

Article

Structure and Magnetic Properties of Ce₃(Ni/Al/Ga)₁₁—A New Phase with the La₃Al₁₁ Structure Type

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Academic Editor: Shujun Zhang

Received: 13 November 2014 / Accepted: 18 December 2014 / Published: 29 December 2014

Abstract: Single crystals of Ce₃(Ni/Al/Ga)₁₁ were obtained from an Al flux reaction. Single crystals of the title compound crystallizing in the orthorhombic space group *Immm* (No. 71, $Z = 2$) with $a = 436.38(14)$, $b = 1004.5(3)$ and $c = 1293.4(4)$ pm. This is a standardized unit cell of the previously published La₃Al₁₁ structure type. Wavelength dispersive microprobe provides the composition of Ce_{3.11(1)}Ni_{0.03(1)}Al_{8.95(1)}Ga_{1.90(1)}. Single crystal refinement provides the composition Ce₃Ni_{0.08}Al_{9.13}Ga_{1.78} with substitution of the Ni and Ga on the Al1 and Al4 sites with the Al2 and Al3 solely occupied by Al. Magnetic susceptibility measurements reveal antiferromagnetic ordering with $T_N = 4.8$ K and there is no evidence for a ferromagnetic ordering that has been reported for Ce₃Al₁₁. The effective magnetic moment was found to be $\mu_{\text{eff}} = 1.9 \mu_B/\text{Ce}$, which is lower than the expected value for trivalent Ce ($2.54 \mu_B/\text{Ce}$).

Keywords: cerium; single crystal; magnetism; aluminum

1. Introduction

In the binary system of Ce–Al, several compounds with unique physical properties have been found. Three of them, CeAl_2 [1] and CeAl_3 [2] as well as $\text{Ce}_3\text{Al}_{11}$ [3], are classified as Kondo compounds showing characteristic Kondo-behavior in the electrical resistivity. $\text{Ce}_3\text{Al}_{11}$ is a well studied compound: resistivity [4] and specific heat [5] have been measured on polycrystalline samples and the magnetic structure has been determined on a single crystal specimen [3,6]. Single crystals show a ferromagnetic ordering at $T_C = 6.2$ K [3] followed by an anti-ferromagnetic ordering at $T_N = 3.2$ K. Electrical resistivity measurements are consistent with the observation of the Kondo effect and the two ordering temperatures seen in the magnetic measurements. Below 3.2 K it is reported that the magnetic structure of the compound becomes modulated with an incommensurate vector of $k = (0\ 0\ k_z)$ [6]. This is attributed to the spins of the two crystallographic distinct Ce sites (Ce1 on $2a$, mmm ; Ce2 on $4g$, $m2m$). One of them is mainly responsible for the magnetic scattering while the second one is responsible for the Kondo scattering. Furthermore, the spins from Ce1 are correlated with the spins of Ce2 since the Ce2 magnetic moment is not fully screened by the conduction electrons. The electrical resistivity [7] and magnetic effects [8] of $\text{Ce}_3\text{Al}_{11}$ were also studied under pressure. Besides the cerium compound, the physical properties of the series of $RE_3\text{Al}_{11}$ with $RE = \text{La–Nd}$ and Sm have been studied [9,10]. During attempts to synthesize CeNiGa_2 from Al-flux reactions, single crystals of the title compound were obtained. In this paper, we report the crystal structure and magnetic properties of $\text{Ce}_3\text{Ni}_{0.08}\text{Al}_{9.13}\text{Ga}_{1.78}$ and compare to $\text{Ce}_3\text{Al}_{11}$.

