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Compressibility and structural stability of CeN from experiment and theory. The B1–B2 transition

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ABSTRACT

The high-pressure structural stability of CeN is investigated by experiment and theory. Experiments are carried out by energy-dispersive X-ray diffraction and synchrotron radiation, using a diamond anvil cell, to a maximum pressure of 77 GPa. The experimental results are in remarkably good agreement with *ab initio* calculations using the full-potential linear muffin-tin orbital method within the generalized gradient approximation (GGA). The experimental zero pressure bulk modulus is $B_0 = 156(3)$ GPa, the pressure derivative being constrained to $B_0{}' = 4.00$. The corresponding calculated data are $B_0 = 158.1$ GPa and $B_0{}' = 3.3$. We report here the first experimental observation of the transformation of CeN from the ambient B1 type crystal structure to the B2 type. The onset of the transition is in the range 65–70 GPa, and the relative volume change at the transition is $\Delta V/V = -10.9(3)\%$. These data compare well with the calculated transition pressure $P_{tr} = 68$ GPa and $\Delta V/V = -10.8\%$. Experimentally, the transition is found to be rather sluggish.

1. Introduction

The rare-earth nitrides constitute a series of compounds crystallizing in the rock-salt type structure. While transition-metal nitrides have been widely studied, comparably little is known about the corresponding rare-earth nitrides. They are hard and brittle materials, stable but very sensitive to oxidation and hydrolysis. There is a current interest in the magnetic, electronic and optical properties of these compounds [1,2]. Rare-earth nitrides also have potential applications in spintronics [3]. Cerium nitride (CeN) is the first member in this series of compounds, and it has rather unusual properties compared with the other rare-earth nitrides. For example, the lattice parameter of CeN is anomalously small, indicating a tetravalent Ce configuration, while trivalence prevails in the other rare-earth nitrides. Thus, CeN is similar to the collapsed α-phase of cerium metal, where the cerium *f* electrons are itinerant, contributing actively to the metallic conduction and cohesive properties [4]. Only a few theoretical or experimental papers have been devoted to the structural and electronic properties of CeN and other rare-earth mononitrides [4–14]. Epitaxial layers of CeN on Mg (0 0 1) have recently been investigated [15].

The pressure-induced transformation from the NaCl (B1) type structure to the CsCl (B2) type structure is well known from studies of the alkali halides [16] and many other compounds. The transformation is sluggish with a strong hysteresis in compression and decompression. It is characterized by the appearance of new diffraction lines, notably the strong 100 and 110 lines of the B2 phase. Empirically, it is found that the spacing of the (2 2 0) lattice planes of the B1 phase is almost equal to the spacing of the (1 1 1) planes of the B2 phase. The same is true for the B1 (3 1 1) and B2 (2 0 0) planes, as well as the B1 (4 0 0) and B2 (2 1 1) planes [17]. These facts imply that the relative volume collapse at the transition is between 8 and 12%.

Several cerium monopnictides are known to transform under pressure from the B1 type structure to the B2 type structure. Thus, CeP has a transition pressure $P_{tr} = 19$ GPa and a relative volume change $\Delta V/V = -10.5\%$ [18]. Similarly, it is found that $P_{tr} = 14$ GPa and $\Delta V/V = -11\%$ for CeAs [19]. CeN has a smaller lattice parameter than CeP and CeAs, and the B1–B2 transition is therefore expected at a higher pressure. No experimental evidence is available up till now, but theoretically the B1–B2 transition has been predicted to occur at 62 GPa by Svane et al. [4], and at 88 GPa by Rukmangad et al. [12]. In contrast, the lanthanum and praseodymium monopnictides

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are known to transform under pressure from the B1 type structure to a distorted B2 type structure [20–27]. LaN is an exception, since it is predicted to undergo a pressure-induced B1–B2 transition at about 27 GPa [28].

