Crystal Structure of $Ce_3Ni_2(BN)_2N$ and Magnetic Behavior of $(CeNi(BN))_2(CeN)_x$ with x = 0, 1

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Abstract. The new compound Ce₃Ni₂(BN)₂N was synthesized by a modified solid state metathesis reaction. The crystal structure of Ce₃Ni₂(BN)₂N was found to be isotypic with the superconducting compound La₃Ni₂(BN)₂N, according to Rietveld refinements performed on X-ray powder data (*I4/mmm*, Z = 2, a = 3.5817(1) Å, c = 20.283(1) Å).

Corresponding solid state reactions of mixtures composed of CeN/NiB and CeNi/BN yielded CeNi(BN) and a mixture of the

Introduction

Quaternary nitridoborate compounds with [BN]ⁿ⁻ ions were reported for the compositions MNi(BN) with M being Ca, La, Ce, Pr, Tm, Yb [1-4] and La₃Ni₂(BN)₂N [4-7]. Compounds MNi(BN) are considered as semiconductors for CaNi(BN) and as metallic for LaNi(BN), whereas $La_3Ni_2(BN)_2N$ is a superconductor with the highest T_c reported at 14.6 K. Structure refinements by neutron powder diffraction [8] and single-crystal X-ray diffraction [7] have indicated slight deficiencies in the nitride content of $La_3Ni_2(BN)_2N_{1-x}$. The structure contains two-dimensional planar [Ni(BN)] layers, separated by rock salt like [LaN] monolayers. Band structure calculations on La₃Ni₂(BN)₂N were, however, reported to show a three-dimensional character of the conductivity behavior of this material, with Fermi surface velocities in the x and z directions of the tetragonal system in approximate 2:1 ratio [9].

The B–N distances in $[BN]^{n-}$ ions range from 138.1(4) pm in CaNi(BN) to approximately 144 pm in La₃Ni₂(BN)₂N (143(3) pm from single-crystal X-ray analysis, and 143.7(4) pm from neutron powder diffraction). Electronic structure calculations have revealed a closely related behavior of $[BN]^{n-}$ and dicarbide ions in compounds,

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two closely related layered structures $(CeNi(BN))_2(CeN)_x$ with x = 0 and 1.

Magnetization experiments on these samples revealed temperature independent paramagnetic behavior for $Ce_3Ni_2(BN)_2N$ and CeNi(BN) without any magnetic ordering down to 5 K.

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allowing insulating (CaC₂), metallic (LaC₂), and superconducting (LnC_2 , Ln = lanthanide) properties [10].

It is, however, surprising that no compound analogous to $La_3Ni_2(BN)_2N$ has been reported until now in which lanthanum is replaced by another rare-earth element, or Ni is replaced by another transition element (except for partial substitutions reported, e.g. with cobalt [11]). Band structure calculations have suggested that the nickel 3d bands fall below the Fermi level, indicating that nickel can be even negatively charged due to partial occupations of 4s and 4p bands. This implies that transition elements having an open 3d shell may be unlikely candidates to substitute for nickel [3].

Former magnetic studies have suggested the presence of a magnetic ordering in the system Ce-Ni-B-N below $T_C = 25$ K [12]. In these experiments CeNi(BN) was the main phase (> 90 %), showing an effect similar to the magnetic ordering reported for the isotypic compound ErNi(BC) at $T_C = 4.5$ K [13]. However, saturation experiments revealed only 0.2 Bohr magnetons per Ce atom being responsible for the magnetic ordering in the CeNi(BN) dominated sample. Careful re-examinations of XRD patterns from several samples have lead to the hypothesis that an unknown compound such as Ce₃Ni₂(BN)₂N could be the reason for the observed magnetic behavior. Following this assumption, we have initiated experiments to explore the Ce/Ni/B/N system in more detail, with the results being reported here.

Experimental Section

Syntheses

All manipulations of the starting materials for reactions in the Ce/Ni/B/N system were performed in an Ar-filled glove box (Braun



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LabMaster 130, M. Braun GmbH) with commercial as well as synthesized materials. Li₃BN₂ used in the reactions was prepared from appropriate amounts of Li₃N (Alfa Aesar, 99.5 %) and α -BN (ABCR, 99.8 %) in a fused (arc melting) copper ampoule (covered in silica) at 775 °C.

