Effects of Structural Defects and Inhomogeneities on Magnetism

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OUTPUT SUMMARY – FY2003-2005

Invited Conference Presentations 5
Other Invited Presentations 9
Contributed Presentations 23
Journal Papers 60
Conference Papers 4

ABSTRACT AND BACKGROUND
Research efforts in the Magnetism focus area are directed toward understanding the interplay between competing energy contributions in determining critical magnetic phenomena. The main goal of the research efforts is to advance current understanding of magnetic interactions on the nano- and meso-scale by experimentally and theoretically investigating novel magnetic compounds that contain well-defined clusters of lanthanide atoms. In addition to advancing fundamental understanding in the magnetism area, such a goal meets the need for understanding the intrinsic interactions affecting magnetic properties at length scales ranging from 0.1 to 10^3 nm. The experimental systems in this research effort are chosen so that the geometry, and therefore properties, of the clusters of atoms and their interactions may be systematically varied and precisely and reproducibly controlled in such a manner that allows for detailed comparison with both first principles calculations and micro-magnetic models.

The ideal system for testing and refinement of theoretical models is a regular array of mono-sized magnetic nano-grains, or on the smallest scale magnetic clusters, located on a simple lattice and separated by a uniform non-magnetic grain-boundary phase. For many years, crystallographers have investigated rare-earth-
based intermetallic compounds. In a significant number of these materials there exist isolated or semi-isolated structures composed of magnetic rare-earth ions in a non-magnetic matrix. These stable crystalline structures contain periodic arrays of identical magnetic atomic configurations. Thus, not only are exchange interactions between magnetic rare-earth ions in the clusters well defined, but so are the interactions between the clusters. These materials have the potential to serve as model systems for understanding the interactions among nano-scaled magnetic clusters. While their crystal structures have been tentatively established, precise determination of the structures and the physical properties of the majority of the compounds have not been investigated nor have they been modeled. Since the systems of interest are metallic, the magnetic exchange interactions are expected to be relatively strong compared with non-metallic materials, and to have a strong dependence on temperature. In some instances, series of compounds of varying composition but closely related crystal structures exist and these are useful for conducting fundamental studies of the relationship between structure and magnetic properties. In these series, the geometry of a magnetic cluster, or equivalently, the geometry of a magnetic sub-cell, changes systematically with composition. This allows the study of the dependence of various magnetic properties such as exchange coupling, Curie temperature, anisotropy, thermal expansion and magnetostriction on crystallographic structure of the material, and in particular the magnetic sub-unit cell size.

One such series of intermetallic compounds consists of the R \((n+2)(n+1)Ni\((n-1)+2Si\(n+1) phases. The values of n for which the phases exist are dependent on R. For R = La and Ce, phases exist at n = 2, 3, 4, and 5; whereas, phases exist at n = 2, 3, and 4 for R=Pr and only at n = 2 for R=Nd. An extensive investigation of this series is currently in progress.

**TECHNICAL HIGHLIGHTS**

- The existence and stoichiometry of the members of the R \((n+2)(n+1)Ni\((n-1)+2Si\(n+1) series as a function of R have been determined. Contrary to reported results none of the compounds exhibit detectable ranges of solid solution and in several instances the actual composition lies outside of the reported range. Precise phase compositions have been determined.

- In order to prepare high purity polycrystalline and single crystal samples of R \((n+2)(n+1)Ni\((n-1)+2Si\(n+1), the Pr-rich part of the Pr-Ni-Si phase diagram has been evaluated using both experimental results and thermodynamic calculations. The primary solidification region for each of the phases has been determined. Significant changes to the binary Pr-Ni phase diagram have been documented. The existence of two congruently melting phases, which under normal conditions do not solidify as a single phase due to kinetic considerations, has been documented.

- Single crystals of R \((n+2)(n+1)Ni\((n-1)+2Si\(n+1) have been prepared for La, Ce and Pr with n = 2, 3 and 4. Single crystals with R = (La\(_{1-x}\)Pr\(_x\)) with n = 2 and x = 0 to 1 have been prepared in order to investigate the Pr crystal field splitting. Single crystals of neighboring compounds of interest have also been prepared.

- Magnetization, specific heat, and thermal expansion measurements reveal that the Pr compounds order magnetically at temperatures more than an order of magnitude higher than neighboring compounds with very similar compositions. There is a large dependence of the magnetic ordering temperature on n with the existence of large magnetocrystalline anisotropy in both the paramagnetic and ordered states. Ni carries no magnetic moment in these compounds, however the magnetic ordering temperatures of the n = 2, 3 and 4 Pr compounds are higher than those usually observed for Pr compounds which do not contain magnetic moment bearing Co or Fe.

- All of the Pr compounds exhibit a component of the magnetization perpendicular to the c-axis which orders at a lower temperature than the c axis component and has no net moment in the ordered state.
A spin flop transition is observed for fields applied perpendicular to the c axis. A unified empirical model has been developed for the magnetic ordering of all three Pr compounds based on the systematic behavior of the materials.

DEVELOPING TOPICS
Investigations have been initiated into other systems which are expected to provide a detailed fundamental basis for the models relating microstructure and bulk magnetic properties.

This research includes other compounds in the R-Ni-Si systems with recognizable clusters but in which spatial arrangements of the clusters are quite different from the current system. For example, the compound Pr$_{14}$Ni$_6$Si$_{11}$ has nearest-neighbor rare earth environments similar to the R$^{(n+1)(n+2)}$Nin$_{(n-1)}$Si$_{(n+1)}$ phases, yet the trigonal-prismatic assemblies of the rare earth atoms in the Pr$_{14}$Ni$_6$Si$_{11}$ material are no longer uniaxial.