2. Results and Discussion

2.1. Synthesis

During attempts to synthesize CeNiGa_2 from the elements in an Al flux, crystals of $\text{Ce}_3(\text{Ni}/\text{Al}/\text{Ga})_{11}$ were isolated from the melt. The stoichiometric composition was determined to be $\text{Ce}_{3.11(1)}\text{Ni}_{0.03(1)}\text{Al}_{8.95(1)}\text{Ga}_{1.90(1)}$ by quantitative wavelength-dispersive X-ray spectroscopy (WDX) measurements via Electron Microprobe Analysis. Although the Ni content is low, elemental mapping is consistent with the presence of Ni in the structure. The composition was homogenous within the measured area ($200 \times 200 \mu\text{m}^2$, Figure 1) and throughout the crystal.

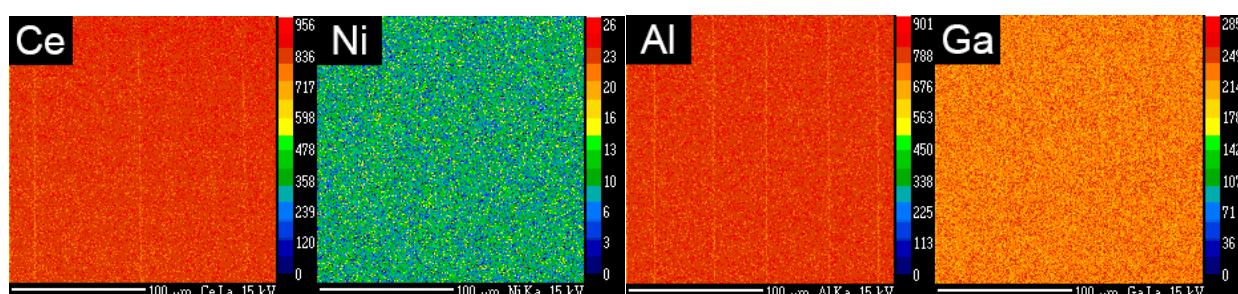


Figure 1. X-ray maps for Ce, Ni, Al and Ga for $\text{Ce}_{3.11(1)}\text{Ni}_{0.03(1)}\text{Al}_{8.95(1)}\text{Ga}_{1.90(1)}$ showing a homogeneous distribution of all elements over the measured area ($200 \times 200 \mu\text{m}^2$).

2.2. Crystal Structure

$\text{Ce}_3(\text{Ni}/\text{Al}/\text{Ga})_{11}$ crystallizes in the orthorhombic space group *Immm* (No. 71) with $a = 436.38(14)$, $b = 1004.5(3)$ and $c = 1293.4(4)$ pm and two formula units ($Z = 2$) in the $\text{La}_3\text{Al}_{11}$ type structure. The unit cell of the presented compound has been standardized and therefore differs from the cited literature. A standardization of the already published compounds has been added, e.g., in the *Pearson* database [11]. Some atom denominations might have changed with respect to the literature, however the standardization is recommended for all compounds of this group. The unit cell of $\text{Ce}_3(\text{Ni}/\text{Al}/\text{Ga})_{11}$ contains two rare-earth sites and four aluminum sites, with two of the Al sites (Al1 and Al4) mixed occupied with Ga or Ni. Al2 and Al3 as well as the two Ce sites are solely occupied by the respective element. The mixed occupied sites were identified by the refinement of the Al occupancies within the structure. The presence of both Ga and Ni is provided by Electron Microprobe Analysis; therefore, the crystallographic sites with higher or lower electron density, with respect to the fully occupied site, were mixed with either Ga or Ni. The mixed occupancy was freely refined to give the stoichiometry of $\text{Ce}_3\text{Ni}_{0.08}\text{Al}_{9.13}\text{Ga}_{1.78}$, similar to the electron microprobe analysis data. The crystal structure can be described as a framework of Al with Ce occupying the pentagonal and hexagonal prismatic voids (Figure 2). The Ce1 polyhedron are slightly distorted fourfold capped hexagonal prisms, with four $(\text{Al}/\text{Ni})_4$ sites and eight $(\text{Al}/\text{Ga})_1$ sites forming the primary polyhedron ($d(\text{Ce}-X) = 329\text{--}331$ pm), while the caps are formed by four Al3 atoms capping four of the six rectangular faces (Figure 3a) formed by two $(\text{Al}/\text{Ni})_4$ and two $(\text{Al}/\text{Ga})_1$ sites ($d(\text{Ce}-X) = 361$ pm). The two remaining rectangular faces (formed by four $(\text{Al}/\text{Ga})_1$ sites) are used to condense the Ce1 with two Ce2 polyhedron in a *trans*-oid fashion. The Ce2 atoms are surrounded by ten plus six atoms ($d(\text{Ce}-X) = 321\text{--}323$ pm plus 357–374 pm) forming a sixfold capped pentagonal prism (Figure 3b). Two faces are mono capped (Al3 over $[(\text{Al}/\text{Ni})_4_2\text{Al}_2]$) and two faces are bicapped (($\text{Al}/\text{Ni})_4$ and $(\text{Al}/\text{Ga})_1$ over $[(\text{Al}/\text{Ni})_4_2(\text{Al}/\text{Ga})_1_2]$). The fifth face formed by four $(\text{Al}/\text{Ga})_1$ sites is again used to condense the Ce2 with the Ce1 polyhedra. The connection between these strands is realized by the atoms capping the two prisms. The shortest Ce–Ce distance is over 400 pm, while the distances within the polyhedron are between 329 and 361 pm (see Table 1). All interatomic distances are in the same range as the ones published for the prototypic $\text{La}_3\text{Al}_{11}$ -type structure [12].