CeN (Alfa Aesar, 99.9 %) was used without a pre-treatment. The employed NiB was produced from reactions of the elements, Ni (Strem, 99.9 %) and B (ABCR, 99.7 %), in an electric arc. Intermetallic CeNi was made by heating equimolar proportions of Ce (Strem, 99.9 %) and Ni metal in a fused Ta ampoule (silica fused) for 12 h at 1000 °C. BN was heated at 700 °C under vacuum for several hours. All subsequent reactions were accomplished in fused Ta ampoules, vacuum-sealed into silica tubes.

Synthesis of Ce₃Ni₂(BN)₂N (sample A)

The new compound $Ce_3Ni_2(BN)_2N$ was synthesized through a modified metathesis reaction [14] by heating a carefully ground mixture of 225.5 mg CeCl₃ (Alfa Aesar, 99.9 %), 79.1 mg NiCl₂ (Strem, 98 %), 21.2 mg Li (Strem, 99.8 %), 76 mg BN (ABCR, 99.8 %), and 18.2 mg Li₃BN₂ (molar ratio: 3 : 2 : 10 : 1 : 1) in a fused Ta ampoule at 1040 °C for one week. When the ampoule was cooled down to room temperature it was opened in air and the product was washed, first with a mixture of acetone/water to remove the co-produced LiCl and then with acetone. An XRD pattern of the resulting dark grey powder was used for a subsequent (Rietveld) structure refinement.

Synthesis of CeNi(BN) (sample B)

CeNi(BN) was synthesized from reactions of eqimolar amounts of CeN and NiB as reported previously [3]. Reactions were carried out in fused Ta tubes near 1200 °C for about three days. The product was identified as CeNi(BN) containing up to 10 % unknown side-phase(s), as estimated from the X-ray powder patterns (with respect to the 100 %-reflection of CeNi(BN)).

In an alternative attempt CeNi and BN were used as starting materials (sample C) using a slight excess of BN (1 : 1.1 molar ratio), being reacted under similar conditions as before. The product contained about 40 % CeNi(BN) and 60 % Ce₃Ni₂(BN)₂N without any side-phases being detectable in the X-ray powder pattern.

Powder diffraction and structure refinement

The XRD patterns of all reaction products were collected with a Stadi-P (Stoe, Darmstadt) powder diffractometer using Cu-K_{a1} radiation (germanium monochromator). The phase contents of samples were estimated from the X-ray patterns shown in Figure 1. Reflections of the unknown or not assigned compound(s) are denoted by an asterisk.

An XRD pattern collected on $Ce_3Ni_2(BN)_2N$ (sample A) was indexed isotypically to $La_3Ni_2(BN)_2N$. The structure refinement of $Ce_3Ni_2(BN)_2N$ was performed with the WinPlotr (FullProf) program package [15] taking into account the three side phases CeB_6 , Ta_2B , and $TaN_{0.04}$, of which the latter results from a partial reaction with the Ta container. Results of the refinement are shown in



Figure 1 Projection of XRD patterns of sample B (CeNi(BN), below) and sample C (mixture of CeNi(BN) and Ce₃Ni₂(BN)₂N, top). Reflections of the unknown product(s) are marked with an asterisk (*).



Figure 2 Rietveld refinement of $Ce_3Ni_2(BN)_2N$. Circles represent measured data; and the calculated pattern is superimposed with the observed pattern. Ticks mark the Bragg reflections ($Ce_3Ni_2(BN)_2N$, CeB_6 , Ta_2B , and $TaN_{0.1}$ from above). The difference curve is shown in the lower part of the graph.

Table 1 Results of the (Rietveld) structure refinement on $Ce_3Ni_2(BN)_2N$.

Formula, formula weight	Ce ₃ Ni ₂ B ₂ N ₃ , 601.37 g/mol
Wavelength	1.5406 Å
Crystal system, Z	tetragonal, 2
Space group	I4/mmm
Unit cell dimensions	a = 3.5817(1) Å,
	c = 20.283(1) Å
Volume	260.19(1) Å ³
Range, step width	$5^{\circ} < 2\Theta < 129.98^{\circ}, 0.02^{\circ}$
Total number of reflections	179
Effective number of reflections	76
Refined parameters for all 4 phases	31
Refined structural parameters (Ce ₃ Ni ₂ (BN) ₂ N)	7
R _p , R _{wp}	3.76 %, 4.76 %
R_{Bragg}^{r} (all phases), R_{Bragg} (Ce ₃ Ni ₂ (BN) ₂ N)	7.21 %, 5.46 %

Table 1 and Figure 2. Atomic positions and equivalent isotropic displacement parameters U_{eq} are presented in Table 2. Selected bond lengths are shown in Table 3.