The magnetic properties of this intermetallic compound are much different from the R$^{(n+1)(n+2)}$Nin$_{(n-1)}$Si$_{(n+1)}$ compounds, as indicated by preliminary bulk measurements. Another example includes an extended homologous series of intermetallic compounds, which are built as distinctly different but closely related one-, two-, or three-dimensional arrangements of filled trigonal prisms and half-octahedra, both containing rare earth atoms in the vertices of these polyhedra.

- Pr$_{1.5}$Ni$_{1+x}$Si$_{3-x}$ where -0.2 < x < 0.4 is a solid solution with the AlB$_2$ structure which corresponds to an infinite assembly of the same trigonal cells which make up the trigonal prisms in R$_{(n+2)(n+1)}$Nin$_{(n-1)}$Si$_{(n+1)}$. However the Curie temperature within the solid solution ranges from 3 to 5K with discontinuous step at x = 0.0. From careful x-ray diffraction measurements on a single crystal, a 1% superlattice peak at 12° in two theta has been detected in the x = 0.0 material suggesting that crystallographic ordering of the non-magnetic atoms, is responsible for a significant change in Curie temperature. Further experiments as well as Linear Density Approximation with a Hubbard correction for strongly correlated electronic orbitals, LDA+U, calculations are currently being performed.

Preliminary investigations have also looked into an alternative approach to advance current understanding of magnetic interactions on the nano- and meso-scale. These consist of experimentally and theoretically investigating systems where defects may be introduced into single crystals in a systematic way. There have been no complete studies of the introduction of controlled defects into single crystals of rare-earth intermetallic compounds. Systematic studies of the interaction of domain walls with defects in such compounds can be performed and compared with detailed theoretical calculations to examine how atomic, nanoscale and microscale interactions affect their magnetic properties. Controlled defects such as vacancies, impurities, and dislocations may readily be introduced into single crystal by controlled annealing, alloying or deformation.

Since most rare earth intermetallic compounds exhibit negligible ductility, it is normally not possible to introduce a high level of defects by deformation. However, investigations of the RM B2 (CsCl-type) intermetallic compounds at Ames Laboratory has shown that twelve of these phases exhibit unprecedented ductility. Although the magnetic behaviors of most of these phases have been known for many years, no one has examined the compounds from a view point of the influence of defects and chemical inhomogeneities on the magnetic behaviors. Most of the RM B2 phases are stoichiometric, fully-ordered line compounds, so it may be difficult to introduce vacancies and excess substitutional metals into the materials, but one can dope the RM phases with interstitial elements to control defects.

- GdAg is a ductile B2 compound that orders antiferromagnetically at 132 K. A second transition at 100 K, resulting in a ferromagnet moment which is 10$^{-4}$ time the total Gd moments in the system has been observed. Magnetization measurements of a single crystal sample before and after annealing and deformation treatments suggest that this transition is due to the ordering of uncompensated Gd moments at
antiphase boundaries within the crystal. If confirmed this represents a unique possibility to study the magnetism 2-dimensional defect structures. LDA+U band structure calculations support the concept that the interactions at such a boundary should be ferromagnetic.

SELECTED PUBLICATIONS


Stoichiometric Studies on $Pr_{(n+1)(n+2)}Ni_{n(n-1)+2}Si_{n(n+1)}$ Compounds


Scope:

An interesting homologous series of $R_{(n+2)(n+1)}Ni_{n(n-1)+2}Si_{n(n+1)}$ compounds exists for rare earth elements of Ce, La, Nd and Pr, where $n$ is the number of small trigonal cells that fits along the side of the prismatic columns in the crystal structure. Depending on the rare earth element, only certain compounds of the series are stable. For example for Pr-Ni-Si, several compounds, such as $Pr_6Ni_2Si_3$ ($n = 2$), $Pr_5Ni_2Si_3$ ($n = 3$), and $Pr_{15}Ni_7Si_{10}$ ($n = 4$) have been identified within this series. This project is directed towards the determination of actual stoichiometry of $Pr_{(n+1)(n+2)}Ni_{n(n-1)+2}Si_{n(n+1)}$ ($n = 2, 3, 4, 5$) compounds.

Research Highlights:

Annealed alloys of $Pr_6Ni_2Si_3$ ($n = 2$), $Pr_5Ni_2Si_3$ ($n = 3$), $Pr_{15}Ni_7Si_{10}$ ($n = 4$) have been prepared in both polycrystalline and single crystal form. The crystals structures of each of these compounds have been determined by powder and single crystal x-ray diffractometry. The crystal structures are hexagonal, $P6_3/m$, see figure 1 for $Pr_5Ni_2Si_3$ ($n = 3$) where chemical bonding within and between trigonal prismatic columns in a three-dimensional lattice are different and can be controlled by varying material’s chemistry. In all cases, single crystal diffraction data supported by Rietveld refinements indicate that the Ni sites located on the $6\bar{3}$ axes (coordinate triplets are $0,0,z$) are partially occupied, therefore yielding Ni-deficient stoichiometries for each of the compounds. The degree of Ni-deficiency varies systematically with $n$: $Pr_6Ni_{1.75}Si_3$ (12.5% for $n = 2$), $Pr_5Ni_{1.85}Si_3$ (7.5% for $n = 3$) and $Pr_{15}Ni_{6.8}Si_{10}$ (2.9% for $n = 4$). Despite the high accuracy of single crystal data, there remains uncertainty as to the occupation of Ni and Si sites in these compounds. Since complex structures can frequently exhibit both site disorder and partial occupancies, the actual phase compositions can differ considerably from those determined either crystal chemistry or by x-ray analyses. Moreover, any slight deviation from the actual stoichiometry can lead to the appearance of a second and/or even third phase.

