(La₃Z_x)Al and (Ce₃Z_x)Al with Z = C, N, O: Preparation, Physical Properties and Chemical Bonding of Metal-rich Perovskites

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Abstract. The inverse cubic Perovskites (La₃O)Al, (La₃N)Al, (Ce₃O)Al, and (Ce₃N)Al are reported together with the solid solution series (Ce₃C_{1-x}N_x)Al. The crystal structure of (La₃N)Al is analyzed in detail based on single crystal X-ray diffraction data (Space group $Pm\bar{3}m$, $a = 509.04(1)$ pm, $Z = 1$, $R_g(F) = 0.008$, $wR(F^2) = 0.018$). Combined X-ray powder diffraction and thermal analysis studies on samples with various N and O contents indicate only small tolerance of the ternary compounds towards Z = N, O deficiency and small solubility of Z in hexagonal α -Ce₃Al. Indications for the existence of a cubic β -Ce₃Al with Cu₃Au structure type could not be derived from any experiment. All studied phases are metals, the Ce compounds contain the rare-earth metal in Ce(4f¹) states according to X-ray absorption spectroscopy and measurements of the magnetic susceptibilities. The Ce moments order antiferromagnetically with T_N decreasing and scaling with increasing unit cell dimension of the compounds. Electronic band structure calculations reveal a trend to increased mixing of Z and La states on going from Z = O via N to C. Formation of a band gap even in the formally electronically balanced (La₃C)Al is mainly prohibited by insufficient charge transfer between the metal species.

Keywords: Invers Perovskites, Rare-earth compounds, Crystal structures, Electronic properties, Chemical Bonding

Introduction

In the binary systems R -Al (R = rare-earth metal) phases with the composition R_3 Al were reported for $R = Y, La - Nd, Sm$ [1 – 6]. La₃Al was found to exist only in the small

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temperature window of $670\text{ K} < T < 790\text{ K}$ with the hexagonal Mg_3Cd structure [2]. A sample prepared at $T = 770\text{ K}$ was observed to show superconductivity below $T_c = 5.8\text{ K}$ [7]. Several reports suggest a cubic La_3Al high-temperature polymorph [8, 9]. According to the majority of phase diagrams available, the binary compounds $R_3\text{Al}$ with $R = \text{Ce}, \text{Pr}$ crystallize in the hexagonal Mg_3Cd (Ni_3Sn) structure type at ambient temperature and transform into a cubic Cu_3Au type modification above $T = 520\text{ K}$ (Ce) and $T > 600\text{ K}$ (Pr), respectively. However, there are observations that quenched melt beads of the Ce containing system exclusively consisted of hexagonal $\alpha\text{-Ce}_3\text{Al}$, while a transformation into a cubic phase on annealing in quartz ampoules [10] or MgO crucibles [11] was apparent. On cooling from ambient temperature, $\alpha\text{-Ce}_3\text{Al}$ shows a 1.8 % volume reduction at $T = 100\text{ K}$ without significant change of the crystal structure, interpreted to be connected to the Kondo effect [10, 12 – 14]. However, different authors claim a structural transition of $\alpha\text{-Ce}_3\text{Al}$ to a monoclinic structure induced by small displacements of the atoms ($P6_3/mmc \rightarrow P112_1/m$) at this temperature [15]. For Nd_3Al only a hexagonal Mg_3Cd type modification is known. The recent discovery of the new binary phase $\text{La}_{16}\text{Al}_{13}$ indicates that binary phase diagrams of these rare-earth metal–aluminium systems in general have to be used with great care [16]. Additionally, in the past, several examples for binary intermetallic compounds were revealed to represent ternary compounds involving unnoticed nonmetallic constituents as, e. g., oxygen. The alkaline-earth metal compounds $(A_3\text{O})E(14)$ with $E(14) = \text{Sn}, \text{Pb}$ [17, 18], formally known as binary phases $A_3E(14)$, and $(A_4\text{O})E(15)_2$ with $E(15) = \text{group 15 elements}$ [19 – 22], in older phase diagrams assigned as $A_2E(15)$, may suffice as examples.

For the systems considered, the phases $R_3\text{Al}$ with cubic Cu_3Au structure type show the identical metal substructure as cubic Perovskites $(R_3Z)\text{Al}$ ($Z = \text{O}, \text{N}, \text{C}$), differences in powder X-ray diffraction intensities are only marginal, just the unit cell parameters may vary slightly on introduction of nonmetallic components Z . However, physical properties as hardness, electrical conductivity, magnetic ordering behavior, and magnetic transition temperatures as well as thermal and chemical stabilities can dramatically depend on Z . Since most reports in literature on $R_3\text{Al}$ phases do not state analytical composition data, the results, particularly on cubic Cu_3Au type phases, should be taken with great care. As can be taken from literature, cubic Perovskites $(R_3\text{C})\text{Al}$ exist with all rare-earth metal elements $R = \text{Sc}, \text{Y}, \text{La} - \text{Lu}$, except $R = (\text{Pm}), \text{Eu}$ [23, 24]. An unexpected small unit cell volume of $(\text{Ce}_3\text{C})\text{Al}$ as compared to the carbides of the other rare-earth metals was interpreted to indicate $\text{Ce}^{4+}(4f^0)$ contributions to be present. Only few nitrides were reported with $R = \text{La} - \text{Nd}, \text{Sm}$ [6, 25], but no ternary nitride formation for $R = \text{Eu} - \text{Lu}$ was observed [6, 26]. Different authors even claimed no formation of any ternary nitrides independent of the choice of R according to their experiments [24]. No borides or oxides with aluminum of the considered formula type have previously been reported. Generally, for the binary modifications of Ce_3Al and for all ternary Perovskites $(R_3Z)\text{Al}$ no information concerning chemical

composition, specifically on the content of Z, is available in literature.

Experimental Details

Since rare-earth metals and all products in this study are air and moisture sensitive, all manipulations were carried out under inert conditions in an argon filled glove box (MBraun, O₂ and H₂O content < 1 ppm). All samples were checked by X-ray powder diffraction and elemental analyses on N and O. For nominal carbides the C content was additionally determined. Exemplary measurements of the carbon content in nominal oxides and nitrides did not indicate any carbon contamination. Detection limits typically were well below $w(\text{C, N, O}) = 0.10\%$. Only Z contents above the detection limits were considered in the given formulas.

