RFe₂Mg_xAl_{8-x} (R = La-Nd and Sm; x≈0.8): Flux synthesis, structure, magnetic and electrical properties

Xiaowei Ma¹, Ping Chai¹, Banghao Chen¹, Eric Lochner², Susan E. Latturner^{*,1}

¹ Department of Chemistry and Biochemistry, Florida State University, Tallahassee, FL 32306

² Department of Physics, Florida State University, Tallahassee, FL 32306

latturne@chem.fsu.edu

phone: 850-644-4074

Abstract

Single crystals of Mg-substituted CeFe₂Al₈ type intermetallics RFe₂Mg_xAl_{8-x} (R = La-Nd and Sm; x≤1) were grown by reacting iron and rare earth metals in 1:1 Mg/Al mixed flux. The structure features mono-capped and bi-capped trigonal prismatic FeAl₆ units. Electronic structure calculations indicate that magnesium substitution reduces the valence electron count, shifting the Fermi level away from a pseudo-gap. This changes the electronic nature of the cerium analog; the previously reported ternary CeFe₂Al₈ shows strong hybridization between the cerium states and the conduction electrons, resulting in no magnetic moment on Ce atoms. On the other hand, magnetic susceptibility measurements on CeFe₂Mg_xAl_{8-x} indicates a localized moment on cerium. The newly synthesized Pr, Nd and Sm analogs exhibit antiferromagnetic ordering at 2.8 K, 7.8 K and 12 K respectively. Solid state ²⁷Al NMR of LaFe₂Mg_xAl_{8-x} exhibits a broad Knight shift at ~1200 ppm, consistent with the metallic behavior shown by electrical resistivity data.

Key words: metal flux, intermetallics, antiferromagnetism, electrical resistivity, cerium valence

1. Introduction

Intermetallic aluminides have been reported to exhibit a variety of useful applications. For instance, Ni_3Al can be used as light-weight automotive body material [1]. $\gamma\text{-TiAl}$ has promising mechanical properties and corrosion resistance as high-temperature engine components [2,3]. FeAl is a possible substitute for stainless steel with excellent corrosion and oxidation resistance [4,5]. Furthermore, aluminides containing rare earths and/or transition metals often possess interesting magnetic and electrical behavior as is seen for compounds such as La_2NiAl_7 [6], RAu_3Al_7 ($\text{R} = \text{Ce-Nd, Sm, Gd-Lu}$) [7], and CeT_2X_8 ($\text{T} = \text{Fe, Co}$; $\text{X} = \text{Al, Ga}$) [8-13]. In particular, CeT_2X_8 ($\text{T} = \text{Fe, Co}$; $\text{X} = \text{Al, Ga}$) as well as the correlated LaT_2Al_8 have received much interest due to possible Kondo lattice behavior. CeFe_2Al_8 crystallizes in the orthorhombic CaCo_2Al_8 structure type in space group $Pbam$, as first characterized by Yarmoljuk et al [8]. In this compound, neither Ce nor Fe shows magnetic ordering based on magnetic measurements, ^{57}Fe Mössbauer spectra and neutron diffraction of CeFe_2Al_8 and LaFe_2Al_8 [9,10]. Instead, hybridization between Ce 4f electrons and the conduction electrons leads to a metallic Fermi-liquid ground state, as characterized by the electrical resistivity, thermoelectric power and heat capacity [11-13].

CeT_2X_8 intermetallics are typically synthesized by direct melting of elements in a stoichiometric ratio, and accurate characterization of physical properties are hindered by the lack of single crystal samples. Compared with the traditional solid state synthesis, the flux method promotes the growth of crystals. Reports on the growth of $\text{CeCo}_{2-x}\text{M}_x\text{Al}_8$ ($\text{M} = \text{Fe, Mn, Ni}$) and $\text{YbNi}_{2-x}\text{Fe}_x\text{Al}_8$ crystals from molten aluminum demonstrate the value of such samples for careful structural and magnetic studies on these compounds [14]. We are exploring the use of Mg/Al mixtures (1:1 molar ratio with a melting point of $\sim 470^\circ\text{C}$) as fluxes; this has enabled the synthesis of rare earth-containing phases such as $\text{R}_5(\text{Mg/Al})_5\text{Fe}_4(\text{Al/Si})_{18}$ ($\text{R} = \text{Gd, Dy and Y}$) and EuMgSn [15,16]. The large single crystals produced in this flux allowed for the study of interesting antiferromagnetic behavior in these compounds. In the present work, we synthesized single crystals of $\text{CeFe}_2\text{Mg}_x\text{Al}_{8-x}$ and $\text{LaFe}_2\text{Mg}_x\text{Al}_{8-x}$ in Mg/Al flux. Mg was incorporated into the structure on a specific Al site. In addition, we successfully expanded the synthesis to Pr, Nd and Sm analogs, which have not been reported so far.

