Examination of magnetic phase transition in $Pr[(n+2)(n+1)]Ni[n(n-1)+2]Si[n(n+1)]$ compounds using thermal expansion and magnetostriction

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Examination of magnetic phase transition in $Pr_{(n+2)(n+1)}Ni_{n(n-1)+2}Si_{n(n+1)}$ compounds using thermal expansion and magnetostriction

by

Sang-Hoon Song

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

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This is to certify that the master's thesis of

Sang-Hoon Song

has met the thesis requirements of Iowa State University

Signatures have been redacted for privacy
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ABSTRACT

In this study, thermal expansion and magnetostriction of members of a homologous series of compounds based on the alloy series Pr\textsubscript{(n+2)(n+1)}Ni\textsubscript{m(n-1)+2}Si\textsubscript{n(n+1)} has been investigated to study the magnetic phase transitions. In order to identify the location of magnetic phase transitions for polycrystalline samples of Pr\textsubscript{5}Ni\textsubscript{2}Si\textsubscript{3} and Pr\textsubscript{15}Ni\textsubscript{7}Si\textsubscript{10}, theoretical calculations based on Debye-Gruneisen model were used to separate the phonon and magnetic contributions to thermal expansion from experimental results on these materials. The results indicate two magnetic transitions in each compound, one corresponding to the Curie temperature and the other at a lower temperature exhibiting characteristics of a spin reorientation transition. From the thermal expansion measurements of Pr\textsubscript{5}Ni\textsubscript{2}Si\textsubscript{3} single crystal, 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, the characteristics of a spin reorientation transition appeared only in the results measured perpendicular to c axis. Based on the experimental results, the expected variation of magnetization with temperature in Pr\textsubscript{5}Ni\textsubscript{2}Si\textsubscript{3} single crystal was calculated using a nearest neighbor exchange interaction approximation. The results are in good agreement with experimental observations given the simplified nature of the assumptions.
1. INTRODUCTION

The role of bonding interactions among atoms within a crystal structure and that of exchange interactions among magnetic moments within a magnetic structure seem very similar; both serve as a foundation for maintaining each structure. Moreover, the responses to thermal energy also resemble each other. While the bonding and exchange energy tend to cause order of structures, thermal energy disturbs the regularity and causes disorder. Therefore the entropy for each structure varies with the distribution in vibration mode (phonon) and spin wave (magnon). Magnetic materials therefore have these two paradigms in one system. In other words, two kinds of structures can exist within a magnetic solid. These two paradigms within one phase sometimes overlap thus showing very similar phenomena simultaneously, one of which corresponds to dimensional change in solids due to thermal expansion and magnetostriction. More interestingly, both phenomena are closely related with transformation in each structure. In this study, members of a magnetic alloy system Pr-Ni-Si have been investigated using thermal expansion and magnetostriction to study their magnetic transformations.

The ternary Pr-Ni-Si alloy system contains the homologous series Pr_{(n+2)(n+1)}Ni_{n(n-1)+2}Si_{n(n+1)}, where R is a rare earth element, in this case Pr, and provides a range of materials with different structures as described by Rogl [1]. The crystal structures of these compounds are closely interrelated because they form trigonal prismatic columns in which the number of trigonal prisms that form the columns is determined by the value of n in the chemical formula. Each prismatic column contains periodic arrays of magnetic elements, in this case Pr atoms, which are separated by layers of non-magnetic elements. This particular crystal structure,
which can be controlled by adjustments of chemical composition, can serve as a model system from which systematic investigation of magnetic interactions between magnetic clusters as well as magnetic moments within the clusters can be made. The crystal structures of Pr$_3$Ni$_2$Si$_3$ (n=3) and Pr$_{15}$Ni$_7$Si$_{10}$ (n=4) are shown at Fig.1.

An investigation of the properties of polycrystalline samples of the n = 3 alloy has recently been reported by Pecharsky et al. [2]. The magnetization and heat capacity measurements, and calculations of the magnetocaloric effect showed that the material is paramagnetic for temperatures down to about 50 K. At this temperature it undergoes an order-disorder transition and below this temperature it is ferromagnetic. A second magnetic transition was indicated from heat capacity measurements at around 25 K. Fig.2 shows the results of magnetization and heat capacity measurements from the literature.

In this study, the previously reported two kinds of magnetic phase transitions have been examined by using thermal expansion and magnetostriction measurements for polycrystalline samples of Pr$_3$Ni$_2$Si$_3$ and Pr$_{15}$Ni$_7$Si$_{10}$. The results showed two anomalies in behavior for both alloys, one corresponding to the onset of ferromagnetic ordering and the other at lower temperature exhibiting characteristics of a spin reorientation transition which is not clearly understood so far. Each of the anomalies for Pr$_{15}$Ni$_7$Si$_{10}$ compounds are observed at a little higher temperature than Pr$_3$Ni$_2$Si$_3$ compounds and those transition temperatures also varied with the applied magnetic field. In order to identify the location of the transitions more precisely theoretical calculations were used to extract the magnetic contribution from the total thermal expansion based on the Debye-Gruneisen model. The resultant magnetic contribution to thermal expansion showed more distinctive anomalies at
the transition temperatures, which made the comparison in the transition temperatures of the samples between Pr$_3$Ni$_2$Si$_3$ and Pr$_{13}$Ni$_7$Si$_{10}$ more clearly. During the procedure to calculate the phonon effect, the Gruneisen parameters for both compounds were calculated using the phonon contribution to heat capacity and thermal expansion, and the bulk modulus measured from acoustic velocity method. The magnetostriction vs. magnetic field curves for each compound showed some interesting behaviors that is considered to be associated with the second magnetic transition at lower temperature.

Single crystal samples of Pr$_5$Ni$_2$Si$_3$ have recently been fabricated, which enabled us to investigate the anisotropy in thermal expansion and magnetostriction. Since the quantity we measured for polycrystalline samples was the average value over a random distribution of local anisotropies, investigation on single crystal samples was essential to understand its anisotropic property. The measurements have been carried out along the directions parallel and perpendicular to the c axis respectively and the results, as predicted, show anisotropic behaviors below the Curie temperature ($T_c$). Magnetostriction measured perpendicular to c axis shows more complex behavior compared with that measured parallel to c axis. The fundamental reason for the complex behavior in the direction perpendicular to c axis has not been understood clearly.

As a theoretical approach to understand these anisotropic behaviors the variation of magnetization with temperature of the Pr$_5$Ni$_2$Si$_3$ compound was calculated using a nearest neighbor exchange interaction approximation. For this calculation it was assumed that only Pr atoms contribute to the magnetization and exchange interaction exists only between the nearest neighbors of the Pr atoms. The sites occupied by Pr atoms were classified into three types depending on the number of nearest neighbors and the mean field acting on each Pr site.
was calculated based on the average exchange interaction energy, which was calculated from the measured Curie temperature, and the magnetic moments on the Pr atoms. The expected M vs. T curves for each type of Pr atom were calculated using the Brillouin function, as well as the average M vs. T curve for the whole triangular array.

Fig. 1. Crystal structures and unit cells of (a) Pr$_5$Ni$_2$Si$_3$ and (b) Pr$_{15}$Ni$_7$Si$_{10}$ showing the trigonal cells which form prismatic columnar assemblies. The length of the sides of the prismatic columns is determined by the value of n in the chemical formula for the compound in the series.
Fig. 2. Heat capacity (left) and inverse magnetic susceptibility (right) of Pr$_5$Ni$_{1.9}$Si$_3$

(*A. O. Pecharsky et. al. in Physical Review B 68, 134452 (2003)*)
2. THEORETICAL BACKGROUND

2.1. Introduction

As temperature changes, the dimensions of material change. In the case of ferromagnetic materials, there are two kinds of contribution to the total dimensional change: thermal expansion and magnetostriction. The electronic contribution is neglected here since it is usually rather small compared with the other terms. Thermal expansion and magnetostriction both are expressed as linear strains so that the total strain can be described as,

\[ \varepsilon = \frac{\Delta l}{l} = \frac{\Delta l(\text{thermal expansion}) + \Delta l(\text{magnetostriction})}{l} \]

Even though the phenomenological appearance due to each effect looks very similar, however the physical origin for each phenomenon is totally different. In the case of thermal expansion, the lattice vibration is the main cause. Therefore the thermal expansion varies with the change in vibration mode depending on the various conditions in the system like temperature or pressure. On the other hand the magnetostriction has totally different fundamental reason that is related with various magnetic parameters. Just as atoms in a grain in a solid are tied to each other by bonding energy, similarly magnetic moments in a domain of a magnetic material are also bonded with each other by exchange energy. Thermal energy tends to disrupt these exchange interactions among the magnetic moments so that the magnetic structure varies with the temperature, which can be compared with the change in vibration mode in a solid as a response to the thermal energy. Since the magnetostriction is closely associated with the magnetic structure in the material therefore investigation of magnetostriction under various conditions should be a useful method to help understand the
magnetic phase transition in magnetic materials.

2.2. Thermal expansion

The coefficient of linear thermal expansion, \( \alpha_L \), is obtained from a measurement of the length change of the material when its temperature is changed under constant pressure. By definition, it is expressed as

\[
\alpha_L = \frac{1}{l} \frac{\partial l}{\partial T}
\]

where \( l \) is the length of the material.

The fundamental reason for thermal expansion is, in short, due to the anharmonic nature of the interatomic interactions in solids. If the atoms in solids vibrate harmonically the mean positions of the atoms would not change even though temperature changes. Fig. 3 illustrates the variation of the potential energy \( \phi \) with interatomic distance. In this picture, the equilibrium separation \( r + \Delta r \) (where \( \frac{d\phi}{dR} = 0 \)) changes as temperature changes, which is due to the asymmetric shape in potential well with respect to interatomic distance.

