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X-RAY DIFFRACTION AND SYNCHROTRON RADIATION

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J. Staun Olsen

Physics Lab. II, University of Copenhagen, Copenhagen, Denmark

L. Gerward

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

U. Benedict

Commission of the European Communities, Joint Research Centre,
European Institute for Transuranium Elements, Karlsruhe

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J. Staun Olsen

Physics Laboratory II, University of Copenhagen, Universitets-
parken 5, DK-2100 Copenhagen, Denmark

L. Gerward

Laboratory of Applied Physics III, Technical University of

Denmark, DK-2800 Lyngby, Denmark

U. Benedict

Commission of the European Communities, Joint Research Centre,

European Institute for Transuranium Elements, Postfach 2266,

D-7500 Karlsruhe, F.R.G.

Abstract

High-pressure x-ray diffraction studies have been performed
on UN powder for pressures up to 34 GPa using synchrotron
radiation and a diamond anvil cell. For the cubic low-pres-
sure phase the bulk modulus $B_0 = (203 \pm 6)$ GPa
and its pressure derivative $B_0' = 6.3 \pm 0.6$ is in good agreement
with other data from the literature. The UN material has been
found to transform to a new phase, UN III, at 29 GPa. The
transformation is of first order nature with a 3.2% decrease
in volume. The UN III phase has been indexed according to a
face-centred rhombohedral cell with $a = 4.657(5)$ Å and
$\alpha = 85.8(2)^\circ$ at 34 GPa. The influence of the 5 f electrons in
the transformation is discussed.
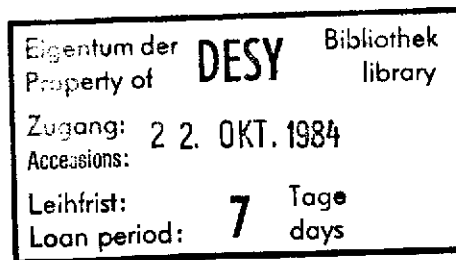
1 Introduction

Uranium nitride (UN) belongs to the actinide pnictide com-
pounds with the rock salt structure (space group Fm$\bar{3}$m). In
the last fifteen years these compounds have been extensively
studied by various methods, mainly because of their magnetic
properties. Temperature induced first-order magnetic phase
transitions have been found in these materials, which usually
are either ferromagnetically or antiferromagnetically ordered
at low temperatures. The 5 f-electrons are primarily respon-
sible for the magnetic behaviour of the actinides and can be
compared with the situation found for the iron-group transition
metals and the rare earths, where the 3 d- and 4 f-electrons,
respectively, determine the magnetic properties. At the moment
we have no precise knowledge about the electronic structure of
all these compounds. In particular, there are great difficul-
ties in describing the 5 f-electrons, because they are neither
well localized at the actinide ions nor completely itinerant
(taking part in the bonding).

UN is a Type I antiferromagnet (van Doorn & du Plessis 1977)
with the Néel temperature T_N = (53.1 ± 0.2) K. In contrast to
other antiferromagnetic uranium compounds it has a rather small
lattice constant and a small value of the ordered moment at
T = 0 K. It is suggested that UN is a band or itinerant anti-
ferromagnet such as chromium metal. Photoelectron spectroscopy
on UN has shown a narrow band of f states near the Fermi level
containing (2.2 ± 0.5) electrons (Norton, Tapping, Creber

& Buyers 1980).   This indicates the possibility of
an intermediate valence for the uranium in UN. Thus the number
of electrons in the 5 f shell may be a non-integer.

Very few high-pressure studies have been reported, even though
this is a clean method to change the interatomic distance. In
the present paper we report some high-pressure experiments on
UN up to 34 GPa at room temperature. The purpose of the experi-
ments has been to compare the high-pressure behaviour with the
results of the other experiments mentioned above, and theoreti-
cal calculations.

2 Experimental

A diamond anvil cell of the Holzapfel-Syassen type was utilized
for the high-pressure studies. A gasket of inconel with a hole
200 μm in diameter and thickness 80 μm enclosed the very fine
UN powder. A 4:1 methanol-ethanol mixture was added to the pow-
der to allow for hydrostatic pressure conditions. The pressure
was determined from the pressure induced wavelength shift of
the fluorescence lines from a small ruby added to the powder.
The uncertainty in the pressure determination is estimated to
0.1 GPa for pressures below 10 GPa. For higher pressures the
uncertainty may be larger because of non-hydrostatic conditions.