2. Experimental section

2.1 Synthesis

Reactants were used as received: Mg and Al metal slugs (99.95%), Fe powder (99+%) from Alfa Aesar, and rare earth metals from Metall (99+%). The synthesis of $\text{RFe}_2\text{Mg}_x\text{Al}_{8-x}$ is similar to that reported in our previous work [15]. Reactants Mg/Al/Fe/R (R = La, Ce, Pr, Nd, Sm) were initially weighed out in a mmol ratio of 15/15/1/1, and loaded into stainless steel crucibles in a dry box. These crucibles were welded shut in an argon-filled glovebox and then flame-sealed in fused silica tubes under vacuum. The ampoules were heated in a muffle furnace from room temperature to 950°C in 10 h; they were held at 950°C for 5 h, cooled to 750°C in 80 h, and held at 750°C for 24 h, at which point they were quickly removed from the furnace, flipped and centrifuged to decant the molten Mg/Al flux off of the product crystals which adhered to the crucible walls. Subsequent reactions were carried out to determine the optimal Mg/Al/Fe/R reactant ratios (15/15/2/1 for R = La and Ce, and 15/15/1/0.5 for R = Pr, Nd and Sm. Reactions with the optimal ratios were carried out in Nb crucibles to obtain high purity samples for further magnetic and electrical measurements.

LaFe_2Al_8 was grown in Al flux in an alumina crucible. A mixture of Al/Fe/La in a mmol ratio of 30/1/1 was loaded in an alumina crucible, which was placed in a silica tube with a wad of quartz wool above it. The silica tube was sealed shut under vacuum. This ampoule was then heated in a muffle furnace from room temperature to 1000°C in 10 h; it was held at 1000°C for 10 h, cooled to 800°C in 80 h, and held at 800°C for 24 h, at which point the crystals were separated from the Al flux using the aforementioned centrifuge method for $\text{RFe}_2\text{Mg}_x\text{Al}_{8-x}$.

2.2 Elemental analysis.

SEM-EDS analysis was performed using a JEOL 5900 scanning electron microscope (30 kV acceleration voltages) equipped with PGT Prism energy dispersion spectroscopy software. Selected crystals were arranged on double-sided carbon tape adhered to an aluminum sample puck. Each crystal was cleaved to expose inner portions to acquire more accurate elemental analysis of the bulk sample and avoid erroneous readings due to residual flux coating on the surface. Several spots on each crystal were analyzed for 60 s at each location. The magnesium content of $\text{RFe}_2\text{Mg}_x\text{Al}_{8-x}$ crystals ranged from 6-8 mol % for all samples.

2.3 X-ray diffraction.

Single crystal diffraction data were collected for each analog at room temperature on a Bruker APEX2 single crystal diffractometer with a Mo K α radiation source. Selected crystal samples were broken into suitable size and small spheroid fragments were mounted on glass fibers for diffraction. Data was processed using the program SAINT and corrected with the SADABS program [17]. Space group assignment was accomplished by XPREP, and refinement of the structure was performed by SHELXTL [18]. The structures were solved in orthorhombic space group *Pbam*; crystallographic data and collection parameters for all the six phases are shown in Table 1. Table 2 shows atom positions and isotropic thermal parameters for LaFe₂Mg_xAl_{8-x}. Further data for LaFe₂Al₈ and other four analogs can be found in the supporting information (Table S1-S6), and 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-429475 (LaFe₂Al₈), CSD-429476 (LaFe₂MgAl₇), CSD-429477 (CeFe₂MgAl₇), CSD-429478 (PrFe₂MgAl₇), CSD-429479 (NdFe₂MgAl₇), or CSD-429480 (SmFe₂MgAl₇). During the refinement, assignment of rare earth and iron sites were straightforward; all lighter element sites (Mg and Al) were initially assigned as aluminum, but assignments were modified based on bond length considerations and elemental analysis. In the final refinement cycles, occupancies of all sites were allowed to vary, but all appeared fully occupied (100 +/- 1%). Powder X-ray diffraction data were collected on a PANalytical X'Pert PRO with a Cu K α radiation source in the temperature range of -160°C to room temperature.

2.4 Solid State ²⁷Al NMR.

²⁷Al MAS NMR spectra were collected on a Varian/Inova 500WB spectrometer (11.7 T) with ²⁷Al resonance frequency of 130.46 MHz. The ²⁷Al shift was referenced to 1M Al(NO₃)_{3(aq)}. Crystals of LaFe₂Mg_xAl_{8-x} were ground with NaCl in a 1:1 ratio by volume in a glove box and the powder was packed into a 4 mm zirconia rotor sealed with an airtight screw cap. Single pulse acquisition was applied with a short RF pulse less than 15°. The spinning speed was 12 kHz and the recycle delay was 0.3 s.

2.5 Electronic structure calculations.

The density of states (DOS) calculations on LaFe_2Al_8 and $\text{LaFe}_2\text{MgAl}_7$ were performed with tight binding - linear muffin tin orbitals - atomic sphere approximation (TB-LMTO-ASA) program package [19]. The calculations were based on structure parameters determined by single X-ray diffraction data; for $\text{LaFe}_2\text{MgAl}_7$, an ordered model was used with the 4g mixed Mg/Al site (see Table 2) fully occupied by magnesium. Six empty Wigner-Seitz spheres were needed to fill the empty space in the structure. The following radii of atomic spheres were used: $r(\text{La}) = 3.88 \text{ \AA}$, $r(\text{Fe}) = 2.56/2.59 \text{ \AA}$, $r(\text{Mg}) = 2.88 \text{ \AA}$, $r(\text{Al}) = 2.56\text{-}3.02 \text{ \AA}$, $r(\text{E}) = 1.28\text{-}1.68 \text{ \AA}$. The basis set contains La (6s, 5p, 4f), Fe (4s, 4p, 3d), Mg(3s, 3p) and Al (3s, 3p) with La (6p), Mg(3d) and Al (3d) being downfolded. The calculation was made for 160 κ points in the irreducible Brillouin zone. Integration over the Brillouin zone was performed by the tetrahedron method [20].