Chemical analyses for N, O and C were carried out via hot-gas-extraction (N, O simultaneous: LECO 436DR; C: LECO RH404). EDXS technique was used for determination of the metal ratio of (La₃N)Al single crystals. All values are averages of at least 3 independent measurements.

The preparation of the binary rare-earth metal nitrides RN was discussed in-depth by Brown et al. [27]. Purification of La and Ce as well as production and characterization of LaN and CeN was previously described [28]. Melt beads with the total compositions La_xAl and Ce_xAl were synthesized from the elements (Al: 99.9999 %, Chempur) by fusion in the appropriate molar ratios in an arc-furnace.

For the preparation of (R₃Z)Al ($R = \text{La, Ce}$; $Z = \text{N, O}$), RN, CeO₂, or La₂O₃ and the respective binary alloys R_xAl were fused together in an arc-furnace in molar ratios allowing the formation of pure ternary compounds. The carbides were produced from melt beads of R, Al and C (Graphite, pressed to pellets). For samples of the nominal composition (R₃Z_x)Al the same procedure was used. The resulting beads were sealed in Ta ampoules in Ar atmosphere, which were successively sealed in evacuated quartz ampoules. This assembly was annealed at temperatures in the range of $870\text{ K} \leq T \leq 1070\text{ K}$ for at least seven days.

La–Al melt beads react with nitrogen to form (La₃N)Al as main phase (next to small amounts of LaN and La₂[AlN₃], depending on the molar ratio $n(\text{La}) : n(\text{Al})$ in the initial mixture) at temperatures in the range of $1070\text{ K} < T < 1270\text{ K}$. At $T > 1300\text{ K}$ the reaction of La–Al melt beads with nitrogen atmosphere produces polycrystalline LaN and hexagonal AlN single crystals. Single crystals of (La₃N)Al were obtained from the reaction of a melt bead La₃Al in nitrogen atmosphere at $T = 1270\text{ K}$.

For X-ray diffraction the powdered samples (XRD) were loaded between two Kapton-foils for protection from moisture and air. The X-ray experiments were carried out on an imaging plate Guinier-Camera (Huber-Diffraction, G 670) equipped with a quartz monochromator (Cu K α_1 -radiation, $6^\circ \leq \Theta \leq 100^\circ$, $4 \times 15\text{ min}$).

The collection of diffraction intensities of a single crystal platelet (La₃N)Al with metallic luster was performed on a

MSC-Rigaku R-Axis Rapid diffractometer. The data are consistent with a primitive cubic unit cell and the space groups $P23$, $Pm\bar{3}$, $P432$, $P\bar{4}3m$, and $Pm\bar{3}m$. The refinement in $Pm\bar{3}m$ led to satisfactory results with no indications for the need of a symmetry reduction.

Differential thermal analysis (DTA) was carried out in automatic analyzers DSC 404 and DSC 449 (Netzsch, thermocouple type S, heating/cooling rate 10 K/min). Samples were sealed in Nb ampoules in Ar atmosphere. Temperature calibration was carried out with five melting points of pure metals.

Measurements of the magnetic susceptibility were performed on a SQUID magnetometer (MPMS-XL7, Quantum Design) at fields $\mu_0 H$ between 2 mT and 7 T in the temperature range 1.8 K – 400 K using ca. 100 mg of single phase products sealed in quartz tubes under 400 mbar He.

Electrical resistivity measurements were carried out on suitable pieces of the single phase products by a conventional dc four-point method between 3.5 K and 320 K. The contacts were made from silver-filled epoxy. All manipulations were carried out in an argon-filled glove box with an integrated cryostat for the resistivity measurement.

For X-ray absorption spectroscopy (XAS) the compounds were ground with three times their volume of dry B_4C to produce homogenous absorbers. Air sensitive samples were loaded in steel capsules, equipped with Be-windows (0.5 mm) and sealed with indium gaskets. The Ce- L_{III} edge measurements were performed in transmission geometry at the EXAFS II beamline E4 at the DORIS III storage ring in the HASYLAB laboratory (Hamburg, Germany). The X-ray beam was monochromatized using a double crystal monochromator, equipped with a Si(111) crystal. With this experimental setup the resolution in the energy region studied is about 1.5 eV. The absorption spectra were measured simultaneously with the spectrum of CeO_2 serving as references for energy calibration.

Calculation Procedure

Scalar relativistic LDA band structure calculations [29] for $(La_3Z)Al$ were carried out using the TB-LMTO-ASA method [30, 31] including combined correction for neglect of interstitial regions and partial waves of higher order. Atomic sphere radii ($(La_3O)Al$: $r(La) = 176$ pm, $r(Al) = 232$ pm, $r(O) = 112$ pm; $(La_3N)Al$: $r(La) = 176$ pm, $r(Al) = 239$ pm, $r(N) = 117$ pm; $(La_3C)Al$: $r(La) = 173$ pm, $r(Al) = 243$ pm, $r(C) = 121$ pm)) were determined by an automatic procedure described in [32]. The valence basis set consisted of $La(6s,5d,4f)$, $Al(3s,3p)$, $O(2p)$, $N(2s,2p)$, $C(2s,2p)$ orbitals. The $La(6p)$, $Al(3d,4f)$ and $Z(3d)$ orbitals were included in the tails of these LMTOs according to the Löwdin downfolding procedure [32]. k -space integration was performed by the tetrahedron method using 84 irreducible k points. Chemical bonding was characterized in terms of two-center orbital interactions using the COHP (Crystal Orbital Hamiltonian Populations) method [33], which is implemented in a separate version of the LMTO-ASA code [34].