![Fig. 3. Variation of the potential energy \( \phi \) with interatomic separation \( R \)]
2.3. Thermodynamic relation

The thermodynamic relationship associated with thermal expansion can be expressed in various ways using Maxwell relations

\[
\left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V, \quad -\left( \frac{\partial S}{\partial P} \right)_T = \left( \frac{\partial V}{\partial T} \right)_P
\]

By definition,

\[
\alpha_L = \frac{1}{3V} \left( \frac{\partial V}{\partial T} \right)_P
\]

and using the Maxwell relations \( \alpha_L \) can be expressed as

\[
\alpha_L = \frac{1}{3V} \left( \frac{\partial V}{\partial T} \right)_P = -\frac{1}{3V} \left( \frac{\partial S}{\partial P} \right)_T = -\frac{1}{3V} \left( \frac{\partial S}{\partial P} \right)_T \left( \frac{\partial V}{\partial P} \right)_T = -\frac{1}{3V} \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V
\]

Since the isothermal bulk modulus \( B \) is

\[
B = -V \left( \frac{\partial P}{\partial V} \right)_T
\]

therefore

\[
\alpha_L = \frac{1}{3B} \left( \frac{\partial P}{\partial T} \right)_V \quad (1)
\]

Since the pressure can be expressed as

\[
P = -\left( \frac{\partial F}{\partial V} \right)_T
\]

where \( F \) is Helmholtz free energy, given by

\[
F = U - TS
\]

Since the entropy \( S \) and internal energy \( U \) are related by
\[
T \left( \frac{\partial S}{\partial T} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V
\]

the pressure can be expressed entirely in terms of the internal energy as follows [3],

\[
P = -\frac{\partial}{\partial V} [U - TS] = -\frac{\partial}{\partial V} [U - T \int_0^T dS - T \int_0^T \frac{\partial}{\partial T} U(T', V)]
\]

where

\[
U = \sum \varepsilon_i n_i
\]

\[
= \sum \left[ \frac{h \nu_i}{k_B T} \right] \exp \left( -\frac{h \nu_i}{k_B T} \right) \approx \sum \left[ \frac{h \nu_i}{k_B T} \exp \left( \frac{h \nu_i}{k_B T} \right) - 1 \right]
\]

In the calculation of summation inside the brackets, Einstein model regarding lattice vibration in solids was used

\[
\varepsilon_{ni} = \frac{1}{2} h \nu + n h \nu
\]

Substituting this into the equation (1), the thermal expansion \( \alpha_L \) can be expressed as

\[
\alpha_L = \frac{1}{3B} \sum_i \frac{\partial^2}{\partial T \partial V} \left[ \frac{h \nu_i}{\exp \left( \frac{h \nu_i}{k_B T} \right) - 1} \right]
\]

The contribution of the mode with frequency \( \nu_i \) to the total specific heat capacity is given by

\[
C^i_v = \frac{\partial}{\partial T} \left[ \frac{h \nu_i}{\exp \left( -\frac{h \nu_i}{k_B T} \right)} \right] \approx \frac{\partial}{\partial T} \left[ \frac{h \nu_i}{\exp \left( \frac{h \nu_i}{k_B T} \right) - 1} \right]
\]
and substituting this into equation (2) results in

$$\alpha_l = \frac{1}{3B} \sum_i - \frac{\partial}{\partial V} C_v^i$$

According to the Gruneisen’s assumption indicating that the fractional change in the frequency of the lattice vibration is proportional to the fractional change in volume, the Gruneisen parameter for the mode with frequency \(v_i\) can be expressed as

$$\gamma^i = \frac{\partial (\log_e v_i)}{\partial (\log_e V)} = -\frac{V}{v_i} \frac{\partial v_i}{\partial V}$$

thus an overall Gruneisen parameter being

$$\gamma = \frac{\sum_i \gamma^i C_v^i}{\sum_i C_v^i}$$

Since the total specific heat capacity is

$$C_v = \frac{1}{V} \sum_i C_v^i$$

therefore using these definitions for \(\gamma\) and \(C_v\), the simple form of Gruneisen function can be obtained

$$\alpha_l = \frac{\gamma C_v}{3B}$$

2.4. Phase transitions

An assembly of atoms or molecules that is homogeneous in chemical composition and physical properties is called as a “phase”. Based on this definition, phase transitions should be accompanied by the change in physical properties like volume, pressure, temperature, energy, and so forth. Phase transitions are classified into first-order and higher
order transitions depending on the existence of singularities in the $n$th-order derivatives of the free energy. In the case of first-order transitions, the transitions can be characterized by discontinuous changes in thermodynamic variables like entropy ($S$) or volume ($V$), which is first derivative of the Gibb’s free energy ($G$)

$$\frac{\partial G}{\partial T} \bigg|_p = -S$$

$$\frac{\partial G}{\partial P} \bigg|_T = -V$$

Rearrangement of these two equations gives the Clausius-Clapeyron relation, given by

$$\frac{dP}{dT} = \frac{\Delta S}{\Delta V} = \frac{\Delta H}{T \Delta V}$$

where $\Delta H$ and $\Delta V$ is the latent heat and volume change involved in the transition respectively. When it comes to second-order transitions, using the same procedure, $dP/dT$ can be expressed with variables which are second-order derivatives of free energy like volume expansion coefficient ($\beta$), specific heat coefficient ($C_p$), and compressibility ($\chi_T$), which is the well known Ehrenfest relation, given by

$$\frac{dP}{dT} = \frac{1}{TV} \frac{\Delta C_p}{\Delta \beta} = \frac{\Delta \beta}{\Delta \chi_T}$$

These different expressions of $dP/dT$ for different order of transition suggest that the existence of latent heat in the transition is a criterion for distinguishing a first order transition from higher order transitions.
2.5. Magnetostriction

Magnetostriction is the change in dimension of a solid, which accompanies change in magnetic structure of the solid. In other words, magnetostriction occurs only when there is a change in magnetic structure in the material. Therefore the magnetostriction is mainly determined by what affects the change in the magnetic structure. Regarding this, magnetostriction can be classified into spontaneous magnetostriction and field induced magnetostriction according to whether the magnetic structure changes spontaneously or is induced by an external magnetic field. This spontaneous magnetostriction can be divided into two groups of magnetostriction due to long-range ordering and that of short-range ordering, depending on the existence of long-range magnetic ordering in the magnetic structure. Though the spontaneous magnetostriction occurs mainly due to the long-range ordering, however, the fact that there exists small amount of magnetostriction due to the short-range ordering even above the ordering temperature should not be ignored. With respect to this close relation between magnetostriction and magnetic structure, the measurements of magnetostriction will give information about magnetic structure of the material.

Magnetostriction is usually expressed as $\lambda$, the fractional change in length

$$\lambda = \frac{\Delta l}{l}$$

in distinction from the mechanical strain $\epsilon$. The maximum magnetostrictive strain that a material can have is called saturation magnetostriction $\lambda_s$ which is the strain relative to the length in demagnetized state measured along the saturated magnetization direction, thus this being an intrinsic property of the material.
The magnetostriction that we measure varies with the measurement angle $\theta$ from the direction of magnetization, which can be described for an isotropic material by the relation

$$\lambda(\theta) = \frac{3}{2} \lambda_s \left( \cos^2 \theta - \frac{1}{3} \right)$$

For the measurement of $\lambda_s$, since it is almost impossible to make the sample to be absolute demagnetized state the magnetostriction with the field parallel to a given direction $\lambda_{//}$, and the magnetostriction with the field perpendicular to the given direction $\lambda_{\perp}$, are measured and the difference is taken.

$$\lambda_{//} = \lambda(0) = \frac{3}{2} \lambda_s \left( \cos^2 0 - \frac{1}{3} \right) = \lambda_s$$

$$\lambda_{\perp} = \lambda(90^\circ) = \frac{3}{2} \lambda_s \left( \cos^2 90^\circ - \frac{1}{3} \right) = \frac{\lambda_s}{2}$$

$$\frac{2}{3} (\lambda_{//} - \lambda_{\perp}) = \frac{3}{2} \left( \lambda_s + \frac{\lambda_s}{2} \right) = \lambda_s$$
3. EXPERIMENTAL METHODS

3.1. Sample preparation

Polycrystalline samples of Pr$_3$Ni$_2$Si$_3$ ($n = 3$) and Pr$_{15}$Ni$_7$Si$_{10}$ ($n = 4$) were prepared by arc melting in an argon atmosphere from high purity components. Pr (99.9+ at. % pure) was prepared by the Materials Preparation Center at Ames Laboratory and had following major impurities (in parts per million atomic): F-222, O-203, Si-120, N-101, Fe-6.8, and Nd-2.2. The other components, Ni (99.88 at. % pure) and Si (99.999 at. % pure), were purchased from commercial vendors. Samples were drop cast after arc melting. The samples were heat treated at different temperatures from 870 K to 1220 K for different periods of time ranging from 5 days to 4 weeks. X-ray powder diffraction analysis of the heat treated samples indicated that, within the sensitivity of the technique, they were single phase alloys.

Synthesis of single crystals of Pr$_3$Ni$_2$Si$_3$ was accomplished using a modified Vertical Gradient Freeze method. Due to the non-congruent melting behavior of the Pr$_3$Ni$_2$Si$_3$ compound, crystals were grown from an alloy of composition Pr$_3$Ni$_{2.5}$Si$_{2.5}$ to avoid the formation of higher melting compounds. Alloys of the appropriate composition were prepared by arc-melting under Ar atmosphere using high purity elements. Crystallographic orientation of the growth direction was determined to be along the c-axis direction using back-reflection Laue methods. Microstructures of the annealed samples were investigated by SEM. Quantitative compositional analysis was done by energy-dispersive spectroscopy (EDS) on JEOL 7830F Auger Microprobe after ion sputtering of the surface and verified the stoichiometry of the compound to be Pr$_5$Ni$_2$Si$_3$. 
3.2. Strain measurements

3.2.1. Introduction

Thermal expansion and magnetostriction have been measured by the strain gauge method. Measurements were carried out under applied magnetic fields of up to $\mu_0 H = 9$ T in the temperature range 5 K - 300 K using a Quantum Design Physical Property Measurement System (PPMS). In the case of polycrystalline samples, measurements were performed in two perpendicular directions of the samples (5 mm cube) separately to examine the effect of texture, from which the isotropy in thermal expansion was confirmed. For the measurements of single crystal samples, strains have been measured parallel and perpendicular to c axis respectively under applied magnetic field along the same direction as strain measured. A “half bridge” configuration was used to compensate for the temperature and field dependence of the strain gauge resistance not caused directly by strain in the sample. The second “dummy” gauge was attached to a copper reference sample, the measured strain being therefore the difference in thermal expansion between the sample and that of copper.