The X-ray experiments were performed using synchrotron radia-
tion from the electron storage ring DORIS at HASYLAB-DESY in
Hamburg. The electron energy was 3.7 GeV. The pressure cell was

placed on an energy-dispersive diffractometer (Staun Olsen, Buras, Gerward & Steenstrup, 1981). Diffraction from the gasket was avoided by reducing the incident beam cross section to 0.1×0.1 mm^2 using tantalum slits. A good geometrical resolution was obtained by using a large distance (35 cm) between sample and detector and a slit (0.4 mm) in front of the detector to define the scattered beam.

The diffraction spectra were analysed in a pure germanium detector (PGT) with an energy resolution of 150 eV (FWHM) at 5.9 keV, and a multichannel pulse-height analyser (Canberra 80) having 2048 channels and covering the energy range up to 70 keV. The energy positions of the diffraction peaks were determined by the peak-search programme of the multichannel analyser. The scattering angle 2θ is a fixed parameter in the energy-dispersive diffraction method. In the present work the angle has been determined from a diffraction spectrum of NaCl at atmospheric pressure in the pressure cell. The estimated uncertainty in the angle determination is less than 0.01°. Once the 2θ scale of the diffractometer has been calibrated, the angle can be changed in units of 0.001° by a stepping motor.

The UN powder has been obtained by grinding sintered UN pellets prepared at the European Institute for Transuranium Elements in Karlsruhe. The material has to be a very fine powder in order to give a diffraction spectrum that is representative for a random powder. This is because the sample volume is very small and the incident synchrotron radiation is highly collimated.

3 Results

The lattice constant at atmospheric pressure and room temperature depends slightly on the carbon content. Muromura & Tagawa (1979) have obtained the extrapolated value 4.8883(2) Å at zero carbon content. This value is in good agreement with the value 4.8887(3) Å found in the present work by the standard Debye-Scherrer-technique and for the UN powder in the pressure cell, using NaCl as a reference material.

Fig. 1a shows an energy-dispersive diffraction spectrum of UN powder at atmospheric pressure. It is seen that the spectrum can be indexed according to the fcc structure up to and including the 420 reflection. Still higher indices have been obtained by increasing the scattering angle 2θ, but in that case some of the low-index lines will overlap with the uranium L-lines. The spectrum in Fig. 1a has been found to be the best compromise, having a sufficient number of peaks for an accurate structure determination and avoiding overlap problems with the fluorescence lines. Notice also the complete absence of any diffraction lines from the gasket. Fig. 2 shows the interplanar spacings as functions of pressure.

4 Discussion

4.1. The cubic phase at P < 29 GPa

It is found thet the diffraction spectra of UN can be indexed according to the fcc structure up to a pressure about 29 GPa. The lattice constant a of the cubic phase has been calculated by a least squares fit to the observed spectrum of diffraction lines for each pressure. The unit cell volume V and the pressure P were fitted to the Murnaghan first-order equation of state (see for example Anderson 1966):

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

where V_0 is the unit cell volume at ambient pressure, B_0 the isothermal bulk modulus and B_0' its pressure derivative, also at ambient pressure. In addition, the Birch first-order equation has been used:

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

The result of the fit to the Murnaghan equation is shown in Fig. 3. The agreement between the fitted curve and the measured points for P < 29 GPa is excellent. Table 1 shows that

the two equations give the same B_0 value within less than 1%. As a final result we quote $B_0 = 203(6)$ GPa and $B_0' = 6.3(2)$. These values are in good agreement with other data from the literature. Padel, Groff & Novion (1970) have found $B_0 = 205.9$ GPa from ultrasonic measurements. Guinan & Cline (1972) determined $B_0 = 191.1$ GPa from measurements of elastic constants. Fournier, Beille, Boeuf, Vettier & Wedgwood (1980) have measured the pressure dependence of the lattice parameter at 4.2 K using neutron diffraction. They quote the value 0.5 Mbar^{-1} for the compressibility, corresponding to $B_0 = 200$ GPa.

Hill (1970) has compared the behaviour of different uranium compounds as a function of the U-U distance in the so-called Hill plot. According to this plot uranium compounds are forming two groups with respect to the magnetic behaviour and the localization of the 5f electrons. The separation of uranium atoms in UN at zero pressure in the cubic phase is equal to 3.46 Å. The distance has decreased to 3.34 Å at the pressure 29 GPa. According to the Hill plot we have then passed the border of the transition region. In this region we expect a nonmagnetic behaviour and a delocalization of the 5f electrons.

