Nd₈Co_{4-x}Al_xGe₂C₃: A case study in flux growth of lanthanide-rich intermetallics

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Abstract

The intermetallic Nd₈Co_{4-x}Al_xGe₂C₃ ($x \approx 0.65$) was prepared from reaction of germanium and carbon in Nd/Co eutectic flux in an alumina crucible. This phase exhibits a new structure type in orthorhombic space group *Pbcm*, with unit cell parameters $a = 8.001(1) \text{ \AA}$, $b = 11.696(2) \text{ \AA}$, $c = 15.020(3) \text{ \AA}$ ($Z = 4$; $R_1 = 0.0234$). The structure features germanium-centered neodymium clusters Ge@Nd₉ which share faces to form layers separated by zigzag chains of cobalt atoms capped by carbon. Density of states calculations confirm that this compound is metallic, and indicate that the cobalt should not have a magnetic moment. This is supported by magnetic susceptibility measurements which show a low temperature ferromagnetic ordering at $T_C = 50 \text{ K}$ due to the Nd³⁺ ions. Magnetization field dependence studies on single crystals indicate this compound is a strong ferromagnet with large anisotropy; the Nd³⁺ magnetic moments align along the *a*-axis.

Keywords: metal flux, intermetallic, carbide, ferromagnet, magnetic anisotropy, lanthanide

1. Introduction

Flux synthesis in molten metal solvents is a highly productive technique for the growth of new complex intermetallic phases as large crystals [1]. Compared with traditional solid-state methods, the flux method not only minimizes the diffusion barrier by bringing reactants into solution, it also enables formation of crystals without lengthy annealing steps. Low-melting main group metals such as In, Ga, Sn, and Al have been widely used as fluxes. Eutectic mixtures of metals have also proven worthy of extensive investigation due to their lowered melting points and the fact that two-component solvents allow for the dissolution of a larger variety of reactants. Mixed metal solvents also allow additional control over the interaction of the flux with the reactants by changing the flux ratio.

Our past investigations have demonstrated that eutectic mixtures of early lanthanide elements ($Ln = \text{La, Ce, Pr, Nd}$) with late first row transition metals ($T = \text{Fe, Co, Ni}$) are excellent solvents for the discovery and crystal growth of complex lanthanide-rich intermetallic compounds [2-8]. For example, both Nd and Co have high melting points, but when combined in a 64%/36% Nd/Co mole ratio a eutectic is formed with a low melting point (566°C)[9]. Reactions of main group elements in this flux yield products such as $\text{Nd}_2\text{Co}_2\text{SiC}$, $\text{Nd}_6\text{Co}_5\text{Ge}_{2.5}\text{Al}_{1.5}$, and the title phase [2,10]. The magnetic properties of these compounds depend on the Co-Co connectivity in the structures, with isolated transition metal sites or dimers being non-magnetic and larger clusters resulting in magnetic coupling to each other or to the lanthanide ions. For example, in $\text{Nd}_2\text{Co}_2\text{SiC}$, magnetic moments only stem from lanthanide elements instead of Co-Co dimers; however the hexagonal cobalt nets in $\text{Nd}_6\text{Co}_5\text{Ge}_{2.5}\text{Al}_{1.5}$ exhibit magnetic ordering from both lanthanide elements and transition metal elements.

The $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$ title phase was initially discovered in an effort to find a germanium-containing analogue of $\text{Nd}_2\text{Co}_2\text{SiC}$. In $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$, each germanium site is surrounded by nine neodymium ions forming a tricapped trigonal prism; these Ge@Nd_9 clusters share edges and faces to form layers which are separated by infinite zigzag cobalt chains capped by carbon. Magnetic susceptibility measurements indicate that the magnetic moments of the five crystallographically unique Nd^{3+} sites order ferromagnetically at low temperature. Measurements on oriented single crystals reveal significant magnetic anisotropy in the ferromagnetic state, with the Nd^{3+} moments aligned preferentially along the a -axis.