Results and Discussion

Preparation and Chemical Behavior

Preparation of the ternary phases (R_3Z)Al (R = rare-earth metal, specifically La, Ce; Z = O, N, C) can in principle be carried out as previously described for the analogous In containing phases [28]. Due to the lower eutectic temperatures in the R -rich part of the Al containing binary phase diagrams compared to the respective In systems [35], generally lower annealing temperatures were applied. The resulting chemical compositions from elemental analyses and unit cell dimensions from X-ray powder diffraction are gathered in Table 3. A general difference of the Al containing systems compared to those with In as constituent is the higher thermal stability of the metal-rich nitrides and the tendency for formation of ternary nitridoaluminates. The latter fact is indicated by the formation of alkali and alkaline-earth metal nitridoaluminates [e. g., 36, 37] as well as of $\text{La}_2[\text{AlN}_3]$ [38], while no ternary compound with a stable covalent In–N bond is known in nitride chemistry. The high thermal stability, even against reaction with nitrogen atmosphere, can be seen in the fact, that La–Al melt beads react with nitrogen to form $(\text{La}_3\text{N})\text{Al}$ as main phase at temperatures in the range of $1070\text{ K} < T < 1270\text{ K}$. According to our experiments $(\text{La}_3\text{N})\text{Al}$ is probably the kinetically favored product when treated under excess nitrogen gas, because the amount decreases with increased reaction duration in favor of formation of the binary metal nitrides LaN and AlN. Corresponding phases in the binary systems R –In either do not react with nitrogen under these conditions (but at higher temperatures), or form $R\text{N}$ and In in a rapid reaction [28, 39]. At $T > 1300\text{ K}$ the reaction of La–Al melt beads with nitrogen atmosphere produces LaN and hexagonal AlN single crystals (needles of several mm in length). Single crystals of $(\text{La}_3\text{N})\text{Al}$ ($a = 509.48(7)\text{ pm}$ compared to $a = 509.04(1)\text{ pm}$ determined from powder X-ray diffraction) were obtained from the reaction of a melt bead La_3Al in nitrogen atmosphere at $T = 1270\text{ K}$. Preparation of oxides, for comparison, was achieved from oxide precursors, while excess oxygen leads to aluminate products. Experiments aiming for ‘ $(\text{Ce}_3\text{C})\text{Al}$ ’ led to samples containing the cubic Perovskite next to unknown phases. On reduction of the carbon amount at a total composition of $(\text{Ce}_3\text{C}_x)\text{Al}$ with $x \approx 0.65$ the highest amount of the cubic Perovskite in a multiphase sample was obtained, while on further reduction of the carbon content hexagonal $\alpha\text{-Ce}_3\text{Al}$ is in equilibrium with the Perovskite carbide.

Crystal Structure Details and Compositions

X-ray powder diffraction performed on the ternary compounds (R_3Z)Al (R = La, Ce; Z = O, N, C) clearly indicate the Cu_3Au type metal substructure. Refinement results of X-ray diffraction intensity data taken on a single crystal $(\text{La}_3\text{N})\text{Al}$ support the structural assignment and reveal the nitride ions located in octahedral holes exclusively formed by La, i. e., a cubic Perovskite type structure. Details con-

cerning the data collection and structure determination for the single crystal are gathered in Tables 1 and 2. No indications for deviations from cubic metric were apparent from the X-ray powder patterns. Discrimination between binary cubic Cu_3Au type compounds and ternary cubic Perovskites for these element combinations based on powder X-ray diffraction is virtually impossible, due to the small scattering power contribution of Z. The same is true for the decision between different $Z = \text{C}, \text{N}, \text{O}$ or of only partially occupied Z sites based on X-ray powder diffraction intensities. The single crystal structure refinements on $(\text{La}_3\text{N})\text{Al}$ led to full occupancy of the N site, EDX analyses on such crystals $(\text{La}_3\text{N})\text{Al}$ resulted in a molar ratio of $n(\text{La}) : n(\text{Al}) = 3 : 1$. Both results support the composition assignment and give no indication for a significant homogeneity range of this ternary compound. Anisotropic refinements of the displacement parameters of La led to strongly oblate ellipsoids with large extension in the directions perpendicular to the N–La direction and $U_{11} = U_{22} \approx 3 \times U_{33}$ (see Table 2 and Figure 1). Such displacement was frequently observed for related binary octahedra framework structures with ReO_3 structure type (e. g., Cu_3N [40] and ReO_3 itself [41, 42]) and a variety of Perovskites ABO_3 , and often associated with atomic/ionic size mismatch in the structure prior distortion. Distortion typically proceeds by static tilting of the octahedra at somewhat lower temperatures or higher pressures. For comparison, the closely related cubic Perovskite nitride $(\text{Ca}_3\text{N})\text{Ti}$ exhibits nearly no anisotropy of Ca ($U_{11} \approx U_{33}$ [43]), indicating a perfect size fit, while, e. g., the nitrides $(\text{Ca}_3\text{N})E$ with $E = \text{P}, \text{As}$ [44, 45] and the oxides $(\text{A}_3\text{O})E$ with $A = \text{Ca}, \text{Sr}, \text{Ba}$ and $E = \text{Si}, \text{Ge}$ [46 – 48] are distorted to orthorhombic unit cells (space group $Pnma$).

The unit cell volumes of the carbides are significantly larger than those of the nitrides, oxides, and particularly the binary (hexagonal) phases. Table 4 gathers volumes per formula unit from literature and the present work. Despite some scatter of the literature data it is apparent, that the reported unit cell of $(\text{Ce}_3\text{C})\text{Al}$ [23, 24] deviates to lower values than expected from those of the oxide and nitride and nearly coincides with that of $(\text{Ce}_3\text{N})\text{Al}$. This observation was discussed to arise from a $\text{Ce}^{4+}(4f^0)$ contribution in the carbide [23], while the volumes of the nitride and oxide are consistent with an exclusive $\text{Ce}^{3+}(4f^1)$ content. The reported unit cell parameters of $a = 502.9 \text{ pm}$ [23] and $a = 500.7 \text{ pm}$ [24] for $(\text{Ce}_3\text{C})\text{Al}$ were in principle reproduced with $a = 503.86(5) \text{ pm}$ in the present work, but on a sample of the solid solution series $(\text{Ce}_3\text{C}_{1-x}\text{N}_x)\text{Al}$ ($(\text{Ce}_3\text{C}_{0.82(2)}\text{N}_{0.12(2)})\text{Al}$ according to chemical analyses, compare Table 3). Data on samples with various carbon contents of bulk compositions ‘ $(\text{Ce}_3\text{C}_x)\text{Al}$ ’ indicate a compound with an approximate composition parameter $x = 0.65$ (see above).

