Flux growth and magnetic properties of rare earth cobalt germanide, $\text{RE}_6\text{Co}_5\text{Ge}_{1+x}\text{Al}_{3-x}$ (RE = Pr, Nd; $x \approx 0.8$)

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Abstract:

The intermetallic compounds $\text{RE}_6\text{Co}_5\text{Ge}_{1+x}\text{Al}_{3-x}$ (RE=Pr, Nd) were synthesized from the reaction of germanium and aluminum in RE/Co eutectic flux. These phases crystallize with the $\text{Nd}_6\text{Co}_5\text{Ge}_{2.2}$ structure type in hexagonal space group $P-6m2$ ($a = 9.203(2)\text{\AA}$, $c = 4.202(1)\text{\AA}$, $R_1 = 0.0109$ for $\text{Pr}_6\text{Co}_5\text{Ge}_{1.80}\text{Al}_{2.20}$; and $a = 9.170(3)\text{\AA}$, $c = 4.195(1)\text{\AA}$, $R_1 = 0.0129$ for $\text{Nd}_6\text{Co}_5\text{Ge}_{1.74}\text{Al}_{2.26}$). The structure features chains of face-sharing Ge@RE_9 clusters intersecting hexagonal cobalt nets linked by aluminum atoms. Magnetic susceptibility measurements indicate that both phases exhibit ferromagnetic ordering of the cobalt layers with T_C in the range of 130-140 K. The magnetic moments of the rare earth ions order at lower temperature (30-40 K). Magnetic measurements on oriented crystals of $\text{Nd}_6\text{Co}_5\text{Ge}_{1.74}\text{Al}_{2.26}$ show a strong preference of the moments to order along the c -axis.

Keywords:

Intermetallic; crystal growth; magnetic anisotropy; flux reaction; ferromagnet; hexagonal net

1. Introduction

Binary and ternary intermetallic compounds based on rare earth elements (RE) in combination with late transition metals (T) have been actively investigated for their interesting magnetic properties [1,2]. Some of these magnetic materials have been widely used in computer hard drives and electric motors such as the current leading materials SmCo_5 and $\text{Nd}_2\text{Fe}_{14}\text{B}$ which feature very high remanence and high coercive field [1,3]. The complex and interesting magnetic nature of these intermetallics can be ascribed to the magnetic moments of localized unpaired electrons on the rare earth ions coupled with the itinerant electron magnetism of the transition metals in the compound [4].

The binary phase diagrams of early rare earth metals combined with late transition metals all feature low-melting eutectics in the rare earth-rich region. These eutectic mixtures can act as fruitful synthesis media for magnetic intermetallics containing two paramagnetic elements. Exploratory metal flux synthesis has proven to be very useful for growth of complex RE/T/M/M' compounds in the form of large single crystals [5,6]. In our previous research, La/Ni eutectic was used for the synthesis of many new intermetallic phases such as $\text{La}_{21}\text{Fe}_8\text{Sn}_7\text{C}_{12}$ and $\text{LaRu}_2\text{Ni}_2\text{Al}$ [7,8]. Ce, Pr, and Nd- rich eutectics are now being explored as fluxes since they contain paramagnetic rare earth ions, which may lead to formation of phases with interesting magnetic properties deriving from both the transition metal and the rare earth ion. The magnetic behavior of the transition metal in RE/T/M/M' compounds is dependent on the extent of T-T bonding in the structure. For example, isolated transition metal sites or small transition metal clusters in intermetallics such as NdCoC_2 , NdCoGe_3 , and $\text{R}_2\text{Co}_2\text{SiC}$ (R=Pr, Nd) tend to be non-magnetic [9-11]. On the other hand, phases containing larger transition metal building blocks, such as the Fe_{13} clusters in $\text{Ce}_{33}\text{Fe}_{13}\text{B}_{18}\text{C}_{34}$, Fe layers in $\text{Nd}_6\text{Fe}_{10}\text{Al}_3$, and Fe networks of $\text{Nd}_2\text{Fe}_{14}\text{B}$, will have strong magnetic moments on the transition metal atoms, and might even exhibit unusual magnetic phenomena such as multiple ordering transitions or spin glass behavior [12,13,3].