2.6 Electrical resistivity.

Electrical resistivity measurements were conducted with a conventional four-probe method on a Physical Property Measurement System (PPMS) by Quantum Design. Single crystals were put on a sample holder puck and four 25 micron diameter gold wires were adhered to the crystal surface with silver paste. Resistivity data were taken from 2 - 300 K with an applied excitation current of 5 mA.

2.7 Magnetic properties.

Magnetic measurements were carried out on a Quantum Design SQUID Magnetic Property Measurement System. Clean crystals were selected and held between two strips of kapton tape, oriented with *c*-axis parallel to the applied field. Temperature dependence of magnetic susceptibility data were collected between 1.8 K and 300 K. A magnetic field of 1000 G was applied for $\text{PrFe}_2\text{Mg}_x\text{Al}_{8-x}$ and $\text{NdFe}_2\text{Mg}_x\text{Al}_{8-x}$, and 1 T for $\text{LaFe}_2\text{Mg}_x\text{Al}_{8-x}$, $\text{CeFe}_2\text{Mg}_x\text{Al}_{8-x}$ and $\text{SmFe}_2\text{Mg}_x\text{Al}_{8-x}$. Field-dependent magnetization data were collected at 1.8 K in the field range of 0 to 7 T.

3. Results and discussion

3.1 Synthesis.

Needle-shaped single crystals of $\text{RFe}_2\text{Mg}_x\text{Al}_{8-x}$ (R = La-Nd and Sm) were grown from

reactions of iron and early rare earth metals in excess Mg/Al flux. An SEM image of a single crystal of $\text{NdFe}_2\text{Mg}_x\text{Al}_{8-x}$ is shown in Figure 1. The clean surface indicates that products can be well separated from the flux by centrifuging above the melting point of the Mg/Al mixture. No apparent impurity peaks were observed in the powder X-ray diffraction pattern of $\text{NdFe}_2\text{Mg}_x\text{Al}_{8-x}$ in the temperature range of -160°C to room temperature (see Figure S1). The reaction yields are 50-60% based on the rare earth reactant.

3.2 Structure.

$\text{RFe}_2\text{Mg}_x\text{Al}_{8-x}$ ($\text{R} = \text{La-Nd}$ and Sm) crystallize in the CaCo_2Al_8 structure type in orthorhombic space group *Pbam*. Previously reported CeFe_2Al_8 and LaFe_2Al_8 polycrystalline samples were synthesized by traditional stoichiometric reactions. Here we have grown single crystal samples of LaFe_2Al_8 from aluminum flux, and single crystals of $\text{RFe}_2\text{Mg}_x\text{Al}_{8-x}$ from reactions in Mg/Al flux; the latter incorporate magnesium into the structure by partial substitution on an aluminum site (the 4g Wyckoff site, as shown in Figure 2).

A distinctive building block in the structure is the FeAl_6 cluster, composed of iron atoms centering a trigonal prism of aluminum atoms. All of these units share trigonal faces, forming chains running along the *c*-direction. All the FeAl_6 clusters are also connected in the *ab*-plane in two different ways: half of them are monocapped by bridging Al sites, similar to the chains of FeAl_6 clusters seen in $\text{R}_5(\text{Mg/Al})_5\text{Fe}_4(\text{Al/Si})_{18}$ ($\text{R}=\text{Gd}$, Dy and Y) and $\text{R}_3\text{Fe}(\text{Mg/Al})_4\text{Si}_2$ [15,16]. The other half are bicapped by two aluminum atoms on both sides.

Figure 3a displays the coordination of the rare earth atoms, which occupy a single crystallographic site in the structure. This 4g site is coordinated by 13 aluminum atoms in the bondlength range of 3.1820(9) to 3.3070(2) Å, forming a capped pentagonal prism. Magnesium occupies a similar pentagonal prism; its coordination environment consists of ten aluminum atoms (the top and bottom of the prism) and three iron atoms capping the sides. Because of their similar electron counts, aluminum and magnesium cannot be accurately distinguished in an X-ray diffraction experiment. The magnesium was assigned to this particular 4g site based on bond lengths; in particular, the single crystal X-ray data refinements of LaFe_2Al_8 and $\text{LaFe}_2\text{Mg}_x\text{Al}_{8-x}$ were compared to determine which particular bond lengths were elongated (see Table 3). All the Mg-related bond lengths for $\text{LaFe}_2\text{MgAl}_7$ are larger than those for LaFe_2Al_8 as expected. The large distance between rare earth and

magnesium (3.927(1) Å at minimum) also favors the site assignment of Mg and answers the question why magnesium only occupies the particular 4g site instead of other aluminum sites. Refining this position as occupied by Mg instead of Al decreases the thermal parameter (U_{eq}) from 0.01619 for Al occupancy to 0.0097 for Mg occupancy in $\text{LaFe}_2\text{MgAl}_7$ (thermal parameters for other analogs are summarized in Table S6). The distances between this Mg site and the surrounding Al sites are between 2.9942(8) Å and 3.153(1) Å, lying in the literature range of Mg-Al bond lengths (2.77 - 3.44 Å) [21-24]. However, considering the similar X-ray scattering factors of magnesium and aluminum, we cannot rule out the possibility that this site is occupied by a mixture of Mg and Al. According to the EDS results, the amount of magnesium in $\text{LaFe}_2\text{Mg}_x\text{Al}_{8-x}$ is around 7%, less than the calculated value (9.1%) if the 4g site is fully occupied by Mg. Therefore, a general stoichiometry $\text{LaFe}_2\text{Mg}_x\text{Al}_{8-x}$ ($x \approx 0.8$) is used.