2. Experimental Methods

2.1 Sample Preparation.

The starting materials were stored and handled in an argon-filled glovebox. Neodymium chips (99.9%, Strem Chemicals), cobalt slugs (99.95%, Alfa Aesar), powders of germanium (99.9%, Strem Chemicals), and acetylene carbon black (99.95%, Strem Chemicals) were used as received. The Nd/Co eutectic flux was made by arc melting slugs of Nd and Co in a 64/36 mole percent ratio under argon; the resulting pellets were flipped and remelted several times to ensure homogeneity, then broken into smaller pieces for use in subsequent flux reactions. Initial reactions were prepared by sandwiching 1 mmol of Ge and 2 mmol of C between layers of Nd/Co eutectic pieces in an alumina crucible (ID 6mm), which was placed into a silica tube. A wad of fiberfrax was placed above the reaction crucible to act as a filter during centrifugation. The silica tube was flame-sealed under vacuum of 10^{-2} Torr. The ampule was then heated to 950°C in 3 h, held at this temperature for 12 h, and then cooled to 850°C in 10 h. The reaction mixtures were subsequently annealed for 48 h at 850°C and then cooled to 700°C in 84 h. At 700°C the ampule was removed from the furnace, quickly inverted, and centrifuged in order to decant the molten flux. This procedure produced the title phase in somewhat low yield. Elemental analysis (see below) indicated incorporation of aluminum, likely due to the reaction of the strongly reducing flux and the alumina crucible. In subsequent reactions, aluminum powder (99.9%, Strem Chemicals) was deliberately added as a reactant, which resulted in significantly better yield. Samples can be left in air for one week to oxidize the flux coating in order to remove traces of flux residue on the surface of the crystals. The $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$ crystals are stable in air for several months, but slowly react with water.

2.2 Elemental Analysis.

Semi-quantitative elemental analysis was performed with energy-dispersive X-ray spectroscopy (EDXS) on a JEOL 5900 scanning electron microscope equipped with PGT Prism energy dispersion spectroscopy software. Flux-grown crystals were mounted onto an aluminum SEM holder with carbon tape, oriented with a flat face perpendicular to the electron beam, and analyzed using a 30kV accelerating voltage and an accumulation time of 40 s. Scans of the surface and interiors of cleaved crystals showed ratios for the Nd, Co, and Ge in agreement with those indicated by the XRD structure solution. The carbon content was not determined due to the

limitation of EDXS with light elements. Small amounts of Al (2-5%) were consistently observed in all the crystals, likely due to contamination from attack on the Al₂O₃ crucible material by the strongly reducing Nd/Co flux.

2.3 X-ray Diffraction.

Small interior shards of this new phase were mounted on glass fibers using epoxy. The single crystal X-ray diffraction data were collected at room temperature on a Bruker AXS APEX2 CCD diffractometer equipped with a Mo-target X-ray tube ($\lambda = 0.71073 \text{ \AA}$). Data processing was then performed using the Bruker SAINT software. An absorption correction was applied to the data with the SADABS program [11]. The structure was solved in the centrosymmetric space group *Pbcm* (No.57) and refined using the SHELXTL software package [12]. Crystallographic data collection parameters are listed in Table 1; atom positions and site occupancies for the title compound can be found in Table 2. One of the two cobalt sites consistently showed significantly less than 100% occupancy; given the presence of aluminum indicated by SEM-EDS analysis, this site was refined as a mixed Co/Al site with 67% of Co and 33% of Al. One of the carbon sites also showed slightly lower than 100% occupancy. However, given the lack of other elements that could mix on a carbon site and the inherent difficulty in refining light element sites that are surrounded by heavy atoms, this site occupancy was fixed to 100%. Further crystallographic data can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (fax: +(49) 7247 808 666; e-mail: crysdata@fiz.karlsruhe.de) on quoting the depository number CSD-429809. Powder X-ray diffraction data were collected at room temperature on a PANalytical X'Pert PRO with a Cu K α radiation source.

2.4 Magnetic susceptibility measurements.

Magnetic susceptibility measurements were carried out using a Quantum Design SQUID Magnetic Property Measurement System. Crystals were selected and held between two strips of kapton type. Temperature-dependent susceptibility data were collected between 1.8K and 300K at 100 G, resetting the magnet before data collection. Field-dependent data were collected at several temperatures using fields up to 5 T; crystals were oriented with *a*-axis parallel and perpendicular to the applied field.

Table 1. Crystallographic data collection parameters for Nd₈Co_{3.35}Al_{0.65}Ge₂C₃.

Crystal system	orthorhombic
Space group	<i>Pbcm</i> (#57)
Cell parameters, Å	<i>a</i> = 8.001(1)
	<i>b</i> = 11.696(2)
	<i>c</i> = 15.020(3)
<i>V</i> , Å ³	1405.5(4)
Formula weight (g/mol)	1550.1
<i>Z</i>	4
Calc. Density (g/cm ³)	7.32
Max. 2Theta (°)	52.13
Radiation	Mo Kα
Temperature (K)	290
Reflections	14969
Unique data/parameters	1454 / 78
Mu (mm ⁻¹)	36.99
R(int)	0.0609
R ₁ /wR ₂ ^a (I>2σ(I))	0.0234 / 0.0432
R ₁ /wR ₂ (all data)	0.0327 / 0.0460
Largest diff peak and hole (e·Å ⁻³)	1.66 / -1.63

^a R₁=Σ(|F_o|-|F_c|) / Σ|F_o|; wR₂=[Σ(w(F_o²-F_c²)²)/Σ(w|F_o|²)^{1/2}].