3.2.2. Strain gauges

Fig. 4. shows a schematic for describing strain gauge. The strain gauge is composed of three parts; foil, lead wire/soldering pad, and matrix. In order to increase the sensitivity in variation of resistance with strain the foil is patterned into a folded shape as shown. For measuring the dimensional change in specimen the strain gauge is bonded on the surface of the specimen and the variation of resistance of the foil is measured. The resistance of the gauge changes with strain ($\varepsilon$) according to the relation,

$$F_G = \frac{\Delta R}{\varepsilon}$$
where $F_G$ is the gauge factor of strain gauge and the strain of the foil is assumed to be the same as that of specimen.

An adhesive M-bond 610 was used for bonding the strain gauge on the surface of specimens. Specimens were annealed at 150°C for 1 hour to cure the bond. For the measurement at low temperatures down to 5 K the strain gauges were made of nickel-chromium alloy (similar to Karma). The resistances of the gauge for measuring polycrystalline and single crystal sample were 350 Ω and 120 Ω respectively. The reason for this difference was due to the size of the single crystal samples (typically 2×2×3 mm$^3$) and the availability of suitably small strain gauges.

Fig. 4. Strain gauge dimensions
3.2.3. Wheatstone bridge circuit

Wheatstone bridge circuit is composed of four resistors which are connected to each other as shown in Fig. 5. With the excitation voltage (E) applied, the output voltage (e₀) varies with the relative resistances of four resistors (R₁, R₂, R₃, R₄).

Specifically, output voltage actually depends on the resistance ratios R₁/R₂ and R₄/R₃ as shown below in equation (3);

\[ E_A = E \left( 1 - \frac{R_4}{R_4 + R_3} \right), \quad E_B = E \left( 1 - \frac{R_1}{R_1 + R_2} \right) \]

\[ e_0 = E_A - E_B = E \left( \frac{R_1}{R_1 + R_2} - \frac{R_4}{R_4 + R_3} \right) \]

\[ \frac{e_0}{E} = \left( \frac{R_1/R_2}{R_1/R_2 + 1} - \frac{R_4/R_3}{R_4/R_3 + 1} \right) \] (3)

In case all four resistors have the same resistance (R₁=R₂=R₃=R₄=R), the output voltage must be zero. When the resistance of one of those resistors changes (R+ΔR), then an output voltage is induced;

\[ \frac{e_0}{E} = \frac{1 + \Delta R}{1 + \Delta R + 1} - \frac{1}{2} = \frac{\Delta R}{4 + 2 \Delta R} = \frac{F_G \varepsilon}{4 + 2 F_G \varepsilon} = \frac{F_G \varepsilon}{4 \left( \frac{2}{2 + F_G \varepsilon} \right)} \approx \frac{F_G \varepsilon}{4} \] (4)

\( e_0/E = \text{dimensionless bridge output, mV/V} \)

\( e_0 = \text{output voltage} \)

\( E = \text{excitation voltage} \)

\( F_G = \text{gage factor of strain gage, } F_G = \frac{\Delta R}{\varepsilon} \)

(where \( \varepsilon = \text{strain} \))
Fig. 5. Basic Wheatstone bridge circuit

This indicates that for small changes in resistance the out-of-balance voltage changes linearly with resistance, and by implication therefore changes linearly with strain.

Fig. 6. shows that errors which come from neglecting the term inside the parenthesis in equation (4) are smaller than 0.3 % when the strain is below 3000 ppm and gage factor is 2.05. Therefore, the output voltage is linearly proportional to $\Delta R/R (= F_G \varepsilon)$.

Fig. 6. Variation of $2/(2+F_G \varepsilon)$ with $\varepsilon$. 
3.2.4. Shunt calibration

In order to calibrate resistance to strain ratio, a shunt calibration method was used. Fig. 7. shows schematic diagram for describing the shunt calibration of single active gauge. Calibration resistor \( R_C \) is connected parallel to gauge \( R_G \) to produce an output voltage simulating strain. The resulting resistance in their arm of the bridge is

\[
\frac{1}{R} = \frac{1}{R_G} + \frac{1}{R_C}
\]

\[
R = \frac{R_G R_C}{R_G + R_C}
\]

The change in resistance \( \Delta R \) due to \( R_C \) is

\[
\Delta R = R - R_G = \frac{R_G R_C}{R_G + R_C} - R_G
\]

\[
\frac{\Delta R}{R_G} = \frac{-R_G}{R_G + R_C}
\]

Since the gauge factor \( F_G \) is by definition,

\[
F_G = \frac{\Delta R / R}{\varepsilon}
\]

therefore,

\[
\frac{\Delta R}{R} = F_G \varepsilon
\]

\[
F_G \varepsilon = \frac{-R_G}{R_G + R_C}
\]

\[
\varepsilon = \frac{-R_G}{F_G (R_G + R_C)} \quad (5)
\]
in which $\varepsilon$ is compressive strain (- strain) simulated by shunting $R_G$ with $R_C$.

Calibrating resistance ($R_C$) connected parallel to the resistance ($R_G$) make the whole resistance to be decreased, in which decreasing in resistance corresponds to the shrink in length of sample, negative strain.

Combining equation (4) and (5) results in the relation between output voltage and simulated strain produced by shunting $R_G$ with $R_C$;

$$\varepsilon = \frac{-R_G}{F_G(R_G + R_C)} = \frac{4}{F_G} \cdot \frac{e_0}{E}$$

For measurement of polycrystalline samples, $R_G$ and $R_C$ were 350 $\Omega$ and 174.8 k$\Omega$ respectively, and the gauge factor $F_G$ was 2.05, as a result, the strain ($\varepsilon$) is - 975 ppm;

$$\varepsilon = \frac{-350}{2.05(350 + 174800)} = -9.75 \times 10^{-4} = -975 \text{ ppm}$$

For measurement of single crystal samples, $R_G$ and $R_C$ were 120 $\Omega$ and 174.8 k$\Omega$ respectively, and $F_G$ was 2.08, as a result, the strain ($\varepsilon$) is - 330 ppm;

$$\varepsilon = \frac{-120}{2.08(120 + 174800)} = -3.3 \times 10^{-4} = -330 \text{ ppm}$$

Since the strain ($\varepsilon$) is linearly proportional to output voltage ($e$), the strain ($\varepsilon(T)$) at a given temperature can be evaluated from the measured output voltage ($e(T)$) using the relationship;

$$\varepsilon(T) = e(T) \cdot \frac{975 \text{ ppm}}{e_0}$$

$e_0$ is the output voltage when simulated strain 975 ppm was produced by shunting $R_G$ (174.8 k$\Omega$) with $R_C$ (350 $\Omega$).
Fig. 7. Wheatstone bridge circuit with the shunt calibration of single active gauge
3.2.5. Half bridge configuration

In order to compensate the temperature and field dependence of the stain gauge resistance a half bridge configuration was used. The half bridge configuration is composed of two active gauges bonded on the specimens and the other two fixed resistors within the measuring equipment as shown in Fig. 8.

As mentioned above, general relationship between output voltage and resistance ratio \((R_1/R_2, R_4/R_3)\) in Wheatstone bridge is;

\[
\frac{e_0}{E} = \left( \frac{R_1/R_2}{R_1/R_2 + 1} - \frac{R_4/R_3}{R_4/R_3 + 1} \right)
\]

\(R_1=\)gauge on test material

\(R_2=\)gauge on reference material

\(R_3, R_4=\)resistors inside the strain gauge indicator

Since the resistance of two resistors inside the strain gauge indicator is constant (for simplicity let \(R_3/R_4 = 1\)) the output voltage that we measure (which is linearly proportional to strain) depends only on the resistance ratio \((R_1/R_2)\) of the active gauges;

\[
\frac{e_0}{E} = \left( \frac{R_1/R_2}{R_1/R_2 + 1} - \frac{1}{2} \right)
\]

Fig. 8. Schematic diagram for half bridge configuration
The resistance of strain gauge depends not only on the strain in sample but also on the temperature or applied magnetic field. These extra effects should be excluded or compensated from the measured values. Considering that these other effects exist, the resistance ratio can be described as below;

\[
\frac{R_1}{R_2}(T) = \frac{R_{\text{TEST}} + R_{\text{STRAIN1}}(T) + \alpha}{R_{\text{REFER}} + R_{\text{STRAIN2}}(T) + \beta}
\]

- \( R_{\text{TEST}} = \) resistance of gauge on test material \textit{at initial temperature} \\
- \( R_{\text{REFER}} = \) resistance of gauge on reference material \textit{at initial temperature} \\
- \( R_{\text{STRAIN1}}(T) = \) resistance of gauge on test material due to the strain in test material at \( T \) \\
- \( R_{\text{STRAIN2}}(T) = \) resistance of gauge on reference material due to the strain in reference material at \( T \) \\
- \( \alpha = \) change in resistance of gauge on test material due to the extra effects \\
- \( \beta = \) change in resistance of gauge on reference material due to the extra effects

Assuming \( \alpha = \beta \) and \( R_{\text{TEST}} = R_{\text{REFERENCE}} = R_3 = R_4 = R \), then;

\[
\frac{e_0}{E}(T, \alpha) = \frac{R_1}{R_1 + R_2} - \frac{R_4}{R_4 + R_3} = \frac{R + R_{\text{STRAIN1}}(T) + \alpha}{2R + 2\alpha + R_{\text{STRAIN1}}(T) + R_{\text{STRAIN2}}(T)} - \frac{1}{2}
\]

\[
\frac{e_0}{E}(T, \alpha = 0) = \frac{R + R_{\text{STRAIN1}}(T)}{2R + R_{\text{STRAIN1}}(T) + R_{\text{STRAIN2}}(T)} - \frac{1}{2}
\]

Therefore, the error due to other effects (\( \alpha \)) at half bridge configuration is;
\[
\Delta \frac{e_0}{E} (T) = \frac{e_0}{E} (T, \alpha) - \frac{e_0}{E} (T, \alpha = 0) \\
= \left( \frac{R + R_{\text{STRAIN1}}(T) + \alpha}{2R + R_{\text{STRAIN1}}(T) + R_{\text{STRAIN2}}(T) + 2\alpha} \right) - \left( \frac{R + R_{\text{STRAIN1}}(T)}{2R + R_{\text{STRAIN1}}(T) + R_{\text{STRAIN2}}(T)} \right) \\
= \frac{\alpha (R_{\text{STRAIN2}}(T) - R_{\text{STRAIN1}}(T))}{4R^2} \\
= \frac{\alpha}{4R} \times F_g (\varepsilon_2 - \varepsilon_1) \\
(6)
\]