Recently, Kanchana et al. [14] published a theoretical work on the lattice dynamics and elastic properties of CeN using *ab initio* density-functional methods. Both the local density approximation (LDA) and the generalized gradient approximation (GGA) were used for the exchange-correlation potential. In particular, these authors are stressing the need for more experimental work in order to clarify the high-pressure behavior of CeN. In the present work, we have undertaken studies of high-pressure energy-dispersive X-ray diffraction in CeN up to 77 GPa using the diamond anvil cell and synchrotron radiation. As the results will show, the GGA calculations of Kanchana et al. [14] are in remarkably good agreement with experiment for CeN. We have therefore focused on those calculations, which have been extended to include the B2 phase and the B1–B2 transition pressure.

2. Experimental procedure

2.1. Sample preparation

Precautions must be taken to prevent the oxidation of powdered rare earth metals and the hydrolysis of the nitride product [29]. CeN was prepared by reacting Ce chips (Ventron Chemicals) with flowing NH_3 gas at 516 °C for about 6 h in a quartz tube. Before the reaction, the Ce chips were washed with cyclohexane C_6H_{12}, which is relatively unreactive. All manipulations were performed in a protective N_2 atmosphere.

2.1.1. High-pressure X-ray diffraction

Room temperature, high-pressure X-ray diffraction (XRD) powder spectra were recorded at beamline F3 of HASYLAB-DESY in Hamburg, Germany, using the white-beam method and synchrotron radiation. The diffractometer, working in the energy-dispersive mode, has been described elsewhere [30]. High pressures were obtained in a Syassen–Holzapfel type [31] diamond-anvil cell. A finely ground powder sample and a ruby chip as a pressure marker were placed in a hole with a diameter of 80 μm in an Inconel gasket, pre-indented to a thickness of 60 μm. Due to the high reactivity of CeN, the pressure cell was loaded in a nitrogen atmosphere, and silicone oil was used as the pressure-transmitting medium. The pressure was determined by the ruby luminescence method, applying the non-linear pressure scale of Mao et al. [32]. Experiments have been performed at different Bragg angles. The Bragg angle of each run was calculated from a zero-pressure spectrum of sodium chloride (NaCl) in the diamond-anvil cell.

Energy-dispersive XRD spectra were recorded at pressures up to 77 GPa. At each pressure, values for the lattice parameter and the unit-cell volume were derived and refined using the PURUM code [33]. The compression curve can be described by the Birch-Murnaghan equation of state [34]:

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

where $x = V/V_0$, V being the volume at pressure P, and V_0 the volume at zero pressure, B_0 is the bulk modulus and B_0' its pressure derivative, both parameters evaluated at zero pressure. Numerical values of B_0 and B_0' were obtained from a non-linear least-squares fit of Eq. (1) to the experimental pressure–volume data points.

3. Theoretical calculations

Total-energy calculations have been carried out using the all-electron full potential (FP) linear muffin-tin orbital method [35,36] for the NaCl and CsCl type crystal structures. In this method, the crystal is divided into two regions: non-overlapping muffin-tin spheres surrounding each atom, and the interstitial region between the spheres. We use a double-*k spdf* LMTO basis (each radial function within the spheres is matched to a Hankel function in the interstitial region of decay constant *k*) for describing the valence bands. The basis functions included in the calculations are Ce (5s, 6s, 5p, 5d, 4f) and N (2s, 2p). The potential is expanded in terms of spherical harmonics within the spheres, and in terms of plane waves in the interstitial region. The GGA [37] has been used for the exchange-correlation potential. The charge density and potential inside the muffin-tin spheres were represented by spherical harmonics up to $l_{max} = 6$, while in the interstitial region, 6566 plane waves with energies up to 147.5 Ry were included in the calculations. Total energies were evaluated as a function of volume with the tetrahedron method for a (22 × 22 × 22) *k*-mesh, corresponding to 328 *k* points in the irreducible Brillouin zone.