Utilizing the revised chemistries determined in this study, attempts to produce single-phase material in well annealed samples still resulted in second and third phase inclusions in the compounds. Therefore, we conducted systematic studies using microstructural analysis by scanning electron microscopy, differential thermal analysis and x-ray and neutron diffraction, to determine the stoichiometry of these series of compounds. We focused on the "$Pr_6Ni_2Si_3$" ($n = 2$) alloy. Using single crystal diffractometry from flux-grown samples, isothermal annealing experiments in which the composition of the alloy was iteratively adjusted closer to the actual composition and quantitative volume fraction analysis of both x-ray and neutron powder diffraction, we were able to confirm that partial Si occupancy of the Ni3 (2a) site is necessary for single phase Pr$_6$Ni$_2$Si$_3$. The actual stoichiometric composition for $n = 2$ alloy in $Pr_{(n+1)(n+2)}Ni_{n(n-1)+2}Si_{n(n+1)}$ series was determined to be Pr$_6$Ni$_{1.6}Si_{3.2}$. 

![Fig. 1 Perspective views of the unit cells of Ce$_6Ni_2Si_3$, Ce$_2NiSi$, and Ce$_{13}Ni_4Si_{13}$ structure types.](image-url)
Impact:
It has been confirmed that partial Si occupancy of the Ni3 (2a) site is necessary for single phase Pr$_n$Ni$_2$Si$_3$. Based on the same site occupancy of Si on the Ni3 site, the stoichiometry of Pr$_5$Ni$_2$Si$_3$ and Pr$_{15}$Ni$_7$Si$_{10}$ compounds were predicted to be of Pr$_{5}$Ni$_{1.85}$Si$_{3.1}$ and Pr$_{15}$Ni$_{6.7}$Si$_{10.2}$, respectively. All alloys contain minimal amounts of second phase compared to ideal stoichiometric compositions from the general formula. For the case of Pr$_{15}$Ni$_{6.7}$Si$_{10.2}$, adjusting the composition to include excess Si has resulted in significant grain growth during long term anneals at 900°C indicating this composition falls well within a single phase region of the phase diagram. The high rates of grain growth have been exploited to synthesize the largest single crystals to date (see Figure 2) of this compound through solid-state techniques.

Future Work:
Large single grains of Pr$_5$Ni$_2$Si$_3$ and Pr$_{9}$Ni$_2$Si$_3$ compounds will be produced by altering the heat treatment process for solid-state grain growth to acquire large single crystals for structural and magnetic property measurement. Further, R$_{(n+2)(n+1)}$Ni$_{n(n-1)+2}$Si$_{(n+1)}$ (R = Ce, La and Nd) series will be investigated to determine if the same systematics for deviation from stoichiometry exist for when other rare-earth metals are substituted for Pr.

Interactions:
This work is in collaboration with the other efforts within the Magnetism focus area.
Thermodynamic Modeling and Flux Growth of Single Crystals of the R-Ni-Si Systems


Scope:
High quality single-phase single crystal/polycrystalline of the series of compounds $R\{n\}(n+1)Ni\{n+2\}Si\{n+1\}$, where R=Pr, or other rare earth metals such as Ce, La, Ni, are needed for the physical properties measurements, and neutron scattering studies to determine the magnetic structures, phonon spectra and crystalline electric field levels. However, due to the lack of detailed phase diagram information, considerable difficulties have been encountered in the preparation of the compounds. Therefore, thermodynamic descriptions for the R(Ce, La, Nd, Pr)-Ni-Si systems are desired by using both experiment and thermodynamic modeling to facilitate the crystal growth by either flux or Bridgman method.

Research Highlights:
The Pr-Ni-Si, Nd-Ni-Si and La-Ni-Si systems have been investigated via experiments and thermodynamic modeling. In the experimental part, alloys for the systems have been prepared and investigated using thermal analysis and scanning electron microscopy. The existence of the reported stoichiometric compounds in the Ni-Pr, Nd-Ni and La-Ni systems has been confirmed. The temperature difference between our studies and the reported results for the La-Ni, Nd-Ni system is not large (20-50 °C). In the Ni-Pr system, however, a significant difference (30-100 °C higher) has been found for both the congruent melting of the compounds and the invariant reactions, especially on the Pr-rich side. For the Pr-Ni-Si and La-Ni-Si systems an isothermal section at 500 °C has been constructed. Polycrystalline single phase Pr$_6$Ni$_2$Si$_3$, Pr$_5$Ni$_2$Si$_3$ and Pr$_{15}$Ni$_7$Si$_{10}$ compounds (“the homologous series of interest”) were obtained by annealing samples of appropriate composition at 900 °C. The experimental phase equilibrium and thermodynamic data in the Ni-Pr, Pr-Si, Nd-Ni and La-Ni systems were analyzed by using thermodynamic models for the Gibbs energies of individual phases. Optimal sets of thermodynamic parameters for three binary systems, Ni-Pr, Pr-Si, Nd-Ni and La-Ni, and the ternary system Pr-Ni-Si, have been obtained. As described below, the knowledge gained from this analysis allowed the preparation of single crystals of all the compounds of interest in the ternary R(La, Pr)-Ni-Si system.

