

# Effect of chemical and external pressure on the structure of intermetallic compound CeNi

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Received 29 June 2006; received in revised form 27 September 2006; accepted 17 October 2006

Available online 20 November 2006

## Abstract

Neutron powder diffraction was employed to study the structural modifications of the intermediate-valence compound CeNi at room temperature induced by either chemical or external pressure. For the first time we were able to record the diffraction pattern resulting from the pressure-induced first-order phase transition occurring in CeNi at 300 K. At pressure  $P = 2$  GPa we observe the coexistence of two phases while only single pressure-induced phase is visible at  $P = 5$  GPa. The results obtained are indicative of a higher symmetry of the collapsed structure as compared to the CrB-type ambient pressure structure of CeNi. The critical pressure range around 2 GPa is found to be in agreement with the previous estimation derived from the thermopower measurements.

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**Keywords:** Rare earth alloys and compounds; Phase transitions; High-pressure; Neutron diffraction

## 1. Introduction

The study of mechanisms of the transitions between different structural modifications for the materials with almost empty or almost filled  $f_{5/2}$  electronic configurations may provide a new insight into the origin of their ground-state properties, especially in the case if the structural transitions involve volume discontinuity driven by electron correlation effects. The intermediate-valence compound CeNi exhibits anomalous behavior of many physical properties including the first-order structural phase transition with volume discontinuity  $\sim 5\%$  [1,2] and well-defined ground-state coherent effects in the magnetic response function observed by the inelastic neutron scattering technique [3]. Thus, CeNi is an attractive model system to investigate the influence of the coherent effects on the mechanism of the volume-collapse phase transitions. However, the CeNi  $P$ – $T$

phase diagram is established only at relatively low pressures ( $< 0.8$  GPa) in the limited temperature range below 150 K and the structure of the high-pressure phase remains unknown. Recent thermopower measurements of CeNi as a function of external pressure at 300 K indicate possible phase transitions to occur at  $\sim 3$  and 8 GPa [4].

In the present work the neutron powder diffraction technique was used to study the pressure-induced phase transition in CeNi as well as the structural modifications of CeNi resulting from the chemical pressure due to either La (negative chemical pressure) or Lu (positive chemical pressure) substitutions for Ce in the CrB-type CeNi lattice.

## 2. Experiment

### 2.1. Chemical pressure

CeNi,  $Ce_{1-x}La_xNi$  ( $0 \leq x \leq 1$ ) and  $Ce_{1-x}Lu_xNi$  ( $0 \leq x \leq 0.4$ ) samples were prepared by arc melting of high purity elements ( $\sim 99.98$ ) in the argon atmosphere. Obtained compositions were then recrystallized in vacuum and founded in cylindrical ingots of a diameter  $\sim 10$  mm. Ingots were then annealed in dynamical vacuum for 120 h. According to X-ray and neutron powder diffraction measurements (see Fig. 1 as an example), all samples were found to

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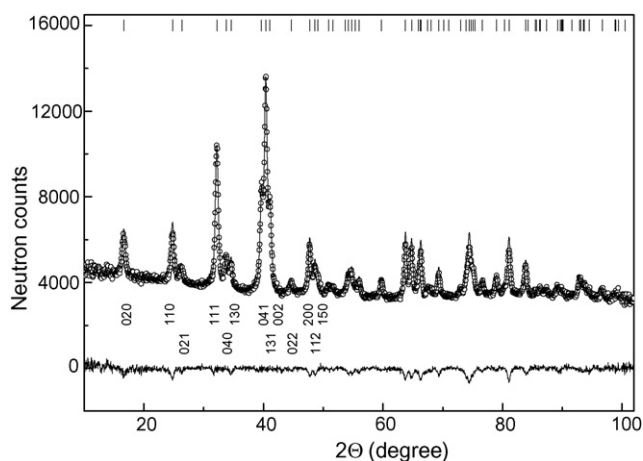


Fig. 1. Neutron powder diffraction pattern of CeNi at ambient pressure and room temperature recorded using D7A diffractometer (Ekaterinburg) with  $\lambda = 1.5324 \text{ \AA}$ .  $hkl$  Miller indexes are indicated below the correspondent Bragg peaks.