Table 2. Atom positions and thermal parameters for Nd₈Co_{3.35}Al_{0.65}Ge₂C₃.

	Wyckoff Site	<i>x</i>	<i>y</i>	<i>z</i>	U _{eq}
Nd1	4(d)	0.44929(8)	0.18017(6)	¼	0.0108(2)
Nd2	8(e)	0.11578(6)	0.31928(4)	0.10970(3)	0.0134(1)
Nd3	8(e)	0.59307(5)	0.41805(4)	0.11606(3)	0.0109(1)
Nd4	4(d)	0.05799(9)	0.04961(6)	¼	0.0183(2)
Nd5	8(e)	0.23854(6)	0.62391(4)	0.08541(3)	0.0122(1)
Co1	8(e)	0.3854(1)	0.1641(1)	0.04912(8)	0.0146(3)
Co2/Al2*	8(e)	0.1017(2)	0.0518(1)	0.0471(1)	0.0173(5)
Ge1	4(d)	0.3152(1)	0.4530(1)	¼	0.0108(3)
Ge2	4(d)	0.1723(1)	0.7834(1)	¼	0.0117(3)
C1	4(c)	0.566(1)	¼	0	0.015(3)
C2	8(e)	0.244(1)	0.108(1)	0.1355(8)	0.041(3)

Co2/Al2*: mixed Co/Al site contains 67.5(9)% Co and 32.5(9)% Al.

2.5 Electronic Structure Calculations.

Density of states (DOS) calculations were carried out with the tight binding-linear muffin tin orbitals-atomic sphere approximation (TB-LMTO-ASA) program package [13]. $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$ was modelled as $\text{La}_8\text{Co}_4\text{Ge}_2\text{C}_3$ (with the Nd sites modelled as La, and the mixed Co/Al site modelled as completely filled with Co) in order to avoid complications from unpaired *f*-electrons or site mixing. The following radii of atomic spheres were used: $r(\text{La}) = 3.88 \text{ \AA}$, $r(\text{Co}) = 2.55 \text{ \AA}$, $r(\text{Ge}) = 2.92 \text{ \AA}$, $r(\text{C}) = 2.55/2.87/3.11 \text{ \AA}$. The basis set includes La 6s, 5d, (6p); Co 4s, 4p, 3d; Ge 4s, 4p, (3d); and C 2s, 2p, (3d); orbitals in parentheses were downfolded. The calculation was made for 585 *k* points in the irreducible Brillouin zone.

3. Results and Discussion

3.1 Synthesis

$\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$ grows from reactions of germanium and carbon in Nd/Co flux in alumina crucibles. The silver crystals are bar-shaped, growing up to 3 mm in length and 1 mm in diameter; the long dimension is along the crystallographic *a*-axis. This compound is stable in dry air for several months, but slowly reacts with water. After centrifuging, some flux residue is left on the crystal surface. The air-sensitivity of the flux can be used to remove this residue by leaving the product in the open air for several days; the flux oxidizes and flakes away from the crystals. However, flux inclusions trapped within the crystals during growth remain problematic, indicated by a small jump in the magnetic susceptibility data at around 200 K (highlighted when plotted as inverse susceptibility; see Figure S1), where the ferromagnetic ordering of flux byproduct Nd_4Co_3 is expected [2,14].

The highest yield of $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$ was obtained from a Nd/Co/Ge/C/Al ratio of 8 : 4.75 : 1 : 2 : 0.5 mmol and a centrifuge temperature of 720 °C, leading to a 40% yield based on germanium. Varying the ratio results in lower yield and decreasing the centrifugation temperature leads to more viscous flux which is difficult to remove. Aside from traces of Nd_4Co_3 from flux residue, no other byproducts were observed in X-ray powder diffraction patterns of reaction products. In the diffraction pattern (see Figure S2), the peak positions are correct but in several cases the intensities are different from the theoretical pattern; the largest deviations are

seen for the (004) and (006) indices, indicating preferred orientation of the powder crystallites. Attempts to synthesize $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$ analogues with other lanthanide metals (from reactions in Pr/Co or Ce/Co eutectic fluxes) were unsuccessful, as were attempts to replace Ge with Si, Sn and Pb (a reaction of Nd/Co/Si/C gives $\text{Nd}_2\text{Co}_2\text{SiC}$ [2], a reaction of Nd/Co/Sn/C produces $\text{Nd}_{21}\text{Co}_8\text{Sn}_7\text{C}_{12}$ with the $\text{La}_{21}\text{Fe}_8\text{Sn}_7\text{C}_{12}$ structure type [4], and a reaction of Nd/Co/Pb/C yields NdPb_3). Stoichiometric synthesis of $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$ was attempted by arc-melting the elements in the correct ratio; this did not form the title phase.