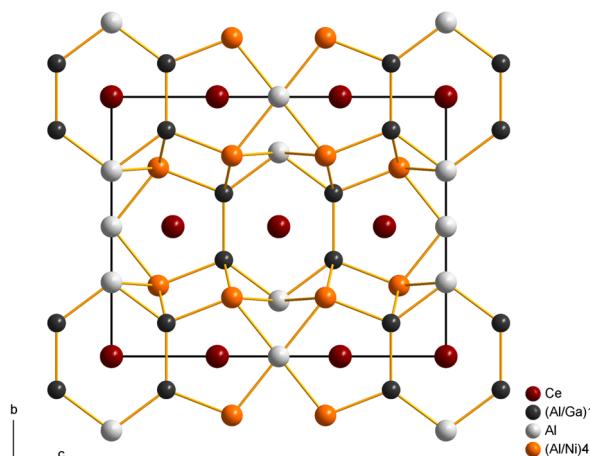


Figure 2. View onto the (011) plane of the unit cell of $\text{Ce}_3\text{Ni}_{0.08}\text{Al}_{9.13}\text{Ga}_{1.78}$ with the Al-framework highlighted. The Ce1 and Ce2 cations are located in the pentagonal and hexagonal voids in the framework.

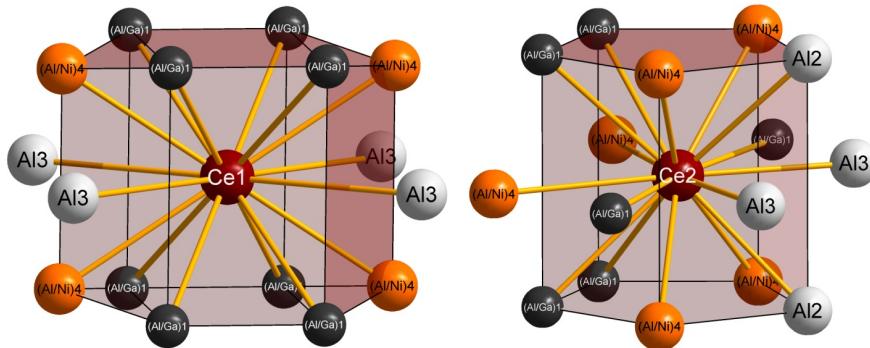


Figure 3. Coordination environments surrounding Ce1 (**a**) in the shape of a fourfold capped slightly distorted hexagonal prism and; Ce2 (**b**) in the shape of a sixfold capped pentagonal prism.