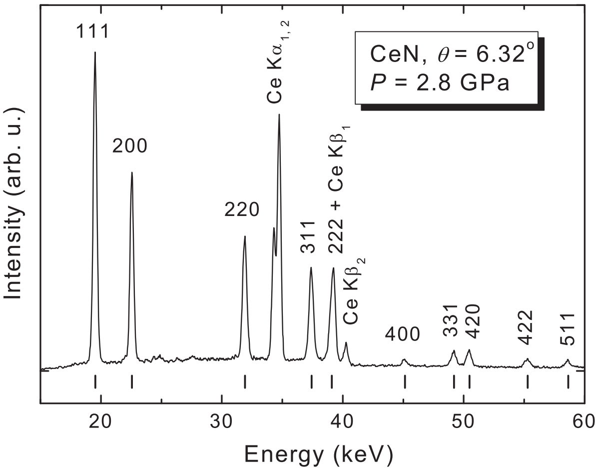

Fig. 1. Diffraction spectrum of CeN at 2.8 GPa. The Bragg angle is $\theta = 6.32°$. The row of bars below the spectrum indicates the positions of the Bragg peaks of the B1 phase.

Table 1
The lattice parameter a_0 of CeN at ambient conditions. The values are experimental except for the last entry.

a_0 (Å)	Reference
5.021(1)[a]	Iandelli and Botti [5]
5.020(4)	Gambino and Cuomo [29]
5.023(1)	Danan et al. [7]
5.020(1)	Brown and Clark [38]
5.019(2)	Schlegel et al. [8]
5.022(2)	Olcese [9]
5.021(2)	Present work, expt.
5.024	Present work, GGA calc.

[a] This lattice parameter was originally stated to be 5.011 in Å units, but was actually in kX units (as seen from the wavelength of Cu Kα also given in that paper). The lower value 5.011 Å has often been incorrectly cited in the literature (*e.g.* Wyckoff [39]).

4. Results and discussion

4.1. Lattice parameter

Fig. 1 shows a diffraction spectrum of the low-pressure phase of CeN. The lattice parameter at ambient conditions, determined as the mean value of several runs, is $a_0 = 5.021(2)$ Å. As shown in Table 1, there is a general consensus among published experimental determinations for a lattice parameter of about 5.020 Å. Table 1 also shows that our experimental value compares very well with the theoretical value $a_0 = 5.024$ Å calculated in the GGA approach [14].

4.1.1. Bulk modulus and the equation of state

Fig. 2 shows experimental and theoretical compression curves of CeN. It is seen that our experimental pressure–volume data are in remarkably good agreement with the calculated curve using the GGA approach. Somewhat lower volumes are predicted by calculations using the LDA for exchange and correlation [14]. Also included in Fig. 2 are the experimental pressure–volume data points of Olcese [9]. These data show a somewhat peculiar behavior with a first steep decrease of volume followed by a constant volume at pressures between 4 and 7.5 GPa. As explained by the author, this surprising result could be due to practical difficulties in the

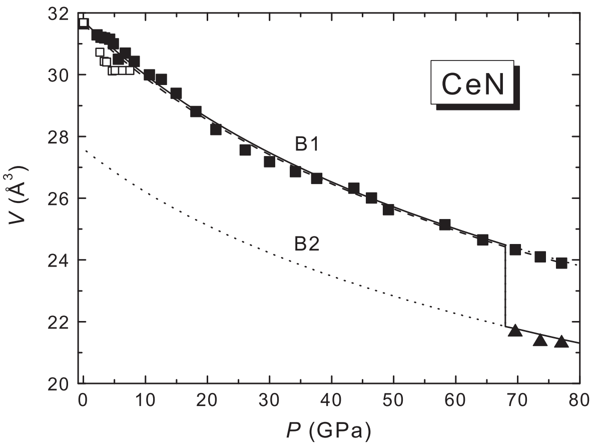

Fig. 2. Compression curves of CeN. V is the volume per formula unit, and P is the pressure. Filled squares denote our experimental data points for the B1 phase, open squares those of Olcese [9]. Filled triangles denote our experimental data points for the B2 phase. The dashed curve is the fit of the Birch-Murnaghan equation to our experimental data for the B1 phase. The full and dotted curves are the results of the GGA calculation. The transition pressure is $P_{tr} = 68$ GPa.

interpretation of the X-ray diffraction patterns at pressures above 5 GPa. Anyway, the pressure range investigated by Olcese [9] is limited to $0 \le P \le 7.5$ GPa, and this is too narrow to draw any definitive conclusions about the high-pressure behavior of CeN.