This phase was initially formed in low yield from the reaction of carbon and germanium in Nd/Co eutectic, with inadvertent incorporation of aluminum from attack on the alumina crucible. This is to be expected from the use of strongly reducing lanthanide-rich fluxes, and can be avoided by selecting other crucible materials (such as tantalum, niobium, or stainless steel). Similar contamination from reduction of the alumina crucible is seen in the flux syntheses of $\text{Ce}_{33}\text{Fe}_{14-x}\text{Al}_x\text{B}_{25}\text{C}_{34}$, $\text{La}_6\text{Fe}_{13-x}\text{Al}_x\text{Sn}_y$, and $\text{La}_{21}\text{Mn}_8\text{Ge}_{6.2}\text{Al}_{0.8}\text{C}_{12}$ [6-8]. While the aluminum in these phases is found to partially occupy a mixed site with a late transition metal or main group metalloid of similar size, incorporation of this dopant is often required to stabilize the structure; the yield is increased if Al is deliberately added as a dopant, and different products are formed in the absence of aluminum (for instance if steel crucibles are used). In some cases, aluminum occupies its own site (as is seen for $\text{LaRu}_2\text{Al}_2\text{B}$, $\text{La}_2\text{Ni}_{1.8}\text{Ru}_{0.2}\text{Al}$, and $\text{La}_6\text{SnNi}_{3.7}\text{Ru}_{0.7}\text{Al}_{3.6}$, all initially isolated from La/Ni flux reactions of Ru, Sn, and B in alumina crucibles [5]) and the yield is dramatically increased upon deliberate addition of aluminum in subsequent reactions.

The majority of research into flux growth of multinary Ln/T/M phases (T = transition metal; M = main group metal) involves reactions of lanthanides with other elements in low-melting flux metals such as Ga, In, Sn, etc. This is an excellent way to grow crystals of known phases or discover new phases, and has been reviewed extensively [1]. In recent years, there have been a number of investigations into reacting lanthanides in excess T/M flux mixtures. Many compounds with the ThCr_2Si_2 structure type have been grown from such mixed fluxes. Examples include the synthesis of LnCo_2Ge_2 from CoGe flux and EuPd_2As_2 from PdAs [15,16]. While the superconducting phases $\text{Ba}_{1-x}\text{A}_x\text{Fe}_2\text{As}_2$ (A = K, Sr, etc) do not contain lanthanides, use of FeAs as a flux has proven useful in growing large single crystals without the problematic substitution and contamination seen for samples grown from tin flux [17]. More complex

structures can also be obtained from mixed fluxes; reactions of Pr in excess Pt/Ge mixture produces large crystals of superconducting $\text{Pr}_2\text{Pt}_3\text{Ge}_5$ up to 10 mm in length [18]. Crystals of quasicrystal approximant $\text{Gd}_{14.34}\text{Au}_{67.16}\text{Ge}_{18.5}$ can be grown from Au/Ge flux, and large single grains of true quasicrystal $\text{Ln}_{8.7}\text{Mg}_{34.6}\text{Zn}_{56.8}$ —with evident pentagonal facets—can be grown from Mg/Zn melts [19, 20]. As would be expected for reactions of a small amount of lanthanide metal in a large excess of T/M flux, the products of such reactions are lanthanide-poor.