Magnetization measurements on single phase samples $(\text{Ce}_3\text{C}_{1-x}\text{N}_x)\text{Al}$ ($x = 0.15$) are consistent with Ce in a pure $\text{Ce}^{3+}(4f^1)$ state (see below), thus leaving substitution of the C site by N and/or O as the most likely reason for the smaller unit cell dimension also for the literature data. Similarly, phase analyses in the systems Ce–Al–N and Ce–Al–O led to the conclusion that $(\text{Ce}_3\text{N})\text{Al}$ and $(\text{Ce}_3\text{O})\text{Al}$ tolerate only small deficiencies x on the Z site in the sense

of $(\text{Ce}_3\text{Z}_{1-x})\text{Al}$. In samples with $Z = \text{N}$, O contents below the nominal amount for the formation of $(\text{Ce}_3\text{Z})\text{Al}$ always hexagonal Ce_3Al was observed as a second phase as is illustrated in Figure 2: DTA measurements on samples with the bulk compositions $(\text{Ce}_3\text{N}_x)\text{Al}$ and $x = 0.2, 0.4, 0.6, 0.8, 1$, annealed at $T = 870$ K and subsequently quenched to ambient temperature are shown. The respective XRD patterns taken prior to the thermal analyses are also plotted. As can be seen from XRD, hexagonal $\alpha\text{-Ce}_3\text{Al}$ is present in all samples with $x < 1$, while the sample with $x = 1$ ($a = 500.92(1)$ pm, $(\text{Ce}_3\text{N}_{1.01(1)})\text{Al}$ according to chemical analyses) gives a diagram fully explained by a cubic Perovskite structure. Qualitatively, the amount of hexagonal $\alpha\text{-Ce}_3\text{Al}$ in the samples decreases with increasing x , while the amount of $(\text{Ce}_3\text{N})\text{Al}$ increases. The relatively weak intensities of the reflections caused by $\alpha\text{-Ce}_3\text{Al}$ compared to those from the ternary Perovskite nitride are due to the mechanical properties of both phases: the binary compound is ductile while the ternary nitride is brittle. Therefore, the microcrystalline powder is enriched in nitride crystallites of suitable size after grinding. Corresponding to these XRD patterns, the DTA curves reveal endothermal signals at $T_{\text{max}} = 925$ K, which represent melting of Ce_3Al . The size of this peak decreases with increasing x conversely to a growing endothermal signal at $T_{\text{max}} = 1340$ K. The XRD patterns of the samples after the thermal analyses show no significant differences to those recorded before the DTA measurements and the sample with $x = 1$ was clearly molten. The DTA signal at $T_{\text{max}} = 1340$ K is thus interpreted as congruent melting point of $(\text{Ce}_3\text{N})\text{Al}$, which exhibits no significant homogeneity range $(\text{Ce}_3\text{N}_x)\text{Al}$ within the $\Delta x = 0.2$ step frame of the experiments. The systematic variation of the DTA peak temperatures from $T_{\text{max}} = 1295$ K for $x = 0.2$ to $T_{\text{max}} = 1340$ K for $x = 1.0$ may indicate the possibility of a small N deficiency, but favorably be connected with the progression of the liquidus. Similar DTA and XRD investigations for the quasi-binary systems $\text{Ce}_3\text{Al}-(\text{Ce}_3\text{O})\text{Al}$ (fig. 3) indicate also small homogeneity ranges for both Ce_3Al and $(\text{Ce}_3\text{O})\text{Al}$, but an incongruent melting at a temperature of 990 K, since the samples after DTA measurements always contained a multitude of binary phases. The experiments also revealed large homogeneity ranges in the sense of substitution of C and O by N in the ternary carbide and oxide, respectively, i. e., $(\text{Ce}_3\text{C}_{1-x}\text{N}_x)\text{Al}$ and $(\text{Ce}_3\text{O}_{1-x}\text{N}_x)\text{Al}$.

Polymorphism of Ce_3Al

Experiments within this study aiming for cubic $\beta\text{-Ce}_3\text{Al}$ always resulted in the hexagonal phase (e. g., quenching from 870 K after annealing in a sealed Ta ampoule for several weeks). There are likewise no indications for a transition of hexagonal $\alpha\text{-Ce}_3\text{Al}$ into a high-temperature polymorph ($\beta\text{-Ce}_3\text{Al}$ with Cu_3Au structure type as was reported in literature) from thermal analyses as discussed above. This observation is in line with the report that $\alpha\text{-Ce}_3\text{Al}$ does not show any discontinuity or aberration in the magnetic susceptibility at the presumed transition temperature to $\beta\text{-Ce}_3\text{Al}$ [11]. This result indicates that the previous observations of cubic $\beta\text{-Ce}_3\text{Al}$ may be due to the presence

of nonmetal stabilized ternary phases. This interpretation is in accordance with the independent observation that quenched melt beads exclusively consisted of α -Ce₃Al, while a transformation into a cubic phase on annealing in quartz ampoules [10] or MgO crucibles [11] was apparent. Speculations on the growth of metastable cubic Cu₃Au type binary compounds, once cubic crystal seeds are formed [23], become likewise unlikely. As was already pointed out in the introduction, phases R_3 Al with $R = Y, La, Sm$ and the Cu₃Au crystal structure frequently observed in literature are also likely to be stabilized by unnoticed C, N and/or O impurities [24]. This becomes particularly apparent in a recent report on cubic La₃Al: X-ray powder diffraction data of a multi-phase mixture, obtained in a synthesis experiment apparently aiming for the ternary nitridoaluminate La₂[AlN₃] [38], consisted mainly of La₂[AlN₃], LaAl and LaN, but contained additionally this cubic phase. We presume a correct composition of (La₃N_{1-x}O_x)Al, as indicated by the reported unit cell parameter of $a = 505.0(1)$ pm [8], compared to the unit cell dimensions of (La₃N)Al of $a = 507.0$ pm [6], $a = 509.04(1)$ pm, or (La₃O)Al of $a = 503.22(2)$ pm (see table 3). The situation for cubic β -Ce₃Al is similar: literature values for the unit cell parameter were reported to cover the range of $498.5 \text{ pm} \leq a \leq 501.3 \text{ pm}$ [3, 49], which is in the order of the value obtained for (Ce₃N)Al ($a = 500.92(1)$ pm) and larger than that for (Ce₃O)Al ($a = 495.74(1)$ pm, see Tables 3 and 4).

Magnetic Properties and Specific Heat

Data of the magnetic susceptibility of (Ce₃O)Al, (Ce₃N)Al, and (Ce₃C_{1-x}N_x)Al ($x = 0.15$) are given in Figure 4 for an external magnetic field of $\mu_0 H = 1$ T. The curvature of $1/\chi(T)$ at temperatures below 100 K and the almost linear variation of all three data sets at high temperatures indicate the presence of the $^2F_{5/2}$ crystal field ground multiplet of the $4f^1$ electronic configuration of Ce. A Curie-Weiss fit in the range of $150 \text{ K} < T < 400 \text{ K}$ results in $\mu_{\text{eff}}/\text{Ce-atom} = 2.74 \mu_B$ and $\Theta = -116 \text{ K}$ for (Ce₃O)Al, $\mu_{\text{eff}}/\text{Ce-atom} = 2.50 \mu_B$ and $\Theta = -37 \text{ K}$ for (Ce₃N)Al, and $\mu_{\text{eff}}/\text{Ce-atom} = 2.62 \mu_B$ and $\Theta = -77 \text{ K}$ for (Ce₃C_{1-x}N_x)Al ($x = 0.15$). These effective magnetic moments are compatible with that of the free Ce³⁺($4f^1$) ion: $\mu_{\text{eff}} = 2.54 \mu_B$ [50].