In the case of a quarter bridge configuration, where only one strain gauge \((R_1)\) is bonded on a test material and the other three resistors \((R_2, R_3, R_4)\) are located inside the measuring equipment so that they all have constant resistance \(R\), the output voltage can be described as follows:

\[
\frac{e_0}{E} (T, \alpha) = \frac{R_1}{R_1 + R} - \frac{R}{R + R} = \frac{R + R_{\text{STRAIN1}}(T) + \alpha}{2R + R_{\text{STRAIN1}}(T) + R_{\text{STRAIN2}}(T)} - \frac{1}{2} \\
\frac{e_0}{E} (T, \alpha = 0) = \frac{R + R_{\text{STRAIN1}}(T)}{2R + R_{\text{STRAIN1}}(T)} - \frac{1}{2}
\]

Therefore, the error due to other effects \((\alpha)\) at quarter bridge configuration is;

\[
\Delta \frac{e_0}{E} (T) = \frac{e_0}{E} (T, \alpha) - \frac{e_0}{E} (T, \alpha = 0) \\
= \left( \frac{R + R_{\text{STRAIN1}}(T) + \alpha}{2R + R_{\text{STRAIN1}}(T) + \alpha} \right) - \left( \frac{R + R_{\text{STRAIN1}}(T)}{2R + R_{\text{STRAIN1}}(T) + R_{\text{STRAIN2}}(T)} \right) \\
= \frac{\alpha R}{(2R + R_{\text{STRAIN1}}(T) + \alpha) (2R + R_{\text{STRAIN1}}(T))} \approx \frac{\alpha R}{4R^2} \\
= \frac{\alpha}{4R} \\
(7)
\]
Equations (6) and (7) show the relative magnitude of error in the half bridge configuration compared to that in quarter bridge configuration. Since the thermal expansion or magnetostriction of the samples used in this research are of the order of ~10^{-3}, then if we use reference materials which show similar strains to the test material (which means small value in “F_0(\varepsilon_2-\varepsilon_1)” at eq. (6)), then the error in half bridge configuration will be at least 10^{-3} times lower than quarter bridge configuration.

3.3. Acoustic velocity measurements

Bulk modulus for polycrystalline samples were determined using acoustic velocity measurements made at 300 K. A Panametrics 5052PR Pulser/Receiver was used to generate and receive the acoustic waves. In order to measure the shear and longitudinal wave velocity, a pair of 1/4" dia 5MHz shear wave contact transducers and a pair of 1/4" dia. 10 MHz longitudinal wave contact transducers were used respectively. The time duration for the acoustic waves to transmit through the samples was calculated using a LeCroy model LT262 350MHz digital storage oscilloscope.

The bulk modulus for the samples were calculated from the measured longitudinal and shear wave velocities using a relation, given by

\[ B = \rho \left( V_L^2 - \frac{4}{3} V_T^2 \right) \]

\( \rho \) = density of the sample

\( V_L \) = longitudinal wave velocity

\( V_T \) = shear wave velocity
4. RESULTS AND DISCUSSION

4.1. Experimental results for polycrystalline Pr$_5$Ni$_2$Si$_3$ and Pr$_{15}$Ni$_7$Si$_{10}$ samples

4.1.1. Thermal expansion

The results of thermal expansion measurements under a zero magnetic field (H = 0) and under a field of $\mu_0 H = 9$ T for polycrystalline Pr$_5$Ni$_2$Si$_3$ and Pr$_{15}$Ni$_7$Si$_{10}$ are shown in Fig. 9. Two kinds of anomalies in thermal expansion were observed around 50 K and 25 K for Pr$_5$Ni$_2$Si$_3$ samples (solid symbols), 65 K and 30 K for Pr$_{15}$Ni$_7$Si$_{10}$ samples (open symbols), which are indicative of magnetic phase transitions. The first derivatives of strain with respect to temperature (Fig. 10.) show the locations of magnetic phase transitions more clearly. For example, the effect of applied magnetic field on the transition temperatures can be easily recognized by the width between the two temperatures where the sign $d\varepsilon/dT$ changes, which suggest that the magnetic phase which exists in this intermediate temperature range between the transition temperatures is stabilized by the presence of an applied magnetic field.
Fig. 9. Thermal expansion results for Pr$_5$Ni$_2$Si$_3$ and Pr$_{15}$Ni$_7$Si$_{10}$ under zero applied magnetic field and under a field of $\mu_0 H = 9$ Tesla
Fig. 10. First derivatives of the strain with respect to temperature $d\varepsilon/dT$ for $\text{Pr}_5\text{Ni}_2\text{Si}_3$ and $\text{Pr}_{15}\text{Ni}_7\text{Si}_{10}$ under zero applied magnetic field and under a field of $\mu_0H = 9$ T
4.1.2. Separation of phonon and magnetic effects from the total thermal expansion

In order to identify the location of magnetic phase transitions more accurately the magnetic contribution needs to be extracted from the total thermal expansion because lattice vibrations, which vary with temperature, also contribute to the thermal expansion. Therefore calculating the phonon contribution to thermal expansion should be done prior to obtaining the magnetic contribution. The Debye-Gruneisen model was used for calculating phonon effect. The specific procedures are described below.

4.1.2.1. Determination of Debye temperature ($\theta_D$)

The Debye temperature was calculated from the specific heat capacity data. Fig. 11 shows the measured specific heat capacity data for $Pr_5Ni_2Si_3$ and $Pr_{15}Ni_7Si_{10}$ respectively. The heat capacity data show the “$\lambda$”-type anomalies around 50 K and 65 K, each of which correspond to ordering temperature for $Pr_5Ni_2Si_3$ and $Pr_{15}Ni_7Si_{10}$ respectively, which is consistent with the thermal expansion data as shown in Fig. 8.

The Debye temperature is by definition the temperature above which thermal vibrations are more important than quantum effects or equivalently the temperature above which most of modes of vibration are fully excited. The magnetic effect has influence on the specific heat capacity thus making the variation of heat capacity with temperature deviate from the “Debye-like” behavior.

Considering this, the Debye temperature was calculated by fitting the specific heat data in the high temperature range (100-300 K) where magnetic contribution can be ignored. Specifically, an extrapolation procedure was developed to determine the locus of values of $C_v(T)$ which will give a limiting value of $C_v = 3N_0k_B$ as $T$ tends to infinity. This extrapolation was achieved by fitting $C_v$ against $1/T$ using the Einstein equation,
\[ C_V = 3N_o k_B \left( \frac{\theta_E}{T} \right)^2 \frac{e^{\theta_E}/T}{(e^{\theta_E}/T - 1)^2} \]

\( \theta_E \) is Einstein temperature, \( N_o \) is # of atoms/mol

and determining the intercept at \( 1/T = 0 \) as shown in Fig. 12.

For fitting procedures, measured \( C_p \) values were used instead of \( C_V \) since the difference between \( C_p \) and \( C_V \) is below 0.3 \% so the error could be ignored. The value of Debye temperature (\( \theta_D \)) was determined by finding the temperature at which \( C_V(\theta_D) = 0.952C_V(\infty) \) using the Debye equation as follows:

\[
C_V(T) = 9N_o k_B \left( \frac{T}{\theta_D} \right)^3 \int_0^{\theta_D} x^4 e^{-x} \frac{1}{(1 - e^{-x})^2} dx ; \quad \theta_D \text{ is the Debye temperature}
\]

at \( T \to \infty \), \( C_V \to 3N_o k_B = 3R = 24.942 \text{(J/mol·K)} \)

at \( T = \theta_D \):

\[
C_V(\theta_D) = 9N_o k_B \left( \frac{1}{\theta_D} \right)^3 \int_0^{\theta_D} x^4 e^{-x} \frac{1}{(1 - e^{-x})^2} dx = 3N_o k_B \times 0.952
\]

The resultant Debye temperature is 201 K and 209 K for \( \text{Pr}_5\text{Ni}_2\text{Si}_3 \) and \( \text{Pr}_{15}\text{Ni}_7\text{Si}_{10} \) respectively.
Fig. 11. Variation of specific heat capacity with temperature of \( \text{Pr}_5\text{Ni}_2\text{Si}_3 \) and \( \text{Pr}_{15}\text{Ni}_7\text{Si}_{10} \)
Fig. 12. Heat capacity plotted against $1/T$ for Pr$_3$Ni$_2$Si$_3$, with extrapolation of data to $1/T = 0$. This allows the high temperature asymptote of $C_v$ (at $T = \infty$) to be determined.
4.1.2.2. Calculation of magnetic contribution to thermal expansion

Once $\theta_D$ was obtained the expected lattice contribution to the thermal expansion was calculated theoretically from the thermal expansion data at different temperatures using the method of Sayetat et al. [4].

The following equation is a fitting equation for the thermal expansion data as a function of temperature.

\[
\frac{l(T) - l(293 \text{ K})}{l(293 \text{ K})} = \frac{l(0 \text{ K}) - l(293 \text{ K})}{l(293 \text{ K})} + \frac{l(0 \text{ K})I_a}{l(293 \text{ K})} \cdot T \cdot \varphi\left(\frac{\theta_D}{T}\right)
\]

where

\[
\varphi\left(\frac{\theta_D}{T}\right) = \frac{3953.632T^4 - 800.60870\theta_D T^3 + 85.07724\theta_D^2 T^2 - 4.4325820\theta_D^3 T + 0.0946173\theta_D^4}{3953.632T^4 - 682.00128\theta_D T^3 + 143.155337\theta_D^2 T^2 + 15.1214918\theta_D^3 T + 0.0946173}\]

Rational approximation for the Debye function; $|\epsilon| < 0.000002$ [5]

$l(0 \text{ K})$ = length of sample at $0 \text{ K}$

$I_a = Ky_kB/V_0$

$K$ = isothermal compressibility

$\gamma$ = Gruneisen’s parameter

$V_0$ = volume of sample at $0 \text{ K}$

In order to calculate only the phonon contribution to thermal expansion the fitting procedure was performed over the temperature range 100-300 K where the magnetic effects could be ignored. This is the same as the fitting procedure for heat capacity data explained above. For the purpose of calculation, the Debye temperature ($\theta_D$) that calculated from the heat capacity data was inserted into the fitting equation to reduce the number of fitting
parameter, from which the error in result is considered to be reduced. This calculation gives a slowly varying background contribution to thermal expansion that would be expected in the absence of magnetic contributions. The results were then extended to lower temperatures using the same equation to determine the expected thermal expansion in the absence of magnetic effects. This is shown in Fig. 13 (a) and 14 (a) together with the experimental data for Pr$_5$Ni$_2$Si$_3$ and Pr$_{15}$Ni$_7$Si$_{10}$ respectively. The differences between the measured thermal expansion (solid symbols) and the calculated phonon effect (solid line) are attributed to magnetic contributions to thermal expansion.