Based on the results of the thermodynamic description of the Pr-Ni-Si system, a liquidus surface has been calculated and the primary solidification regions for Pr$_6$Ni$_2$Si$_3$, Pr$_5$Ni$_2$Si$_3$ and Pr$_{15}$Ni$_7$Si$_{10}$ have been predicted, Figure 1. Isotherms for the compounds Pr$_6$Ni$_2$Si$_3$, Pr$_5$Ni$_2$Si$_3$ and Pr$_{15}$Ni$_7$Si$_{10}$ and compositions in their primary solidification fields that exhibit favorable temperature ranges for crystal growth have been calculated. Flux growth experiments with compositions derived from these isotherms have been performed using sealed Ta crucibles. The samples were cooled...
at a rate of approx. 1-5 °C/hr from temperatures higher than the liquidus down to temperatures higher than the invariant-reactions temperatures. The slow cools were followed by decanting of the residual liquid, yielding single crystals well-separated from the remaining liquid. Single-crystal rods of several cubic mm in size have thus been prepared for the homologous series of interest, Pr$_6$Ni$_2$Si$_3$, Pr$_5$Ni$_2$Si$_3$ and Pr$_{15}$Ni$_7$Si$_{10}$, see Figure 2. Similar success has been attained in the La-Ni-Si using this approach.

As a result of thermal analyses and of the calculations of the liquidus surface, single crystals of other ternary rare earth - transition metal - silicides have been synthesized in addition to the targeted compounds of the homologous series. Experiments to determine physical and magnetic properties of these compounds are ongoing.

**Impact:**

A strong improvement in single crystal synthesis of intermetallic compounds-flux growth method, yielding crystals suitable for studies that require larger single crystals, has been developed through the combination of thermodynamic modeling and thermal analysis. The liquidus surface calculated from the thermodynamic models helps the rapid identifying primary region the compounds of interest. The operating temperature range in flux growth method can be determined by thermal analysis. The flux technique, applicable to a wide variety of materials, provides a quick screening of compounds, often gives uniform stoichiometries and a high degree of structural perfection.

**Future work:**

More detailed phase equilibria studies will be conducted in the Ce-Ni-Si and Nd-Ni-Si system to further refine the primary solidification phase fields of the compound series $R_{(n+1)(n+2)}Ni_{(n+1)}Si_{(n+1)}$. These studies will include reinvestigating the Ce-Ni, Ce-Si and Nd-Si binary systems, and the Ce-Ni-Si and Nd-Ni-Si ternary systems via experiments and thermodynamic modeling. The experimental work will be done using thermal analysis, microstructural characterization and electron microprobe analysis. In addition, isothermal phase equilibria studies will be conducted at selected temperatures to determine exact compositions of single and conjugate phases together with the ranges of solid solutions. Thermodynamic models for Ce-Ni, Ce-Si and Nd-Si binary systems, and Ce-Ni-Si and Nd-Ni-Si ternary systems will be developed and the liquidus surface for the Ce-Ni-Si and Nd-Ni-Si systems will be calculated. The results will be used to optimize alloy composition selection for single crystal synthesis by flux growth techniques as well as identifying other promising synthesis methods for bulk crystal growth. In addition, the physics of nucleation and growth of single crystals during the flux method will be analyzed to optimize process parameters such as cooling rates and cooling profile to optimize yield and maximize size of crystals prepared. We will also broaden the work on phase relations work and on synthesis method development to other compounds in the alloy systems. For example, experiments will carried out to confirm the possibility of partial substitution of the Pr with other rare earths, e.g. Ce, Nd, and La, to grow $(R, R')_{(n+1)(n+2)}Ni_{(n+1)}Si_{(n+1)}$ single crystals/polycrystalline phases.

**Interactions:**

This work is in collaboration with the Magnetism focus group.
Magnetization Studies of Pr\(_{(n+1)(n+2)}\)Ni\(_{n(n-1)+2}\)Si\(_{n(n+1)}\) Single Crystals

**Personnel:** R.W. McCallum, T.A. Lograsso, K.A. Gschneidner, Jr., and V.K. Pecharsky (PI’s MEP); P.C. Canfield and B.N. Harmon (PI’s CMP); Y. Janssen, M. Huang, and Y-B. Lee (Postdocs); and A.O. Tsokol, D. Wu, and K.W. Dennis (Asst. Sci.)

**Scope:**

The homologous series Pr\(_{(n+2)(n+1)}\)Ni\(_{n(n-1)+2}\)Si\(_{n(n+1)}\) consists of three members, Pr\(_6\)Ni\(_2\)Si\(_3\), Pr\(_5\)Ni\(_2\)Si\(_3\), and Pr\(_{15}\)Ni\(_7\)Si\(_{10}\), for \(n = 2, 3,\) and \(4\), and where \(n\) is the number of small trigonal cells that fit along the side of the prismatic columns in the crystal structure. Magnetization measurements of single crystals of the three compounds show a highly anisotropic magnetic behavior that varies systematically as a function of \(n\). Separate ordering temperatures are observed for the components of the magnetization parallel and perpendicular to the crystallographic \(c\)-axis.

**Research Highlights:**

Magnetic properties of single crystals of nominal compositions Pr\(_6\)Ni\(_2\)Si\(_3\) \((n = 2)\), Pr\(_5\)Ni\(_2\)Si\(_3\) \((n = 3)\), Pr\(_{15}\)Ni\(_7\)Si\(_{10}\) \((n = 4)\) have been studied. Between 100 and 400 K, the paramagnetic dc susceptibility, \(\chi\), parallel and perpendicular to the \(c\)-axis is reasonably approximated by a Curie-Weiss law for all three compounds. The paramagnetic moment, determined from the polycrystalline average, is close to the free-ion moment for Pr\(^{3+}\) for all three compounds. This suggests that, in these compounds, Ni does not have a magnetic moment. This is further supported by measurements on single crystals of the La analogs that show a weak, temperature-independent, paramagnetism. In all cases, the Weiss temperature, \(\theta\), proportional to the strength of the magnetic interactions, is higher for \(H \parallel c\) than for \(H \perp c\). For \(H \parallel c\), \(\theta||\) increases with increasing \(n\), while for \(H \perp c\), \(\theta\perp\) decreases with increasing \(n\). All three compounds order magnetically below 100K. For \(H \parallel c\) the compounds show ferromagnetic order and the Curie temperature, \(T_C\), scales with \(n\) (the size of the prismatic column): \(T_C = 46, 55,\) and \(70\) K for \(n = 2, 3,\) and \(4\), respectively. \(T_C\) is in good agreement with \(\theta||\) for the three compounds. For \(H \perp c\), a peak occurs in the low-field magnetization as a function of temperature, at 33, 27, and 11 K for \(n = 2, 3,\) and \(4\), respectively.