(Ce₃O)Al orders antiferromagnetically at $T_N = 9(1) \text{ K}$, (Ce₃N)Al at $T_N = 6(1) \text{ K}$, while (Ce₃C_{1-x}N_x)Al ($x = 0.15$) shows no indication for a magnetic order above $T = 2 \text{ K}$. These transition temperatures, in principle, decrease with increasing unit cell parameters and thus with increasing distances $d(\text{Ce}-\text{Ce})$. In a magnetization isotherm at $T = 1.8 \text{ K}$ (well below T_N) (Ce₃N)Al shows a clear two-step metamagnetic behavior. The first quite pronounced step starting at 1.2 T is followed by a second weaker one between 3.5 T and 4.5 T. The magnetization reaches only $2.9 \mu_B$ at a field $\mu_0 H$ of 7 T. For (Ce₃O)Al a metamagnetic transition step at a field below 1.0 T is barely visible. Similar to (Ce₃C_{1-x}N_x)Al ($x = 0.15$), hexagonal α -Ce₃Al (and ‘cubic Ce₃Al’) is known to show no magnetic order above $T = 4 \text{ K}$ and an effective magnetic moment of $\mu_{\text{eff}}/\text{Ce-atom} = 2.52 \mu_B$ at high temperatures [11].

A measurement of the heat capacity on $(\text{Ce}_3\text{C}_{1-x}\text{N}_x)\text{Al}$ ($x = 0.15$) down to temperatures of 1.8 K shows no phase transitions but a steep increase in c_p/T below 4.5 K. Since $\text{Ce}(4f^1)$ is a Kramers ion, where the minimum degeneracy is that of a doublet, application of a magnetic field leads to a splitting of the crystal field ground state. Therefore, a distorted two-level Schottky anomaly develops with increasing field (Figure 5). The entropy contained in the Schottky anomaly is around $k_B N_A \ln 2$, thus confirming that the ground state is a doublet. Only measurements at lower temperatures can clarify whether the upturn ($\propto T^{-2}$) in zero field indicates a magnetic ordering in the ground state doublet (in which the short-range order tail is seen in zero field). The energy splitting of the ground doublet necessary to reproduce the upturn in c_p/T below 4.5 K is well below $k_B \cdot 1$ K. Subtraction of a Debye lattice term (Debye temperature 250 K) produces a large multi-level Schottky anomaly with a maximum of $\approx 20 \text{ J mol}^{-1} \text{ K}^{-1}$ height at ≈ 31 K. A crystal field level scheme with the doublet ground state and a quasi-quartet excited state at $k_B \cdot 83$ K (two doublets near that energy) nicely reproduces this Schottky anomaly.

A sample of $(\text{La}_3\text{N})\text{Al}$ (which contained small amounts of La and LaN) displayed Pauli paramagnetism ($\chi_0 \approx +90 \cdot 10^{-6} \text{ emu mol}^{-1}$, after subtraction of diamagnetic increments $\chi_p \approx +160 \cdot 10^{-6} \text{ emu mol}^{-1}$). This corresponds to an electronic density of states of $\approx 5 \text{ states eV}^{-1}$ at E_F which has to be compared with $2.9 \text{ states eV}^{-1}$ found in electronic structure calculations (*vide infra*).

X-ray Absorption Spectroscopy

For independent information on the electronic state of cerium we measured XAS spectra on the $\text{Ce}-L_{\text{III}}$ threshold. The applied range of photon energies makes it possible to measure in transmission geometry, thus to obtain data of the bulk material less obscured by surface impurities. Fig. 6 shows the $\text{Ce}-L_{\text{III}}$ edge of $(\text{Ce}_3\text{O})\text{Al}$, $(\text{Ce}_3\text{N})\text{Al}$ and $(\text{Ce}_3\text{C}_{1-x}\text{N}_x)\text{Al}$ together with the spectrum of CeO_2 as a reference. Clearly the positions of the absorption edges of the Perovskite compounds coincide in energy, while the edge of CeO_2 is shifted to higher energies. No indications for a $\text{Ce}^{4+}(4f^0)$ contribution at increased energies is visible from the spectra of the Perovskites indicating an identical $\text{Ce}^{3+}(4f^1)$ state. Additionally shown is the spectrum of the sample ‘ $(\text{Ce}_3\text{C}_{0.7})\text{Al}$ ’ with the highest content of a cubic Perovskite compound in a carbide sample as stated above. The occurrence of exclusively $\text{Ce}^{3+}(4f^1)$ contributions to the spectrum indicates that the reported small volume of ‘ $(\text{Ce}_3\text{C})\text{Al}$ ’ is not correlated with an increased valence state of Ce, but is due to a C deficiency.

Electrical Resistivity

The electrical resistivity $\rho(T)$ (figure 7 a) of $(\text{Ce}_3\text{N})\text{Al}$ is $\approx 1 \mu\Omega \text{ m}$ at 300 K and decreases linearly with decreasing temperature indicating metallic conductivity. The residual resistivity $\rho_0 \approx 0.25 \mu\Omega \text{ m}$ is higher than that of the La compounds, but still of the usual order of magnitude found

in similar compounds. No clear discontinuity is visible around T_N as can be expected from the small deGennes factor of $\text{Ce}^{3+}(4f^1)$. Figure 7 b shows the electrical resistivity of $(\text{Ce}_3\text{C}_{1-x}\text{N}_x)\text{Al}$ ($x = 0.15$) to be considerably larger ($\rho(300\text{ K}) \approx 2.4\ \mu\Omega\text{ m}$) and to decrease nonlinearly and with little temperature dependence down to about $T = 50\text{ K}$. Below this temperature $\rho(T)$ increases again. Together with the absence of magnetic order above temperatures of 1.8 K (in $\mu_0H = 10\text{ mT}$) and the heat capacity data, the temperature dependence of the electrical resistivity leads to conclude on some kind of frustration of magnetic exchange due to disorder. Competing ferromagnetic and antiferromagnetic interactions could be induced by slightly different distances $d(\text{Ce}-\text{Ce})$ due to disorder in the C, N sublattice. Structural disorder may also explain the large absolute resistivity of this material.