4.2 The rhombohedral phase at P > 29 GPa

A phase transformation has been found at about 29 GPa as mentioned in Section 3. It is assumed that the new structure is a slight distortion of the face-centred cubic structure of the low-pressure phase. The diffraction peaks from the cubic phase split into two or more new lines or broaden. Noticeable exceptions are the 200 and 400 lines, which remain unchanged in the

high-pressure phase (see Fig. 1 and 2). This behaviour is ex-
pected, when a cubic unit cell is deformed into a rhombohedral
one. We therefore conclude that the uranium atoms form a face-
centred rhombohedral lattice. The positions of the nitrogen
atoms cannot be determined in the present investigation because
of their small scattering power. Fig. 1b shows a diffraction
spectrum of the high-pressure phase indexed according to the
face-centred rhombohedral cell. There are no unindexed
lines in the spectrum. All the calculated lines are observed
except the 222 line. However, the 222 line is expected in a
spectral region where the strong 113 and $\bar{1}13$ peaks are overlap-
ping.

The space group is $R\bar{3}m$ (No. 166) where the notation and the
number of the space group are those given in the International
Tables for X-ray Crystallography (1969). The space group is
one of the maximal non-isomorphous subgroups of $Fm\bar{3}m$. The
customary description of the lattice is a primitive rhombohedral
cell or a triple-hexagonal cell with 3 point positions in 3(a):
$000, \frac{2}{3}\frac{1}{3}\frac{1}{3}, \frac{1}{3}\frac{2}{3}\frac{2}{3}$. In the ideal case of an fcc lattice one has
$c_H/a_H = 2.449$, where a_H and c_H are the lattice constants of
the triple-hexagonal cell. In the present work we are using
the larger face-centred rhombohedral cell with 4 point posi-
tions per unit cell. The reason for this is to facilitate the
comparison with the low-pressure phase of the NaCl-type.
Actually the space group is denoted $F1\bar{3}2/m$ when the structure
is described as being derived from the NaCl structure.

The unit cell parameters a and α of the rhombohedral structure
have been determined from the energies of the Bragg peaks in the
diffraction spectra using the method of least squares. The re-
finement programme PURUM (Werner 1969) has been very useful for
this purpose. Table 2 lists the observed and calculated inter-
planar spacing at 34 GPa. The calculated unit cell parameters
at 34 GPa are a = 4.657(5) Å and α = 85.8(2)$^{\circ}$, where the uncer-
tainties are the standard errors of the fit. The goodness of the
fit is characterized by

$$\sum (d_{obs} - d_{calc})^2/(n - 2) = 3.2 \times 10^{-5} \ \text{Å}^2 \qquad (3)$$

where n is the number of reflexions. Alternatively, we have cal-
culated a reliability factor:

$$100 \sum |d_{obs} - d_{calc}|/\sum d_{obs} = 0.28\% \qquad (4)$$

These results show that the present structure determination is considerably better than a previous high-pressure study of US (Staun Olsen, Steenstrup, Gerward, Benedict, Spirlet & Andreetti 1984). The present work is comparable with a high-pressure study of YbH_2 (Staun Olsen, Buras, Gerward, Johansson, Lebech, Skriver & Steenstrup 1984), where a reliability factor about 0.3% was obtained. Table 3 shows the unit cell dimensions for all measured pressures.

The unit cell volume is shown as a function of pressure in Fig. 3. The fit to the Murnaghan equation for the low-pressure cubic phase has been extrapolated to P > 29 GPa as shown by the broken line. It is seen that there is a discontinuity of the volume at the phase transition at about 29 GPa. Therefore we conclude that it is a first order transition. There is a 3.2% volume decrease when the structure changes from cubic to rhombohedral.

The highest pressure obtained in the present work is 34 GPa and we have too few measurements to determine the equation of state for the high-pressure phase. There is very little hysteresis in the phase transition as indicated by the measurements for decreasing pressure (open symbols in Fig. 2 and 3).

4.3. Comparison with theoretical calculations.

The equation of state for UN has been computed by Brooks and Glötzel (1980) in the atomic sphere approximation. In Fig. 4 we have compared the theoretical equation of state with

our experimental measured values of volume as function of pressure. We see some deviation between the two curves. The theoretical equilibrium lattice parameter is 4.86 A compared with the experimental value 4.89 A. The theoretical bulk modulus 237 GPa calculated by means of the theoretical equation of state corresponds reasonably well to the experimental B_0 value 203 ± 6 GPa. No theoretical calculations showing any phase transformation are available for the time being. It is interesting that the U-U distance in UN is close to the critical distance given by Hill. The transformation seen in the case of UN is much more evident than in the case of US. The measured phase transformation can be an argument for that not all 5 f electrons take part in binding at normal temperature and pressure, and that they change their behaviour at about 29 GPa.