In this work, crystals of $\text{RE}_6\text{Co}_5\text{Ge}_{1+x}\text{Al}_{3-x}$ (RE=Pr, Nd) were grown from reactions in RE/Co flux. These phases form with the $\text{Nd}_6\text{Co}_5\text{Ge}_{2.2}$ structure type which was previously reported in 1986 [14,15]. However, the previous work only described the approximate stoichiometry and structure. Investigations of magnetic behavior were not carried out, possibly

due to the lack of pure sample and large crystals. The large crystals grown from flux allow for extensive magnetic characterization. The structure features 2-D hexagonal cobalt nets capped by aluminum atoms. Magnetic susceptibility measurements show that for the both analogues, the magnetic moments of the cobalt atoms order ferromagnetically at high temperature, and the magnetic moments of the rare earth ions order at low temperatures.

2. Experimental Section

2.1 Sample Preparation. The starting materials were stored and handled in an argon-filled glovebox. Praseodymium chips (99.9%, Strem Chemicals), neodymium chips (99.9%, Strem Chemicals) cobalt slugs (99.95%, Alfa Aesar), powders of germanium (99.9%, Strem Chemicals), and aluminum (99.95%, Strem Chemicals) were used as received. The Pr/Co eutectic flux was made by arc melting pieces of Pr and Co in a 66/34 mole ratio on a water-cooled copper hearth under argon; the resulting eutectic ingot button was flipped and remelted several times to ensure homogeneity. The brittle ingot was then fractured with a hammer into smaller pieces (1 mm^3) for use in flux reactions. Nd/Co eutectic was made in a similar way, by arc melting a mixture of Nd/Co chunks in a 64/36 mole ratio [16].

$\text{Pr}_6\text{Co}_5\text{Ge}_{1.80}\text{Al}_{2.20}$ was prepared by sandwiching 1 mmol of Ge and 1 mmol of Al between a total of 1.5 g of Pr/Co eutectic in an alumina crucible (ID 6 mm), which was placed in a silica tube. A second alumina crucible was filled with Fiberfrax ceramic fiber wool and inverted 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 $950\text{ }^\circ\text{C}$ in 3 h, held at this temperature for 12 h, and then cooled to $850\text{ }^\circ\text{C}$ in 10 h. The reaction mixture was subsequently annealed for 48 h at $850\text{ }^\circ\text{C}$ and then cooled to $650\text{ }^\circ\text{C}$ in 84 h. At $650\text{ }^\circ\text{C}$ the ampule was removed from the furnace, quickly inverted, and centrifuged in order to decant the molten flux. The Nd analogue $\text{Nd}_6\text{Co}_5\text{Ge}_{1.74}\text{Al}_{2.26}$ was subsequently synthesized in a similar fashion from reaction of 2 mmol of Ge powder layered between Nd/Co eutectic ($\sim 1.5\text{ g}$). To remove traces of flux residue from the surface of the crystals, samples can be left in air to preferentially oxidize the flux coating. Products were then kept in a drybox to prevent any further oxidation, although these crystals will not degrade if left in air for several months.

2.2 Elemental Analysis. Semiquantitative 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. Analysis of several spots on 5 – 10 crystals of each analog showed an average RE/Co/Al/Ge ratio of 50% : 36% : 7% : 7%. This is a slightly higher rare earth and cobalt content than that indicated by the XRD structure solution (40% : 33% : 12% : 15%, vide infra), likely due either to traces of RE/Co flux residue on the surface of the crystals, or to a lower sensitivity of the EDS technique to light elements in a heavy matrix.

2.3 X-ray Diffraction studies. Powder X-ray diffraction was used to test for the presence of unreacted starting materials or formation of byproducts; data were collected on pulverized samples at room temperature on a PANalytical X-Pert PRO diffractometer with a Cu K α source. For structure determination, small shards were broken off of larger crystals of RE₆Co₅Al_{1+x}Ge_{3-x} and were mounted on glass fibers using quick-drying 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 ($\lambda = 0.71073\text{\AA}$). Full spheres of diffraction data were collected, with individual frames collected at 20 seconds per frame and a frame width of 0.3°. Data processing was then performed using the Bruker SAINT software [17]. An absorption correction was applied to the data with the SADABS program. The structure was solved in the hexagonal space group *P*-6m2 and refined using the SHELXTL software package [18]. Crystallographic and data refinement parameters are shown in Table 1. For both compounds, siting assignments were straightforward for the rare earth and cobalt positions, as well as one of the germanium sites; refinement of these site occupancies resulted in values at or close to 100%. However, a 3k site (assigned as a partially occupied germanium site in the parent structure Nd₆Co₅Ge_{2.2}) [14,15] was assigned as a mixed Ge/Al site in accordance with the EDS data (see Table 2 and discussion). 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 numbers CSD-430645 (for Nd₆Co₅Ge_{1.74}Al_{2.26}) and CSD-430646 (for Pr₆Co₅Ge_{1.80}Al_{2.20}).