The electrical resistivity of $(\text{La}_3\text{Al})\text{N}$ is $0.67\ \mu\Omega\text{ m}$ at 300 K and the residual resistivity is as low as $0.04\ \mu\Omega\text{ m}$. The measurement reveals a temperature dependence typical for metals.

Electronic band structure calculations

In order to elucidate some principle features and trends of the electronic structures we performed scalar relativistic LDA band structure calculations. For reasons of simplicity we restricted these to the lanthanum compounds $(\text{La}_3\text{O})\text{Al}$, $(\text{La}_3\text{N})\text{Al}$, and $(\text{La}_3\text{C})\text{Al}$ using experimental lattice parameters (Table 4).

From analyses of the densities of states (DOS) of the valence bands (Figure 8, $Z(2s)$ bands omitted in the discussion due to low energy positions) it is evident that they can not simply be interrelated by the frozen band approximation. This is mainly due to the different energetic positions and energy bandwidths of the $Z(2p)$ bands. The energy of the bands increases with respect to E_F according to $E(\text{O}(2p)) < E(\text{N}(2p)) < E(\text{C}(2p))$, which is the common trend expected from the first atomic ionization potentials, atomic electronegativities and atomic charge dependence of band positions. The $2p$ bandwidth increases along O to C, which is caused by mixing with $\text{La}(5d)$ minority band states forming partially covalent bonds (see below). While for $Z = \text{O}, \text{N}$ the $2p$ bands are lying well below E_F , the combined effect of increasing energetic position and bandwidth leads for $(\text{La}_3\text{C})\text{Al}$ to a situation with the $\text{C}(2p)$ band closely below the Fermi level with even some contributions at E_F .

The $\text{Al}(3s)$ band can be characterized to a good approximation as a pure $3s$ band, which remains at roughly the same energy position well below E_F for all three compounds. The seemingly very different DOS diagrams result from the fact that the broader $Z(2p)$ band DOS contributions are overlapping in energy with narrower $\text{Al}(3s)$ band contributions, partly for $(\text{La}_3\text{O})\text{Al}$, and completely for $(\text{La}_3\text{N})\text{Al}$, while for $Z = \text{C}$ they are located clearly above the $\text{Al}(3s)$ band.

$\text{Al}(3p)$ bands are located in the upper energy region roughly between -3 eV and $+2\text{ eV}$, where they are strongly mixed with $\text{La}(5d)$ contributions. The energies of filled $\text{Al}(3p)$ bands mark the region where metal-metal bonding takes

place. Exclusively for $(\text{La}_3\text{C})\text{Al}$ this region partially overlaps with the energy region of $Z(2p)$ bands, and, in contrast to $Z = \text{O}, \text{N}$, a DOS contribution of the $Z(2p)$ at E_F results.

The total densities of states at the Fermi level are 3.0 states/eV ($Z = \text{O}$), 2.9 states/eV ($Z = \text{N}$) and 4.9 states/eV ($Z = \text{C}$). The significantly larger value for $Z = \text{C}$ is due to the position of E_F located on the falling flank of a DOS peak, while E_F lies between this and the next higher energy peak for $Z = \text{O}, \text{N}$. This difference is directly related to the fewer number of valence electrons for $(\text{La}_3\text{C})\text{Al}$ compared to the compounds with O and N . Therefore, the number of states at the Fermi level can be chemically tailored by formation of substitution phases according to, e. g., $(\text{La}_3\text{C}_{1-x}\text{N}_x)\text{Al}$.

In order to further characterize chemical bonding within this local DOS picture we calculated energy-resolved Crystal Orbital Hamiltonian Populations (COHP) indicating three significant interatomic two-centre orbital interactions (Figure 9): COHP($Z(2p)$ – $\text{La}(5d)$) diagrams corroborate the picture of partially covalent bonding between elements Z and La , where the strength of orbital interactions increases from O to C explaining the above mentioned trend in $Z(2p)$ bandwidth. Orbital interactions Z – La are clearly optimized, in the sense that all available bonding contributions are exhausted either well below E_F for $Z = \text{O}, \text{N}$, or just at E_F for $Z = \text{C}$, and only neglectable antibonding contributions occur for $Z = \text{N}, \text{O}$.

In the projected DOS for $\text{Al}(3p)$ a pseudo gap occurs in the Fermi level region, which is covered in the total DOS by large $\text{La}(5d)$ contributions. This splitting of $\text{Al}(3p)$ states is caused by $\text{Al}(3p)$ – $\text{La}(5d)$ orbital interactions, which give bonding contributions below and antibonding contributions above the pseudo gap (Figure 8). For $(\text{La}_3\text{O})\text{Al}$ the Fermi level lies within that pseudo gap, so that orbital interactions Al – La are optimized in the sense of separation of bonding from antibonding contributions by the Fermi level. Starting already for $Z = \text{N}$, but especially for $(\text{La}_3\text{C})\text{Al}$, E_F increasingly cuts the falling flank of the partial $\text{Al}(3p)$ DOS below the pseudo gap and thus, increasingly significant bonding contributions are lost (located above E_F). This is not compensated by a corresponding gain of competing bonding interactions. It has been discussed previously for isostructural $(\text{La}_3\text{N})\text{In}$ [28] that these heteroatomic intermetallic interactions play an important role for the electronic structure of the compound since they are sizeable and numerous (each Al atom has 12 La neighbors). The electronic structures of $(\text{La}_3\text{N})\text{In}$ and $(\text{La}_3\text{N})\text{Al}$ are very similar and the conclusions derived for the former compound are valid for the latter as well.

