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In this study, the thermal expansion and Gruneisen parameter of polycrystalline "$Pr_5Ni_2Si_3$" and "$Pr_{15}Ni_7Si_{10}$" 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 $R_{(n+2)(n+1)}Ni_{n(n-1)+2}Si_{n(n+1)}$, 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] 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 "$Pr_6Ni_2Si_3$" ($n=2$), "$Pr_5Ni_2Si_3$" ($n=3$), and "$Pr_{15}Ni_7Si_{10}$" ($n=4$). An investigation of a polycrystalline sample of the $n=3$ alloy has recently been reported by Pecharsky *et al.*[2] The present paper reports on an investigation of the properties of polycrystalline $Pr_5Ni_2Si_3$ and $Pr_{15}Ni_7Si_{10}$, 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 $Pr_5Ni_{1.9}Si_3$ and $Pr_{15}Ni_{6.8}Si_{10}$, which will hereafter be referred to by their ide-

alized stoichiometries $Pr_5Ni_2Si_3$ and $Pr_{15}Ni_7Si_{10}$, respectively, 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). Thermal expansion was measured using strain gauges. Measurements were carried out under applied magnetic fields of up to 9 T in the temperature range 5–300 K. A "half bridge" configuration was used to compensate for the temperature and field dependence of the strain gauge resistance which is 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. The bulk elastic modulus was determined from measurements of acoustic velocity at a temperature of 300 K and the density of the specimens.

III. RESULTS AND DISCUSSIONS

The results of thermal expansion measurements under a zero magnetic field (H=0) for polycrystalline $Pr_5Ni_2Si_3$ and $Pr_{15}Ni_7Si_{10}$ are shown in Fig. 1. Anomalies in thermal expansion occurred in the temperature range below 50 K for $Pr_5Ni_2Si_3$ and below 65 K for $Pr_{15}Ni_7Si_{10}$, which are indicative of magnetic phase transitions from a higher temperature paramagnetic state to a lower temperature magnetically ordered state.

The phonon contributions to the heat capacity and thermal expansion were calculated using the Debye–Gruneisen theorem. Specifically, the Debye temperature θ_D was first calculated from the heat capacity data in the high tempera-
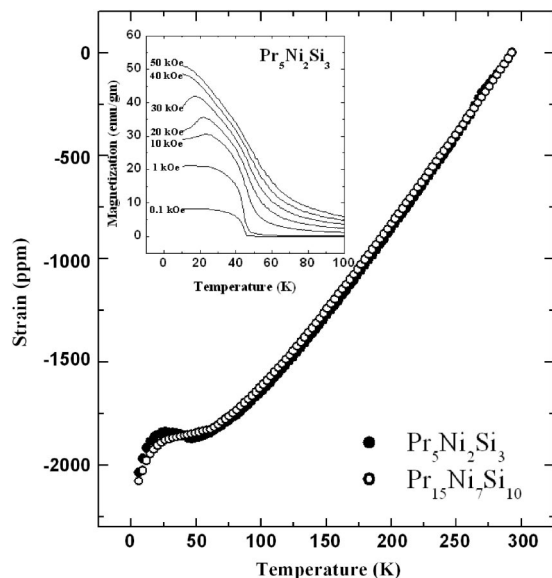
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FIG. 1. Temperature-dependent thermal expansion of polycrystalline $Pr_5Ni_2Si_3$ (solid circles) and $Pr_{15}Ni_7Si_{10}$ (open circles) under zero applied magnetic field. The inset shows detailed results of the variation of magnetization with temperature over the range 10–100 K at different constant field strengths.