The use of lanthanide/transition metal eutectics has proven to be a highly productive way to synthesize lanthanide-rich intermetallic products. These mixtures are excellent solvents for a wide variety of elements, and the products typically incorporate a large proportion of lanthanide in addition to smaller amounts of other reactants present. Compounds produced from our work in Ln/T flux reactions are listed in table 3 along with associated reaction parameters. In addition to our work [2-8], there are few other accounts of lanthanide-rich flux usage. The Kauzlarich group used a Ce/Ni eutectic to synthesize $\text{CeRu}_{1-x}\text{Ni}_x\text{Al}$ ($x = 0.5$) which exhibits cerium fluctuating valence [21]. The “flux creep-up method” investigated by Samata, et al. is likely related. These researchers use Sm/Fe melts to grow crystals of Sm_xFe_y and $\text{Sm}_x\text{Fe}_y\text{M}_z$ phases, including the previously unknown SmFe_7 and $\text{Sm}_{12}\text{Fe}_{14}\text{Al}_5$. They report that the slightly porous boron nitride crucibles allow the molten flux to creep up the walls, allowing crystals to slowly precipitate at the bottom [22]. Late lanthanide elements do not interact with transition metals with the dramatic melting point lowering seen for early lanthanides, but eutectics do form. Mixtures of Dy, Gd, or Tb with nickel have eutectics in the 600 – 700 °C range; these were used by the Chan group to grow crystals of the highly complex $\text{Ln}_{117}\text{Ni}_{53-y}\text{Sn}_{112-y}$ phases. The stability of these phases permitted the removal of the Ln/Ni flux by soaking the cooled reaction mixture in $\text{H}_2\text{O}/\text{EtOH}$ to etch away the flux. They noted that attempting to use tin flux for the growth of isostructural $\text{Gd}_{117}\text{Co}_{56}\text{Sn}_{112}$ phases resulted in GdCoSn_2 instead [23]. The Canfield group reported crystal growth of late lanthanide $\text{Ln}_2\text{Cu}_2\text{In}$ compounds using the self-flux method; this was referred to as a Ln/Cu/In ternary melt, but the amount of indium used was small (reaction mixtures were $(\text{Gd}_{0.5}\text{Cu}_{0.5})_{1-x}\text{In}_x$ with $0.05 < x < 0.15$), so it can be viewed as growth from a Ln/Cu flux [24]. Use of a more indium-rich flux mixture would likely have yielded indides such as GdCu_6In_6 or GdCu_5In_7 . This work raises the accurate point that in reality these flux reactions are occurring in a complex multinary phase space (involving ternary or quaternary phase diagrams, many of which are not known). However, using a large enough excess of the flux mixture will

make the system quasi-binary, and this also prevents possible rising of the melting point if one of the flux components is consumed (by incorporation into crystallizing products) more quickly than the other.

Table 3. Lanthanide/transition metal eutectic flux reactions and observed products [from refs 2-8]. Flux mixture is indicated by reactants in parentheses.

Reactants	Reactant ratio (mmol)*	Heating profile**	Products
(La/Ni)/Fe/M/C, M = Sn, Bi, Sb, Te, or Ge	(9.7:2.5):0.8:0.7:1.2	(a)	La ₂₁ Fe ₈ M ₇ C ₁₂
(La/Ni)/Fe/Al/M, M = main group metals	(9.7:2.5):1.5:0.5:0.3	(a)	La ₆ Fe _{13-x} Al _x M _y
(La/Ni)/Mn/Al/M, M = main group metals	(9.7:2.5):1.5:0.5:0.3	(a)	La ₆ Mn _{13-x} Al _x M _y
(La/Fe)/Al	(9.8:2.2):1	(b)	LaFe _{13-x} Al _x
(Nd/Fe)/Al	(7.6:1.9):1	(b)	Nd ₆ Fe _{13-x} Al _x
(La/Ni)/Ru/Al/B	(9.7:2.5):2:2:1	(c)	LaRu ₂ Al ₂ B
(La/Ni)/Sn/Ru/Al	(9.7:2.5):1:1:1	(d)	La ₆ SnNi _{3.67} Ru _{0.76} Al _{3.6}
(La/Ni)/La/Ru/Sn/C (Al leached from alumina crucible)	(9.7:2.5):1:1:1:1	(c)	La ₂ Ni _{2-x} Ru _x Al
(La/Ni)/La/Mn/C/M, M=Ge, Sn, Sb, Te, Bi	(9.7:2.5):0.25:0.3:0.5:0.25	(a)	La ₂₁ Mn ₈ M ₇ C ₁₂
(La/Ni)/La/Mn/Sn/C	(9.7:2.5):2.1:0.8:0.7:1.2	(a)	La ₁₄ Sn(MnC ₆) ₃
(La/Ni)/La/Mn/C	(9.7:2.5):1.1:0.3:1.8	(a)	La ₁₁ (MnC ₆) ₃
(Ce/Fe)/Al/B/C	(9.8:2):1:1.2:1.2	(e)	Ce ₃₃ Fe _{14-x} Al _x B ₂₅ C ₃₄
(Pr/Fe)/B/C	(9.6:2.5):1.2:1.2	(a)	Pr ₃₃ Fe ₁₃ B ₁₈ C ₃₄
(Nd/Co)/Si/C	(8.4:4.7):1:2	(e)	Nd ₂ Co ₂ SiC
(Pr/Co)/Si/C	(8.4:4.7):1:2	(a)	Pr ₂ Co ₂ SiC

*some ratios reflect excess lanthanide metal added in some cases to compensate for its incorporation into products.