3.3 Electronic properties

3.3.1 Electronic structure calculations

The calculated total and partial density of states (DOS) of $\text{LaFe}_2\text{MgAl}_7$ and LaFe_2Al_8 with TB-LMTO-ASA is shown in Figure 4. $\text{LaFe}_2\text{MgAl}_7$ contains one less valence electron than LaFe_2Al_8 , which shifts the Fermi level lower; it is further away from a pseudo-gap, and as a result a higher density of states is found at the Fermi level (E_F) compared to LaFe_2Al_8 (~23 states/eV·cell at E_F for $\text{LaFe}_2\text{MgAl}_7$, vs. ~20 states/eV·cell for LaFe_2Al_8). A sharp peak at ~4 eV corresponds to the f-orbital states of electropositive lanthanum ions. Shifting the Fermi level lower also shifts it further away from the rare earth states, which may have an impact on the ability of conduction electrons to interact with f-electron states. Bands derived from iron d-orbitals lie predominantly below E_F in the energy range between -3 and 0.7 eV; spin polarization and a resultant itinerant moment on iron is therefore not expected for this compound. The aluminum states are broadly distributed below and above the E_F and the contribution of Mg is negligible. The presence of pseudo-gaps at ~0.7 eV for $\text{LaFe}_2\text{MgAl}_7$ and ~0.5 eV for LaFe_2Al_8 are indicative of their polar nature; such pseudo-gaps are commonly seen in complex intermetallic compounds due to the partial charge transfer between electropositive and electronegative metals. In general, the pseudo-gap tends to be

located at or near E_F for stable structures [25]. Here in the case of $\text{LaFe}_2\text{MgAl}_7$ and LaFe_2Al_8 , the presence of magnesium slightly alters the electronic distribution and destabilizes the structure to some extent.

3.3.2 Solid state ^{27}Al NMR.

The solid state ^{27}Al MAS NMR of $\text{LaFe}_2\text{Mg}_x\text{Al}_{8-x}$ is shown in Figure S2; an XRD powder pattern of this sample (Figure S3) indicates it is free of impurities. NMR measurements on other $\text{RFe}_2\text{Mg}_x\text{Al}_{8-x}$ analogs were not performed to avoid paramagnetic shifts caused by localized $4f$ electrons. The MAS spectrum for $\text{LaFe}_2\text{Mg}_x\text{Al}_{8-x}$ shows a broad metallic peak at ~ 1200 ppm, corresponding to all the aluminum content. Deconvolution of this peak was not possible; the eight aluminum sites in the structure have similar coordination environments and their NMR resonances will occur at similar frequencies. The large Knight shift is in accordance with the metallic character of $\text{LaFe}_2\text{Mg}_x\text{Al}_{8-x}$ as shown by the DOS at the E_F (see Figure 4). Many reported intermetallic aluminides such as $\text{Al}_{85}\text{Ni}_{11}\text{Y}_4$ and $\text{Y}_5(\text{Mg}/\text{Al})_5\text{Fe}_4\text{Al}_x\text{Si}_{18-x}$ show similar Knight shifts in the range of 1100-1300 ppm [15,26].

3.3.3 Magnetic properties.

The temperature-independent Pauli paramagnetism of $\text{LaFe}_2\text{Mg}_x\text{Al}_{8-x}$ (shown in Figure S4) indicates that iron does not have a magnetic moment in this compound. This is consistent with the DOS calculations (Figure 4) and is in agreement with magnetic behavior reported for LaFe_2Al_8 and CeFe_2Al_8 in the literature [9,10]. Accordingly, the magnetic susceptibility of $\text{LaFe}_2\text{Mg}_x\text{Al}_{8-x}$ was subtracted from that of $\text{RFe}_2\text{Mg}_x\text{Al}_{8-x}$ ($\text{R}=\text{Ce}, \text{Pr}, \text{Nd}$ or Sm) in order to fit each to the Curie-Weiss law, and the resulting temperature-dependent magnetic susceptibilities of these four compounds are shown in Figure 5. Magnetic parameters derived from this data are shown in Table 4.

Figure 5a shows the temperature-dependent magnetic susceptibility of $\text{CeFe}_2\text{Mg}_x\text{Al}_{8-x}$. The zero-field-cooled (ZFC) and field-cooled (FC) curves overlap well when a magnetic field of 1T is applied. The linear temperature dependence of inverse susceptibility obeys the Curie-Weiss law above 150 K, and the calculated magnetic moment of $\sim 2.4 \mu_B$ is close to the theoretical effective value of Ce^{3+} ($2.5 \mu_B$). This indicates that the cerium ions in $\text{CeFe}_2\text{Mg}_x\text{Al}_{8-x}$ are trivalent and have a localized moment. This is distinctly different from

the non-Curie Weiss behavior reported for the unsubstituted CeFe_2Al_8 , which indicates fluctuating $\text{Ce}^{3+}/\text{Ce}^{4+}$ valence due to strong hybridization between the Ce f -states and the conduction electrons [10-13]. It is notable that the data for $\text{CeFe}_2\text{Mg}_x\text{Al}_{8-x}$ shows a large negative Weiss constant (-155 K) but no magnetic ordering down to 1.8 K. This might indicate magnetic frustration, although the lack of FC/ZFC splitting argues against this. Another possibility is that Al/Mg mixed sites in the vicinity of the rare earth ions result in non-Fermi liquid behavior as postulated for other doped or disordered cerium intermetallics such as $\text{Ce}_{1.33}\text{Pt}_4\text{Ga}_{10}$, $\text{Ce}(\text{Ru}_{1-x}\text{Rh}_x)_2\text{Si}_2$, and $\text{CePtSi}_{0.9}\text{Ge}_{0.1}$; further studies would be needed to confirm this [27,28].