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 θ_D were obtained, 201 K for $Pr_5Ni_2Si_3$ and 209 K for $Pr_{15}Ni_7Si_{10}$, 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.*[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 $Pr_5Ni_2Si_3$, 31 K and 58 K for $Pr_{15}Ni_7Si_{10}$ 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[4]
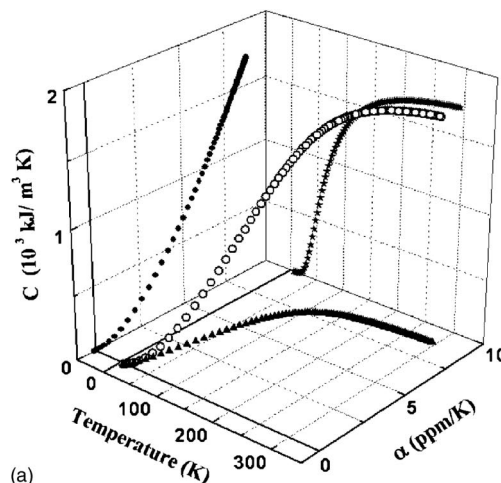
(a)
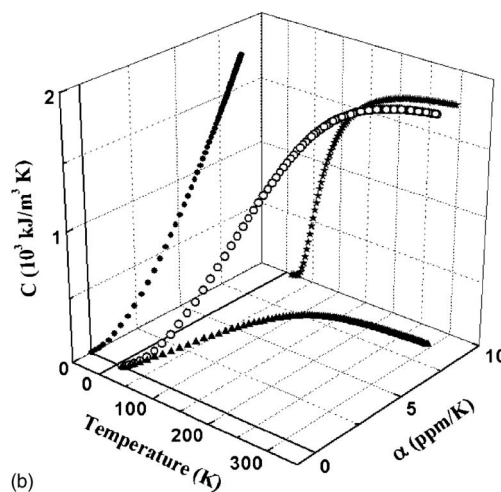
(b)

FIG. 2. The calculated phonon contribution to heat capacity and thermal expansion coefficient of polycrystalline (a) $Pr_5Ni_2Si_3$ and (b) $Pr_{15}Ni_7Si_{10}$ using the Debye-Gruneisen theorem. The symbols *, ▲, ● show the projections of the data on the C-T, α-T, and α-C planes, respectively.

$$\alpha = \gamma \frac{C}{3K},\qquad(1)$$

where α is the thermal expansion coefficient, C is the specific heat capacity, K is the bulk elastic modulus, and γ 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 $Pr_5Ni_2Si_3$ and 68.6 GPa for $Pr_{15}Ni_7Si_{10}$. The Gruneisen parameter was then calculated for each compound from Eq. (1) using known values of C and α assuming no structural or magnetic changes in the alloys. The results are shown in Fig. 4(b).

Magnetostriction of polycrystalline $Pr_5Ni_2Si_3$ and $Pr_{15}Ni_7Si_{10}$ were measured. The results for these two compounds were very similar[5] and showed a positive magnetostriction at all temperatures in which the amplitude of magnetostriction under a 9 T field decreased with temperature for both samples. Inflection points on the λ-H curve were observed at low temperatures, at 10 K for $Pr_5Ni_2Si_3$ and at
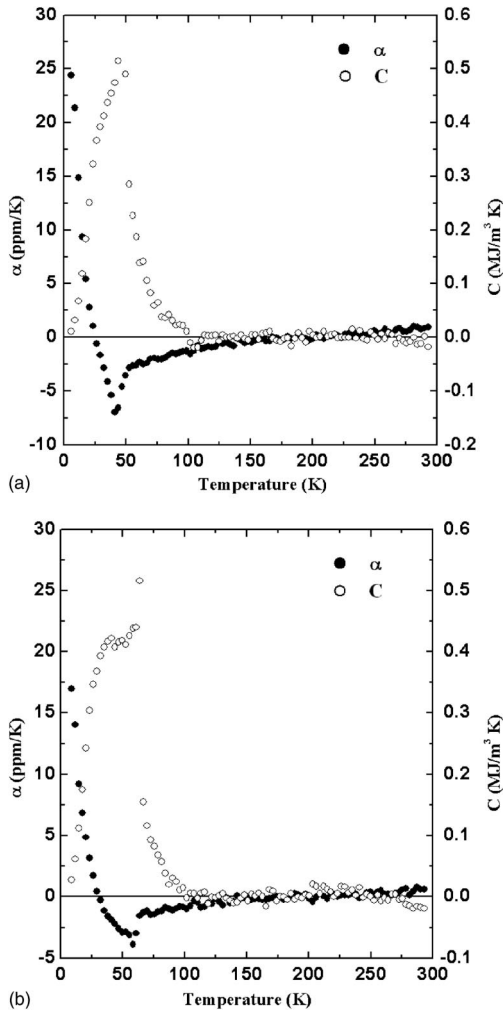
FIG. 3. The magnetic contribution to heat capacity/thermal expansion coefficient obtained from the difference between the total heat capacity/thermal expansion coefficient and the phonon contribution for (a) $Pr_5Ni_2Si_3$ and (b) $Pr_{15}Ni_7Si_{10}$ shown in Fig. 2.