The nature of the magnetic order in these materials may be further clarified by studying the magnetization as a function of applied fields at 5 K (Fig 2). For the three compounds, for \(H \parallel c\), the magnetization saturates rapidly and is weakly field dependent, as typical for ferromagnets. As with the Curie temperature, the saturation magnetization (Fig. 3) depends strongly on \(n\). The observed values are much lower, between 25 and 50\%, than the theoretical value of \(gJ = 3.2\mu_B/\text{Pr}\). These reduced values may result from non-collinear magnetic order and/or from a reduced ordered Pr moment due to crystal field splittings. For \(H \perp c\), for all three compounds, when \(H < 2T\), \(dM/dH\) is small. Between 2 T and 3 T, for all three compounds, a metamagnetic transition is observed, while for \(H > 3T\) \(dM/dH\) is also small (Fig.3).

These results (combined with the results of a powder neutron diffraction study on Pr\(_5\)Ni\(_2\)Si\(_3\)) are consistent
with the magnetization process of a conical spiral. This magnetic structure has a ferromagnetic component parallel to the \( c \)-axis, and an antiferromagnetic, helical, component perpendicular to it. The metamagnetic transitions observed for \( H \perp c \) then correspond to the destruction of the helical component: the spins which are partially anti-parallel to the applied field are forced into a parallel orientation. The low values of \( dM/dH \), in fields both above and below this transition, indicate that the ferromagnetic component parallel to the \( c \)-axis is not easily rotated by the perpendicular field.

Within this picture, the peak in the low-field magnetization for \( H \perp c \) corresponds to the ordering temperature of the helical component perpendicular to the \( c \)-axis. The values for the Weiss temperature \( \theta_{\perp} \), are positive rather than negative, as expected for antiferromagnets. This also fits within the picture of the helical component of the magnetic structure, that are generally caused by more than one relevant magnetic interaction. Here, the helix is caused by competing magnetic interactions, of which the strongest are ferromagnetic, resulting in an overall positive interaction parameter and Weiss temperature.

**Impact:**

The highly systematic variation of the magnetic properties of the compounds in the homologous series \( \text{Pr}_{(n+2)(n+1)}\text{Ni}_{(n-1)+2}\text{Si}_{n+1} \) with respect to the size of the trigonal prisms, which are the building block of the structure, shows clear evidence of competing magnetic interactions. This systematic behavior results from the variation of the relative strengths of the competing reactions with the scale of the unit cell. This allows long range interactions to be changed while the nearest neighbor surroundings of the Pr atoms are essentially unchanged.

**Future Work:**

Studies of single crystals of dilute alloys of \( \text{La}_{1-x}\text{Pr}_x\text{Ni}_2\text{Si}_3 \) are being conducted in order to separate the effects of crystal field splitting from those of the magnetic interactions allowing the determination of the crystal field levels. Studies of \( \text{Pr}_2\text{NiSi}_3 \) and \( \text{Pr}_{14}\text{Ni}_6\text{Si}_{11} \) are also being conducted as these materials represent alternative stacking of the trigonal structural components. Both empirical and first principle models are being evaluated to establish a detailed understanding of these interactions.

**Interactions:**

In addition to the members of Magnetism Focus area of MEP, this collaboration includes researchers from Condensed Mater Physics. The neutron diffraction experiments are being conducted in collaboration with Dr. Anna Llobet Megias of the Lujan Neutron Scattering Center, LANL.
Thermal Expansion and Magnetostriction in $\text{Pr}_{(n+2)(n+1)}\text{Ni}_{(n+1)}\text{Si}_{(n+1)}$ Compounds

Personnel: D.C. Jiles (PI), J.E. Snyder (PI), R.W. McCallum (PI), and T.A. Lograsso (PI)

Scope:

The principal aim of this effort is to determine by a systematic investigation the thermoelastic and magneto-elastic properties of the homologous series of $\text{Pr}_{(n+2)(n+1)}\text{Ni}_{(n+1)}\text{Si}_{(n+1)}$ compounds. This effort is in close collaboration with the phase stability, structural, magnetization, heat capacity, and neutron diffraction investigations within the Magnetism focus area. Measurements have been performed on both polycrystalline and single crystal samples. Phonon and magnetic contributions to the total thermal expansion have been separated through the use of the Debye-Gruneisen model. Two magnetic phase transitions have been identified from the anomalous behavior of the magnetic contribution to the thermal expansion. In order to gain further insight, theoretical calculations of the expected variation of magnetization with temperature were performed using a “nearest neighbor” exchange interaction model. The strength of the exchange interactions varies with location of the Pr atom in the unit cell and the number of exchange interactions varies systematically with chemical composition. A variety of magnetic behaviors and transition temperatures are expected based on these theoretical calculations. The theoretical and experimental investigations of the variation of magnetic phase transitions with composition in this alloy system may provide a model system for understanding magnetic properties of more complicated structures.