The phonon contribution has been subtracted from the measured thermal expansion as shown in Fig. 13 (b) and 14 (b). Since the other electronic contributions to thermal expansion are negligible in comparison with the magnetostrictive component, the resultant is the magnetic contribution to the thermal expansion. The derivative with respect to temperature of this resultant magnetic contribution to the thermal expansion is shown in Fig. 13 (c) and 14 (c). This derivative will be strongly dependent on any changes in the magnetic structure and it can be seen that magnetic transitions are indicated where distinct changes occurred in the slope of the curve of the magnetic component of thermal expansion against temperature. From this the magnetic transition temperatures were found to occur at 45 K and 25 K for Pr$_5$Ni$_2$Si$_3$ and 58 K and 31 K for Pr$_{15}$Ni$_7$Si$_{10}$ respectively.
Fig. 13 (a) Comparison of the experimental thermal expansion data on Pr$_5$Ni$_2$Si$_3$ in zero field with calculated phonon contribution to thermal expansion using the Gruneisen-Debye model and the equations of Sayet et al. [4] (b) The magnetic contribution to thermal expansion obtained from the difference between the total thermal expansion and the phonon contribution (c) Derivative of the magnetic contribution to thermal expansion with respect to temperature

Fig. 14 (a) Comparison of the experimental thermal expansion data of Pr$_{13}$Ni$_7$Si$_{10}$ in zero field with the calculated phonon contribution to thermal expansion (b) The magnetic contribution to thermal expansion obtained from the difference between the total thermal expansion and the phonon contribution (c) The derivative of the magnetic contribution to thermal expansion
4.1.3. Determination of Gruneisen parameter

Gruneisen established the experimental pattern of behavior for many crystalline materials [6]. He showed that the ratio of the thermal expansion coefficient (α) to the heat capacity (C) is roughly constant with temperature (T). The ratio of α to C is known as the “Gruneisen parameter” and it is expressed in the dimensionless form as

\[ \gamma = 3K \frac{\alpha}{C} \]

where α is the thermal expansion coefficient, C is the specific heat capacity, and K is the bulk elastic modulus.

When Gruneisen reported this relationship he investigated the effect of lattice vibrations of non-magnetic materials only therefore the effect of magnetic interactions in magnetic materials can make the results deviate from this model. With respect to this the Gruneisen parameter of Pr₅Ni₂Si₃ and Pr₁₅Ni₇Si₁₀, which showed magnetic ordering temperature, should be determined with the magnetic effect being precluded.

Fig.15. shows the expected temperature dependence of both heat capacity and thermal expansion coefficient in the absence of magnetic effects which were obtained from fitting procedures that was explained in the former chapters. The calculated phonon contributions to α and C show the similarity in behavior, which is usually observed at non-magnetic metals [7].
Fig. 15. The calculated phonon contribution to heat capacity and thermal expansion coefficient of (a)Pr$_5$Ni$_2$Si$_3$ and (b)Pr$_{15}$Ni$_7$Si$_{10}$ using the Debye-Gruneisen theorem. The symbols *, △, •, show the projections of the data on the C-T, α-T and α-C planes respectively.
In order to determine the relationship between thermal expansion coefficient and specific heat capacity more precisely the variation of $\alpha$ with $C$ was plotted and the results are shown in Fig. 16 (a) for both compounds. These show behavior that is consistent with the Gruneisen assumption [6]

$$\alpha = \gamma \frac{C}{3K} \quad (8)$$

where $\gamma$ is the Gruneisen parameter. Since the Gruneisen parameter and bulk modulus are relatively insensitive to temperature, the thermal expansion coefficient and heat capacity have essentially a linear relationship. The bulk modulus $K$ for each compound was calculated from acoustic velocity measurements made at 300 K. The values obtained were 68.9 GPa for $\text{Pr}_5\text{Ni}_2\text{Si}_3$ and 68.6 GPa for $\text{Pr}_{15}\text{Ni}_7\text{Si}_{10}$. The Gruneisen parameter was then calculated for each compound from equation (8) using known values of $C$ and $\alpha$ assuming no structural or magnetic changes in the alloys. The results are shown in Fig. 16 (b).

Fig. 16 (a) Comparison of the calculated phonon effect of $\text{Pr}_5\text{Ni}_2\text{Si}_3$ and $\text{Pr}_{15}\text{Ni}_7\text{Si}_{10}$. (b) Comparison of the calculated Gruneisen parameter of $\text{Pr}_5\text{Ni}_2\text{Si}_3$ and $\text{Pr}_{15}\text{Ni}_7\text{Si}_{10}$ with temperature. Bulk moduli for $\text{Pr}_5\text{Ni}_2\text{Si}_3$ and $\text{Pr}_{15}\text{Ni}_7\text{Si}_{10}$ are 68.9 and 68.6 GPa respectively.
4.1.4. Magnetostriction

The magnetostriction of Pr$_5$Ni$_2$Si$_3$ is shown in Fig. 17 (a). Magnetostriction was measured at temperature intervals of ten degrees from 10 K to 70 K under an applied magnetic field up to $\mu_0H = 9$ T. The results show a positive magnetostriction at all temperatures. This is consistent with the results of calculations of thermal expansion in Fig. 9, which showed a positive contribution to strain from the magnetic ordering.

The magnetostriction amplitude under a $\mu_0 H = 9$ Tesla field decreased from $360 \times 10^{-6}$ at 10 K to $130 \times 10^{-6}$ at 50 K, but note that even in the paramagnetic regime a field induced strain of $30 \times 10^{-6}$ was observed at $\mu_0 H = 9$ T which is higher than the magnetostriction observed in many ferromagnetic materials. An inflection point on the $\lambda$-$H$ curve, meaning a maximum in $d\lambda/dH$, was observed around $\mu_0 H = 3$ T at lower temperatures (10 K and 20 K) but was not seen at 30 K and higher temperatures.

The magnetostriction of Pr$_{15}$Ni$_2$Si$_{10}$ is shown in Fig. 17 (b). The results show similar behavior to Pr$_5$Ni$_2$Si$_3$ in which the amplitude of magnetostriction was always positive but decreased with increasing temperature. An inflection point on $\lambda$-$H$ curve was observed around $\mu_0 H = 3.8$ T at low temperatures (10 K and 20 K).
Fig. 17. Magnetostriction of (a) Pr$_5$Ni$_2$Si$_3$ and (b) Pr$_{15}$Ni$_7$Si$_{10}$ in fields of up to $\mu_0 H = 9$ Tesla at different temperatures over the range 10 - 70 K
4.2. Experimental results for single crystal Pr$_5$Ni$_2$Si$_3$ sample

4.2.1. Thermal expansion

Fig. 18. shows thermal expansion measured parallel and perpendicular to the c axis under zero magnetic field, with the thermal expansion and calculated phonon contribution for polycrystalline samples shown for comparison. Thermal expansion curves for polycrystalline and single crystal samples are consistent with each other in the high temperature region where the magnetic effect is not present. This indicates that the lattice contribution to thermal expansion is isotropic.

The thermal expansion data measured from single crystal samples were used for calculations of thermal expansion expected for polycrystalline samples by averaging the total local anisotropies over all directions under the assumption that all the grains are randomly distributed inside the polycrystalline samples. Since this compound has a hexagonal structure, the averaged strain in the polycrystal is given by,

$$\varepsilon_{\text{poly}} = \frac{1}{3} \varepsilon_{\parallel c} + \frac{2}{3} \varepsilon_{\perp c}$$

where $\varepsilon_{\text{poly}}$ is average thermal expansion for polycrystalline sample, $\varepsilon_{\parallel c}$ is thermal expansion measured parallel to the c axis and $\varepsilon_{\perp c}$ is thermal expansion measured perpendicular to the c axis.

The results of this calculation have been compared with the experimental results, which show excellent agreement between measured and calculated values of strain for a randomly oriented polycrystalline sample.
The single crystal thermal expansion data below the Curie temperature in Fig. 18 show anisotropy, with different behavior depending on the direction of measurement of strain, whether parallel or perpendicular to the c axis.

The magnetic contribution to thermal expansion along different directions was calculated from the total thermal expansion in the directions parallel and perpendicular to the c axis by applying the same procedure as described previously for the polycrystalline samples. Specifically the isotropic phonon contribution to thermal expansion was subtracted from the total thermal expansion along different directions. The results of these calculations are shown in Fig. 19, in which the polycrystalline data have been included for comparison. The same value of strain, irrespective of the direction of measurement, was observed at the Curie temperature and above. The magnetic contribution to this thermal expansion in directions parallel and perpendicular to the c axis, which correspond to spontaneous magnetostriction $\lambda_{\parallel c}$ and $\lambda_{\perp c}$ respectively, showed different behavior as temperature decreased below the Curie temperature; note that the spontaneous magnetostriction $\lambda$ is distinguished from the total measured strain $\varepsilon$ which comprises magnetic and phonon contributions. $\lambda_{\perp c}$ increases as T decreases from 50 K down to 25 K, then decreases below 25 K making a local maximum in the graph, while $\lambda_{\parallel c}$ decreases monotonically. In this respect, the second transition at the lower temperature (25 K) is considered to be associated with the variation of the distribution of preferred orientation of magnetic moments along directions perpendicular to c axis. From this it seems reasonable to conclude that the anomaly in thermal expansion observed around 25 K and 30 K for polycrystalline Pr$_5$Ni$_2$Si$_3$ and
Pr$_{15}$Ni$_7$Si$_{10}$ samples respectively is due to $\lambda_{\perp c}$ only, not being caused by $\lambda_{\parallel c}$ which shows monotonic behavior.