A fit of the Birch-Murnaghan equation of state to our experimental data points for the B1 type phase (Fig. 2) gives the zero-pressure bulk modulus $B_0 = 156(3)$ GPa, the pressure derivative being constrained to $B_0' = 4.00$. This experimental result compares very well with the calculated values $B_0 = 158.1$ GPa and $B_0' = 3.3$ in the GGA approach. It is also in good agreement with the bulk modulus 159 GPa predicted by Svane et al. [4], and with the preliminary experimental bulk modulus 153 GPa reported earlier by Jakobsen et al. [11]. To our best knowledge, there are no other experimental values of the bulk modulus of CeN published in the literature. Table 2 shows our experimental results together with a number of calculated values of the bulk modulus of CeN.

4.2. The B1–B2 transition

Fig. 3 shows the diffraction spectrum of CeN at our maximum pressure 77 GPa. The strongest peak of the B2 phase, namely the 1 1 0 peak, would be expected to appear between the 2 0 0 and 2 2 0 peaks of the B1 phase. Inspection of the diffraction spectrum shows that there is indeed a new peak at the expected position 28.6 keV. The B2 (1 0 0) peak, visible as a shoulder to the left of the B1 (1 1 1) peak, further confirms the presence of the B2 phase. Using a peak-fitting program, the B2 (1 0 0) and B1 (1 1 1) peaks could be resolved, and the position of the B2 (1 0 0) peak determined as 20.1 keV. Moreover, the B2 (2 1 0) peak is barely visible at 45.3 keV.

The B2 (1 1 0) peak is visible also in the diffraction spectra at 70 and 74 GPa, whereas the B2 (1 0 0) can be resolved only at 77 GPa. Pressure–volume data points for the B2 phase at these pressures are included in Fig. 2. We conclude that the onset of the B1–B2 transition is in the range 65–70 GPa. We have not observed the fully transformed high-pressure phase, but it has been possible to determine the relative volume change at the transition, which is $\Delta V/V = -10.9(3)$ %. To our best knowledge, this is the first experimental observation of the pressure-induced B1–B2 transition in CeN.

Fig. 4 shows the calculated total energy of CeN in the B1 and B2 structures as functions of the unit-cell volume. The common tangent of the two curves defines the points of equal enthalpy of the two phases (at $T = 0$ K), and thus marks where the B1–B2 transition occurs. The slope of this curve corresponds to a theoretical transition pressure of 68 GPa, in excellent agreement with the present experimental result. Svane et al. [4] have investigated the B1–B2 transition in CeN by a similar but less accurate method, leading to a transition pressure of 62 GPa. The relative volume change at the B1–B2 transition is $\Delta V/V = -10.8\%$ according to the present calculations, also in very good agreement with experiment. Table 2 summarizes experimental and theoretical data for the B1–B2 transition in CeN.