Research Highlights:

In order to identify the location of magnetic phase transitions for polycrystalline samples of $\text{Pr}_5\text{Ni}_2\text{Si}_3$ and $\text{Pr}_{15}\text{Ni}_7\text{Si}_{10}$, theoretical calculations based on the Debye-Gruneisen model were used to separate the phonon and magnetic contributions to the experimentally determined thermal expansion. The results indicate two magnetic transitions in each compound, one corresponding to the onset of ferromagnetic order and the other at a lower temperature exhibiting characteristics of a spin reorientation transition. From the thermal expansion measurements of $\text{Pr}_5\text{Ni}_2\text{Si}_3$ single crystal (Fig. 1), a temperature-dependent anisotropy in thermal expansion was observed in the temperature range below the Curie temperature. This is due to the negative and positive magnetic contributions to the thermal expansion along the directions parallel and perpendicular to the $c$-axis, respectively. In addition, evidence of the second transition appeared only in the results measured perpendicular to the $c$-axis. This is supported by the neutron diffraction results from Los Alamos National Laboratory, which indicate that the low temperature transition appears to be related to ordering of the magnetization components in the direction perpendicular to the $c$-axis.

Magnetostriction measurements of a $\text{Pr}_5\text{Ni}_2\text{Si}_3$ single crystal measured with $H_{\text{applied}} \parallel c$-axis [Fig. 2(a)] and $H_{\text{applied}} \perp c$-axis [Fig. 2(b)] with the strain measured along the applied field direction clearly document the anisotropic behavior. The magnetostriction for $H \parallel c$ shows no hysteresis and negative values for all temperatures. However, the magnetostriction for $H \perp c$ shows a

![Fig. 1](image-url) Variation of the magnetic contribution to thermal expansion of single crystal $\text{Pr}_5\text{Ni}_2\text{Si}_3$ with temperature measured parallel and perpendicular to $c$ axis under zero magnetic field.
mixture of negative and positive values varying with applied field. Hysteresis and an inflection point (peak in $d\lambda/dH$) are observed for lower temperatures (below 30 K) but not at higher temperatures (in between the two transition temperatures), consistent with results for polycrystalline samples. Interpretation of all the complex features of the single crystal magnetostriction results is currently in progress.

Based on the experimental results, the expected variation of magnetization with temperature for $\text{Pr}_2\text{Ni}_2\text{Si}_3$ single crystal was modeled using a nearest neighbor exchange interaction approximation. The mean field acting on each atomic site was calculated based on the exchange energy that was obtained from the experimentally measured Curie temperature ($T_c$). From this, the expected $M$ vs. $T$ curves for each Pr site were calculated using the Brillouin function, as well as the average $M$ vs. $T$ curve for the whole triangular array. The results indicate that the $M$ vs. $T$ curve for the corner atoms exhibited very different behavior from that of the other types of Pr atoms on the center or edge sites. This is considered to be the cause of the second magnetic phase transition observed at the lower temperature. More precise calculations are being performed in which the exchange interactions vary from site to site in the unit cell.

Fig. 2 Magnetostriction of single crystal $\text{Pr}_2\text{Ni}_2\text{Si}_3$ samples measured (a) parallel and (b) perpendicular to c axis at different temperatures.

Impact:
Thermal expansion and magnetostriction measurements show good agreement with the magnetization, heat capacity, and neutron diffraction investigations of the $\text{Pr}_2\text{Ni}_2\text{Si}_3$ and $\text{Pr}_2\text{Ni}_2\text{Si}_{10}$ members of the $\text{Pr}_{(n+2)(n+1)}\text{Ni}_{n(n-1)+2}\text{Si}_{n(n+1)}$ homologous series. Theoretical calculations show that the Curie temperature and other magnetic transition temperatures can be understood in terms of the variety of exchange interactions in the unit cell.

Future Work:
Further analysis will be undertaken of single crystal magnetostriction measurements to extract hexagonal magnetostriction constants. Single crystal thermal expansion and magnetostriction measurements for $\text{Pr}_2\text{Ni}_2\text{Si}_3$ ($n=2$) and $\text{Pr}_2\text{Ni}_2\text{Si}_{10}$ ($n=4$), will be performed in order to compare systematic variation among the different members of the $\text{Pr}_{(n+2)(n+1)}\text{Ni}_{n(n-1)+2}\text{Si}_{n(n+1)}$ homologous series. Most importantly thermal expansion measurements of the non-magnetic analogs $\text{La}_{(n+2)(n+1)}\text{Ni}_{n(n-1)+2}\text{Si}_{n(n+1)}$, will be performed in order to compare the theoretical calculation of phonon contribution to thermal expansion with experimental measurements where there is no ferromagnetic contribution.

Interactions:
Research has been performed in close collaboration with Ames Laboratory investigators involved in sample fabrication, thermodynamic, structural, magnetization, and heat capacity investigations, and with the neutron diffraction investigations performed at Los Alamos National Laboratory.
Theory/Computation in support of $\Pr_{(n+1)(n+2)}\text{Ni}_{n(n-1)+2}\text{Si}_{n(n+1)}$ Studies

Personnel: B.N. Harmon (PI CMP), R.W. McCallum (PI), and Y-B. Lee (Postdoc)

Scope:
With typically large magnetic single ion anisotropy, rare earth elements are often key components of hard permanent magnets. The strongly correlated 4f electrons and their often non-collinear ordering in complex crystal structures present challenging problems for detailed, accurate calculations. Yet the development of new magnetic materials, particularly with structure and functionality at the nano-scale, has placed a high premium on understanding how rare earth elements “work” in complex structures. The physics of rare earth 4f moments subject to strong crystal fields and coupled to each other via the conduction electrons is not new. The difficulty has been calculations precise enough that theory and experiment can engage in the reliable design and analysis of nano-scale magnetic components. Modern computational capabilities have advanced (by a six orders of magnitude in the last 20 years) to such an extent that a concerted effort to develop and apply modern techniques toward complex materials containing rare earth elements is timely. The goal of this theory/computational project is to initiate such an effort. The homologous series $\Pr_{(n+1)(n+2)}\text{Ni}_{n(n-1)+2}\text{Si}_{n(n+1)}$ is a prototype system with Pr atoms residing in a variety of crystal sites. As describe earlier, the Pr atoms form vertical prisms of various sizes, and can be considered as nano-scale components in a larger crystal. The big advantage is that these nano-components order, and can be studied by highly precise x-ray and neutron scattering techniques. Likewise the periodicity of the single crystal allows the use of highly precise electronic structure techniques, although, with the very large number of atoms per unit cell, the calculations are anything but routine.