Table 2 Atomic positions and equivalent isotropic displacement parameters U_{eq} (in Å²) of Ce₃Ni₂(BN)₂N.

Atom	Wyckoff- position	х	у	Ζ	U_{eq}
Ce2	2a	0	0	0	0.0108(7)
Ce1	4e	1/2	1/2	0.87306(9)	0.0089(6)
Ni	4d	0	1/2	3/4	0.020(2)
N2	2b	1/2	1/2	0	0.020(3)
N1	4e	0	0	0.1143(9)	0.020(3)
В	4 <i>e</i>	0	0	0.198(1)	0.020(3)

Table 3 Selected bond length (in Å) of $Ce_3Ni_2(BN)_2N$.

Ce2-N2	2.533(1)	4 x	
Ce2-N1	2.32(2)	2 x	
Ce1-N2	2.575(2)	2 x	
Ce1-N1	2.546(2)	4 x	
Ni-Ni	2.533(1)	4 x	
Ni-B	2.08(1)	4 x	
N1-B	1.69(3)	1 x	

Details on the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, Germany, D-76344 Eggenstein-Leopoldshafen (Fax: (+49)7247-808-666; E-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD 41973 for Ce₃Ni₂(BN)₂N.

Magnetic measurements

The magnetic susceptibilities of samples A - C were measured with a SQUID magnetometer (Quantum Design, MPMS). Some 50 mg of each sample were placed into a gelatin capsule and cooled down to 5 K in the absence of a magnetic field. A magnetic field of 500 Oe was applied when the samples were warmed up to 300 K (Zero Field Cooled signal). In a following step the samples were cooled down to 5 K in the applied field (Field Cooled signal). At lower temperatures the step size between the data points was reduced. The field dependency of the magnetization was measured at 5 K resulting in a hysteresis behavior.

Results and Discussion

Crystal structure of Ce₃Ni₂(BN)₂N

The Rietveld refinement of Ce₃Ni₂(BN)₂N was performed in the space group *I4/mmm* by using the atomic positions of the isotypic La₃Ni₂(BN)₂N [7] as starting parameters. Due to the small scattering contributions of the light elements (boron and nitrogen) in the X-ray experiment, their isotropic displacement parameters were restrained to refine equivalent. The tetragonal structure of Ce₃Ni₂(BN)₂N contains square planar layers of Ni atoms (d_{Ni-Ni} = 2.533(1) Å). The centers of these squares are capped alternately from above and below by boron atoms of the BN units (d_{B-N} = 1.69(3) Å). As a result, every Ni atom is coordinated in a distorted tetrahedral fashion by boron atoms (d_{Ni-B} = 2.08(1) Å, \angle B-Ni-B = 105(1)° and 118.7(5)°). The nitrogen atoms of the BN units are surrounded by five Ce atoms forming a square pyramid which is the typical



Figure 3 Comparison of tetragonal crystal structures representing CeNi(BN) (left) and $Ce_3Ni_2(BN)_2N$ (right). Cerium atoms are shown dark grey, nickel atoms light grey, boron black, and nitrogen white.

