Single crystal growth of $PrNiGe_2$ compounds

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Abstract

We report on the magnetic characterization of a praseodym intermetallic $PrNiGe_2$. Several single crystals are grown by the Czochralsky method from Ni- deficient sample as the initial one. X-ray analysis of the sample indicated the $CeNiSi_2$-type structure as the only phase. The unit-cell volume V tends to decrease as decreasing x. The magnetic measurements clearly indicate that $PrNi_xGe_2$ exhibits a ferromagnetic orderings at 14 K, which is independent with of composition of Ni. A strong anisotropy along the three principal crystallographic directions was observed, reflecting the orthorhombic symmetry of the crystal structure. The b-axis was found to be the easy axis of magnetization.

1 Introduction

A lot of investigations have been reported on a series of ternary compounds $R_xT_yX_z$ (R: rare earth, T: transition metal and X: p element). In these compounds, the Ruderman-Kittel-Kasuya-Yoshida (RKKY) interaction and Kondo effect compete each other. Competition between the RKKY interaction and Kondo effect was discussed by Doniach as a function of $|J_{cf}|D(\epsilon_F)$, where $|J_{cf}|$ is the magnitude of the magnetic $c-f$ exchange interaction and $D(\epsilon_F)$ is the density of the states at the Fermi energy ϵ_F [1–6].

The ternary compounds $CeTX_2$ (T = transition metal and X = Si, Ge, Sn) form a large family having the orthorhombic $CeNiSi_2$-type layered structure, which is constructed from deformed fragments of the $CeGa_2Al_2$ and α-$ThSi_2$ structures [7–9]. The lattice parameter along b-axis is extremely large compared to those along a- and c- axes, and it is expected that highly anisotropic magnetic property exists. Indeed, these compounds have received considerable interest of a great variety of magnetic behaviors [10–12]. There are not so many reports on single crystal growth due to the difficulty in obtaining single phase samples. On the other hand, the magnetic properties of polycrystals of RT_xGe_2 (T: Fe, Co, Ni, Cu, $x < 1$) have been investigated in a previous study, and it seems to be easier to grow polycrystals when the amount of T is reduced [13–16]. $PrNiGe_2$ is known to order ferromagnetically below 13 K [17]. In this study, we have grown a single crystal of $PrNi_xGe_2$ and report the anisotropic magnetic properties here.

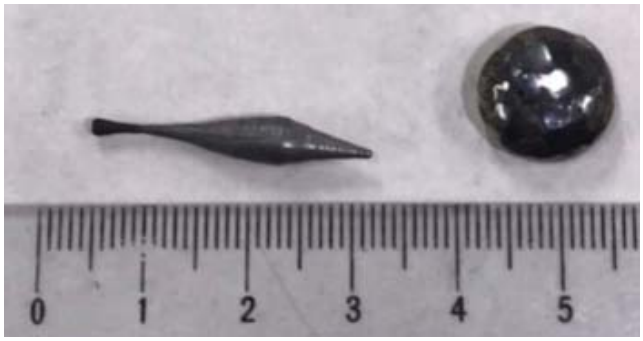

Figure 1: Photograph of a single crystal ingot of $PrNi_{0.8}Ge_2$.

2 Experimental

The polycrystalline samples of $PrNi_xGe_2$ ($x = 0.6$, 0.8, and 1.0) were prepared as starting materials by arc-melting praseodym (99.9%), nickel (99.99%) and germanium (99.999%) in a tetra-arc furnace under argon atmosphere. To improve homogenity, the ingot was turned over and remelted several times. The weight loss is negligible. Single crystals were grown by a Czochralski pulling method. The pulling parameter was kept constant during the growth (pulling rate: 10 mm/h; seed rotation speed: 10 rpm; crucible-rotation speed: 5 rpm). An ingot was 2-3 mm in diameter and 30 mm in length as shown in Figure 1. Its homogeneity and chemical composition were checked by microprobe analysis, which was made using JEOL SEM and Oxford Instrument EDX at Venture Business Laboratory Kanazawa University, based on the measurement of the Ce $L_{\alpha 1}$, Ni $K_{\alpha 1}$ and Ge $K_{\alpha 1}$ X-ray emission lines. The experimental atomic percentages of $PrNi_xGe_2$ are obtained to be Pr 25.3%, Ni 23.7% and Ge 50.9% for $x = 1.0$, Pr 30.0%, Ni 26.6% and Ge 43.3% for $x = 0.8$, and Pr 21.5%, Ni 16.4% and Ge 61.9% for $x = 0.6$, respectively. These results are closed to the theoretical value (Pr 25.0%, Ni 16.7% and Ge 58.3%), and the composition of Ni tends to decrease as decreasing x.