Table 1. Interatomic distances for $\text{Ce}_3\text{Ni}_{0.08}\text{Al}_{9.13}\text{Ga}_{1.78}$.

Ce1–	Count	d (in pm)	Ce2–	Count	d (in pm)
(Al/Ni)4	4×	328.51(12)	(Al/Ni)4	4×	320.65(9)
(Al/Ga)1	8×	330.61(7)	Al3	2×	320.71(11)
Al3	4×	360.38(13)	(Al/Ga)1	4×	321.04(7)
–	–	–	Al2	2×	322.59(7)
–	–	–	(Al/Ni)4	2×	356.68(12)
–	–	–	(Al/Ga)1	2×	373.95(13)
(Al/Ga)1–	Count	d (in pm)	Al2–	Count	d (in pm)
(Al/Ga)1	1×	258.29(13)	(Al/Ni)4	4×	291.13(11)
(Al/Ni)4	2×	263.85(9)	Al3	4×	306.60(11)
Al3	1×	264.35(11)	Ce2	4×	322.59(7)
(Al/Ni)4	1×	272.17(12)	–	–	–
Ce2	2×	321.04(7)	–	–	–
Ce1	2×	330.61(7)	–	–	–
Ce2	1×	373.95(13)	–	–	–
Al3–	Count	d (in pm)	(Al/Ni)4–	Count	d (in pm)
(Al/Ga)1	2×	264.35(11)	(Al/Ga)1	3×	263.85(9)
(Al/Ni)4	4×	283.76(8)	Al3	2×	283.76(8)
Al2	2×	306.60(11)	Al2	1×	291.13(11)
Ce2	2×	320.71(11)	Ce2	2×	320.65(9)
Ce1	2×	360.39(13)	Ce1	1×	328.51(12)
–	–	–	Ce2	1×	356.68(12)

2.3. Magnetic Properties

The magnetic susceptibility $M(T)/H = \chi(T)$ data are summarized in Figure 4a and the inverse susceptibility $\chi(T)^{-1}$ in Figure 4c. Figure 4b shows $\chi(T)$ below 9 K. The crystallographic orientation of the crystal was not determined. The presented compound orders antiferromagnetically at $T_N = 4.8$ K, slightly higher than $\text{Ce}_3\text{Al}_{11}$ ($T_N = 3.2(1)$ K). The ferromagnetic transition observed in $\text{Ce}_3\text{Al}_{11}$ at $T_C = 6.2$ K was not observed in $\text{Ce}_3\text{Ni}_{0.08}\text{Al}_{9.13}\text{Ga}_{1.78}$. This may be related to the Ga- and Ni-substitution of the system and the introduction of disorder in the Al sublattice. It is also possible that the slight

difference in electronic composition with the small amount of Ni incorporation may be important. A fit of the inverse susceptibility data in the region above 50 K using the Curie-Weiss law, revealed an effective magnetic moment of $\mu_{\text{eff}} = 1.9(1) \mu_B$ per cerium atom and a Weiss constant of $\theta_p = -21(1)$ K, consistent with antiferromagnetic interactions in the paramagnetic region.

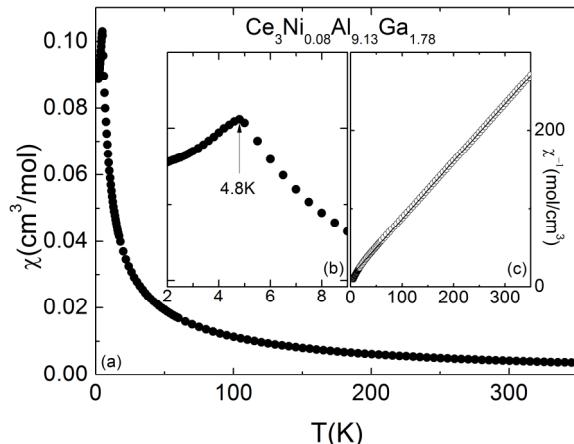


Figure 4. Magnetic susceptibility $\chi(T)$ (a); magnetic susceptibility below 9 K (b); and inverse magnetic susceptibility $\chi(T)^{-1}$ (c) vs. temperature for $\text{Ce}_3\text{Ni}_{0.08}\text{Al}_{9.13}\text{Ga}_{1.78}$.