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Table 1 The bulk modulus B_0 of cubic UN and its pressure derivative B_0' at ambient pressure. The uncertanties are the standard deviations of the least squares fit to the equation of state.

Equation of state	B_0 (GPa)	B_0'
Murnaghan first-order	203 ± 6	6.2 ± 0.6
Birch first-order	203 ± 7	6.5 ± 1.0
Weighted average value	203 ± 6	6.3 ± 0.6

Table 2 Diffraction spectrum of UN powder, P = 34 GPa.
hkℓ = indexing using a face-centred rhombohedral unit cell with a = 4.657(5) Å and α = 85.8(2)°.
HKL = indexing using the customary triple-hexagonal unit cell with a_H = 3.169(4) Å, c_H = 8.640(14) Å and c_H/a_H = 2.726(6) (space group R$\bar{3}$ m).

d_{obs} (Å)	d_{calc} (Å)	hkℓ	HKL	intensity
2.890	2.880	111	00.3	m
2.620	2.616	$\bar{1}$11	10.1	s
2.313	2.317	200	10.2	s
1.706	1.698	220	10.4	m
1.579	1.585	$\bar{2}$20	11.0	m
1.462	1.462	113	10.5	m
	1.440	222	00.6	not observed
1.384	1.388	$\bar{1}$13	11.3	m
1.359	1.355	$\bar{1}\bar{1}$3	20.1	w
1.317	1.308	$\bar{2}$22	20.2	w
1.152	1.158	400	20.4	m
1.125	1.126	133	10.7	w
1.075	1.075	$\bar{1}$33	20.5	m

Table 3. Unit cell dimensions for UN

P(GPa)	a(A)		V(A³)
Face-centred cubic			
0	4.8887(3)		116.84(2)
1.53	4.880(4)		116.2(3)
2.69	4.872(4)		115.6(3)
5.15	4.853(4)		114.3(3)
6.66	4.839(4)		113.3(3)
7.64	4.833(4)		112.9(3)
8.63	4.827(4)		112.5(3)
10.20	4.819(4)		111.9(3)
12.77	4.805(4)		110.9(3)
13.01	4.800(4)		110.6(3)
16.00	4.782(4)		109.4(3)
18.36	4.777(5)		109.0(3)
21.0	4.763(9)		108.1(3)
22.2	4.753(9)		107.3(6)
23.6	4.747(8)		106.9(4)
27.9	4.726(10)		105.6(7)
28.8	4.723(13)		105.4(9)
Face-centred rhombohedral		$\alpha(°)$	
28.8	4.686(15)	86.1(3)	102.2(9)
31.0	4.677(10)	86.4(3)	101.7(7)
32.1	4.673(10)	86.4(2)	101.4(7)
34.0	4.657(6)	85.8(2)	100.2(4)

Figure captions

Fig. 1 X-ray energy-dispersive diffraction spectra of UN powder obtained with synchrotron radiation (electron energy 3.7 GeV, electron current 20-40 mA). Scattering angle $2\theta = 11.17°$. High-energy part magnified 10X in intensity.

(a) Rock salt structure at atmospheric pressure.

(b) Rhombohedral structure at 34 GPa.

Fig. 2 Interplanar spacing of UN as functions of pressure. The indices of the f.c.c. structure are given on the left-hand side and those of the f.c. rhombohedral structure on the right-hand side. Filled symbols denote measurements for increasing pressure and open circles denote decreasing pressure.

Fig. 3 Unit cell volume of UN as a function of pressure. The curve for the cubic phase has been calculated from the Murnaghan equation using $B_0 = 203$ GPa and $B_0' = 6.3$. The curve has been extrapolated for P > 29 GPa as shown by the broken line. Triangles denote the rhombohedral high-pressure phase. Open symbols denote measurements for decreasing pressure.

