

For P > 35 GPa we have also used other scattering angles in order to shift the diffraction peaks on the energy scale. In this way we find a broad peak where the original 111 peak would be expected.

4. Discussion

The observed diffraction spectra could be indexed according to the rock-salt structure up to about 20 GPa. Fig. 3 shows the calculated unit cell volume V as a function of pressure. The V(P) data were fitted to Murnaghan's equation of state:

$$P = (B_0/B_0') \left[(V_0/V)^{B_0'} - 1 \right] \tag{1}$$

where B_0 is the isothermal bulk modulus and B_0' its pressure derivative at ambient pressure.

For comparison also the Birch equation has been used:

$$P = \frac{3}{2} B_0 \left[(a_0/a)^7 - (a_0/a)^5 \right] \{ 1 + \frac{3}{4} (B_0' - 4) \left[(a_0/a)^2 - 1 \right] \}$$

Table 1 shows the best results obtained by non linear least square fits to the two equations.

It is seen that B_0 and B_0' determined from the two equations of state agree very well. However, they differ by about 50% from the literature data. A possible explanation is that the use of synchrotron radiation gives a great improvement in the counting statistics of the diffraction spectra. Moreover, a large number of spectra, specially at low pressure, is necessary to obtain a reasonable accuracy in the fit to the equation of state.

The result of the fit to Murnaghan's equation is shown as full curve in Fig. 3. The agreement between the fitted curve and the measured

points is excellent. From about 20 GPa and upwards the observed
diffraction peaks could not be indexed according to the rock-salt
structure. The 222 peak disappears. Whether the 111 peak also dis-
appears, is not quite clear because a possible diffraction peak at
the corresponding energy would overlap with the thorium $L_{\gamma 1}$ fluore-
scence peak. But the intensity of the latter peak is not noticeable
increased in the pressure range 20-35 GPa, thus allowing only for a
weak possible overlapping peak. Around 36 GPa, peak broadening and
appearance of new peaks is observed.

Grosshans, Vohra & Holzapfel (6) have shown that for Pr, La, Y
distortion of the fcc lattice is possible at very high pressure.
They suggest that the distortion results from a phase transformation
of second order nature, which can be described by a soft phonon
mode with $\vec{q} = (2\pi/a_{fcc})(\frac{1}{2},\frac{1}{2},\frac{1}{2})$, where a_{fcc} is the lattice parameter
of the fcc phase. The soft phonon mode results in a hexagonal six-
layers sequence ABCA'B'C'. In accordance with this model we have
indexed the diffraction spectrum at 40.1 GPa using a unit cell
in the hexagonal representation where $a = a_{fcc}/\sqrt{2}$ and $c = 2\sqrt{3} \, a_{fcc}$.
In this way all observed lines could be indexed. The calculated
interplanar distances are shown in Table 2 together with the measured
values. The agreement is good, and we see that the spectrum consists
of groups of peaks that we cannot separate with our resolution. The
actual positions of the atoms in the unit cell are still unknown.
A complete structure determination would require more fundamental
work on intensity calculations using high-pressure energy-diffraction
and synchrotron radiation. It may be noted, however, that the spectra
obtained in the present work represent a great improvement as compared
to conventional diffractometry with respect to counting statistics
and exposure times.

The behaviour of ThS is different from that of US at high pressure
> 15 GPa: In US it was necessary to change a distorted fcc cell
even more, and use an orthorhombic cell for the high pressure phase.

This difference could result from the presence of 5f electrons in US.

5. Conclusions

The rock-salt structure of ThS is stable up to about 20 GPa. The
bulk modulus B_0 = 145(6) and its pressure derivative B_0' = 5.4(1.0)
have been determined from the observed V(P) data. The value for B_0
disagrees with about 50% from a previously published value.
For P > 20 GPa and up to the maximum pressure 4o GPa we observe a
new phase ThS II. The phase transformation is thought to be of second
order nature. The diffraction spectra of ThS II can be indexed
according to a distorted fcc structure where the close-packed planes
have the six-layers sequence ABCA'B'C'. This may be explained by a
soft phonon mode with $q = (2\pi/a_{fcc})(\frac{1}{2},\frac{1}{2},\frac{1}{2})$.