The samples were checked by conventional x-ray powder diffraction experiments using Cu-K_α radiation. The single crystalline state was confirmed using back-scattering Laue technique. The dc magnetic susceptibility was measured in the temperature range 2.0-300 K using a Quantum Design MPMS-5 superconducting quantum interference device magnetometer. The specific heat was measured by utilizing the Heat Capacity option on a Physical Properties Measurement System.

3 Results and Discussion

Figure 2 shows X-ray powder diffraction pattern of $PrNi_xGe_2$. All diffraction peaks can be indexed in the orthorhombic $CeNiSi_2$ type layered structure (space group Cmcm), as shown in the calculated spectrum. The determined lattice parameters a, b, and c are gathered in Table 1, and are consistent with those of previous reports [13, 17]. The unit-cell volume V tends to decrease as decreasing x.

The specific heat of $PrNi_xGe_2$ single crystal is shown in Figure 3. All samples show an anomaly reaching a maximum of $\sim$14 J $mol^{-1}K^{-1}$ at 12 K. It is consistent with the previous result of $PrNiGe_2$ polycrystalline sample [17], which is associated with the onset of ferromagnetic order. A small anomaly is observed only in $PrNi_{0.6}Ge_2$ at $\sim$17 K, indicating some magnetic impurity may be included because the sample deviate from stoichiometry.

Figure 4 shows the temperature dependence of M/H in a magnetic field of 1 kOe and the

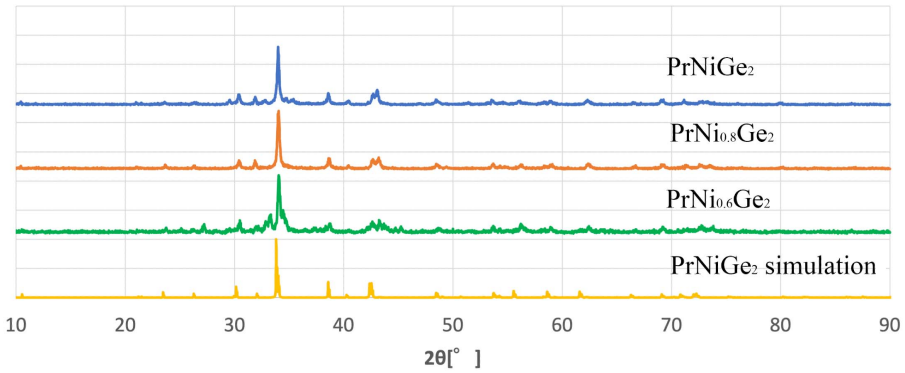

Figure 2: The X-ray powder diffraction pattern of $PrNi_xGe_2$ and the calculated spectrum.

Table 1: Lattice parameters in the orthorhombic structure of XRD patterns and the unit cell volume of $PrNi_xGe_2$.

x	a (Å)	b (Å)	c (Å)	V (Å^3)
1.0	4.25	16.73	4.30	305.9
0.8	4.25	16.80	4.18	298.1
0.6	4.25	16.80	4.18	288.9

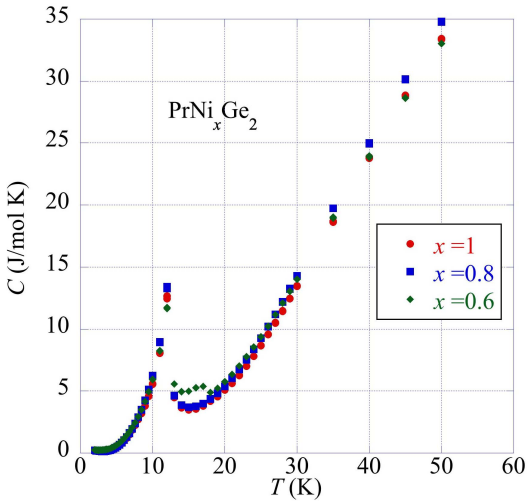

Figure 3: The specific heat of $PrNi_xGe_2$.