Table 1  
The crystal lattice parameters of CeNi as a function of La and Lu substitutions for Ce

	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )
Ce <sub>0.6</sub> Lu <sub>0.4</sub> Ni	3.693(2)	10.286(3)	4.310(2)	163.7
Ce <sub>0.8</sub> Lu <sub>0.2</sub> Ni	3.746(2)	10.407(3)	4.342(2)	169.2
Ce <sub>0.9</sub> Lu <sub>0.1</sub> Ni	3.759(1)	10.461(3)	4.352(1)	171.15
Ce <sub>0.95</sub> Lu <sub>0.05</sub> Ni	3.7699(5)	10.495(1)	4.3568(5)	172.4
CeNi	3.7858(6)	10.548(1)	4.3631(6)	174.2
Ce <sub>0.9</sub> La <sub>0.1</sub> Ni	3.8014(6)	10.571(1)	4.3683(7)	175.6
Ce <sub>0.8</sub> La <sub>0.2</sub> Ni	3.819(1)	10.587(2)	4.370(1)	176.7
LaNi	3.9048(5)	10.792(1)	4.3900(5)	185.0

be of single phase with the CrB-type of crystal structure (the  $Cmcm$  space group).

In order to study the effect of chemical pressure, neutron powder diffraction patterns for the samples under study were recorded at room temperature using D7A diffractometer (Institute for Metal Physics, Ekaterinburg) with  $\lambda = 1.5324 \text{ \AA}$ . The results are summarized in Table 1 and Fig. 2.

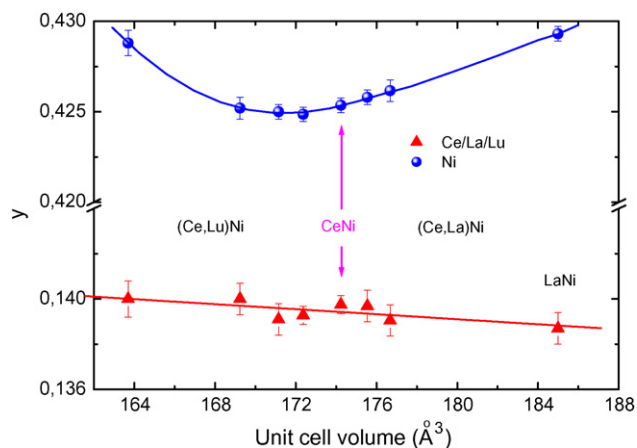


Fig. 2. Position parameter  $y$  for Ce/La/Lu and Ni ions as a function of the unit cell volume at room temperature and ambient pressure for the  $Ce_{1-x}La_xNi$ – $CeNi$ – $Ce_{1-x}Lu_xNi$  series.

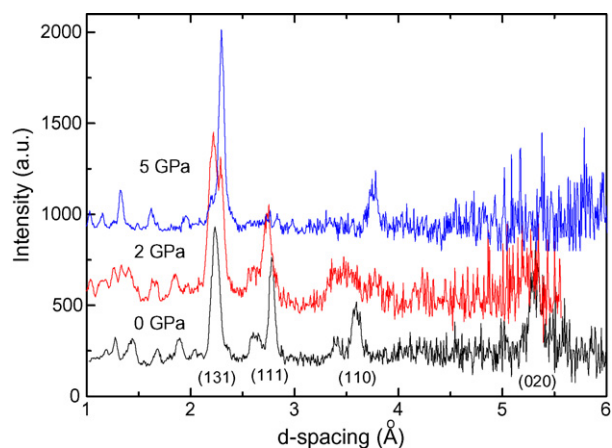


Fig. 3. Structural spectra for CeNi at ambient pressure, at 2 and 5 GPa measured at room temperature using DN-12 time-of-flight high-pressure spectrometer (Dubna). ( $hkl$ ) indexes correspond to the  $Cmcm$  space group.