The temperature dependence of magnetic susceptibilities for Pr, Nd or Sm analogs are shown in Figure 5b, 5c and 5d. All three phases exhibit antiferromagnetic transitions with the Néel temperatures at 2.8 K, 7.8 K and 12 K for Pr, Nd and Sm analogs respectively. The inverse susceptibility data for $\text{PrFe}_2\text{Mg}_x\text{Al}_{8-x}$ and $\text{NdFe}_2\text{Mg}_x\text{Al}_{8-x}$ can be well fitted to the Curie-Weiss law at above 100 K and the calculated magnetic moments ($\sim 3.7 \mu_B$ for $\text{PrFe}_2\text{Mg}_x\text{Al}_{8-x}$ and $\sim 3.5 \mu_B$ for $\text{NdFe}_2\text{Mg}_x\text{Al}_{8-x}$) are close to the theoretical value ($3.6 \mu_B$) for Pr^{3+} and Nd^{3+} ions. The positive Weiss constants of 44 K for $\text{PrFe}_2\text{Mg}_x\text{Al}_{8-x}$ and 47 K for $\text{NdFe}_2\text{Mg}_x\text{Al}_{8-x}$ indicate the presence of ferromagnetic interactions at high temperature, although antiferromagnetic coupling forces become dominant at low temperature and lead to ordering at the Neel temperature. The magnetic susceptibility data for $\text{SmFe}_2\text{Mg}_x\text{Al}_{8-x}$ are distinctly different. There is an evident splitting between the ZFC and FC curves at and below T_N . The inverse susceptibility data for $\text{SmFe}_2\text{Mg}_x\text{Al}_{8-x}$ does not show Curie-Weiss behavior at high temperatures. This is often the case for samarium-containing phases, due to mixing of the ground state ($J=5/2$) and the low-lying first excited state ($J=7/2$) of Sm^{3+} ions (van Vleck behavior).

Figure 6 displays the field dependence of magnetization for $\text{RFe}_2\text{Mg}_x\text{Al}_{8-x}$ ($\text{R}=\text{Ce}$, Pr, Nd and Sm) at 1.8 K. $\text{CeFe}_2\text{Mg}_x\text{Al}_{8-x}$ and $\text{SmFe}_2\text{Mg}_x\text{Al}_{8-x}$ present a linear dependence of magnetization with the field, rising to magnetization values of $0.22 \mu_B$ and $0.06 \mu_B$ at 7 T respectively, which are far from being saturated. The low magnetic response for $\text{CeFe}_2\text{Mg}_x\text{Al}_{8-x}$ and $\text{SmFe}_2\text{Mg}_x\text{Al}_{8-x}$ compared to $\text{NdFe}_2\text{Mg}_x\text{Al}_{8-x}$ and $\text{PrFe}_2\text{Mg}_x\text{Al}_{8-x}$ is also reflected by their low magnetic susceptibilities, as indicated in Figure 5. The low

magnetization for the Ce phase is likely indicative of Ce^{3+} cations in a paramagnetic state; it is not as low as the $0.02 \mu_B$ value observed by Strydom et al for the strongly hybridized intermediate-valent CeFe_2Al_8 at 2 K and 7 T [11]. $\text{NdFe}_2\text{Mg}_x\text{Al}_{8-x}$ also shows linear magnetization at low applied fields and then a strong spin reorientation occurs, as indicated by the sharp jump at ~ 4 T. However saturation was not achieved at 7 T. $\text{PrFe}_2\text{Mg}_x\text{Al}_{8-x}$ exhibits similar metamagnetic behavior at even lower fields, and the magnetization is close to saturated by 7 T.

3.3.4 Electrical resistivity.

Temperature dependence of electrical resistivity for $\text{RFe}_2\text{Mg}_x\text{Al}_{8-x}$ (R= La - Nd, Sm) were carried out in the temperature range of 2 - 300 K. All five phases exhibit metallic behavior at temperatures above 50 K, with resistivity rising linearly along with temperature. Accordingly, only the data below 40 K is shown in Figure 7. No anomaly was observed for $\text{CeFe}_2\text{Mg}_x\text{Al}_{8-x}$, comparable to the reported resistivity data for CeFe_2Al_8 [11]. $\text{PrFe}_2\text{Mg}_x\text{Al}_{8-x}$ and $\text{NdFe}_2\text{Mg}_x\text{Al}_{8-x}$ also approach their residual resistivity at 2 K. Notably, $\text{LaFe}_2\text{Mg}_x\text{Al}_{8-x}$ shows a minimum at ~ 20 K, which has never been mentioned by the literature on LaFe_2Al_8 . It is unclear whether this $\rho_{\min}$ is attributed to the magnesium incorporation or the poor crystal quality, as reflected by its low residual resistivity ratio (RRR) $= \rho_{300\text{K}}/\rho_{\min} = 1.6$ (see Table 4). However, it is reported that an irregular phononic behavior was observed at ~ 25 K from the temperature-variable specific heat for LaFe_2Al_8 , which likely correlates to the $\rho_{\min}$ of $\text{LaFe}_2\text{Mg}_x\text{Al}_{8-x}$ [11]. $\text{SmFe}_2\text{Mg}_x\text{Al}_{8-x}$ exhibits a correlation between the magnetic ordering and electrical conduction. The electrical resistivity experienced a sharp increase at ~ 11 K, consistent with the antiferromagnetic ordering at 12 K.