Table 1. The bulk modulus and its pressure derivative for ThS

Murnaghan equation	$B_0 = 145.7 \pm 5.3$ GPa $B_0' = 5.2 \pm 1.0$
Birch equation	$B_0 = 145.2 \pm 5.6$ GPa $B_0' = 5.4 \pm 1.0$
Average value	$B_0 = 145 \pm 6$ GPa $B_0' = 5.4 \pm 1$
K.Govinda Rajan et al. (2)	$B_0 = 220$ GPa.

Table 2. Diffraction spectrum of ThS powder, P = 40.1 GPa. The distorted fcc phase has been indexed using a hexagonal representation with $a = a_{fcc}/\sqrt{2}$ and $c = 2\sqrt{3}\ a_{fcc}$.
Lattice parameters are a = 380(3)pm, c = 1861(20)pm.

d measured	Intensity	d calculated	hkl (distorted fcc)	Equivalent hkl (fcc)
3.097	m	3.102	006	111
2.638	s	2.687	104	200
2.457	w	2.465	105	
2.317	w	2.327	008	
1.962	s	1.900	108	220
1.829	w	1.817	110 113	
1.627	s	1.620	202 116	311/222
1.322	m	1.343 1.330	208 1,1,1o	400
1.200	w	1.202	214	420
1.152	w	1.154	216	
1.031	w	1.034	306	422
0.980	w	0.992 0.970	308 2,1,12	511

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Figure captions

Fig. 1. Energy-dispersive x-ray diffraction spectrum of ThS
        at P = 0 GPa

Fig. 2. Interplanar spacings of ThS as functions of pressure.
        The indices of the fcc phase are indicated to the left
        and those of the distorted fcc phase to the right. Filled
        circles denote increasing pressure, open circles decreas-
        ing pressure.