## 2.2. High-pressure neutron measurements

Using the time-of-flight high-pressure neutron spectrometer DN-12 (IBR-2 pulsed reactor, Frank Laboratory of Neutron Physics, Dubna) and a sapphire anvil cell, we were able to record the pressure-driven evolution of elastic neutron spectra of CeNi at 300 K up to  $P = 5 \text{ GPa}$  (Fig. 3). Ambient pressure spectrum shows the pure CrB-type diffraction pattern, the same as in Fig. 1. A shift and/or splitting of some spectral lines as well as appearance of additional maxima at  $P = 2 \text{ GPa}$  indicate clearly the development of the pressure-induced phase transition. At 5 GPa the diffraction pattern changes significantly. The number of relatively intensive peaks is reduced as compared to ambient pressure diffraction pattern. In particular, the (1 1 1) and (0 2 0) peaks are absent at 5 GPa. Thus, we can assume a single-phase character of the 5 GPa diffraction pattern associated with a new phase of CeNi resulting from a first-order pressure-induced phase transition.

## 3. Discussion

La substitutions for Ce expand the crystal lattice in all the main crystallographic directions, while substitutions with Lu lead to the lattice compression. The main structural elements of the CrB structure are the zig-zag chains of Ce and Ni ions propagating along the  $c$  crystallographic direction. Respectively, the lattice parameter  $c$  varies much less due to chemical pressure than the  $a$  and  $b$  parameters.

CeNi primitive cell contains two Ce and two Ni ions. Ce and Ni are both located at (4c) (0,  $y$ , 1/4) positions. Fig. 2 demonstrates the variation of the atomic coordinate  $y$  for the rare earth ions Ce/La/Lu and Ni as a function of the unit cell volume derived from the Rietveld refinement of the neutron diffraction patterns. While  $y_{Ce/La/Lu}$  increases slightly and almost linearly with decrease in the unit cell volume,  $y_{Ni}$  shows nonmonotonous behavior. It decreases also almost linearly when going from LaNi to CeNi, reaches its minimum for the slightly compressed (as compared to the stoichiometric CeNi) composition  $Ce_{0.95}Lu_{0.05}Ni$  and then grows again. It should be noted, that in CeNi both  $y_{Ce}$  and  $y_{Ni}$  position parameters exhibit significant changes within the temperature range between 80 and 120 K, whereas for LaNi the values of these parameters remain almost temperature independent [5]. Although at ambi-

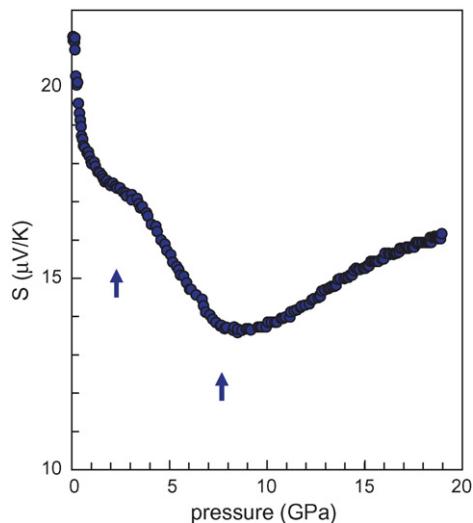


Fig. 4. Thermopower  $S$  as a function of pressure for CeNi (from Ref. [4]). The phase transitions are assumed to occur around  $\sim 3$  and  $\sim 8$  GPa (arrows), i.e. in the regions of broad singularities of  $S$  vs.  $P$  curve.

ent pressure CeNi exhibits clear signatures of the crystal lattice instability upon cooling [5,6], a structural phase transition does not occur down to very low temperature. The question whether the compressed Lu-doped compositions undergo a phase transformation upon cooling at ambient pressure or not remains to be open.