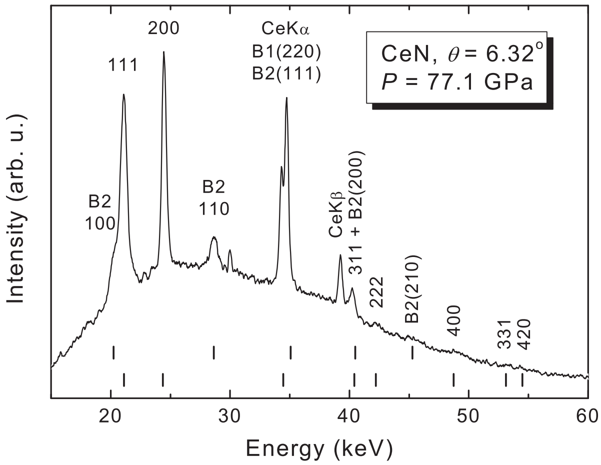

Fig. 3. Diffraction spectrum of CeN at 77.1 GPa showing new peaks due to the B2 phase. The Bragg angle is $\theta = 6.32^\circ$. The bars below the spectrum indicate the positions of the Bragg peaks of the B2 phase (upper row) and the B1 phase (lower row). The 2 2 0 peak of the B1 phase and the 1 1 1 peak of the B2 phase are hidden behind the Ce Kα fluorescence peak. The very small peak at 30.0 keV is due to the inconel gasket of the pressure cell.

The B1–B2 transition is not instantaneous as suggested by theory, but rather slow in practice. Thus, a major fraction of the sample is still in the B1 phase at 77 GPa, the maximum pressure of the present work (Fig. 3). Pressures well above 80 GPa would be necessary in order to get the sample fully transformed into the B2 phase. We would expect a large hysteresis in the pressure–volume curves when the B2 phase transforms back to the B1 phase. Usually, the experimental transition pressure is defined as midway between the transitions in compression and decompression, but this has not been possible to measure in the present work. Thus, the

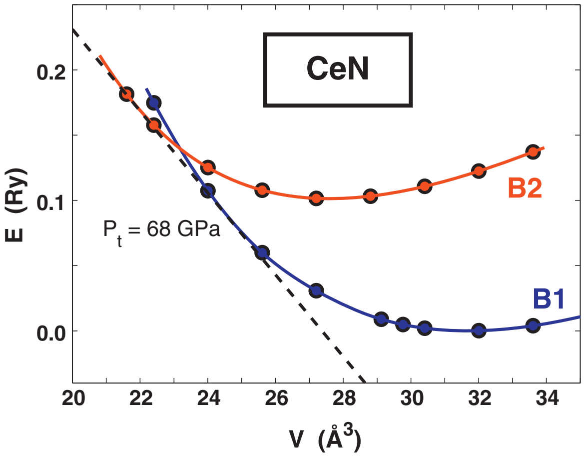

Fig. 4. Total energy (in units of Rydberg per formula unit, and calculated with the GGA total energy functional) of CeN as a function of the unit-cell volume. The B1 and B2 structures are considered, and zero energy is defined as the minimum energy of the B1 phase. The common tangent defines the structural transition pressure $P_{tr} = 68$ GPa, with a calculated volume change $\Delta V/V = -10.8\%$ at the transition.

Table 2
Values of the bulk modulus B_0 and its pressure derivative B_0' for the low-pressure (B1) phase of CeN. Also included are values of the transition pressure, P_{tr}, and the relative volume change, $\Delta V/V$, at the transition.

B_0 (GPa)	B_0'	P_{tr} (GPa)	$\Delta V/V$ (%)	Reference
153(5)				Jakobsen et al. [11], expt., preliminary.
156(3)	4.00	65–70[a]	−10.9(3)	Present work, expt.
159.0		62	−5	Svane et al. [4,40], theory, LDA.
140.2		88	−5.8	Rukmangad et al. [12], theory, interionic potentials.
158.1	3.3			Kanchana et al. [14], theory, GGA.
158.1	3.3	68	−10.8	Present work, theory, GGA.

[a] Onset of the transformation.

comparison between the experimental and calculated transition pressures should be regarded as tentative at the present stage.

5. Conclusions

The lattice parameter, the equation of state, and the bulk modulus of CeN, as determined by high-pressure X-ray diffraction, are in remarkably good agreement with the GGA calculations of Kanchana et al. [14]. Those calculations have therefore been extended to the B2 phase, including the B1–B2 transition pressure. Experimentally, the onset of the pressure-induced B1–B2 transformation occurs in the range 65–70 GPa with a volume collapse of 10.9(3)%, in good agreement with the calculated transition pressure. In practice, the transition is rather sluggish, and a pressure well above 80 GPa would be necessary to achieve a full transformation into the B2 type structure.

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