3. Experimental Section

3.1. Synthesis

During recent molten metal flux growth experiments that were designed to produce CeNiGa_2 , we found crystals of $\text{Ce}_3(\text{Ni/Al/Ga})_{11}$ instead of the desired phase. The single crystals were grown from elements with purities >99.9% in a molten Al flux. The elements were combined in the ratio Ce:Ni:Ga:Al of 1:1:2:20 in an alumina crucible which was sealed under vacuum in a quartz ampoule. The ampoule was heated to 1175 °C over 14 h, kept at this temperature for six hours, and cooled to 700 °C at a rate of 3 K/h. The majority of the flux was subsequently removed by spinning the ampoule in a centrifuge. Single crystals of the title compounds show metallic luster and are stable in air over weeks.

3.2. X-ray Crystallography

The single-crystal X-ray diffraction data was collected on a crystal with $0.08 \times 0.12 \times 0.22 \text{ mm}^3$ at 90 K using a Bruker SMART 1000 CCD diffractometer (Bruker, Billerica, MA, USA) employing graphite-monochromatized Mo-K α radiation ($\lambda = 71.073 \text{ pm}$). The datasets were collected in full sphere with 0.3° scans in ω , and exposure time of 20 s per frame using the SMART software (Bruker, Billerica, MA, USA). Lorentz and polarization effects were corrected using the SAINT program and absorption corrections were applied based on fitting a function to the empirical transmission surface as sampled by multiple equivalent reflections (program SADABS). The structure solution was obtained by direct methods and refined by full-matrix least-squares refinement using the SHELX software package (see Table 2). Details of the crystal structure refinement (atomic coordinates and anisotropic displacement parameters) are given in Tables 1 and 3.

Table 2. Crystallographic data and details of the structure refinement for Ce₃Ni_{0.08}Al_{9.13}Ga_{1.78}.

Empirical formula	Ce ₃ Ni _{0.08} Al _{9.13} Ga _{1.78}
Temperature	90(2) K
Crystal dimensions (μm^3)	80 \times 120 \times 220
Crystal system, space group	Orthorhombic, <i>Imm</i> ₃ (No. 71)
Lattice constants, <i>a</i> (pm) <i>b</i> (pm) <i>c</i> (pm)	436.38(14) 1004.5(3) 1293.4(4)
Formula units (<i>Z</i>)	2
Calculated density, <i>D_x</i> (g/cm ³)	4.702
Volume, <i>V</i> (Å ³)	566.9(3)
Diffractometer, radiation and wavelength	Bruker SMART 1000 CCD, Mo-Kα, $\lambda = 71.073$ pm
$\pm h_{\max}$; $\pm k_{\max}$; $\pm l_{\max}$	5, 12, 16
Θ_{\max} (°)	27.09
F(000)	706
Absorption coefficient μ (mm ⁻¹)	17.13
Data correction	Background, polarization and Lorentz factors
Reflections, unique	3007, 389
<i>R</i> _{int} / <i>R</i> _σ	0.030/0.018
Reflections with $ F_o \geq 4\sigma(F_o)$	377
Structure determination and refinement	Programs SHELXS-97 and SHELXL-97 [13]
Scattering factors	International Tables, Vol. C [14]
<i>R</i> ₁ / <i>R</i> ₁ with $ F_o \geq 4\sigma(F_o)$	0.012/0.011
<i>wR</i> ₂ /Goodness of Fit (GooF)	0.025/1.114
Extinction (g)	0.0016(1)
Residual electron density, max. ρ (e ⁻ · 10 ⁶ pm ⁻³) min.	0.64, -0.52

Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum (FIZ) Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (Fax: +49-7247-808-666; E-Mail: crysdata@fiz-karlsruhe.de), on quoting the depository number 428063.