2.4 Magnetic susceptibility measurements. Magnetic susceptibility measurements were carried out on a Quantum Design SQUID Magnetic Property Measurement System. Crystals were selected and held between two strips of kapton tape. Temperature-dependent susceptibility data were collected between 1.8K and 300K at 100 G. Field-dependent data were collected at several temperatures using fields up to 5 T; crystals were oriented with *c*-axis parallel to the applied field. For Nd₆Co₅Ge_{1.74}Al_{2.26}, both field-dependent and temperature-dependent data were collected on large crystals oriented with *c*-axis either parallel or perpendicular to the applied field.

Table 1. Crystallographic data collection parameters for RE₆Co₅Ge_{1+x}Al_{3-x} phases.

	Pr ₆ Co ₅ Ge _{1.80} Al _{2.20}	Nd ₆ Co ₅ Ge _{1.74} Al _{2.26}
Formula weight (g/mol)	1330.1	1347.4
Crystal system	hexagonal	
Space group	<i>P</i> -6 <i>m</i> 2	
Unit cell parameters	<i>a</i> = 9.203(3) Å, <i>c</i> = 4.202(1) Å	<i>a</i> = 9.170(3) Å, <i>c</i> = 4.195(1) Å
Unit cell volume (Å ³)	308.2(2)	305.4(2)
Z	1	
Calc. Density (g/cm ³)	7.166	7.325
Crystal dimensions (mm)	0.06 × 0.05 × 0.03	0.05 × 0.03 × 0.02
Collection temp (K)	297	
Index ranges	-11 ≤ <i>h</i> ≤ 11, -12 ≤ <i>k</i> ≤ 12, -5 ≤ <i>l</i> ≤ 5	-12 ≤ <i>h</i> ≤ 11, -11 ≤ <i>k</i> ≤ 12, -5 ≤ <i>l</i> ≤ 5
Reflections collected	3564	3523
Unique data/parameters	333 / 25	332 / 25
μ (mm ⁻¹)	34.14	35.89
<i>R</i> ₁ , <i>wR</i> ₂ for <i>I</i> ≥ 2σ(<i>I</i>)	0.0109 / 0.0210	0.0129 / 0.0265
<i>R</i> ₁ , <i>wR</i> ₂ for all data	0.0111 / 0.0211	0.0130 / 0.0266
Residual peak/hole (e ⁻ Å ⁻³)	0.61 / -0.64	0.70 / -0.64

Table 2. Atom positions and atomic displacement parameters for Pr₆Co₅Ge_{1.80}Al_{2.20}.

	Wyckoff Site	<i>x</i>	<i>y</i>	<i>z</i>	U _{eq}	Occupancy
Pr1	3 <i>k</i>	0.13117(3)	0.86883(3)	½	0.0121(1)	1
Pr2	3 <i>j</i>	0.48356(3)	0.51644(3)	0	0.0108(1)	1

Co1	<i>3j</i>	0.84633(7)	0.15367(7)	0	0.0149(2)	1
Co2	<i>1e</i>	2/3	1/3	0	0.0150(4)	1
Co3	<i>1a</i>	0	0	0	0.0144(4)	1
Ge1	<i>1d</i>	1/3	2/3	½	0.0098(3)	1
Al2/Ge2	<i>3k</i>	0.7624(1)	0.2376(1)	½	0.0118(4)	0.732(4) / 0.268(4)

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 [19]. $\text{Nd}_6\text{Co}_5\text{Ge}_{1.74}\text{Al}_{2.26}$ was modeled as $\text{Nd}_6\text{Co}_5\text{GeAl}_3$, with the mixed Ge/Al site modelled as being fully occupied by Al. The following radii of atomic spheres were used: $r(\text{Nd}) = 3.54/3.70 \text{ \AA}$, $r(\text{Co}) = 2.55 \text{ \AA}$, $r(\text{Ge}) = 2.92 \text{ \AA}$, $r(\text{Al}) = 2.71 \text{ \AA}$. The basis set includes Nd (6s, 5d; 4f orbitals treated as core orbitals), Co (4s, 4p, 3d), Ge (4s, 4p, 3d), and Al (3s, 3p), with Nd 6p, Ge 3d, and Al 3d being downfolded. The calculation was made for $18 \times 18 \times 18$ k points in the irreducible Brillouin zone.