Fig. 3. Unit cell volume of ThS as a function of pressure. The
        curve shows the result of a fit to Murnaghan's equation
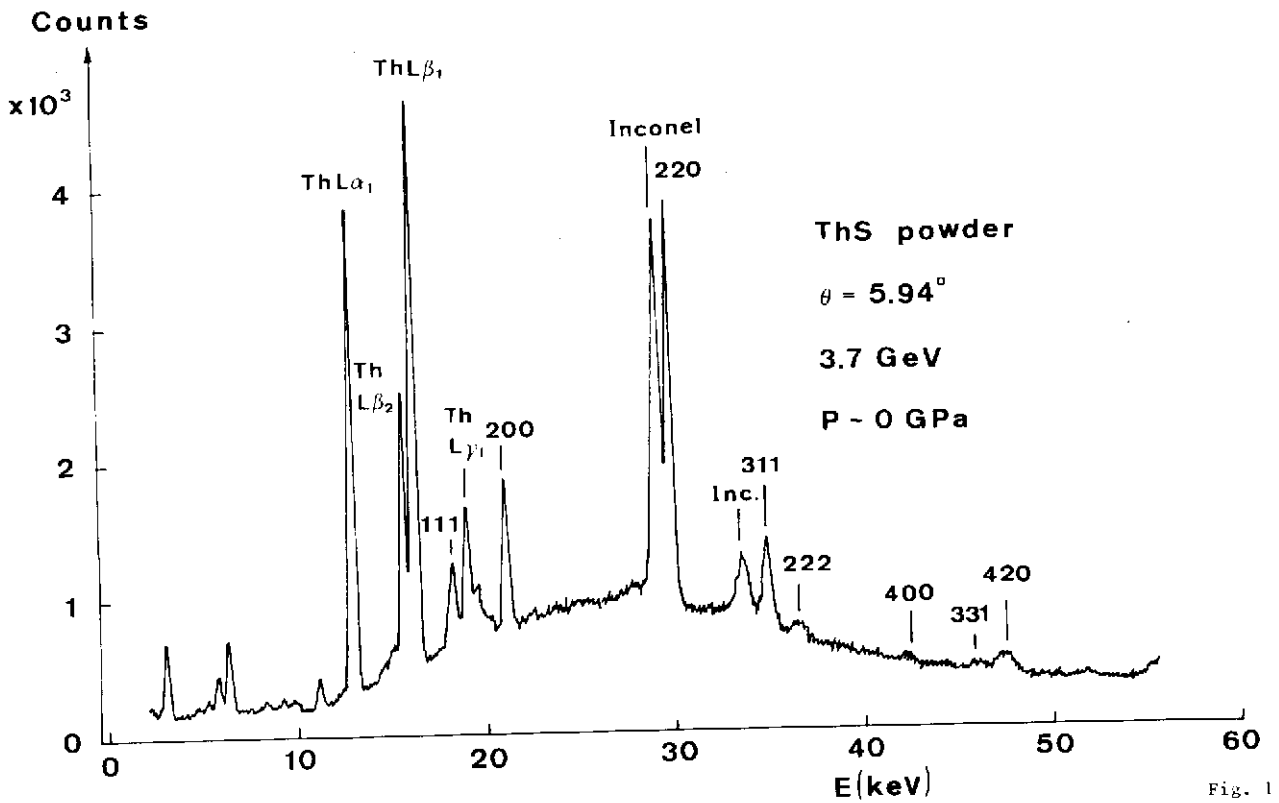   of state.
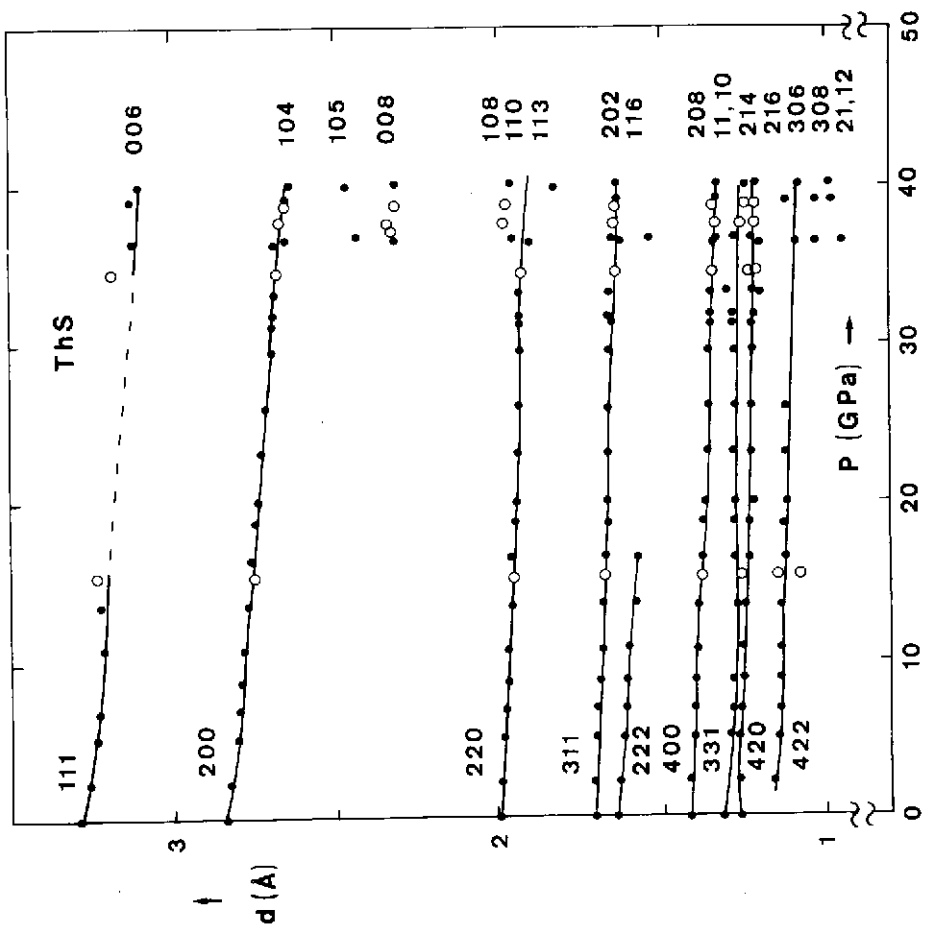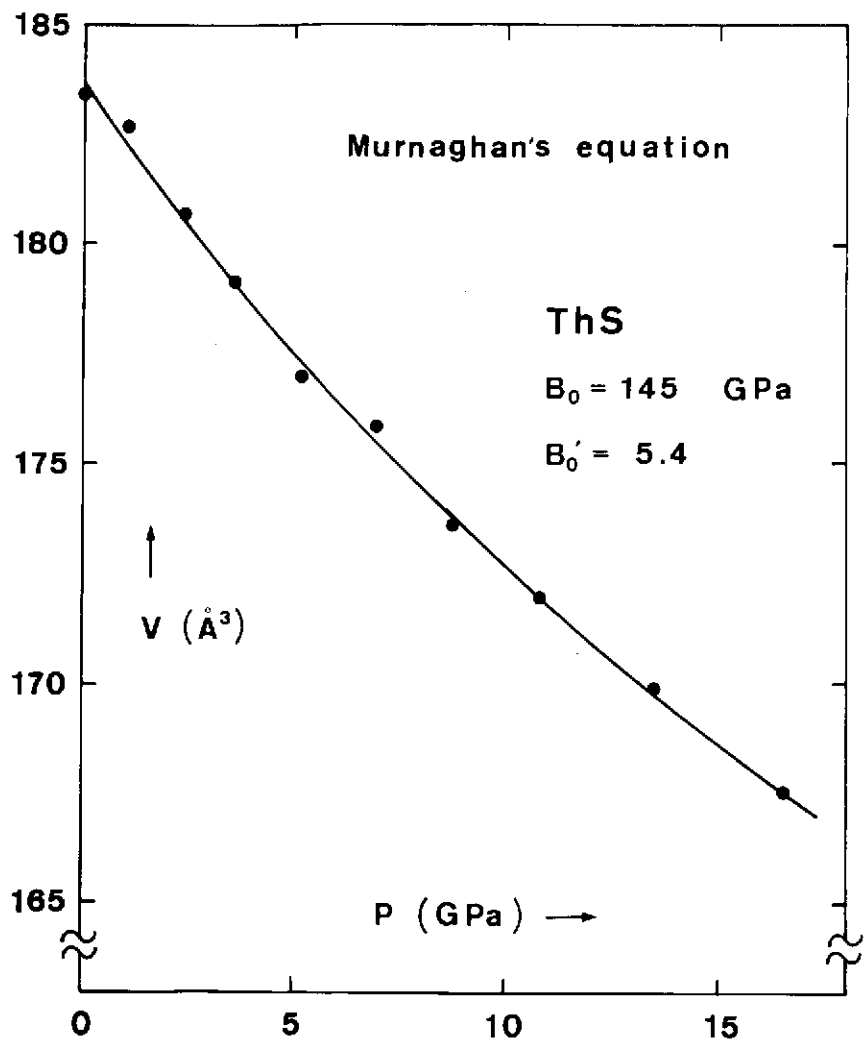
Fig. 2

ThS

d (Å)

P (GPa) →

006, 104, 105, 008, 108, 110, 113, 202, 116, 208, 11,10, 214, 216, 306, 308, 21,12

111, 200, 220, 311, 222, 400, 331, 420, 422

Fig. 2

Counts

x10³

ThLβ₁

ThLα₁

Inconel

220

Th Lβ₂

Th Lγ₁

200

111

311

Inc.

222

400

331

420

ThS powder

θ = 5.94°

3.7 GeV

P ~ 0 GPa

E(keV)

Fig. 1

Fig. 3