Fig. 4 Comparison between experimental and calculated equation of state for UN. ———·——— experimental values, ----------- theoretical values.
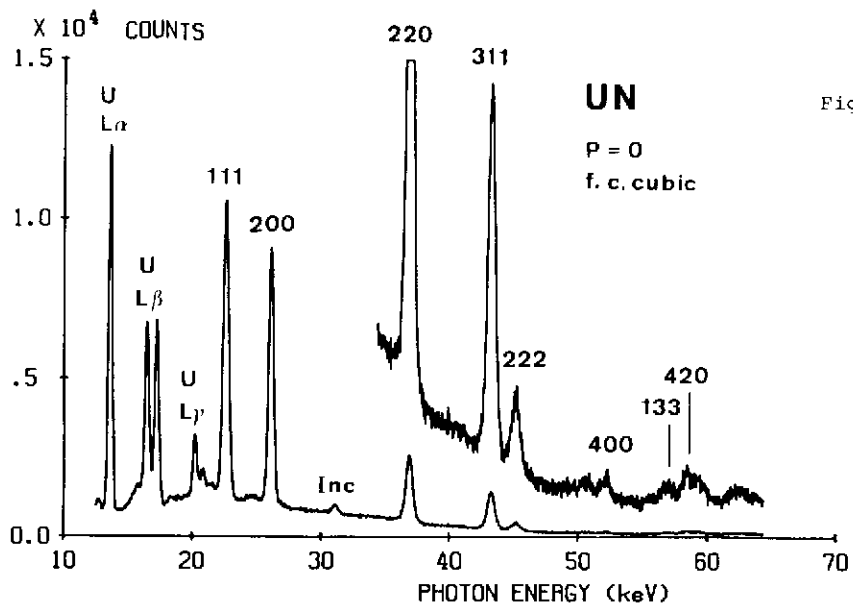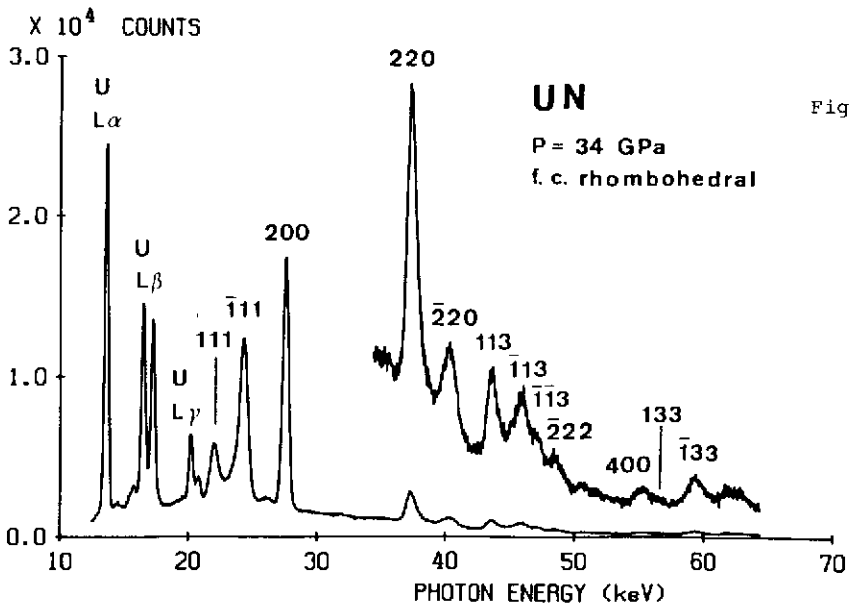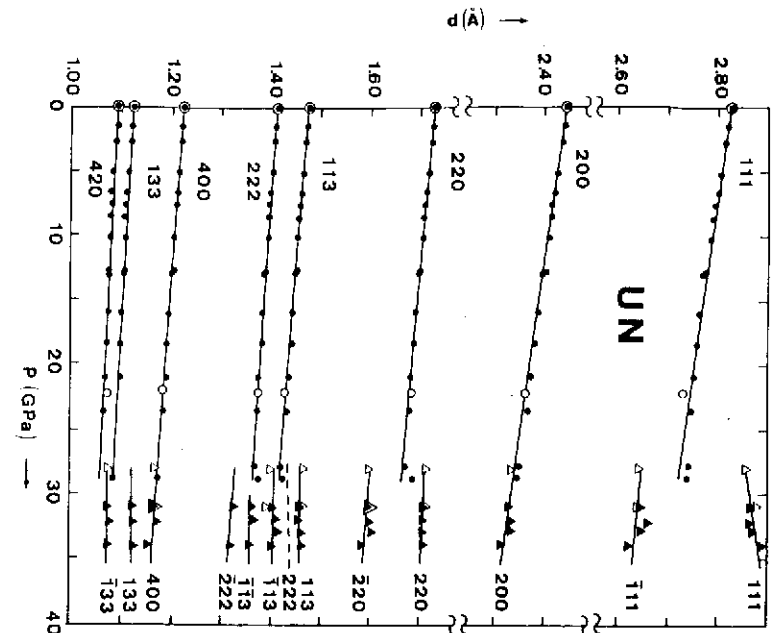
Fig. 1a

UN

P = 0

f. c. cubic

Fig. 1b

UN

P = 34 GPa

f. c. rhombohedral

Fig. 2

UN

Fig. 3

UN

● ○ f. c. cubic

▲ △ f. c. rhombohedral

Fig. 4