Research Highlights:
This is a relatively new project (last six months), so that only a number of calculations and analyses have been completed. We use the full potential linear augmented plane wave (LAPW) method, modified by the addition of a Hubbard like Coulomb parameter to account for the strong correlation of the localized 4f electrons on the rare earth atoms. This is the so-called LDA+U method, which has been shown to greatly improve the calculated electronic structure for many rare earth containing compounds (see *Electronic Structure and Magneto Optical Properties of Solids*, V. Antonov, B.N. Harmon, and A. Yaresko. Kluwer Academic Press, 2004). The first calculation was for $\Pr_5\text{Ni}_2\text{Si}_5$. This material has 20 Pr atoms per unit cell, with four different Pr sites. Some of the early experimental data is presented in neighboring sections of this document, as are details and pictures of the crystal structure. The initial calculations were for ferromagnetic order. Each of the 4f spin moments on the Pr are aligned parallel, and the electronic structure iterated to self-consistency. The goal here is to check how strongly the Pr 5d electrons respond to the local 4f spins. Surprisingly, there is a large difference in the local 5d moments (0.1983, 0.1457, 0.1520, and 0.0776 for Pr1, Pr2, Pr3, and Pr4 respectively.) The key to understanding these 5d-moment values is the respective site-projected 5d density of states (DOS) near the Fermi level. The situation for Pr1 is shown in figure 1 below. The paramagnetic DOS (obtained with no net spin on the 4f electrons) has a large peak at the Fermi level (spin up DOS = spin down DOS). When the two 4f electrons have their spin aligned, the exchange interaction causes the 5d spin up and spin down bands to split, and this yields a relatively large 5d moment and a lower DOS at the Fermi energy for the spin aligned state. For Pr4 the 5d bands are broader and the paramagnetic DOS at $E_F$ is considerably smaller.
Experimentally, the Pr moments are not aligned, but rather form a complex magnetic arrangement, with only components of the 4f and 5d spin along the crystallographic c-axis. Calculations with non-collinear magnetic moment arrangements are planned, but first we wanted to determine if there was any nesting of the Fermi surface, which might suggest the periodicity of the moment arrangement. $\chi(q)$ calculations yield a peak in q-space at the spanning wavevector for any nesting, and if the nesting is strong, the wavevectors at the peaks in $\chi(q)$ are candidates for the new periodicity of the magnetic moments, which need not be commensurate with the underlying crystal lattice. The results of such calculations are shown in Fig.2 right.

**Impact:**
The nesting peaks provide neutron scattering experiments the regions in q-space to look for new peaks caused the magnetic ordering. The preliminary calculations indicate large differences in the 5d electronic structure at different Pr sites, helping to account for the unusually rich results obtained experimentally.

**Future Work:**
Calculations for crystal field effects and non-collinear order are planned, as are continuing calculations in support of the experimental effort.

**Interactions:**
This effort is a collaboration between researchers from Condensed Mater Physics and members of Magnetism focus area of MEP.
Magnetic Interactions in Pr\(_{(n+1)(n+2)}\)Ni\(_{n(n-1)+2}\)Si\(_{n(n+1)}\)

Personnel: R.W. McCallum, T.A. Lograsso, K.A. Gschneidner, Jr., and V.K. Pecharsky (PI’s MEP); P.C. Canfield and B.N. Harmon (PI’s CMP); Y. Janssen and Y-B. Lee (Postdocs); A.O. Tsokol, D. Wu, and K.W. Dennis (Asst. Sci.); and A. Llobet Megias (PI LANL)

Scope:

The homologous series Pr\(_{(n+2)(n+1)}\)Ni\(_{n(n-1)+2}\)Si\(_{n(n+1)}\) consists of three members, with \(n\)=2, 3, and 4, where \(n\) is the number of small trigonal cells that fit along the side of the prismatic columns in the crystal structure. Both single phase and single crystal samples of the three compounds have been prepared and DC magnetization, specific heat, thermal expansion, and magnetostriction measurements have been performed. The highly anisotropic properties of the three compounds vary systematically with \(n\). Initial neutron diffraction measurements and Linear Density Approximation with a Hubbard correction for strongly correlated electronic orbitals, LDA+U, calculations provide insight into the nature of the magnetic interactions and the resulting order.

Research Highlights:

Magnetization and specific heat measurements of samples with nominal compositions Pr\(_3\)Ni\(_2\)Si\(_3\) (\(n\)= 2), Pr\(_3\)Ni\(_2\)Si\(_3\) (\(n\)= 3), and Pr\(_{15}\)Ni\(_7\)Si\(_{10}\) (\(n\)= 4) show that the main ordering of these materials is ferromagnetic with the moments ordered along the crystallographic c-axis. The respective ordering temperatures of 39, 48 and 64 K, determined by specific heat, are in excellent agreement with those determined by Arrott plots from the magnetization. Moreover, a clear Invar effect is seen in the thermal expansion at the corresponding temperatures. Magnetization measurements with H\(\perp\)c indicate that there is a component of the magnetization perpendicular to c ordering at a temperature below the main ordering event. This ordering, which is accompanied by a weak anomaly in the specific heat, appears antiferromagnetic, resulting in zero net moment perpendicular to c. Application of a 3 T field perpendicular to the c-axis results in an apparent spin-flop transition with a field independent moment perpendicular to c for fields >3T.