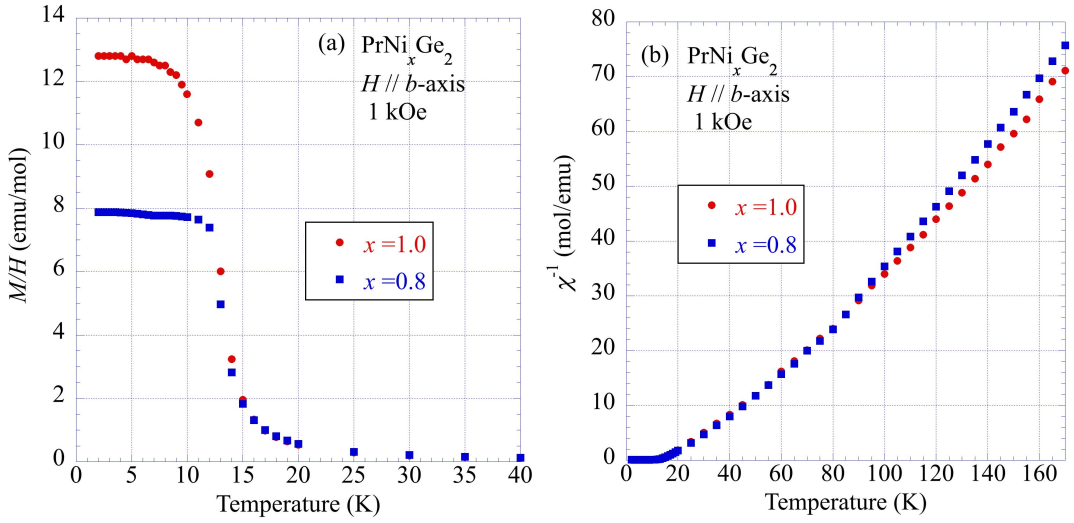

Figure 4: (a) M/H and (b) the inverse magnetic susceptibility as a function of temperature in a magnetic field of 1 kOe along b—axis of $PrNi_xGe_2$.

Table 2: Magnetic data for $PrNi_xGe_2$ compounds.

	$PrNiGe_2$ b-axis	$PrNi_{0.8}Ge_2$ a-axis	$PrNi_{0.8}Ge_2$ b-axis	$PrNi_{0.8}Ge_2$ c-axis
Θ (K)	46.1	−6.1	48	−6.0
μ_{rmeff} (μ_B)	3.47	3.06	3.34	2.99
χ_0 (10^{-3}emu/mol)	1.93	1.63	1.88	1.78
M[5T, 5K] (μ_B)	2.55	0.679	2.89	0.982

inverse magnetic susceptibility of $PrNi_xGe_2$. A strong decrease in magnetization is observed at around 13 K for both x=1.0 and 0.8 samples, which is consistent with the result of specific heat measurement. The magnetic susceptibilities of those compounds in the paramagnetic state are fitted using the following formula:

$$M/H(T) = \frac{N\mu_{\text{eff}}^2}{3k_B(T-\Theta)} + \chi_0, \tag{1}$$

where N is the Avogadro number, k_B is Boltzmann's constant, Θ is the paramagnetic Curie temperature, and χ_0 is a temperature-independent part of the magnetism including the diamagnetic core correction, the Pauli susceptibility of the electron gas, or the Van Vleck temperature independent paramagnetism. Θ, χ_0, and the effective magnetic moment μ_{eff} are given in Table 2. The χ_0 values are relatively large for both x=1.0 and 0.8 compounds while the μ_{eff} values are in good agreement with the Hund's rule ground state for Pr^{3+} ion (3.58 μ_B).