**Heating profiles:

- (a) 3h to 950°C, hold for 12h, 10h to 850°C, hold for 48h, 84h to 600°C, centrifuge
- (b) 3h to 1050°C, hold for 12h, 10h to 950°C, hold for 48h, 84h to 815°C, centrifuge
- (c) 3h to 1000°C, hold for 12h, 10h to 850°C, hold for 48h, 84h to 650°C, centrifuge
- (d) 3h to 1000°C, hold for 12h, 10h to 850°C, hold for 48h, 84h to 600°C, centrifuge
- (e) 3h to 950°C, hold for 12h, 10h to 850°C, hold for 48h, 84h to 700°C, centrifuge

Figure 1. (a) Structure of $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$ viewed down the a -axis. Large grey spheres are Nd; red, blue, and black spheres represent Co, Ge, and C, respectively, and Ge@Nd_9 clusters are shown as blue polyhedra. (b) Layer of face-sharing Ge@Nd_9 clusters, viewed down the c -axis.

3.2 Structure

$\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$ exhibits a new structure type in orthorhombic space group $Pbcm$, shown in Figure 1. The major structural building blocks in $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$ are the layers of germanium-centered neodymium clusters Ge@Nd_9 and the infinite zigzag cobalt carbide chains that separate them. Each of the two crystallographically unique Ge sites is surrounded by 9 Nd^{3+} cations in tricapped trigonal prismatic coordination (it can also be viewed as a monocapped square antiprism; see figure 1b). Clusters comprised of a main group element surrounded by 8-10

lanthanide cations have been observed in many compounds produced from reactions of such elements in Ln/T eutectics. For instance, Sn@La₉ clusters are found in La₂₁Fe₈Sn₇C₁₂ and La₁₄Sn(MnC₆)₃, and Ge@Nd₉ clusters are found in Nd₆Co₅Ge_{2.5}Al_{1.5} [3, 4, 10]. The formation and stability of such M@Ln_n units is likely due to electron transfer; the relatively electronegative main group element is partially reduced by the lanthanide-rich flux to become negatively charged, and the resulting anion surrounds itself with Ln³⁺ cations. Similar M@Ln_n clusters are found in other lanthanide-rich compounds, with the size of the coordinating lanthanide cluster dependent on the relative radii of the M and Ln ions. For instance, octahedral C@Ce₆ and Al@Sm₆ units are found in Ce₃₃Fe₁₃B₂₅C₃₄ and Sm₁₂Fe₁₄Al₅, respectively [8, 22]. Square antiprismatic Sb@Gd₈ clusters are found in Gd₅Ir₂Sb [25], and the compound La₈Co₂In₃ features In@La₁₁ units [26].

The Ge@Nd₉ clusters in Nd₈Co_{4-x}Al_xGe₂C₃ share faces to form 2-D slabs that are stacked perpendicular to the *c*-axis and separated by cobalt/carbon building blocks. The Nd-Ge distances range from 3.142 Å to 3.296 Å, falling in the Nd-Ge bond range 3.1-3.4 Å observed in NdCo_{0.83}Ge₂ and NdCoGe₃ [27, 28]. The Nd-Nd distances within these slabs range from 3.5 – 3.9 Å. However, a shorter distance is found between the slabs, with Nd3 sites on one slab being 3.35 Å away from Nd5 sites on a neighboring slab. This variety of Nd-Nd distances may be the source of the complex magnetic behavior arising from the Nd sublattice of this compound (see section 3.3).

The cobalt/carbon layers that separate the Nd/Ge slabs are unique. These layers are comprised of parallel infinite zigzag chains of cobalt atoms which run in the *b*-axis direction; see Figure 2. The Co-Co distances in this chain are 2.477 Å, 2.494 Å, and 2.621 Å, all within the Co-Co bond range 2.4-2.9 Å observed for other intermetallic phases such as Nd₂Co₂SiC, Nd₆Co₅Ge_{2.2}, and NdCo₂Ge₂ [2, 15, 29]. Three out of every four of the Co-Co linkages are bridged by carbon in a bidentate manner to form triangles; the Co-C distances are 1.834 Å, 1.874 Å and 1.915 Å. The “non-bridged” Co₂-Co₂ linkage has a bond distance of 2.477 Å. The Co₂ site features partial substitution by aluminum which is consistently seen at a level of 30 – 35% Al in refinement of single crystal XRD data of several samples of Nd₈Co_{4-x}Al_xGe₂C₃ from different synthesis batches in which different amounts of aluminum were added as a reactant.

Figure 2. Cobalt/carbon chains viewed down the [101] direction. Black spheres represent carbon; red and magenta spheres represent cobalt and Co/Al mixed sites respectively.