3. Results and discussion

3.1 Synthesis.

The intermetallic compounds $\text{RE}_6\text{Co}_5\text{Ge}_{1+x}\text{Al}_{3-x}$ (RE=Pr, Nd) are produced from reactions of germanium and aluminum in RE/Co flux, forming as silver, faceted rectangular rods up to ~2 mm in length and 0.8 mm in diameter. Products form as aggregates of crystals with a very small amount of powder. The crystalline samples of these compounds are very stable in dry air for months, but react slowly with water. The reaction yield is about 40% for the Pr analogue and 60% for the Nd analogue based on germanium. X-ray powder diffraction studies indicate that the products of flux reactions are predominantly single phase (see Figure S1, supporting information). The Pr analogue only forms if both Al and Ge reactants are present; $\text{Pr}_6\text{Co}_5\text{Ge}_{1.80}\text{Al}_{2.20}$ was synthesized from the reactions of 1 mmol of germanium powder and 1 mmol of aluminum powder in Pr/Co flux, which gives the best yield. The Nd analogue can be grown without Al reactant; however, the SEM/EDS results still indicate an aluminum content around 5%. Therefore Al contamination from etching of the alumina crucible by the strongly

reducing flux appears to be incorporated into the products. Polycrystalline samples of $\text{Nd}_6\text{Co}_5\text{Ge}_{1.74}\text{Al}_{2.26}$ can be produced by arc melting synthesis (a stoichiometric ratio of Nd chunks, Co slugs, and Ge powder wrapped in Al foil and arc melted). This produces $\text{Nd}_6\text{Co}_5\text{Ge}_{1.74}\text{Al}_{2.26}$ as the major product. Attempts to make the analogues of the title phases with other rare earth metals such as La or Ce (either by arc melting stoichiometric mixtures, or from flux reactions of Ge and Al in La/Co or Ce/Co eutectics) were not successful, likely due to the larger size of La^{3+} and Ce^{3+} cations. However, a structural analog $\text{La}_6\text{Ni}_{3.7}\text{Ru}_{0.8}\text{Al}_{3.6}\text{Sn}$ can be isolated (from reactions of Ru, Sn, and Al in La/Ni flux) [8], presumably stable because of the incorporation of larger elements on all sites (La, Ru, and Sn compared to Nd, Co, and Ge). This features a 3D $[\text{Ni}_{3.67}\text{Ru}_{0.76}\text{Al}_{3.6}]^3_\infty$ network with hexagonal channels accommodating Sn@La_9 clusters.

3.2 Structure

The $\text{RE}_6\text{Co}_5\text{Ge}_{1+x}\text{Al}_{3-x}$ title phases crystallize with the $\text{Nd}_6\text{Co}_5\text{Ge}_{2.2}$ structure type (hexagonal space group $P-6m2$) shown in Figure 1. Atom positions are listed in Table 2. The structure of $\text{RE}_6\text{Co}_5\text{Ge}_{1+x}\text{Al}_{3-x}$ can be viewed as a hexagonal Co/Ge/Al framework with large channels hosting chains of face-sharing germanium-centered rare earth clusters Ge@RE_9 (@ = encapsulated). Formation of such clusters is likely promoted by the partially reduced nature of the germanium; as the most electronegative element in the reaction mixture, it will accept electrons from the strongly reducing RE/Co flux and become anionic, and will be surrounded by RE^{3+} cations. Similar M@RE_9 clusters are observed in $\text{La}_{21}\text{Fe}_8\text{M}_7\text{C}_{12}$ (M=Sn, Bi, Sb, Te, Ge), $\text{RE}_6\text{Fe}_{13-x}\text{Al}_x\text{M}_y$ (RE=La, Nd, M = main group element), and $\text{Nd}_8\text{Co}_{3.3}\text{Al}_{0.7}\text{Ge}_2\text{C}_3$. [7,13,20] In these structures, the main group elements are surrounded by nine rare earth atoms in a monocapped square antiprism coordination. The tricapped trigonal prismatic Ge@Nd_9 units in $\text{Nd}_6\text{Co}_5\text{Ge}_{1+x}\text{Al}_{3-x}$ feature a much smaller range of Ge-Nd bond lengths (3.1756(9) Å, 3.210(1) Å) compared to the monocapped square antiprismatic Ge@Nd_9 clusters in $\text{Nd}_8\text{Co}_{3.3}\text{Al}_{0.7}\text{Ge}_2\text{C}_3$ (3.026(1) – 3.367(1) Å). The Ge-Pr bond lengths of 3.1856(7) Å and 3.222(1) Å for $\text{Pr}_6\text{Co}_5\text{Ge}_{1+x}\text{Al}_{3-x}$ are within the range seen for phases such as $\text{Pr}_2\text{Ge}_2\text{In}$ and $\text{PrFe}_{0.54}\text{Ge}_3$. [21,22] These clusters share opposing trigonal faces to form chains running in the c -axis direction. Short RE-RE distances of 3.5799(8) – 3.622(1) Å are found both within and between these chains, so rare earth interactions are not limited to 1- or 2- dimensions.