Homoatomic two-center metal orbital interactions are significant only for La . As may be expected, they are far from being exhausted at E_F and increase well beyond. The occurrence of sizeable and similar interactions COHP(La – La) for all three compounds is the puzzling feature that deteriorates simple formal charge assignment efforts. The electronic structure of $(\text{La}_3\text{C})\text{Al}$ is to be contrasted with isostructural and—at first glance—iso-electronic $(\text{Ca}_3\text{N})\text{Bi}$ [43]. In the latter case a formal charge assignment was justified by the non-occurrence of sizeable interactions COHP(Ca – Ca) for for-

mal Ca^{2+} species, the optimization of N–Ca net orbital interactions in the picture of a partial covalent bonding according to $\text{N}^{3-}\text{--Ca}^{2+}$, the optimization of Bi–Ca net orbital interactions (neglecting Bi(6*d*) contributions), and the characteristic compensation of bonding and antibonding contributions below E_F for formal Bi^{3-} species. This way of electron counting within the framework of semiconductor bonding covered by the $(8 - N)$ rule is experimentally corroborated by the existence of an electronic band gap [44]. The only common features of the electronic structures of $(\text{Ca}_3\text{N})\text{Bi}$ and $(\text{La}_3\text{C})\text{Al}$ are the optimization of N–Ca and C–La bonding and the characteristic compensation of bonding and antibonding contributions $\text{COHP}(\text{Bi--Bi})$ and $\text{COHP}(\text{Al--Al})$, respectively. The occurrence of significant contributions $\text{COHP}(\text{La--La})$ below E_F already rules out semiconducting properties for $(\text{La}_3\text{C})\text{Al}$ and the observed electronic conductivities of the various compounds fits these expectations. The reason for the significant and conceptually important electronic La population for $(\text{La}_3\text{C})\text{Al}$ are large covalent bonding contributions C–La and Al–La caused by similar orbital energies. In principle, these orbital interactions could have been optimized at the present electron count creating a bonding-antibonding band gap, if there were no additional bonding interactions La–La that can not be exhausted at E_F . Therefore, a band gap is prevented. From this discussion it becomes evident that a formal charge assignment $(\text{La}^{3+})_3\text{C}^{4-}\text{Al}^{5-}$ would be in contradiction with the electronic structure. At most, formal charge assignments $(\text{La}_3\text{Al})^{2+}\text{O}^{2-}$, $(\text{La}_3\text{Al})^{3+}\text{N}^{3-}$, and $(\text{La}_3\text{Al})^{4+}\text{C}^{4-}$ can be justified, where—besides the electronic octet situation for species Z—the successive electronic depopulation of the metal substructure becomes evident along O to C. A way to compensate a corresponding loss of metal–metal bonding interactions is the creation of point defects on the Z site, in particular for the carbide. Thus, e. g., 25 atom% C-deficient $(\text{La}_3\text{C}_{0.75})\text{Al}$ would to be written according to $(\text{La}_3\text{Al})^{3+}(\text{C}^{4-})_{0.75}$, i. e., the electronic situation was expected to be closely related to the nitride.

Conclusions

The binary phases La_3Al and Ce_3Al apparently do not exist in a stable cubic Cu_3Au type modification at ambient pressure. Reports are likely due to unnoticed impurities and formation of cubic Perovskites $(R_3Z)\text{Al}$ ($Z = \text{O}, \text{N}, \text{C}$). Particularly the nitrides readily form at higher temperatures and even melt congruently. The ternary nitrides and oxides tolerate only small Z deficiencies. The carbide of $R = \text{Ce}$ apparently exhibits intrinsic carbon deficiency, resulting in a smaller unit cell as compared to the Perovskite carbides of other rare-earth metals. Large homogeneity ranges in the sense of solid solutions between the respective ternary oxide, nitride and carbide of the same rare-earth metal are apparent. All ternary compounds considered are metals, Ce is present in a $\text{Ce}^{3+}(4f^1)$ electronic state. The Ce moments order antiferromagnetically with T_N roughly decreasing and scaling with increasing unit cell dimension of the compounds, i. e., with increasing distance $d(\text{Ce--Ce})$. Electronic band structure calculations performed for the analogues

lanthanum compounds with compositions $(\text{La}_3\text{Z})\text{Al}$ reveal a trend to increasing mixing of Z and La states on going from O via N to C. Formation of a band gap even in the formally electronically balanced $(\text{La}_3\text{C})\text{Al}$ is mainly prohibited by insufficient charge transfer between the metal species and corresponding La–La bonding.

Fig. 1. Crystal structure of $(\text{La}_3\text{N})\text{Al}$. Displacement ellipsoids are depicted with 99 % probability. N: dark grey sphere, Al: light grey spheres, La: ellipsoids, the unit cell and the octahedral coordination of N are indicated.

Fig. 2. DTA measurements (left) and XRD patterns (right) on samples of the bulk compositions $'(\text{Ce}_3\text{N}_x)\text{Al}'$ with $x = 0.2, 0.4, 0.6, 0.8, 1$. The thermal effect at $T = 925$ K represents congruent melting of Ce_3Al according to the phase diagram [35]. The signal at $T = 1340$ K is interpreted as congruent melting of $(\text{Ce}_3\text{N})\text{Al}$. The XRD patterns depicted were taken prior the DTA measurements, showing reflection profiles of hexagonal $\alpha\text{-Ce}_3\text{Al}$ decreasing with increasing N content and of $(\text{Ce}_3\text{N})\text{Al}$ increasing with increasing N content. The patterns after the thermal analyses do not show significant differences.

Fig. 3. DTA measurements (left) and XRD patterns (right) on samples of the bulk compositions $'(\text{Ce}_3\text{O}_x)\text{Al}'$ with $x = 0.2, 0.4, 0.6, 0.8, 1$. The thermal effect at $T = 925$ K represents congruent melting of Ce_3Al according to the phase diagram [35]. The signal at higher temperature is interpreted as decomposition of $(\text{Ce}_3\text{O})\text{Al}$. The XRD patterns depicted were taken prior the DTA measurements, showing reflection profiles of hexagonal $\alpha\text{-Ce}_3\text{Al}$ decreasing with increasing O content and of $(\text{Ce}_3\text{O})\text{Al}$ increasing with increasing O content.

Fig. 4. Inverse magnetic susceptibility of $(\text{Ce}_3\text{O})\text{Al}$ ($T_N = 9$ K), $(\text{Ce}_3\text{N})\text{Al}$ ($T_N = 6$ K) and $(\text{Ce}_3\text{C}_{1-x}\text{N}_x)\text{Al}$ ($x = 0.15$, no apparent magnetic order above $T = 2$ K) measured in an external field of $\mu_0 H = 1$ T as a function of temperature.

Fig. 5. $(\text{Ce}_3\text{C}_{1-x}\text{N}_x)\text{Al}$ ($x = 0.15$): a) Specific heat capacity $c_p(T)$ as a function of temperature (left) and b) c_p/T in different external magnetic fields vs. temperature (right). Circles: zero external field, squares: $\mu_0 H = 1$ T, diamonds: $\mu_0 H = 2$ T, triangles up: $\mu_0 H = 4$ T, triangles down: $\mu_0 H = 7$ T, asterisks: $\mu_0 H = 9$ T.