In 1985 Gignoux and Voiron demonstrated the existence in CeNi of a first-order phase transition under pressure associated with a large volume discontinuity [1,2]. The  $P$ - $T$  phase diagram was determined up to 0.8 GPa and 150 K. Since that time however to the best of our knowledge neither the phase diagram out of this limited  $P$ - $T$  domain nor the crystal structure of the pressure-induced phase were published. The only indirect evidence of unchanged crystal symmetry across the transition was obtained from the de Haas-van Alphen effect under pressure [7], which reveals that the topology of the Fermi surface of CeNi is not change after transition, but the cyclotron effective mass is strongly reduced.

The main result of the present study is the direct observation of the pressure-induced phase transition in CeNi at room temperature. Although the structural identification of the pressure-induced phase is by no means trivial because of a rather limited number of well-reserved Bragg peaks, there are no doubts that the 5 GPa diffraction pattern cannot be described in terms of the ambient pressure  $Cmcm$  space group. Therefore, the structure of pressure-induced phase does not belong to the orthorhombic CrB-type and has, most probably, a higher symmetry. From Fig. 3 it follows that at 300 K the phase transition starts at or just below  $P=2$  GPa, while the 5 GPa pressure range lies above the transition region. According to our previous thermopower measurements the room temperature phase transitions in CeNi were assumed to occur at  $\sim 3$  and  $\sim 8$  GPa [4]. Since the singularities of thermopower versus pressure dependence around 3 and 8 GPa are rather broad (Fig. 4), the critical pressure values  $\sim 2$  and  $\sim 3$  GPa derived

by two different techniques are in reasonable agreement. At the same time, our structural data are not consistent with the results derived from the de Haas-van Alphen effect in CeNi [7]. One cannot exclude, however, a temperature-driven phase transitions in CeNi within the pressure range  $2 \text{ GPa} < P < 5 \text{ GPa}$ , so that the CeNi structures can be different at room and at low temperatures.

The neutron diffraction data for  $\text{Ce}_{1-x}\text{La}_x\text{Ni}$ -CeNi- $\text{Ce}_{1-x}\text{Lu}_x\text{Ni}$  series listed in Table 1 (lattice parameters  $a$ ,  $b$  and  $c$ ) and shown in Fig. 2 (position parameters) were extrapolated to their values correspondent to the volume compression down to  $\Delta V/V_0 = -25\%$  (where  $V_0 = 174.2 \text{ \AA}^3$  is the unit cell volume of CeNi) and used for the electronic structure calculations in terms of the spin-polarized relativistic density functional theory in generalized gradient approximation (full potential linearized augmented plane wave version). For a few values of  $\Delta V/V_0$  the minimum of the full energy  $E$  was determined as a function of  $y_{\text{Ni}}$  (this parameter demonstrates the most pronounced variation in Fig. 2). At  $\Delta V/V_0 = -25\%$   $E_{\text{min}}$  was found at  $\Delta y_{\text{Ni}} = 0.002$  with respect to its stoichiometric value  $y_{\text{Ni}} = 0.4254$ . Although  $\Delta y_{\text{Ni}} = 0.002$  turns out to be much less than the extrapolated value  $\Delta y_{\text{Ni}} \sim 0.015$ , no signature of the phase instability was detected since the steepness of the  $E$  versus  $y_{\text{Ni}}$  dependence remains unchanged at any  $|\Delta V/V_0| \leq 25\%$ . It cannot be excluded that a single-electron theory fails to predict a crystal lattice instability in CeNi driven by electronic correlations.

#### 4. Conclusion

Neutron powder diffraction study of the structural variation of intermediate-valence compound CeNi due to chemical pressure-induced by either La or Lu substitutions for Ce revealed nonmonotonous variation of the Ni position parameters  $y_{\text{Ni}}$  which has a minimum near the stoichiometric CeNi composition. For the first time we were able to detect a pressure-induced first-order structural phase transformation in CeNi by direct experimental technique. The results obtained suggest that the symmetry of the pressure-induced phase is higher than the orthorhombic CrB-type structure of ambient pressure phase of CeNi.

#### Acknowledgements

This work was performed under auspices of Russian Federal Agency for Atomic Energy (State Contract #6.06.19.19.06.988). Financial support by RFBR (grant #05-08-33456-a) is gratefully acknowledged.

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