Carbon-capping of transition metal atoms, dimers, or clusters is a defining feature of carbometalates containing lanthanide metals, transition metals, and carbon. The Jeitschko and Kniep groups have been particularly prolific in the synthesis of these $\text{Ln}_x\text{T}_y\text{C}_z$ phases and published an excellent review in 2007 [30]. The majority of structures described in that review contained limited or no T-T bonding; the transition metals were instead surrounded by carbon atoms, which linked to other transition metal sites to form a $[\text{T}_y\text{C}_z]^{n-}$ network. Examples include the corner-sharing TC_4 tetrahedra that link together to form the infinite polyanionic layers $\infty[(\text{T}_2\text{C}_3)^{6-}]$ ($\text{T}=\text{Cr}, \text{Mo}$) of $\text{Ho}_2\text{Cr}_2\text{C}_3$ and $\text{Er}_2\text{Mo}_2\text{C}_3$, and the corner-sharing ReC_5 trigonal bipyramids and ReC_4 squares that comprise the anionic network in $\text{U}_5\text{Re}_3\text{C}_8$. Carbon-capped clusters of transition metals (which exhibit not only T-C but also T-T bonding) are seen in flux-grown intermetallics $\text{La}_{21}\text{Fe}_8\text{Sn}_7\text{C}_{12}$ (which features Fe_4 tetrahedra capped on all edges by carbon

atoms) and $\text{Ce}_{33}\text{Fe}_{13}\text{B}_{25}\text{C}_{34}$ (containing Fe_{13} clusters capped by borocarbide chains) [4, 8]. In recent years Dashjav et al. have discovered two very interesting compounds in the Dy/Fe/C system, both of which feature Fe-Fe bonded units capped with carbon. $\text{Dy}_{15}\text{Fe}_8\text{C}_{25}$ features Fe_6 planar triangles capped with both carbon and C_2 units [31]. A 1-D chain of iron atoms (bridged by C_2 units) is found in $\text{Dy}_{5.64}\text{Fe}_2\text{C}_9$ [32]. The looping cobalt carbide chain in $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$ bears some resemblance to this latter compound. The potential magnetic properties of such 1-D transition metal building blocks are of interest.

3.3 Magnetic Properties

Figure 3 shows the temperature dependence of the magnetic susceptibility data for $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$ with an applied field of 100 Oe and the crystal oriented with a -axis either parallel or perpendicular to the field. The most distinctive feature of the susceptibility data is the sharp rise below $T_C = 50$ K due to ferromagnetic ordering of the Nd^{3+} magnetic moments. The orientation dependence of this transition reveals a strong preference of the Nd moments to be magnetized along the a -axis. Another feature is the large field-cooled (FC) and zero-field cooled (ZFC) splitting seen for both crystal orientations. The ZFC magnetization is close to zero at low temperature in either orientation, indicating random orientation of ferromagnetic domains below T_C (and cancellation of net moment) when cooled in the absence of an external field. The field-cooled susceptibility is significantly larger when the crystal is oriented with a -axis parallel to the applied field, supporting a preference for magnetic domains to align along that axis.

Figure 3. Temperature-dependent magnetic susceptibility data for $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$ measured at an applied field of 100 Oe with the crystal aligned with a -axis parallel or perpendicular to the applied field.

The high temperature magnetic susceptibility data for $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$ show a small but distinct increase in the susceptibility at 200 K (more visible in the inverse susceptibility plot, see Figure S1). This can be attributed to small Nd/Co flux inclusions in the crystal, which form Nd_4Co_3 upon solidification; this phase is known to undergo ferromagnetic ordering at 202 K.[14] After correcting for a small amount of this ferromagnetic impurity, the high temperature data above 210 K can be fit to the Curie-Weiss law, yielding a magnetic moment of $4.0 \mu_B$ per Nd^{3+} , a Weiss constant of 58 K (in agreement with the temperature of the observed transition) when $H//a$, and a magnetic moment of $3.9 \mu_B$ and a Weiss constant of 32 K when $H \perp a$. The observed magnetic moment is higher than the theoretical value of $3.2 \mu_B$ for Nd^{3+} , but this is likely due to the surface contamination instead of being an indication of magnetic moments on the cobalt sites. When $H//a$, the observed values for μ_{eff} , θ , and T_C are larger compared to when $H \perp a$. This indicates that the Nd^{3+} magnetic moments tend to align along the a -axis.

Figure 4. Field-dependent magnetization data for $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$ at various temperatures, with the crystal aligned with a -axis parallel to the applied field.