Fig. 6. XAS spectra at the Ce- L_{III} edge of $(\text{Ce}_3\text{O})\text{Al}$, $(\text{Ce}_3\text{N})\text{Al}$, $(\text{Ce}_3\text{C}_{0.85}\text{N}_{0.15})\text{Al}$, $(\text{Ce}_3\text{C}_{0.7})\text{Al}$ and CeO_2 for energy reference.

Fig. 7. Electrical resistivity of a) $(\text{Ce}_3\text{N})\text{Al}$, b) $(\text{Ce}_3\text{C}_{1-x}\text{N}_x)\text{Al}$ ($x = 0.15$) as function of temperature measured on polycrystalline pieces of the samples.

b)

Fig. 8. Total DOS and local DOS projections for a) (La₃O)Al, b) (La₃N)Al and c) (La₃C)Al.

a)

b)

Fig. 9. COHP(E) diagrams of selected interatomic interactions for a) (La₃O)Al, b) (La₃N)Al and c) (La₃C)Al. Dash-dotted line refers to ordinate axis on the right side and represents the integrated COHP curve (ICOHP).

Table 1. Crystallographic data for (La₃N)Al^a.

Formula weight (g mol ⁻¹)	457.70
Crystal size (mm ³)	0.05 × 0.12 × 0.22
Color	Grey metallic
Crystal system	cubic
Space group	<i>Pm</i> $\bar{3}$ <i>m</i>
Lattice parameters (pm) from powder data (single crystal)	509.04(1) (509.48(7))
Cell volume (10 ⁶ pm ³), <i>Z</i>	131.90, 1
$\rho_{\text{X-ray}}$ (g cm ⁻³), μ (mm ⁻¹)	5.75, 23.78
Radiation	MoK α (71.073 pm)
Diffractionmeter	Rigaku AFC7
Image plate distance (mm)	42.41
Scans, step (deg.)	ω , ϕ , 0.8
<i>N</i> (images)	370
Absorption correction	multi scan
Temperature (K)	296
2 θ_{max} (deg)	66.02
<i>hkl</i> range	$-7 \leq h \leq 7$ $-6 \leq k \leq 7$ $-6 \leq l \leq 7$
No. of measured reflections, <i>R</i> _{int}	1865, 0.049
No. of independent reflections	74
No. of refined parameters	6
Program	SHELXL-97
<i>R</i> _{gt} (<i>F</i>)	0.008
<i>wR</i> (<i>F</i> ²)	0.018
GooF	1.61
Extinction coefficient	0.087
Largest peaks in difference electron density map	0.45, -0.61
$\Delta\rho_{\text{max}}, \Delta\rho_{\text{min}}$ (10 ⁻⁶ pm ⁻³)	

^aAdditional material to this structure refinement can be ordered referring to no. CSD-415803, name of the authors, and citation of the paper at the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (crysdata@fiz-karlsruhe.de). The list of *F*_o/*F*_c-data is available from the author up to one year after the publication has appeared.

Table 2. Positional and displacement parameters (in 10⁴ pm²) for (La₃N)Al^a.

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₃₃
La	3 <i>c</i>	½	½	0	0.0129(1)	0.0041(1)
Al	1 <i>a</i>	0	0	0	0.0090(6)	<i>U</i> ₁₁
N	1 <i>b</i>	½	½	½	0.00067(6)	<i>U</i> ₁₁

^aFor all sites: *U*₁₁ = *U*₂₂, *U*₁₂ = *U*₁₃ = *U*₂₃ = 0

Table 3. Lattice parameters and results of chemical analyses^a.

Compound	<i>a</i> [pm]	Chemical analysis
(La ₃ O)Al	503.22(2)	(La ₃ N _{0.0124(3)} O _{0.85(5)})Al
(La ₃ N)Al ^{a)}	509.04(1)	(La ₃ N _{0.98(4)})Al
(Ce ₃ O)Al	495.74(1)	(Ce ₃ N _{0.023(3)} O _{0.952(3)})Al
(Ce ₃ N)Al	500.92(1)	(Ce ₃ N _{1.01(1)})Al
(Ce ₃ C _{1-x} N _x)Al, <i>x</i> = 0.15	503.86(5)	(Ce ₃ C _{0.82(2)} N _{0.12(2)})Al

^a*a* = 509.48(7) pm from single crystal data, the structure refinements led to full occupancy of the N site, thus to the composition of (La₃N)Al.

Table 4. Volumes per formula unit for *R*₃Al and (*R*₃Z)Al.

Composition (according to lit.) ^a	Unit cell volume/formula unit (pm ³)	Reference
(La ₃ □)Al cub	128.79	[8]
(La ₃ □)Al cub	132.11	[9]
(La ₃ □)Al hex	126.21	[51]
(La ₃ □)Al hex	123.57	[2]
(La ₃ □)Al hex	124.96	[52]
(La ₃ □)Al hex	123.82	[7]
(La ₃ □)Al hex	123.36	[53]
(La ₃ O)Al cub	127.43	this work
(La ₃ N)Al cub	130.32	[6]
(La ₃ N)Al cub	131.90	this work
(La ₃ C)Al cub	133.35	[23]
(Ce ₃ □)Al cub	125.98	[48]
(Ce ₃ □)Al cub	123.88	[3, 4, 54]
(Ce ₃ □)Al cub	123.50	[9]
(Ce ₃ □)Al cub	121.88	[55]
(Ce ₃ □)Al cub	124.70	[2]
(Ce ₃ □)Al hex	116.42	[56]
(Ce ₃ □)Al hex	116.96	[49]
(Ce ₃ □)Al hex	116.20	[52]
(Ce ₃ □)Al hex	117.13	[3, 4, 54, 57]
(Ce ₃ □)Al hex	115.81	[2]
(Ce ₃ O)Al cub	121.83	this work
(Ce ₃ N)Al cub	125.69	this work
(Ce ₃ N)Al cub	125.60	[6]
(Ce ₃ C _{1-x} N _x)Al <i>x</i> = 0.15 cub	127.91	this work
(Ce ₃ C)Al cub	127.19	[23]
(Ce ₃ C)Al cub	125.53	[24]

^ahex: Mg₃Cd structure type, cub: Cu₃Au or cubic Perovskite structure type for binary or ternary compounds, respectively. Note, that for the literature data generally no experimental confirmation of the composition is available.

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