Figure 1. Crystal structure of $\text{RE}_6\text{Co}_5\text{Ge}_{1+x}\text{Al}_{3-x}$ viewed down the c -axis. Magenta polyhedra represent Ge@RE_9 clusters; yellow, red, and blue spheres represent RE, Co, and Ge/Al sites respectively.

Figure 2. Cobalt sites in $\text{RE}_6\text{Co}_5\text{Ge}_{1+x}\text{Al}_{3-x}$ make 2-D hexagonal layers which are stacked along the c -axis; cobalt-cobalt bond distances are highlighted.

The cobalt sites in the structure comprise 2-D hexagonal nets in the ab -plane, shown in Figure 2. These are stacked along the c -axis with an interlayer distance equal to the c -axis parameter ($4.202(1) \text{ \AA}$); these nets are linked by a mixed Ge/Al site. Positioning of the cobalt atoms and RE^{3+} ions are of particular interest since these atoms can give rise to magnetic ordering. The Co2 and Co3 sites form the nodes of the hexagonal net, with Co1 atoms occupying the edges. Each Co3 site is bonded to three Co1 sites with a Co-Co distance of $2.450(1) \text{ \AA}$, similar to Co-Co bond lengths in $\text{NdCo}_{0.4}\text{Si}_{1.6}$ and NdCo_2B_2 [23,24]. Each Co2 site is also

bonded to three Co1 sites at longer distances of 2.864(1) Å; these Co2-Co3 bonds are bridged by the Ge/Al sites which link the cobalt nets along the *c*-axis. The resulting hexagonal channels are 10 Å diameter, and are filled by the Ge@RE₉ chains (see Figure 1).

Compared with Nd₆Co₅Ge_{2.2} [14,15] which was reported to have a unit cell volume of 311.81 Å³, Nd₆Co₅Ge_{1.74}Al_{2.26} has a slightly smaller volume (305.45 Å³). In the original report on Nd₆Co₅Ge_{2.2}, the 3*k* site was assigned as partially filled (40%) by germanium. In our initial refinements of the flux-grown title phases, similar refinement of this site as partially occupied Ge led to 54% and 52% occupation, resulting in stoichiometries of Pr₆Co₅Ge_{2.61} (with R₁ = 0.0115) and Nd₆Co₅Ge_{2.57} (with R₁ = 0.0138). However, the presence of aluminum was indicated by elemental analysis for both compounds, so this 3*k* site was instead modelled as fully occupied by a mixture of Ge and Al. This refined to occupancies of 26.8% Ge and 73.2% Al for Pr₆Co₅Ge_{1.80}Al_{2.20} (R₁ = 0.0109) and 24.8% Ge and 75.2% Al for Nd₆Co₅Ge_{1.74}Al_{2.26} (R₁ = 0.0129). This improved the overall fit, and is in agreement with Ge/Al site mixing seen in other intermetallics such as PrAl_xGe_{2-x} and REAl_{3-x}Ge_x [25,26]. This Ge/Al mixing was consistently seen in R₆Co₅Ge_{1+x}Al_{3-x} products of reactions with a variety of Ge/Al synthesis ratios (including Nd/Co/Ge reactions with aluminum *not* added as a reactant but instead leached from the crucible). The originally reported synthesis of Nd₆Co₅Ge_{2.2} involved arc melting on a copper hearth, so no aluminum was present. The slight volume discrepancy between Nd₆Co₅Ge_{2.2} and Nd₆Co₅Ge_{1.74}Al_{2.26} therefore indicates that a 3*k* site containing 40% Ge and 60% vacancies is slightly larger on average than one containing 25% Ge and 75% Al.