4. Conclusion

CeM_2Al_8 (M = Mn, Fe, Co, Ni) compounds have been widely studied due to the potential for strong hybridization of conduction electrons at the Fermi level with cerium 4f electrons, which can lead to fluctuating valence and Kondo effect. The flux growth of $\text{RFe}_2\text{Mg}_x\text{Al}_{8-x}$ as large crystals from Mg/Al melts has allowed for the study of electronic properties and better understanding of the effects of doping. Magnesium is incorporated on

one aluminum site in the structure; electronic structure calculations indicate that such doping modifies the valence electron count sufficiently to affect the nature of the interaction between rare earth states and the conduction electrons. While CeFe_2Al_8 shows extensive hybridization, leading to fluctuating valence and the quenching of magnetic moment on the cerium ions, substitution of some aluminum by magnesium is sufficient to move the Fermi level away from the $4f$ states and eliminate the hybridization. Accordingly, $\text{CeFe}_2\text{Mg}_x\text{Al}_{8-x}$ exhibits a stable Ce^{3+} moment. Previous explorations of substitutions on the transition metal site have been reported, but this is the first evidence that substitution on the main group metal site can also have significant effects on magnetic and electronic properties of RM_2Al_8 phases.

Acknowledgements

This research was supported by funding from the National Science Foundation (Division of Materials Research) through grant numbers DMR-05-47791, DMR-11-06150, and DMR-14-10214. This work made use of the NMR facilities in the Department of Chemistry and Biochemistry at FSU, and also used the PPMS and SEM Facilities of the Physics Department at FSU.

References

- [1] S.C. Deevi, V.K. Sikka, *Intermetallics* 4 (1996) 357-375.
- [2] R.N. Wright, B.H. Rabin, W. H. McFerran, *J. Mater. Res.* 7 (1992) 2733-2738.
- [3] R.G. Blair, E.G. Gillan, N.K. Nguyen, D. Daurio, R.B. Kaner, *Chem. Mater.* 15 (2003) 3286-3293.
- [4] C.G. McKamey, J.H. DeVan, P.F. Tortorelli, V.K. Sikka, *J. Mater. Res.* 6 (1991) 1779-1805.
- [5] C. Xu, W. Gao, M. Hyland, H. Gong, *Corros. Sci.* 43 (2001) 1891-1903.
- [6] D. Gout, T. J. Barker, O. Gourdon, G. J. Miller, *Chem. Mater.* 17 (2005) 3661-3667.
- [7] S.E. Lattner, D. Bilc, J.R. Ireland, C.R. Kannewurf, S.D. Mahanti, M.G. Kanatzidis, *J. Solid State Chem.* 170 (2003) 48-57.
- [8] I.P. Yarmoljuk, R.M. Rykhal, O.S. Zarechnjuk, *II vsesojuznaya konferentsiya po kristallografi i intermetallicheskih soedineniy*, Lvov (1974) 39.
- [9] M. Kolenda, M.D. Koterlin, M. Hofmann, B. Penc, A. Szytula, A. Zygmunt, J. Zukrowski, *J. Alloys Compd.* 327 (2001) 21-26.
- [10] I. Tamura, T. Mizushima, Y. Isikawa, J. Sakurai, *J. Magn. Mater.* 220 (2000) 31-38.

- [11] S. Ghosh, A.M. Strydom, *Acta Phys. Pol. A.* 121 (2012) 1082-1084.
- [12] M.D. Koterlin, B.S. Morokhivskii, R.V. Lapunova, O.M. Sichevich, *Sov. Phys. Solid State.* 31 (1989) 1826-1827.
- [13] M.D. Koterlin, B.S. Morokhivskii, N.G. Babich, N.I. Zakharenko, R.R. Kut'yanskiĭ. *Phys. Solid State.* 38 (1996) 1924-1925.
- [14] a) L.J. Treadwell, P. Watkins-Curry, J.D. McAlpin, D.J. Rebar, J.K. Hebert, J.F. DiTusa, J.Y. Chan, *Inorg. Chem.* 54 (2015) 963-968. b) X. Wu, M. Francisco, Z. Rak, T. Bakas, S.D. Mahanti, M.G. Kanatzidis, *J. Solid State Chem.* 181 (2008) 3269-3277.
- [15] X. Ma, B. Chen, S.E. Latturmer, *Inorg. Chem.* 51 (2012) 6089-6095.
- [16] X. Ma, J. Lu, J.B. Whalen, S.E. Latturmer, *Inorg. Chem.* 52 (2013) 3342-3348.
- [17] SAINT, Version 6.02a, Bruker AXS, Inc., Madison, WI (2000).
- [18] G.M. Sheldrick, SHELXTL NT/2000, Version 6.1, Bruker AXS, Inc., Madison, WI, (2000).
- [19] O. Jepsen, A. Burkhardt, O.K. Andersen, *The program TB-LMTO-ASA, version 4.7*; Max-Planck-Institut für Festkörperforschung: Stuttgart, Germany (2000).
- [20] P.E. Blöchl, O. Jepsen, O.K. Andersen, *Phys. Rev. B* 49 (1994) 16223-16233.
- [21] G. Kreiner, S. Spiekermann, *J. Alloys Compd.* 261 (1997) 62-82.
- [22] C. Ravi, C. Wolverton, *Acta Mater.* 52 (2004) 4213-4227.
- [23] C. Kranenberg, D. Johrendt, A. Mewis, *Solid State Sci.* 4 (2002) 261-265.
- [24] H. Perltz, A. Westgren, *Arkiv för kemi, Mineralogi, och, Geologi, B.* 15(1) (1942) 1-8.
- [25] a) P. Ravindran, R. Asokamani, *Bull. Mater. Sci.* 20 (1997) 613-622. b) J. Dshemuchadse, D. Y. Jung, W. Steurer, *Acta Crystallogr, Sect. B* B67 (2011) 269-292.
- [26] M.D.H. Lay, A.J. Hill, P.G. Saksida, M.A. Gibson, T.J. Bastow, *Acta Mater.* 60 (2012) 79-88.
- [27] R. T. Macaluso, M. Shatruk, P. Chai, H. Hong, C. Wangeline, K. Ryan, P. Holton, J. Allaz, G. Morrison, B. Fulfer, F. Fronczek, J.Y. Chan, *J. Alloys. Compds.* 600 (2014) 193-198.
- [28] G. R. Stewart, *Rev. Mod. Phys.* 73 (2001) 797-855.