FIG. 4. (a) Comparison of the calculated phonon effect of $Pr_5Ni_2Si_3$ and $Pr_{15}Ni_7Si_{10}$. (b) Comparison of the calculated Gruneisen parameter of $Pr_5Ni_2Si_3$ and $Pr_{15}Ni_7Si_{10}$ with temperature. Bulk moduli for $Pr_5Ni_2Si_3$ and $Pr_{15}Ni_7Si_{10}$ are 68.9 and 68.6 GPa, respectively.

20 K for $Pr_{15}Ni_7Si_{10}$. These are consistent with the existence of magnetic phase transitions at these temperatures. Furthermore, the inflection points in both λ-H and M-H curves occurred under similar applied field strength of around 3 T for $Pr_5Ni_2Si_3$ and 4 T for $Pr_{15}Ni_7Si_{10}$. 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 $Pr_5Ni_2Si_3$ and $Pr_{15}Ni_7Si_{10}$. 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 $Pr_5Ni_2Si_3$, 58 K for $Pr_{15}Ni_7Si_{10}$) and spin reorientation transition at a lower temperature (25 K for $Pr_5Ni_2Si_3$, 31 K for $Pr_{15}Ni_7Si_{10}$). 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
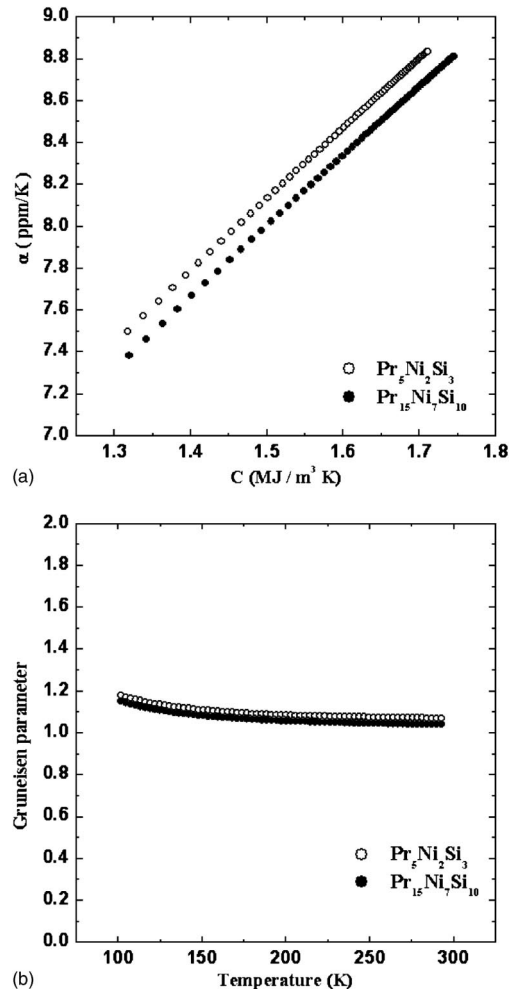
the Gruneisen parameter was then determined from thermal expansion, heat capacity, and the bulk elastic modulus for each compound.

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