3.3 Magnetic Properties

Figure 3 shows the magnetic susceptibility data for RE₆Co₅Ge_{1+x}Al_{3-x} with the *c*-axis (which is oriented along the longest dimension of the rod-shaped crystals) parallel to applied field. Both phases are paramagnetic above 200 K. The inverse susceptibility of Pr₆Co₅Ge_{1.80}Al_{2.20} in the range of 200-300 K was fitted to the Curie-Weiss law, yielding an effective moment of 4.01 μ_B per Pr ion and Weiss constant θ of 113 K. Similar fitting of the high temperature data of Nd₆Co₅Ge_{1.74}Al_{2.26} gives a moment of 3.98 μ_B per Nd and Weiss constant of 131 K. Both the magnetic moments of the title phases are larger than the theoretical values for RE ions (3.58 μ_B for Pr³⁺, and 3.28 μ_B for Nd³⁺). This indicates that the cobalt sites contribute to the magnetic moment. Upon cooling below 200 K, both phases exhibit a distinct ferromagnetic

transition and associated field-cooled/zero field-cooled (FC/ZFC) splitting, with $T_C=130$ K for the Pr analogue and $T_C=140$ K for the Nd analogue. The relatively high ordering temperature indicates it is most likely due to the cobalt sublattice. The observed ordering temperatures are in agreement with the Weiss constants calculated from the Curie-Weiss fits of the high temperature data. As the temperature is further lowered, the rare earth moments order; this occurs at 25 K for the Pr analogue and 30 K for Nd analogue.

Figure 3. (a) Temperature dependence of magnetic susceptibility data for $\text{Pr}_6\text{Co}_5\text{Ge}_{1.80}\text{Al}_{2.20}$ and (b) temperature dependence of magnetic susceptibility data for $\text{Nd}_6\text{Co}_5\text{Ge}_{1.74}\text{Al}_{2.26}$, both measured on crystals aligned with c -axis parallel to applied field of 100 Oe. Filled symbols represent magnetic susceptibility, and empty symbols represent inverse susceptibility data.

Magnetization measurements were carried out to further explore these phenomena. Figure 4 is the field dependence data for $\text{Pr}_6\text{Co}_5\text{Ge}_{1.80}\text{Al}_{2.20}$ taken at several different temperatures. Above the $T_C=130$ K, the field dependence (at 150 K) is characteristic of a paramagnet. Below that temperature (at 80 K), weak ferromagnetism is observed, although no saturation or hysteresis is seen. Below the rare earth ordering temperature (30 K), a slight hysteresis becomes apparent which increases as the temperature is further lowered. The system becomes a somewhat strong ferromagnet at 5 K and 1.8 K (with a remanant magnetization of $0.79 \mu_B$ and a coercive field of 0.95 T at 1.8 K; full saturation at high fields is not achieved). Figure 5 shows magnetization data at different temperatures for $\text{Nd}_6\text{Co}_5\text{Ge}_{1.74}\text{Al}_{2.26}$. Compared with the Pr analogue, it is a slightly softer ferromagnet (indicated by the smaller hysteresis), owing to the smaller single-ion magnetic anisotropy of Nd^{3+} .

Figure 4. Magnetization data for $\text{Pr}_6\text{Co}_5\text{Ge}_{1.80}\text{Al}_{2.20}$ at various temperatures spanning the ferromagnetic transition with crystal aligned with c -axis parallel to applied field