Table 1. Crystallographic data and collection parameters for RFe₂Mg_xAl_{8-x} (R = La-Nd and Sm)

	LaFe ₂ Al ₈	LaFe ₂ Mg _x Al _{8-x}	CeFe ₂ Mg _x Al _{8-x}	PrFe ₂ Mg _x Al _{8-x}	NdFe ₂ Mg _x Al _{8-x}	SmFe ₂ Mg _x Al _{8-x}
Crystal system	Orthorhombic					
Space group	<i>Pbam</i>					
Cell parameters, Å	<i>a</i> = 12.557(3)	<i>a</i> = 12.6060(6)	<i>a</i> = 12.5468(15)	<i>a</i> = 12.5309(8)	<i>a</i> = 12.5224(17)	<i>a</i> = 12.4860(8)
	<i>b</i> = 14.427 (4)	<i>b</i> = 14.4369(7)	<i>b</i> = 14.4221(17)	<i>b</i> = 14.3804(9)	<i>b</i> = 14.4173(19)	<i>b</i> = 14.3996(9)
	<i>c</i> = 4.0708(10)	<i>c</i> = 4.0653(2)	<i>c</i> = 4.0551(5)	<i>c</i> = 4.0430(2)	<i>c</i> = 4.0381(6)	<i>c</i> = 4.0202(3)
<i>V</i> , Å ³	737.5(3)	739.85(6)	733.78(15)	728.55(7)	729.04(18)	722.81(8)
<i>Z</i>	4					
Calc. Density (g/cm ³)	4.201	4.164	4.209	4.247	4.274	4.367
2Theta (max)	56.79	56.56	56.30	56.41	56.44	56.39
Radiation	Mo Kα					
Temperature (K)	290					
Reflections	8073	7994	7840	7839	7478	7774
Unique data/parameters	1012/70	1006/70	996/70	987/70	995/71	974/70
Mu (mm ⁻¹)	10.42	10.35	10.82	11.34	11.77	12.81
R(int)	0.0371	0.0283	0.0237	0.0241	0.0326	0.0214
R ₁ /wR ₂ ^a (I>2(I))	0.0192/0.0351	0.0152/0.0334	0.0149/0.0339	0.0130/0.0260	0.0192/0.0563	0.0123/ 0.0249
R ₁ /wR ₂ (all data)	0.0271/0.0371	0.0180/0.0344	0.0159/0.0343	0.0164/0.0269	0.0216/0.0572	0.0153/0.0257
Largest diff peak and hole (e·Å ⁻³)	0.682/-0.807	0.781/-0.489	0.734/-0.619	0.417/ -0.567	1.237/-1.761	0.533/ -0.559

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

Table 2. Atom positions and isotropic thermal parameters for $\text{LaFe}_2\text{Mg}_x\text{Al}_{8-x}$.

	Wyckoff Site	x	y	z	U_{eq}^{a}
La1	$4g$	0.33957(1)	0.31876(1)	0	0.00970(7)
Fe1	$4g$	0.14643(3)	0.09899(3)	0	0.0090(1)
Fe2	$4g$	0.03343(3)	0.40942(3)	0	0.0104(1)
Al1	$2d$	0	0.5	0.5	0.0082(3)
Al2	$4h$	0.33274(7)	0.49374(6)	0.5	0.0097(2)
Al3	$2a$	0	0	0	0.0093(3)
Al4	$4h$	0.02555(7)	0.13241(6)	0.5	0.0084(2)
Al5	$4h$	0.15795(7)	0.38047(7)	0.5	0.0094(2)
Al6	$4g$	0.09290(7)	0.25459(6)	0	0.0090(2)
Al7	$4h$	0.23285(7)	0.17219(6)	0.5	0.0099(2)
Al8	$4h$	0.45152(7)	0.17862(6)	0.5	0.0096(2)
Mg9/Al9	$4g$	0.33412(8)	0.04676(7)	0	0.0074(2)

^a U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Bond lengths in $\text{LaFe}_2\text{Mg}_x\text{Al}_{8-x}$ and LaFe_2Al_8 .