Table 3. Atomic coordinates and equivalent isotropic thermal displacement parameters for Ce₃Ni_{0.08}Al_{9.13}Ga_{1.78}.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>U</i> _{eq} /pm ²
Ce1	0	0	0	40(1)
Ce2	0	0	0.31629(2)	43(1)
(Al/Ga)1 ^a	0	0.37143(5)	0.33596(3)	60(2)
Al2	1/2	0	1/2	79(3)
Al3	0	0.21444(12)	1/2	63(2)
(Al/Ni)4 ^b	0	0.27297(9)	0.13992(7)	70(3)

^a Mixed occupation Al/Ga = 0.55(1):0.45(1); ^b mixed occupation Al/Ni = 0.98(1):0.02(1).

3.3. Electron Microprobe Analysis (EMPA)

Single crystals were mounted in epoxy and polished for the electron microprobe analysis. The samples were measured using a Cameca SX-100 electron microprobe (Cameca, Gennevilliers Cedex, France) equipped with five wavelength-dispersive spectrometers. The microprobe was operated at 10 nA current with a 15 kV accelerating potential. Net elemental intensities for Ce, Ni, Al and Ga were

determined by quantitative WDX with respect to CeO₂, elemental Ni, Al₂O₃, and GaAs. Atomic percentages were measured at twelve points of the sample and added up to a total of 100%.

3.4. Magnetization

Single crystals of the sample were attached to the specimen holder using Kapton foil (McMaster Carr, 9630 Norwalk Blvd. Santa Fe Springs, CA, USA). The magnetization M(T,H) measurements were carried out for temperatures $T = 2\text{--}350\text{ K}$ under an applied magnetic field 1 kOe using a quantum design magnetic property measurement system (MPMS, QuantumDesign, San Diego, CA, USA).

4. Conclusions

The synthesis and magnetic properties of Ce₃(Ni/Al/Ga)₁₁ with the composition Ce₃Ni_{0.08}Al_{9.13}Ga_{1.78} is reported. The title compound is isostructural to La₃Al₁₁ and crystallizes in the orthorhombic space group *Imm*_m (No. 71) with the standardized setting and lattice parameters of $a = 436.38(14)$, $b = 1004.5(3)$, and $c = 1293.4(4)$ pm. The compound exhibits mixing of Ni and Ga in specific sites (Al1, Al4) on the Al framework. The magnetization data show that the compounds orders antiferromagnetically at $T_N = 4.8\text{ K}$ with an effective magnetic moment of $\mu_{\text{eff}} = 1.9\text{ }\mu_{\text{B}}$ per cerium atom, but no ferromagnetic ordering as observed in Ce₃Al₁₁ has been found. This has been attributed to the disorder introduced by the substitution of Ni and Ga in the Al framework.

Acknowledgments

This work was funded by NSF DMR-1100313. Work at Los Alamos National Laboratory was performed under the auspices of the US Department of Energy, Office of Basic Energy Sciences, Division of Materials Sciences and Engineering, PECASE funding from the US DOE, Office of Basic Energy Sciences (OBES), Division of Material Science and Engineering.

Author Contributions

Tian Shang carried out the experimental work (synthesis). Oliver Janka determined the crystal structure and prepared the manuscript. Joe D. Thompson performed the magnetization measurements. Ryan Baumbach and Eric D. Bauer discussed and analyzed the magnetization measurements. Susan M. Kauzlarich provided oversight of the structure and elemental analysis, useful discussions, revisions and reviewing of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

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