To further investigate the magnetic anisotropy of $\text{Nd}_6\text{Co}_5\text{Ge}_{1.74}\text{Al}_{2.26}$, magnetic measurements were carried out for a single crystal of this compound with the crystal oriented with c -axis parallel and then perpendicular to the applied field (Figure 6). The data show a

strong preference for the cobalt magnetic moments to align along the c -axis. The temperature-dependent data (Figure 6a) features a distinctly larger rise of susceptibility below $T_C=140$ K and FC/ZFC splitting when the crystal is aligned with c -axis parallel to the applied field, compared to the data for the perpendicular orientation. The Curie-Weiss fit of the data above 150 K yield an effective moment of $3.88 \mu_B$ per Nd atom, and a Weiss constant of $\theta = 123$ K for c -axis alignment perpendicular to the field; these are slightly smaller values than those from the parallel orientation data ($\mu_{\text{eff}}=3.98 \mu_B$, $\theta = 131$ K). This also indicates that the magnetic moments align predominantly along the c -axis. It is notable that the jump in the susceptibility below 50 K due to ordering of the Nd^{3+} moments is apparent in both orientations of the crystal; this may indicate that the Nd^{3+} moments are aligned at a canted orientation instead of along the c -axis or in the ab -plane (neutron diffraction data are needed to determine this). The field dependent data for a $\text{Nd}_6\text{Co}_5\text{Ge}_{1.74}\text{Al}_{2.26}$ crystal measured at 1.8 K with $H//C$ exhibits larger coercivity (0.2 T) and remanance ($2.77 \mu_B$), compared to a coercivity of nearly zero and a non-saturated magnetization of $1.81 \mu_B$ with $H \perp C$.

Figure 5. Magnetization data for $\text{Nd}_6\text{Co}_5\text{Ge}_{1.74}\text{Al}_{2.26}$ at various temperatures, with c -axis of the crystal aligned parallel to the applied field.

Figure 6. Anisotropic magnetic properties of $\text{Nd}_6\text{Co}_5\text{Ge}_{1.74}\text{Al}_{2.26}$. Data in red taken with crystal aligned with c -axis parallel to applied field; data in black taken with crystal aligned with c -axis perpendicular to applied field. (a) Temperature dependent data measured with an applied field of 100 Oe. (b) Field dependent data measured at 1.8 K.

3.4 Electronic structure calculations

The model compound $\text{Nd}_6\text{Co}_5\text{GeAl}_3$ was used to calculate total and partial density of states (DOS) data; the resulting DOS diagram is shown in Figure 7. The nonzero DOS at the Fermi energy indicates that this compound is metallic. Nd $5d$ states have their most significant

contribution to the DOS above E_F , whereas orbitals from Co, Ge, and Al are dominant below the E_F . Germanium and aluminum have almost zero contribution to the DOS at the Fermi level. The Ge states contribute to states between -1 and -5 eV which are hybridized with states from surrounding rare earth atoms; this demonstrates that germanium atoms are partially negatively charged and strongly interact with neighboring Nd^{3+} or Pr^{3+} cations in the Ge@RE_9 clusters. The data indicate only a small contribution from the Co 3d electrons at the Fermi level. This does not agree with the experimental magnetic data—the observed ordering of cobalt moments at 150 K indicates the presence of a partially filled and spin-polarized cobalt 3d band at E_F . While the Fermi level does cut through the broad cobalt bands that span from -3 to 2 eV, it does not cut through a region of high density of states, which is generally needed for spin polarization to occur. This incongruity might stem from the difference between the ordered model compound used for the calculation and the actual material which contains a Ge/Al mixture on the 3k site. Changing the Ge/Al ratio will affect the number of valence electrons, which may shift the Fermi level to an area of the cobalt band with high enough DOS to promote spin polarization and a magnetic moment on cobalt.

Figure 7. Total and partial densities-of-states (DOS) data calculated for $\text{Nd}_6\text{Co}_5\text{GeAl}_3$.

4. Conclusion

We have demonstrated that metal fluxes composed of RE/Co mixtures are excellent solvents for main group elements, allowing for the synthesis of complex magnetic intermetallics.

The title structures feature 2-D hexagonal sheets of cobalt atoms which exhibit ferromagnetic ordering. Neutron diffraction studies at different temperatures are planned to explore in more detail the magnitude and alignment of magnetic moments of each of the three cobalt sites and the two unique rare earth sites, and their contribution to the overall magnetic behavior of the compounds. Partial iron substitution into the cobalt sites is also possible as an avenue to modify the magnetic ordering of the cobalt layers; preliminary susceptibility measurements on $\text{Pr}_6(\text{Co/Fe})_5\text{Ge}_{1+x}\text{Al}_{3-x}$ indicate complex magnetic behavior.

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