Bond	Bond length (Å)	
	$\text{LaFe}_2\text{Mg}_x\text{Al}_{8-x}$	LaFe_2Al_8
La(1) - Al(2) $\times 2$	3.2436(7)	3.237(1)
La(1) - Al(3)	3.3071(2)	3.2992(6)
La(1) - Al(4) $\times 2$	3.1820(7)	3.180(1)
La(1) - Al(5) $\times 2$	3.1887(7)	3.180(1)
La(1) - Al(6)	3.2446 (9)	3.230(1)
La(1) - Al(7) $\times 2$	3.2279(7)	3.224(1)
La(1) - Al(8) $\times 2$	3.1963(7)	3.192(1)
Fe(1) - Al(2) $\times 2$	3.5514(6)	2.552(1)
Fe(1) - Al(3)	2.3345(4)	2.3382(7)
Fe(1) - Al(4) $\times 2$	2.5858(6)	2.594(1)
Fe(1) - Al(6)	2.3454(9)	2.348(1)
Fe(1) - Al(7) $\times 2$	2.5367(6)	2.5373(9)
Fe(1) - Mg(9)/Al(9)	2.483(1)	2.467(1)
Fe(2) - Fe(2)	2.7478(9)	2.776(1)
Fe(2) - Al(1) $\times 2$	2.4534(3)	2.4636(6)
Fe(2) - Al(5) $\times 2$	2.6019(6)	2.600(1)
Fe(2) - Al(6)	2.3577(9)	2.351(1)
Fe(2) - Al(8) $\times 2$	2.6102(6)	2.6059(9)
Fe(2) - Mg(9)/Al(9) $\times 2$	2.591(1)/2.592(1)	2.579(1)/2.580(1)
Mg(9)/Al(9) - Al(1) $\times 2$	2.9933(7)	2.978(1)
Mg(9)/Al(9) - Al(2) $\times 2$	3.023(1)	3.023(1)
Mg(9)/Al(9) - Al(5) $\times 2$	3.147(1)	3.149(1)
Mg(9)/Al(9) - Al(7) $\times 2$	3.007(1)	3.005(1)
Mg(9)/Al(9) - Al(8)	3.154(1)	3.158(1)

Table 4. Magnetic and electrical data for $\text{RFe}_2\text{Mg}_x\text{Al}_{8-x}$ ($\text{R} = \text{La-Nd}$ or Sm)

	$\text{LaFe}_2\text{Mg}_x\text{Al}_{8-x}$	$\text{CeFe}_2\text{Mg}_x\text{Al}_{8-x}$	$\text{PrFe}_2\text{Mg}_x\text{Al}_{8-x}$	$\text{NdFe}_2\text{Mg}_x\text{Al}_{8-x}$	$\text{SmFe}_2\text{Mg}_x\text{Al}_{8-x}$
Magnetic moment, μ_B per R^{3+} ion	N/A	2.4	3.7	3.5	N/A
Weiss Constant, K	N/A	-155	44	47	N/A
Néel temperature, K	N/A	N/A	2.8	7.8	12
Resistivity at 293 K, $\times 10^{-4} \Omega \cdot \text{cm}$	1.09	2.75	5.54	2.02	4.08
Residual resistivity ratio, (RRR)	1.6	1.3	1.4	2.2	1.7

Figure Captions.

Figure 1. SEM image of a single crystal of $\text{NdFe}_2\text{Mg}_x\text{Al}_{8-x}$

Figure 2. Structure of $\text{RFe}_2\text{Mg}_x\text{Al}_{8-x}$ ($\text{R} = \text{La-Nd}$ or Sm) a) viewed down the c -axis and b) viewed down the b -axis. Rare earth, magnesium and aluminum atoms are purple, green and cyan respectively. Iron coordination polyhedra shown in red.

Figure 3. Coordination environments of a) rare earth atoms and b) the mixed Mg/Al site in the $\text{RFe}_2\text{Mg}_x\text{Al}_{8-x}$ ($\text{R} = \text{La-Nd}$ or Sm) structure.

Figure 4. Total and partial density of states of $\text{LaFe}_2\text{MgAl}_7$ and LaFe_2Al_8 . The Fermi level is set at 0 eV; dashed line highlights the pseudogap energy.

Figure 5. Temperature dependence of magnetic susceptibilities of (a) $\text{CeFe}_2\text{Mg}_x\text{Al}_{8-x}$, (b) $\text{PrFe}_2\text{Mg}_x\text{Al}_{8-x}$, (c) $\text{NdFe}_2\text{Mg}_x\text{Al}_{8-x}$ and (d) $\text{SmFe}_2\text{Mg}_x\text{Al}_{8-x}$. Filled symbols are susceptibility data and empty symbols are inverse susceptibility data.

Figure 6. Field dependence of magnetization for $\text{RFe}_2\text{Mg}_x\text{Al}_{8-x}$ ($\text{R} = \text{Ce, Pr, Nd}$ or Sm) at 1.8 K.

Figure 7. Temperature dependence of electrical resistivity for $\text{RFe}_2\text{Mg}_x\text{Al}_{8-x}$ ($\text{R} = \text{La-Nd, Sm}$)

Figure 1

Figure 2

Figure 3

(a)

(b)

Figure 4

Figure 5

Figure 6

Figure 7