Preliminary powder neutron diffraction measurements on Pr\(_3\)Ni\(_2\)Si\(_3\) (\(n\)= 3) confirmed the overall ferromagnetic nature of the ordering. The measurements determined the component of the magnetization parallel to the c-axis and indicate that this component is less than the full moment value for Pr of 3.2 \(\mu_B\) for all sites. Moreover, as is clear from the table, the value for the sites at the corners of the prism, Pr1, is only about 25% of the expected value. The total moment along the c-axis is in excellent agreement with that determined from magnetization. The reduced projected moment on the corner sites may be attributed to crystal field splitting and/or to a large component perpendicular to c. The latter case is consistent with the magnetization measurements, in which ordering was observed perpendicular to c. A diffuse peak observed in neutron diffraction measurements below this

<table>
<thead>
<tr>
<th>Site</th>
<th>(\mu_B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pr1</td>
<td>0.75</td>
</tr>
<tr>
<td>Pr2</td>
<td>2.42</td>
</tr>
<tr>
<td>Pr3</td>
<td>2.81</td>
</tr>
<tr>
<td>Pr4</td>
<td>2.24</td>
</tr>
<tr>
<td>Average (Neutrons)</td>
<td>2.01</td>
</tr>
<tr>
<td>Average (Magnetization)</td>
<td>1.98</td>
</tr>
</tbody>
</table>

Unit cell of Pr\(_3\)Ni\(_2\)Si\(_3\) (n=3). The trigonal prisms are shifted with respect to each other by \(\frac{1}{2}\) a unit cell along the c-axis.

Table: c-axis component of the magnetic moments on the various Pr sites from neutron diffraction.
ordering temperature suggests an incommensurate spiral ordering.

From the low-temperature magnetization measurements, this spiral results in a fully compensated moment within the ab plane. The application of a sufficient field in the plane destroys the spiral causing a spin-flop transition with the in-plane component of the magnetization along the field vector. Initial LDA+U band theory calculations for the Pr$_5$Ni$_2$Si$_3$ compound indicate roughly equal moments on all Pr sites. Assuming that the value of the average moment on all Pr sites is constant, the moments on the corner sites must be tilted at approximately 70° with respect to the c-axis. Based on this assumption, the in-plane saturated moment after the spin-flop perpendicular to the c-axis may be calculated. The calculated moment was found to be consistent with the moment measured using DC magnetization.

Assuming the moments in Pr$_6$Ni$_2$Si$_3$ ($n = 2$) and Pr$_{15}$Ni$_7$Si$_{10}$ ($n = 4$) are the same as for corresponding sites in Pr$_5$Ni$_2$Si$_3$ ($n = 3$), and that the moment of the corner sites are tilted at $\sim$ 70° with respect to the c-axis, the low-temperature magnetization may be calculated. For the $n=2$ compound, these assumptions yield excellent agreement with the magnetization measured for H||c. For $n = 4$ the agreement is reasonable. Furthermore, at 5K, the perpendicular component of the magnetization in an applied field after the spin-flop transition is in good agreement with experiment. The similarity of the corner sites for the three structures is supported by the fact that the field at which the transition occurs is similar for all three compounds. On the other hand, the ordering temperatures, both parallel and perpendicular to the c-axis vary systematically with $n$.

In a nearest-neighbor picture three types of sites contribute to the magnetic structure of these compounds. As discussed above, the corner sites, Pr1 in the figure, exhibit a conical spiral structure. The antiferromagnetic interaction required may result from the fact that the Pr-Pr distance between corner sites is less than those in hcp-Pr, which orders antiferromagnetically. The surroundings of the center sites, Pr4, are identical with those in the AlB$_2$ compound Pr$_2$NiSi$_3$. Since Pr$_2$NiSi$_3$ orders at $\sim$5K, it is probable that these sites do not significantly contribute to the high ordering temperature. This leaves the sites on the sides of the prism, Pr2 and Pr3. The number of these sites increases with $n$, as does the ordering temperature, suggesting that these sites play a major role in determining $T_c$. The Pr-Pr nearest neighbor distances for the side sites are larger than that of Pr but smaller than those in the AlB$_2$ structure.

**Impact:**

The complex magnetism exhibited by representatives of the homologous series Pr$_{(n+2)(n+1)}$Ni$_{(n+1)}$Si$_{(n+1)}$ with $n= 2, 3, and 4$, shows a systematic behavior with respect to the size of the trigonal prisms which are the building block of the structure. This systematic behavior provides a new tool by which magnetism is controlled via varying atomic structure rather than via traditional elemental substitutions, and allows for a rigorous test of the theoretical models needed to explain the high ordering temperature and complex magnetic behavior of these materials.

**Future Work:**

In order to determine the exact nature of the magnetic order in the Pr$_{(n+2)(n+1)}$Ni$_{(n+1)}$Si$_{(n+1)}$ series where, $n = 2, 3, and 4$, a set of high quality samples has been prepared for neutron diffraction measurements at LANL. Concurrently, LDA +U band theory calculations are being performed for all members of the series for comparison with the experimental results. Single crystals of R$_{(n+2)(n+1)}$Ni$_{(n+1)}$Si$_{(n+1)}$ with R = La and Ce and $n = 2, 3 and 4$ have been prepared for comparison with the Pr series. For Nd, only the $n=2$ compound exists and it is being investigated.

**Interactions:**

This collaboration includes researchers from Condensed Matter Physics. The neutron diffraction experiments are being conducted in collaboration with Dr. Anna Llobet Megias of the Lujan Neutron Scattering Center, LANL.