coordination pattern for terminal nitrogen atoms in all known nitridoborate ions ($d_{Ce-N} = 2.546(2)$ Å 4x and 2.32(2) Å 1x). Furthermore, the unit cell of $Ce_3Ni_2(BN)_2N$ contains isolated nitride ions which are surrounded by six cerium atoms forming a slightly elongated octahedron $(d_{Ce-N} = 2.533(1) \text{ Å } 4x \text{ and } 2.575(2) \text{ Å } 2x)$. Figure 3 displays a structural comparison of the unit cells of CeNi(BN) and Ce₃Ni₂(BN)₂N. For better comparison of both structures we use a non-standard setting of the CeNi(BN) unit cell with Ce at the origin. The structure of Ce₃Ni₂(BN)₂N can be derived from the structure of CeNi(BN) by inserting one CeN-layer to yield (CeNiBN)₂CeN. The refined B-N distance of the BN-unit of Ce₃Ni₂(BN)₂N was around 0.25 Å longer than the B–N distance in $La_3Ni_2(BN)_2N$. The single-crystal structure determinations on CaNi(BN) and La₃Ni₂(BN)₂N provide some informations on the variation of the B-N distance of the BN unit with respect to the electronic situation. The B-N distance increases from 1.38 A in CaNi(BN) to approximately 1.44 A in La₃Ni₂(BN)₂N due to a partial occupation of the antibonding π^* level of the BN anion. In dicarbides we note a similar behavior of C-C-distances, increasing from about 1.20 Å in CaC_2 to 1.28 Å in LaC_2 (and 1.30 Å in CeC_2). Within the series of tetragonal MNi(BN) compounds (M = Ca, Y, La, Ce, Pr, Tm, Yb) [2] it has been shown that the cerium compound has lattice parameters which suggest a high content of Ce⁴⁺ ions in the structure. The presence of Ce⁴⁺ ions in the structure of Ce₃Ni₂(BN)₂N should let us expect an increased occupation of the antibonding π^* levels of the BN anion, and therefore longer B-N distances than obtained in La₃Ni₂(BN)₂N (1.44 Å). The refined B-N

distance of 1.69 Å in Ce₃Ni₂(BN)₂N is, however, beyond our expectations (approx. 1.50 Å) and the refined prolongation may be an overestimation, due to limited precision in the light atom X-ray refinement next to heavy atoms in the structure and due the relatively low number of observables for the structure refinement from powder data. An overestimation of this distance has been also a shortcoming in the earlier electron diffraction refinements on La₃Ni₂(BN)₂N [16], and has established a structure description that has overlooked the B–N bonding characteristics.

Magnetism

Magnetic measurements were performed for all samples A-C. The new $Ce_3Ni_2(BN)_2N$ (sample A) showed a temperature independent paramagnetic behavior.

The CeNi(BN) sample (B) showed the same behavior as obtained in previous experiments [2, 12]: Temperature independent paramagnetism was obtained in the temperature range from 300 to 25 K. Below 25 K the susceptibility increases rapidly and indicates cooperative interactions. Below 10 K both the ZFC (zero field cooled) and FC (field cooled) signals separate from each other (Figure 4). The field dependency of the magnetization at 5 K showed a weak hysteresis which indicates cooperative interactions, too. The small values of the magnetization at higher fields are remarkable. Former samples have shown a saturation magnetization corresponding to only 0.2 Bohr magnetons per cerium atom, assuming CeNi(BN) is responsible for the magnetic behavior. From the magnetization of sample B only 0.13 Bohr magnetons per cerium atom were calculated, ignoring the small inclusion of an unknown phase.



Figure 4 Temperature dependence of the magnetic susceptibility of samples A-C in an applied field of 500 Oe. Sample A: empty squares, sample B: empty triangles, sample C: filled squares. Note that the results from the measurements A and C both coincide. Sample B shows magnetic ordering below 25 K (ZFC and FC signal).

According to the magnetic behavior of sample C, which is a mixture of CeNi(BN) and Ce₃Ni₂(BN)₂N, it becomes clear that both CeNi(BN) and Ce₃Ni₂(BN)₂N show TIP behavior. This type of magnetic behavior has been also found for LaNi(BN), whereas PrNi(BN) showed paramagnetic behavior with a moment of 3.8 Bohr magnetons (which is close to the theoretical value of Pr^{3+}) [2]. From these findings we can assume that the cerium compounds contain Ce^{4+} rather than Ce^{3+} . This is in agreement with the results of the structure analysis and the elongated B–N distances within the BN units. Figure 4 shows a comparison of mass susceptibilities of the samples A – C. Hence, the unknown byproduct(s) must be accountable for the magnetic ordering obtained below $T_{C} = 25$ K.

Conclusion

The new compound $Ce_3Ni_2(BN)_2N$ was synthesized and shown to crystallize isotypic with the superconducting compound $La_3Ni_2(BN)_2N$. Magnetic measurements on samples containing CeNi(BN) and $Ce_3Ni_2(BN)_2N$ have revealed temperature independent paramagnetism without any cooperative magnetic effects down to 5 K. However, an unknown compound that has been present and in former samples of CeNi(BN) [12] as an impurity has shown magnetic ordering behavior (below 25 K).

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