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$Nd_8Co_{4-x}Al_xGe_2C_3$: A case study in flux growth of lanthanide-rich intermetallics

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ABSTRACT

The intermetallic $Nd_8Co_{4-x}Al_xGe_2C_3$ ($x \approx 0.65$) 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 $a=8.001(1)$ Å, $b=11.696(2)$ Å, $c=15.020(3)$ Å ($Z=4$; $R_1=0.0234$). The structure features germanium-centered neodymium clusters Ge@Nd_9 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 $T_C=50$ K due to the Nd^{3+} ions. Magnetization field dependence studies on single crystals indicate this compound is a strong ferromagnet with large anisotropy; the Nd^{3+} magnetic moments align along the *a*-axis.

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=La, Ce, Pr, Nd) with late first row transition metals (T=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 Nd_2Co_2SiC, $Nd_6Co_5Ge_{2.5}Al_{1.5}$, 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 Nd_2Co_2SiC, magnetic moments only stem from lanthanide elements instead of Co–Co dimers; however the hexagonal cobalt nets in $Nd_6Co_5Ge_{2.5}Al_{1.5}$ exhibit magnetic ordering from both lanthanide elements and transition metal elements.

The $Nd_8Co_{4-x}Al_xGe_2C_3$ title phase was initially discovered in an effort to find a germanium-containing analog of Nd_2Co_2SiC. In $Nd_8Co_{4-x}Al_xGe_2C_3$, 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-

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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 mol% 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 6 mm), 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 $Nd_8Co_{4-x}Al_xGe_2C_3$ 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 a PGT Prism energy dispersion spectroscopy system. 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 30 kV 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 Al_2O_3 crucible material by the strongly reducing Nd/Co flux.

2.3. X-ray diffraction

Small shards cleaved from larger crystals 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 (λ=0.71073 Å). 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 Kα radiation source.

Table 1
Crystallographic data collection parameters for $Nd_8Co_{3.35}Al_{0.65}Ge_2C_3$.

Crystal system	Orthorhombic
Space group	*Pbcm (#57)*
Cell parameters (Å)	a=8.001(1) b=11.696(2) c=15.020(3)
V (Å^3)	1405.5(4)
Formula weight (g/mol)	1550.1
Z	4
Calc. Density (g/cm^3)	7.32
Max. 2θ (deg)	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] ($I>2\sigma(I)$)	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] $R_1=\Sigma(|F_o|-|F_c|)/\Sigma|F_o|$; $wR_2=[\Sigma[w(F_o^2-F_c^2)^2]/\Sigma(w|F_o|^2)^2]]^{1/2}$.

Table 2
Atom positions and thermal parameters for $Nd_8Co_{3.35}Al_{0.65}Ge_2C_3$.

	Wyckoff Site	*x*	*y*	*z*	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.

2.4. 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 1.8 K and 300 K 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.

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]. $Nd_8Co_{4-x}Al_xGe_2C_3$ was modeled as $La_8Co_4Ge_2C_3$ (with the Nd sites modeled as La, and the mixed Co/Al site modeled as completely filled with Co) in order to avoid complications from unpaired *f*-electrons or site