Magnetization measurements were carried out to further explore the nature of the magnetic ordering for $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$. Magnetization data collected at different temperatures with $H//a$ are shown in Figure 4. Above the Curie temperature (at 150K and 80K), the field

dependence is linear, as expected for a paramagnet. At the Curie temperature (50K), the rapid rise of magnetization with field, saturation, and lack of hysteresis indicates the onset of soft ferromagnetic ordering. As the temperature is lowered, the compound becomes a harder ferromagnet, indicated by increases in the magnitude of the coercive field and the saturation magnetization. At 20K, the remanent magnetization is $1\mu_B$, the saturation magnetization is $2.09\mu_B$, and the coercive field is 0.05T. When the temperature is lowered to 1.8K, the hysteresis increases dramatically as the system becomes a very hard ferromagnet, with roughly equivalent remanent and saturation magnetizations of $2.2\mu_B$ and a coercive field of 1.97 T. Data collected at 1.8 K for the crystal aligned with $H \perp a$ (Figure 5) shows even larger coercivity (4.0 T) but the saturation magnetization is substantially lower ($0.34\mu_B$). This is further evidence that the magnetic moments prefer to align along a -axis. Similar lowered remanent magnetization and larger coercivity when the field is applied perpendicular to the easy axis of magnetization was also observed for $\text{Ce}_{0.95}\text{Bi}_{0.05}\text{Co}_{1.85}\text{As}_2$ [33].

Figure 5. Field-dependent magnetization data for $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$ at 1.8K with the crystal aligned with a -axis parallel or perpendicular to the applied field.

3.4 DOS calculations

Calculated total and partial density of states (DOS) diagrams are shown for the model compound $\text{La}_8\text{Co}_4\text{Ge}_2\text{C}_3$ (see Figure 6). The nonzero DOS at the Fermi energy indicates that this compound is metallic. The 5d states of the lanthanide element have their most significant contribution to the DOS above E_F , whereas orbitals from Co, Ge, C are dominant below the E_F . The resulting pseudogap at E_F is characteristic of “polar” intermetallics containing electropositive metals in combination with more electronegative metals and metalloids. The data reveal only a small contribution from the Co 3d electrons at the Fermi level. Despite the presence of Co-Co bonding in the cobalt chains, the lack of cobalt orbital contributions at E_F indicates that spin polarization will not occur; therefore the cobalt atoms will not have a significant magnetic moment and should not contribute to the magnetic behavior of this compound.[34] This is in agreement with the magnetic data described in section 3.3. Carbon and germanium have almost zero contribution to the DOS at the Fermi level and are thus largely anionic. The Ge states are predominantly seen between -1 and -3 eV and are hybridized with states from surrounding lanthanide atoms (which supports the view of germanium being partially negatively charged and strongly interacting with neighboring Nd^{3+} cations in the $\text{Ge}@\text{Nd}_9$ clusters). The carbon atom orbitals contribute to states between -3 and -5 eV which are hybridized with cobalt states and lanthanide states, in agreement with their coordination environment.

Figure 6. Densities-of-States (DOS) data calculated for model compound $\text{La}_8\text{Co}_4\text{Ge}_2\text{C}_3$

4. Conclusion

Ln/T eutectic fluxes have proven to be excellent media for exploratory synthesis and crystal growth of complex Ln/T/M/M' intermetallic phases. Reactions of germanium and carbon with small amounts of aluminum in Nd/Co flux have yielded the novel ferromagnetic compound $\text{Nd}_8\text{Co}_{4-x}\text{Al}_x\text{Ge}_2\text{C}_3$. The tendency for heavy main group elements to be reduced and coordinated by Ln^{3+} cations was observed in this compound, which contains $\text{Ge}@\text{Nd}_9$ clusters. The high Ln content and short Ln-Ln distances in flux-grown Ln/T/M/M' products can lead to intriguing magnetic behavior at low temperatures, with strongly anisotropic hard ferromagnetism seen for the title compound. Conversely, the relatively low concentration of transition metal in the synthesis mixture often leads to formation of small building blocks such as dimers, chains, and small clusters of transition metals (often capped by light elements, yielding T_xC_y species which are surrounded by Ln cations). The limited T-T bonding often precludes the formation of a stable magnetic moment on the transition metal, as is the case for the undulating 1-D chain of cobalt atoms capped by carbon in the title phase; the magnetic data and DOS calculations indicate the cobalt d-electrons do not contribute significantly at E_F and do not have a magnetic moment. Compared to the large numbers of carbometalates with no T-T bonding, and the wide variety of transition metal-rich intermetallics such as $\text{Nd}_2\text{Fe}_{14}\text{B}$ and SmCo_5 , Ln/T/M/M' intermetallics with low-dimensional transition metal building blocks are relatively rare. Further discovery and exploration of new phases containing small T_xC_y clusters may shed light on the minimum size at which a transition metal cluster becomes magnetic.

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Face-sharing
 Ge@Nd_9 clusters

Carbon-capped
cobalt chains