![Graph](image)

Fig. 18. Variation of thermal expansion of single crystal Pr$_5$Ni$_3$Si$_3$ with temperature measured parallel and perpendicular to c axis under zero magnetic field. Experimental data of polycrystalline samples are included for comparison with the calculated values for polycrystalline samples using the measured data of single crystal samples.
Fig. 19. Variation of the magnetic contribution to thermal expansion of single crystal Pr$_5$Ni$_2$Si$_3$ with temperature measured parallel and perpendicular to c axis under zero magnetic field, which is obtained from the difference between the total thermal expansion and the phonon contribution. The data obtained from polycrystalline samples using the same procedures are included for comparison.
4.2.2. Magnetostriction

The results of the magnetostriction measurement for the single crystal Pr$_3$Ni$_2$Si$_3$ sample are shown in Fig. 20. Magnetostriction was measured (a) parallel and (b) perpendicular to the c axis with applied magnetic field along the same direction as the measured strain. While the results on the polycrystalline sample showed a positive magnetostriction at all temperatures as shown in Fig. 17, the single crystal sample showed more complex behavior. The magnetostriction measured along the c axis shows negative values without any hysteresis at all temperatures. However, the magnetostriction measured perpendicular to c axis shows mixture of negative and positive values varying with applied field and temperature. Hysteresis and inflection point (peak in dλ/dH) in magnetostriction are observed in graphs for lower temperatures (below 30 K) and do not appear at higher temperatures, which was also seen at λ-H curves of polycrystalline sample (Fig. 17). Interpretation of these features has not been complete so far and more investigation on these anisotropic features is needed.
Fig. 20. Magnetostriction of single crystal Pr$_5$Ni$_2$Si$_3$ samples measured (a) parallel and (b) perpendicular to $c$ axis at different temperatures.
4.2.3. Magnetization vs. Temperature curve

The M-T curves of Pr$_5$Ni$_2$Si$_3$ single crystal are shown in Fig. 21. These have been calculated in terms of the net number of Bohr magnetons per Pr atom. The theoretical magnetic moment per Pr atom is 3.58 Bohr magnetons. The fact that the maximum value of magnetization under a field of $\mu_0 H = 5$ T is 55 % (for $M_{//c}$) and 29 % (for $M_{\perp c}$) of this value indicates that the values of magnetization measured in both directions were not saturated even at a field of $\mu_0 H = 5$ T and the easy axis in magnetization is tilted closer to the $c$ axis then to the axis perpendicular to $c$ axis. Besides the maximum value of magnetization, the results measured in two perpendicular directions show clearly different behavior. For example, while $M_{//c}$-T curve shows normal ferromagnetic behavior with Curie temperature ($T_C$) around 48 K, however, $M_{\perp c}$-T curve shows different anomaly making a local maximum around 25 K which is the same temperature to the transition temperature that was observed in the $\lambda_{\perp c}$-T curve (Fig. 18, 19). This anisotropy in magnetic property is not easy to understand with the current data we obtained so far. With respect to this, simulation of M-T curves has been performed using a nearest neighbor exchange interaction approximation in exchange interaction, which is explained in the following chapter.
Fig. 21. Variation of the magnetization of Pr$_5$Ni$_2$Si$_3$ single crystal with temperature measured (a) parallel and (b) perpendicular to c axis under various magnetic fields
4.3. Calculation of expected variation of M with T in Pr$_5$Ni$_2$Si$_3$ single crystal

4.3.1. Approach 1: Exchange energy vs. thermal activation

In order to calculate the expected variation of M with T in Pr$_5$Ni$_2$Si$_3$ single crystal exchange energy for each atomic site was determined using a nearest neighbor exchange interaction approximation. For this calculation, it was assumed that

1) only Pr atoms contribute to magnetization and the magnetic moment per Pr atom is 3.58 $\mu_B$

2) exchange interaction exists only between the first nearest neighbors and it is expressed as

$$ E_{ex} = -2J_{NN} \sum_{i,j} J_i J_j $$

where $J_{NN}$ is the exchange interaction constant between nearest neighbors, and $J_i, J_j$ is total angular momentum at ith and jth site.

The Pr atoms in the triangular basal plane of the columnar structure of Pr$_5$Ni$_2$Si$_3$ compound (Fig.1 (a)) can be classified into three groups by the number of nearest neighbors: Pr atoms at the center sites of the triangular plane with six nearest neighbors, those along the edges of the triangular plane with four nearest neighbors, and those at the corners of the triangular plane with two nearest neighbors. Each type of Pr atoms is indicated as red, blue and green circles in Fig. 22. The total exchange energy in this triangular unit consisting of 10 Pr atoms can be calculated by the summation of each exchange interaction

Since the total # of exchange interaction/triangular plane = total # of nearest neighbors/triangular plane = 18/triangular plane, and $J$ of Pr atom in the compound = 4, therefore

$$ E_{ex} = 18 \times (-2J_{NN} \cdot 4^2) = -576J_{NN} $$
In fact this exchange energy is equal to the thermal energy at the Curie temperature ($T_c$), from which $J_{NN}$ was calculated using the measured $T_c$ of this compound, 48 K:

$$E_{ex} = -576J_{NN} = \text{thermal energy at } T_c = 3k_B T_c \times \# \text{ of Pr atoms in the triangular plane} = 30k_B T_c$$

$$\therefore J_{NN} = 3.4526 \times 10^{-23} (J)$$

In this calculation, the thermal energy of each atom is assumed to be $3k_B T$ due to the 6 degrees of freedom; 3 for vibration and 3 for rotation.

Since the effective magnetic field that each atom experiences from the nearest magnetic moments depends on the number of nearest neighbors on each site, the effective magnetic field for each atomic site can be expressed as below,

- $E^c_{ex}$ = the exchange energy that the center atom experiences
  $$= 6 \times (-J_{nn} \cdot J^2)$$
- $E^e_{ex}$ = the exchange energy that each side atom experiences
  $$= 4 \times (-J_{nn} \cdot J^2)$$
- $E^a_{ex}$ = the exchange energy that each vertex atom experiences
  $$= 2 \times (-J_{nn} \cdot J^2)$$

$$E^c_{ex} = 6 \times (-J_{nn} \cdot J^2) = m \cdot \mu_0 H^c_{\text{eff}} = m \cdot \mu_0 \alpha_c M$$
$$E^e_{ex} = 4 \times (-J_{nn} \cdot J^2) = m \cdot \mu_0 H^e_{\text{eff}} = m \cdot \mu_0 \alpha_e M$$
$$E^a_{ex} = 2 \times (-J_{nn} \cdot J^2) = m \cdot \mu_0 H^a_{\text{eff}} = m \cdot \mu_0 \alpha_a M$$

where

$H^c_{\text{eff}}, H^e_{\text{eff}}, H^a_{\text{eff}}$ are the molecular fields on each site

$\alpha_c, \alpha_e, \alpha_a$ are the molecular field constants on each site
Reminding the fact that each atomic site experiences different effective field the total magnetization can be expressed as follow:

\[ m_{\text{triangle}} = m^c + m^e + m^a \]

\[ = m^c B_j \left[ \frac{m_0 \mu_0 (H + H_{\text{eff}}^c)}{k_B T} \right] + m^e B_j \left[ \frac{m_0 \mu_0 (H + H_{\text{eff}}^e)}{k_B T} \right] + m^a B_j \left[ \frac{m_0 \mu_0 (H + H_{\text{eff}}^a)}{k_B T} \right] \]

\[ = 1m^c B_j \left[ \frac{m_0 \mu_0 (H + H_{\text{eff}}^c)}{k_B T} \right] + 6m^c B_j \left[ \frac{m_0 \mu_0 (H + H_{\text{eff}}^e)}{k_B T} \right] + 3m^c B_j \left[ \frac{m_0 \mu_0 (H + H_{\text{eff}}^a)}{k_B T} \right] \]

where

\[ B_j(x) = \left( \frac{2J+1}{2J} \right) \coth \left( \frac{(2J+1)x}{2J} \right) - \left( \frac{1}{2J} \right) \coth \left( \frac{x}{2J} \right) \] Brillouin function

The resultant M-T curve of these calculations is shown in Fig. 23. and these results are consistent with experimentally measured Curie temperature of 48 K, however, the second phase transition observed at lower temperature could not be observed in these simulated curves because detailed variations in the exchange coupling, which lead to differences in orientations of the three groups of Pr atoms, were not taken into account.
Fig. 22. Schematic picture describing three types of Pr atoms in the base plane of prismatic columnar structure of Pr$_3$Ni$_2$Si$_3$ single crystal.
Fig. 23. Simulated M vs. T curves using Brillouin function for the Pr$_5$Ni$_2$Si$_3$ compound. Red/blue/green symbols represent the magnetization due to the Pr atoms at the center/edge/corner sites in unit of Bohr magnetons. The black symbols are the sum of these three contributions, which is the total magnetic moments of 10 Pr atoms in the triangular plane.
4.3.2. Approach 2: Different exchange energy on different sites

In the previous calculation the exchange energy between the nearest neighbors was assumed to be constant for all Pr atomic sites. However, the resultant M vs. T curve based on this calculation does not exhibit the anomaly around 25 K which was observed in the experimentally measured M vs. T curve perpendicular to c axis (Fig. 21 (b)). This suggests that the assumptions need to be modified. At first, the assumption that the strength of all the exchange interactions are the same seems unrealistic therefore the exchange energy between the nearest neighbors was classified into three types:

\( E_{ex} \) (center-side); exchange energy between the atoms at the center and side sites

\( E_{ex} \) (side-side); exchange energy between the atoms at the side sites

\( E_{ex} \) (side-corner); exchange energy between the atoms at the side and corner sites

The number of exchange interactions for each type is six in the triangular unit plane (Fig. 22). Since the Pr atoms in the corner site have the smallest number of nearest neighbor the exchange energy of the corner atoms was assumed to be negative; \( E_{ex} \) (side-corner) < 0.