The isothermal magnetization of $PrNi_xGe_2$ measured at T = 5.0 K along the three principal crystallographic directions is shown in figure 5 (a). For $H//b$-axis the magnetization increases more rapidly with field than along the other two directions, thus indicating the b-axis as the easy axis of magnetization. Hysteretic behaviour is observed especially along b-axis, confirming the ferromagnetic ground state. At 5.0 K the magnetization saturates to 2.55 μ_B/Pr and 2.89 μ_B/Pr for $PrNiGe_2$ and $PrNi_{0.8}Ge_2$, respectively, which is larger than that of a $PrNiGe_2$ porycrystalline sample [18]. The saturation moment of the free Pr^{3+} ion ($g_J J\mu_B = 3.20\mu_B$) is relatively close to the saturation magnetization of $PrNi_{0.8}Ge_2$.

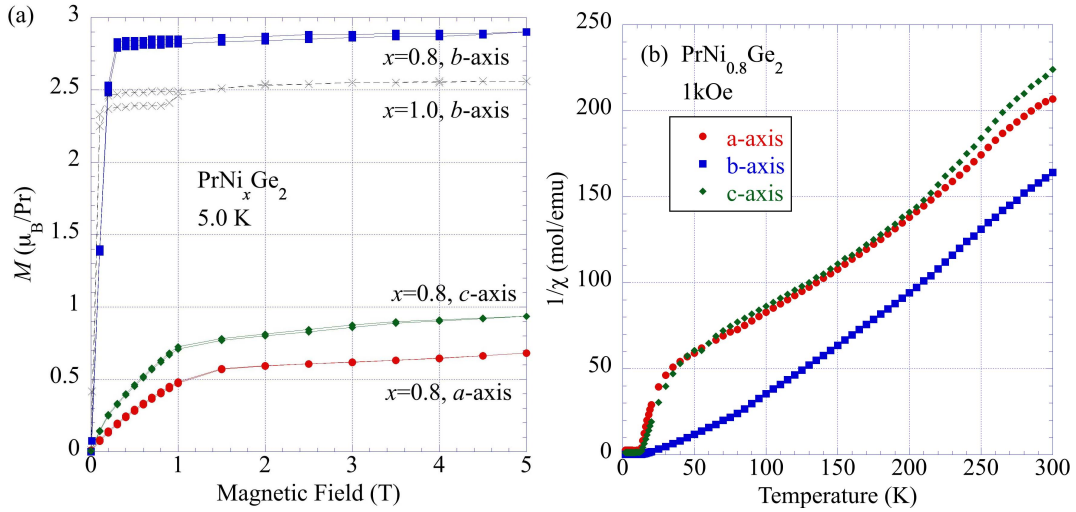

Figure 5: (a) The inverse magnetic susceptibility as a function of temperature (b) The field dependence of the magnetization of $PrNi_{0.8}Ge_2$ at 5.0 K in a magnetic field of 1 along a-, b-, and c-axes of $PrNi_{0.8}Ge_2$.

Figure 5 (b) show the temperature dependences of the inverse magnetic susceptibility of $PrNi_{0.8}Ge_2$. The anisotropy in the magnetic susceptibility along the three principal directions is clearly evident. The magnetic susceptibilities in the paramagnetic state are fitted using the formula (1). The Weiss temperature Θ is positive for b-axis, as expected for a ferromagnetic ordering compound. On the other hand, Θ is negative for a- and c-axes.

4 Summary

In this study $PrNiGe_2$ single crystals are grown by the Czochralsky method from Ni- deficient sample as the initial one. X-ray analysis of the sample indicated the $CeNiSi_2$-type structure as the only phase. The specific heat and the magnetic measurements clearly indicate that $PrNi_xGe_2$ exhibits a ferromagnetic orderings at 12 K, which is independent with of composition of Ni. A strong anisotropy along the three principal crystallographic directions was observed, reflecting the orthorhombic symmetry of the crystal structure. The b-axis was found to be the easy axis of magnetization. From the result of the magnetic susceptibility along the b- plane, the effective magnetic moment is close to the value expected for the free Pr^{3+} ions, while a temperature-independent part of the magnetism remains.

Acknowledgements

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