Based on the average exchange interaction constant \( J_{NN} \) of \( 3.4526 \times 10^{-23} \) (J) which was calculated in approach 1, various combinations of values in exchange energy for each type of interaction were examined for simulating M vs. T curves. The resultant simulated M vs. T curves are shown in Fig. 24 (a) – (e). These results suggest that the second magnetic transition observed around 25 K in the experimental data is likely due to an antiferromagnetic exchange interaction between some of the lattice sites which results in different behavior of the Pr atoms at the corner sites.
Fig. 24 (a) Simulated M vs. T curves using Brillouin function for the Pr₅Ni₂Si₃ compound assuming that the exchange interaction constant $J_{NN}$ for center-side/side-side/side-corner is $4 \times 10^{-23}$ (J), $4 \times 10^{-23}$ (J), $-4 \times 10^{-23}$ (J) respectively. Red/blue/green symbols represent the magnetization due to the Pr atoms at the center/edge/corner sites in unit of Bohr magnetons. The black symbols are the sum of these three contributions, which is the total magnetic moments of 10 Pr atoms in the triangular plane.
Fig. 24 (b) Simulated M vs. T curves using Brillouin function for the Pr$_5$Ni$_2$Si$_3$ compound assuming that the exchange interaction constant $J_{NN}$ for center-side/side-side/side-corner is $4 \times 10^{-23} (J) / 4 \times 10^{-23} (J) / -2 \times 10^{-23} (J)$ respectively. Red/blue/green symbols represent the magnetization due to the Pr atoms at the center/edge/corner sites in unit of Bohr magnetons. The black symbols are the sum of these three contributions, which is the total magnetic moments of 10 Pr atoms in the triangular plane.
Fig. 24 (c) Simulated M vs. T curves using Brillouin function for the Pr$_5$Ni$_2$Si$_3$ compound assuming that the exchange interaction constant $J_{NN}$ for center-side/side-side/side-corner is $4 \times 10^{-23}$ (J) / $3 \times 10^{-23}$ (J) / $2 \times 10^{-23}$ (J) respectively. Red/blue/green symbols represent the magnetization due to the Pr atoms at the center/edge/corner sites in unit of Bohr magnetons. The black symbols are the sum of these three contributions, which is the total magnetic moments of 10 Pr atoms in the triangular plane.
Fig. 24 (d) Simulated M vs. T curves using Brillouin function for the Pr$_5$Ni$_2$Si$_3$ compound assuming that the exchange interaction constant $J_{NN}$ for center-side/side-side/side-corner is $4 \times 10^{-23}$ (J)/ $3 \times 10^{-23}$ (J)/ $1 \times 10^{-23}$ (J) respectively. Red/blue/green symbols represent the magnetization due to the Pr atoms at the center/edge/corner sites in unit of Bohr magnetons. The black symbols are the sum of these three contributions, which is the total magnetic moments of 10 Pr atoms in the triangular plane.
Fig. 24 (e) Simulated M vs. T curves using Brillouin function for the Pr$_5$Ni$_2$Si$_3$ compound assuming that the exchange interaction constant $J_{NN}$ for center-side/side-side/side-corner is $5 \times 10^{-23}$ (J) / $4 \times 10^{-23}$ (J) / $-1 \times 10^{-23}$ (J) respectively. Red/blue/green symbols represent the magnetization due to the Pr atoms at the center/edge/corner sites in unit of Bohr magnetons. The black symbols are the sum of these three contributions, which is the total magnetic moments of 10 Pr atoms in the triangular plane.
5. CONCLUSIONS

Thermal expansion and magnetostriction of some of the Pr-Ni-Si compound system have been investigated in order to study the magnetic phase transformation. Theoretical calculations were used to separate the phonon and magnetic contributions to thermal expansion from experimental results on polycrystalline samples of Pr$_5$Ni$_2$Sb and Pr$_{15}$Ni$_7$Si$_{10}$. The calculated magnetic contribution to thermal expansion revealed the two magnetic phase transitions for each composition: magnetic order/disorder transition at a higher temperature (41 K for Pr$_5$Ni$_2$Sb, 58 K for Pr$_{15}$Ni$_7$Si$_{10}$) and spin reorientation transition at a lower temperature (25 K for Pr$_5$Ni$_2$Sb, 31 K for Pr$_{15}$Ni$_7$Si$_{10}$).

Anisotropy in thermal expansion was observed in the Pr$_5$Ni$_2$Sb single crystal sample below the Curie temperature, where the strain perpendicular to the c-axis, $\epsilon_{\perp c}$ increased as temperature decreased from the Curie point down to 25 K, then decreased below 25 K. On the other hand, the strain parallel to the c-axis, $\epsilon_{/c}$ decreased monotonically as temperature was reduced. Assuming that the phonon contribution to thermal expansion remains isotropic below the Curie point, this feature indicates that this compound shows negative and positive spontaneous magnetostriction in directions parallel and perpendicular to the c axis respectively (i.e. $\lambda_{/c}<0$, $\lambda_{\perp c}>0$) below the Curie temperature, which is consistent with the M vs. T curves of Pr$_5$Ni$_2$Si$_3$ single crystal.

Expected variation of magnetization with temperature of Pr$_5$Ni$_2$Si$_3$ single crystal was calculated using a nearest neighbor exchange interaction approximation. Three types of Pr atoms were classified with respect to the number of nearest neighbors and M vs. T curves for each type as well as the average M vs. T curve for the whole triangular array were simulated.
The results show 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.
APPENDIX. AUTHOR’S PUBLICATIONS AND PRESENTATIONS

PUBLICATIONS


Jiles, D. C.; Song, S. H.; Snyder, J. E.; Pecharsky, V. K.; Lograsso, T. A.; Wu, D.; Pecharsky, A. O.; Mudryk, Ya.; Dennis, K. W.; McCallum, R. W. “Thermal Expansion and Magnetostriction in Pr$_{(n+2)(n-1)}$Ni$_{(n-1)}$$_2$Si$_{(n+1)}$ Compounds” accepted by Journal of Magnetism and Magnetic Materials.

PRESENTATIONS


Thermal Expansion and Magnetostriction in 
Pr$_5$Ni$_2$Si$_3$ Compounds 

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Abstract—The thermal expansion and magnetostriction of polycrystalline and single crystal Pr$_5$Ni$_2$Si$_3$ were investigated over the temperature range 5-300 K. The results show two magnetic phase transitions, one corresponding to the Curie temperature and the other at a lower temperature exhibiting characteristics of a spin reorientation transition. In the temperature range below the Curie temperature, the thermal expansion in single crystal samples exhibited a temperature dependent anisotropy. Specifically negative and positive magnetic contributions to the thermal expansion were observed along the directions parallel and perpendicular to the c axis respectively.

Index Terms—Thermal expansion, Magnetostriction, Rare earth, Spin reorientation, Single crystal

I. INTRODUCTION

The ternary Pr-Ni-Si system contains an unusual and interesting homologous series Pr$_{(2n+2)x(n+1)}$Ni$_{(2n-1)}$Si$_{(n+1)}$ that have recently been discovered to be magnetic [1]. This alloy system exhibits a hexagonal structure formed of trigonal prismatic columns in which the number of small trigonal prisms that fit along each side of the basal plane of the larger trigonal prism of the unit cell, is determined by the value of n in the chemical formula. Therefore the size of the trigonal prismatic magnetic “cluster” can be controlled by adjustments of chemical composition, providing a model system for systematic investigation of magnetic properties which vary with the size of the cross section of the trigonal columns, with the other structural conditions remaining the same.

This series includes the identifiable compounds Pr$_5$Ni$_2$Si$_3$ (n=2), Pr$_5$Ni$_2$Si$_4$ (n=3), and Pr$_5$Ni$_2$Si$_{10}$ (n=5). Investigations of crystal structure, magnetization, specific heat capacity and magnetoelastic effect of polycrystalline Pr$_5$Ni$_2$Si$_3$ have been reported by Pecharsky et al. [1]. Thermal expansion investigations of polycrystalline Pr$_5$Ni$_2$Si$_3$ and Pr$_5$Ni$_2$Si$_{10}$ have recently been reported, in which theoretical calculations have been used to extract the magnetic contribution to thermal expansion [2].

The present paper reports on an investigation of the properties of both polycrystalline and single crystal Pr$_5$Ni$_2$Si$_3$ in which the magnetic phase transitions were examined by measurements of thermal expansion and magnetostriction. Two magnetic phase transitions have been observed in this compound at 48 K and 25 K. The higher temperature transition is known to be the magnetic order/disorder transition.

Single crystal samples of Pr$_5$Ni$_2$Si$_3$ have recently been produced for the first time. These enabled us to investigate the directional dependence of thermal expansion and magnetostriction. Since the quantity measured for polycrystalline samples is the average value over randomly distributed local anisotropies, investigating single crystal samples is essential for understanding its anisotropic characteristics.

II. EXPERIMENTAL METHODS

The polycrystalline samples of Pr$_5$Ni$_2$Si$_3$ were prepared by arc melting in an argon atmosphere from high purity components: Pr (99.9+ at. % pure), Ni (99.88 at. % pure), Si (99.99 at. % pure). The single crystal samples of Pr$_5$Ni$_2$Si$_3$ were synthesized using a vertical gradient freeze method. Thermal expansion and magnetostriction were measured using strain gauges. Measurements were carried out under applied magnetic fields of up to 9 T in the temperature range 5-300 K. Thermal expansion and magnetostriction of single crystal samples were measured parallel and perpendicular to the c axis under applied magnetic field along the same direction as the strain was measured.

III. RESULTS AND DISCUSSIONS

A. Polycrystalline samples

The results of thermal expansion measurements under zero magnetic field and under a field of 9 Tesla ($\mu_0$H=9 T) are shown in Fig.1. Two kinds of anomalies in thermal expansion are observed around 50 K and 25 K indicating magnetic phase transitions.
expansion, in which positive strains are observed above the Curie temperature indicating the magnetovolume effect due to local short range order of magnetic moments which does not disappear immediately at the Curie temperature as long range order does [3]. The transition temperatures were determined from locations at which distinct changes occur in the slope of the thermal expansion curve. Thus magnetic transitions were observed at 48 K and 25 K.

B. Single crystal samples

Fig. 3. shows thermal expansion measured parallel and perpendicular to the c axis under zero magnetic field, with the thermal expansion and calculated phonon contribution for polycrystalline samples shown for comparison. Thermal expansion curves for polycrystalline and single crystal samples are consistent with each other in the high temperature region where the magnetic effect is not present. This indicates that the lattice contribution to thermal expansion is isotropic.

The thermal expansion data measured from single crystal samples were used for calculations of thermal expansion expected for polycrystalline samples by averaging the total local anisotropies over all directions under the assumption that all the grains are randomly distributed inside the polycrystalline samples. Since this compound has a hexagonal structure, the averaged strain in the polycrystal is given by,

$$\varepsilon_{\text{poly}} = \frac{1}{3} \varepsilon_{\parallel c} + \frac{2}{3} \varepsilon_{\perp c}$$

where $\varepsilon_{\text{poly}}$ is average thermal expansion for polycrystalline sample, $\varepsilon_{\parallel c}$ is thermal expansion measured parallel to the c axis and $\varepsilon_{\perp c}$ is thermal expansion measured perpendicular to the c axis. The results of this calculation have been compared with the experimental results in Fig. 3, which shows excellent agreement between measured and calculated values of strain for a randomly oriented polycrystalline sample.

The single crystal thermal expansion data below the Curie temperature in Fig. 3 show anisotropy, with different behavior depending on the direction of measurement of strain, whether parallel or perpendicular to the c axis. It seems reasonable to conclude that this anisotropy in thermal expansion is due to the magnetic ordering and that the non-magnetic phonon contribution remains isotropic below the Curie temperature.

To extract the magnetic contribution from the total thermal expansion, the phonon contribution to thermal expansion was calculated using the Debye-Gruneisen theory. This is indicated as a solid line in Fig. 1. This phonon contribution was then subtracted from the measured total thermal expansion. Details of the theoretical calculations have been reported elsewhere [2]. Fig. 2 shows the resultant magnetic contribution to thermal expansion.
Experimental data of polycrystalline samples are included for comparison with the calculated values for polycrystalline samples using the measured data of single crystal samples.

The magnetic contribution to thermal expansion along different directions was calculated from the total thermal expansion in the directions parallel and perpendicular to the c axis by applying the same procedure as described above for the polycrystalline samples. Specifically the isotropic phonon contribution to thermal expansion was subtracted from the total thermal expansion along different directions. The results of these calculations are shown in Fig. 4., in which the polycrystalline data have been included for comparison. The same value of strain, irrespective of the direction of measurement, was observed at the Curie temperature and above. The magnetic contribution to this thermal expansion in directions parallel and perpendicular to the c axis, which correspond to spontaneous magnetostriction $\lambda_{\text{sp}}$ and $\lambda_{\text{le}}$ respectively, show different behavior as temperature decreases below the Curie temperature. $\lambda_{\text{le}}$ increases as T decreases from 50 K down to 25 K, then decreases below 25 K making a local maximum in the graph, while $\lambda_{\text{sp}}$ decreases monotonically. In this respect, the second transition at the lower temperature (25 K) is considered to be associated with the variation of the distribution of preferred orientation of magnetic moments along directions perpendicular to c axis.

IV. CONCLUSIONS

Two kinds of magnetic phase transitions were observed in $\text{Pr}_3\text{Ni}_2\text{Si}_3$ from the results of thermal expansion and magnetostriction measurements, using both polycrystalline and single crystal samples. The magnetic order/disorder transition was observed at 48 K and the spin reorientation transition at 25 K.

Anisotropy in thermal expansion was observed from single crystal samples below the Curie temperature, where the strain perpendicular to the c-axis, $e_x$, increases as temperature decreases from the Curie point down to 25 K, then decreases below 25 K. On the other hand, the strain parallel to the c-axis, $e_{\text{par}}$, decreases monotonically as temperature is reduced. Assuming that the phonon contribution to thermal expansion remains isotropic below the Curie point, this feature indicates that this compound shows negative and positive spontaneous magnetostriction in directions parallel and perpendicular to the c axis respectively (i.e. $\lambda_{\text{le}}<$0, $\lambda_{\text{sp}}$>0) below the Curie temperature.

Below the second transition temperature (25 K) the thermal expansion behavior perpendicular to the c axis exhibits characteristics of a spin reorientation transition, which is associated with change in anisotropy energy with temperature.

Expected thermal expansion for polycrystalline samples was calculated from the measured single crystal data and the results were consistent with the experimental measurements for polycrystalline samples.

From the comparison of the results from polycrystalline and single crystal samples, it can be seen that the second magnetic transition causes the anomaly in thermal expansion perpendicular to the c axis that was observed below 25 K.

REFERENCES


Thermal expansion and Gruneisen parameters in some Pr–Ni–Si compounds

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In this study, the thermal expansion and Gruneisen parameter of polycrystalline “Pr$_5$Ni$_2$Si$_3$” and “Pr$_{15}$Ni$_7$Si$_{10}$” were investigated over the temperature range of 5−300 K. Calculations of the phonon contribution to thermal expansion were made, which allowed the magnetic contribution to thermal expansion to be calculated from the difference between the total thermal expansion and the phonon contribution. This resulted in a temperature-dependent magnetic contribution to thermal expansion that varied with the magnetic ordering of the material. The results show two magnetic transitions in each compound, the higher temperature transition corresponding to the Curie temperature and the lower temperature transition resulting from a spin reorientation. © 2005 American Institute of Physics. [DOI: 10.1063/1.1853894]

I. INTRODUCTION

In the study of structure/property relationships in magnetic materials it is advantageous to have materials with closely related but different structures whereby systematic changes in structure can be related to magnetic properties. The ternary Pr–Ni–Si alloy system contains the homologous series R$_{n+2}$(n+1)Ni$_n$(n+2)Si$_{n+1}$, where R is a rare earth element, in this case Pr, and provides a range of materials with different structures as described by Rogl. We are therefore investigating this series of alloys because it provides a suitable series of related magnetic compounds in which there are systematic changes in the crystal structure from one composition to the next. The Pr series contains the identifiable compounds “Pr$_5$Ni$_2$Si$_3$” (n=2), “Pr$_3$Ni$_2$Si$_3$” (n=3), and “Pr$_{15}$Ni$_7$Si$_{10}$” (n=4). An investigation of a polycrystalline sample of the n=3 alloy has recently been reported by Pecharsky et al. The present paper reports on an investigation of the properties of polycrystalline Pr$_5$Ni$_2$Si$_3$ and Pr$_{15}$Ni$_7$Si$_{10}$ in which the results of thermal expansion measurement have been analyzed and compared with the expected thermal expansion contributions due to lattice vibrations in the absence of magnetic ordering. The differences have been attributed to magnetic contributions to the thermal expansion and have been used to locate the temperatures of magnetic phase transitions in these compounds.

II. EXPERIMENTAL METHODS

The polycrystalline samples of Pr$_5$Ni$_2$Si$_3$ and Pr$_{15}$Ni$_7$Si$_{10}$, which will hereafter be referred to by their ide-
ture range (100–300 K) where magnetic contributions could be ignored since the material was in a paramagnetic state throughout this temperature range. For this calculation, an approximate equation for the Debye function was used at high temperatures. Values of $\theta_D$ were obtained, 201 K for Pr$_5$Ni$_2$Si$_3$ and 209 K for Pr$_{15}$Ni$_7$Si$_{10}$, respectively, and from these the expected variation of heat capacity with temperature in the absence of magnetic effects was calculated over the whole temperature range. The expected phonon contribution to thermal expansion in the absence of magnetic effects was calculated over the same temperature range as the heat capacity measurements (100–300 K) using the method of Sayetat et al.\textsuperscript{3} These calculations gave a thermal expansion that varied slowly with temperature as would be expected in the absence of magnetic contributions. The results of these calculations, showing the expected temperature dependence of both heat capacity and thermal expansion coefficient in the absence of magnetic effects, are shown in Fig. 2.

Once the results of heat capacity and thermal expansion in the absence of magnetic effects were calculated the phonon contribution was subtracted from the measured total heat capacity and thermal expansion as shown in Fig. 3. Since the other electronic contributions to these properties are negligible in comparison, the differences are due to the magnetic contributions to the heat capacity and thermal expansion, which are strongly dependent on any changes in the magnetic order. The results indicated magnetic transitions at temperatures of 25 K and 41 K for Pr$_5$Ni$_2$Si$_3$, 31 K and 58 K for Pr$_{12}$Ni$_7$Si$_{10}$ where rapid changes in these properties occurred.

The variation of thermal expansion coefficient with heat capacity are shown in Fig. 4(a) for both compounds. These show behavior that is consistent with the Gruneisen assumption\textsuperscript{1}

\begin{equation}
\alpha = \gamma \frac{C}{3K}
\end{equation}

where $\alpha$ is the thermal expansion coefficient, $C$ is the specific heat capacity, $K$ is the bulk elastic modulus, and $\gamma$ is the Gruneisen parameter. Since the Gruneisen parameter and bulk modulus are relatively insensitive to temperature, the thermal expansion coefficient and heat capacity have essentially a linear relationship.

The bulk modulus $K$ for each compound was calculated from acoustic velocity measurements made at 300 K. The values obtained were 68.9 GPa for Pr$_5$Ni$_2$Si$_3$ and 68.6 GPa for Pr$_{12}$Ni$_7$Si$_{10}$. The Gruneisen parameter was then calculated for each compound from Eq. (1) using known values of C and $\alpha$ assuming no structural or magnetic changes in the alloys. The results are shown in Fig. 4(b).

Magnetostriiction of polycrystalline Pr$_5$Ni$_2$Si$_3$ and Pr$_{12}$Ni$_7$Si$_{10}$ were measured. The results for these two compounds were very similar\textsuperscript{5} and showed a positive magnetostriiction at all temperatures in which the amplitude of magnetostriiction under a 9 T field decreased with temperature for both samples. Inflection points on the $\lambda-H$ curve were observed at low temperatures, at 10 K for Pr$_5$Ni$_2$Si$_3$ and at
20 K for Pr$_5$Ni$_2$Si$_3$. These are consistent with the existence of magnetic phase transitions at these temperatures. Furthermore, the inflection points in both $\lambda$-$H$ and $M$-$H$ curves occurred under similar applied field strength of around 3 T for Pr$_5$Ni$_2$Si$_3$ and 4 T for Pr$_{15}$Ni$_7$Si$_{10}$. These results provide further confirmation of a second magnetic transition at lower temperature as suggested by the thermal expansion results.

IV. CONCLUSIONS

Theoretical calculations were used to separate the phonon and magnetic contributions to thermal expansion from experimental results on Pr$_5$Ni$_2$Si$_3$ and Pr$_{15}$Ni$_7$Si$_{10}$. The calculated magnetic contribution to thermal expansion revealed the two magnetic phase transitions for each composition: magnetic order/disorder transition at a higher temperature (41 K for Pr$_5$Ni$_2$Si$_3$, 58 K for Pr$_{15}$Ni$_7$Si$_{10}$) and spin reorientation transition at a lower temperature (25 K for Pr$_5$Ni$_2$Si$_3$, 31 K for Pr$_{15}$Ni$_7$Si$_{10}$). These results are consistent with those of magnetostriction measurements and with previously published heat capacity data and magnetic property measurements. In addition, the bulk elastic modulus was determined for each compound from acoustic velocity measurements and the Gruneisen parameter was then determined from thermal expansion, heat capacity, and the bulk elastic modulus for each compound.

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