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Structure dependence of magnetic properties of $\text{Pr}_5\text{Si}_2\text{Ge}_2$

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Abstract

The crystal structure and magnetic and electronic transport properties of the ternary intermediate compound $\text{Pr}_5\text{Si}_2\text{Ge}_2$ were investigated by means of x-ray powder diffraction, magnetic and electrical resistance measurements. The compound has two polymorphs: $\alpha\text{-Pr}_5\text{Si}_2\text{Ge}_2$ crystallizing in a monoclinic structure with space group $P112_1/a$, for the as-cast sample, and $\beta\text{-Pr}_5\text{Si}_2\text{Ge}_2$ crystallizing in a tetragonal structure with space group $P4_12_12$, for the sample annealed at 1273 K. The average interatomic distances of magnetic Pr atoms and the amounts of covalent (Si, Ge)–(Si, Ge) bond pairs in these two phases are different, which may be responsible for their different magnetic properties. The Curie temperatures T_C of $\alpha\text{-Pr}_5\text{Si}_2\text{Ge}_2$ and $\beta\text{-Pr}_5\text{Si}_2\text{Ge}_2$ are 38 and 50 K, respectively. An irreversibility between zero-field-cooling and field-cooling magnetization curves is observed. The zero-field resistance of these two phases exhibits an anomaly near T_C . On the basis of the results of magnetic and electrical resistance measurements, it is inferred that both of these phases exhibit spin-glass-like behaviour. The magnetic properties and structure dependence of the $\text{Pr}_5\text{Si}_2\text{Ge}_2$ can be elucidated well using the Ruderman–Kittel–Kasuya–Yosida model.

The intimate relationship between crystal structure and magnetism has made the $\text{Gd}_5(\text{Si}_{1-x}\text{Ge}_x)_4$ pseudobinary alloys a unique system [1–10]. The discovery of a giant magnetocaloric effect (MCE) in the composition range of $x \leq 0.5$ triggered a subsequent extensive investigation of the crystallographic, magnetic and transport properties of these materials. In the composition range $0.24 \leq x \leq 0.5$, the MCE is related to a first-order structural phase transition from a high-temperature monoclinic (paramagnetic) to a low-temperature orthorhombic (ferromagnetic) structure [4, 5]. The alloys with $x \leq 0.2$ also

exhibit a first-order magnetostructural transformation between two different orthorhombic structures [6]. In both cases, the high-temperature phase and low-temperature phase are structurally correlated, and the structural transition is accompanied by a magnetic transition [7, 8]. In this paper we report a novel ternary intermediate compound $\text{Pr}_5\text{Si}_2\text{Ge}_2$, which crystallizes in two different structures depending on the heat treatment. In contrast to the reported scenario for $\text{Gd}_5(\text{Si}_{1-x}\text{Ge}_x)_4$, the two phases of $\text{Pr}_5\text{Si}_2\text{Ge}_2$ are not structurally correlated, although they are both ferromagnetic (FM) and exhibit a spin-glass-like behaviour at low temperature.

Two $\text{Pr}_5\text{Si}_2\text{Ge}_2$ alloys were prepared by arc melting the corresponding mixtures of pure components (with purity better than 99.9% for Pr, 99.9999% for Si and Ge) on a water-cooled copper hearth under an argon atmosphere. Each alloy was arc melted 4–5 times with the button being turned over after each melting to improve the homogeneity of the alloy. There was no heat treatment of sample 1. Sample 2 was sealed in an evacuated quartz tube and annealed for one week at 1273 K; this was followed by a water quench. The chemical compositions of the as-cast (sample 1) and heat-treated (sample 2) samples were both determined by means of an inductively coupled plasma atomic emission spectroscopy (ICP-AES, TJA Co.), which gave $\text{Pr}_5\text{Si}_{2.04(2)}\text{Ge}_{2.03(2)}$ for the as-cast sample and $\text{Pr}_5\text{Si}_{2.02(2)}\text{Ge}_{1.99(2)}$ for the heat-treated sample, in good consistency with the nominal composition. Phases were identified by means of x-ray powder diffraction (XRD). The XRD data used to refine the structural parameters were collected on a Rigaku D/max 2500 diffractometer with Cu $K\alpha$ radiation (50 kV, 250 mA) and a graphite monochromator. A step scan mode was employed with a step width of $2\theta = 0.02^\circ$ and a sampling time of 1 s. The Rietveld powder diffraction profile-fitting technique was used to refine the crystal structure of $\text{Pr}_5\text{Si}_2\text{Ge}_2$ compound using the program DBW-9411 [11, 12]. The temperature dependence of the magnetization and field dependence of the magnetization were measured by a superconducting quantum interference device (SQUID) magnetometer. The dc electrical resistance was measured by the standard four-probe method.

The XRD investigation reveals that samples 1 and 2 have different structures. Sample 1 crystallizes in a monoclinic structure with space group $P112_1/a$ (α - $\text{Pr}_5\text{Si}_2\text{Ge}_2$), but sample 2 crystallizes in a tetragonal structure with space group $P4_12_12$ (β - $\text{Pr}_5\text{Si}_2\text{Ge}_2$). For comparison, the XRD patterns of α - $\text{Pr}_5\text{Si}_2\text{Ge}_2$ and β - $\text{Pr}_5\text{Si}_2\text{Ge}_2$ are shown in figure 1. The XRD result reveals that there is about 3 wt% β - $\text{Pr}_5\text{Si}_2\text{Ge}_2$ phase in the α - $\text{Pr}_5\text{Si}_2\text{Ge}_2$ phase. The lattice parameters derived from the Rietveld refinement are: $a = 7.8282(1)$ Å, $b = 15.2072(3)$ Å, $c = 7.9902(1)$ Å and $\gamma = 93.82(0)^\circ$ for α - $\text{Pr}_5\text{Si}_2\text{Ge}_2$; and $a = 7.9725(1)$ Å and $c = 14.8855(1)$ Å for β - $\text{Pr}_5\text{Si}_2\text{Ge}_2$. Figure 2 presents the projection of the crystal structure of α - $\text{Pr}_5\text{Si}_2\text{Ge}_2$ along the c -axis and that of β - $\text{Pr}_5\text{Si}_2\text{Ge}_2$ along the b -axis. The typical distances of the (Si, Ge)–(Si, Ge) pairs are illustrated in figure 2, from which we see that in the α - $\text{Pr}_5\text{Si}_2\text{Ge}_2$ phase only three quarters of the (Si, Ge)–(Si, Ge) pairs become covalently bonded, while all of the (Si, Ge)–(Si, Ge) pairs are covalently bonded in β - $\text{Pr}_5\text{Si}_2\text{Ge}_2$. Unlike in the case of $\text{Gd}_5\text{Si}_2\text{Ge}_2$ [7, 8], the projections of these two structures indicate that these two phases are not structurally correlated. The detailed structural information including atomic parameters and interatomic distances has been published elsewhere [13, 14]. In order to determine the relative stability of these two phases, the as-cast sample 1 and heat-treated sample 2 were sealed in an evacuated quartz tube and annealed for two months at 873 K; this was followed by a water quench. However, an investigation of their XRD shows that no structural changes occur in these two samples due to this annealing.

The temperature dependence of the magnetization was measured during warming under 0.05 T after cooling down from room temperature without an applied field (zero-field cooled (ZFC)) or under an applied field (field cooled (FC)) and the results are shown in figure 3. The irreversibility between the ZFC and FC magnetization curves is a characteristic of spin-glass-

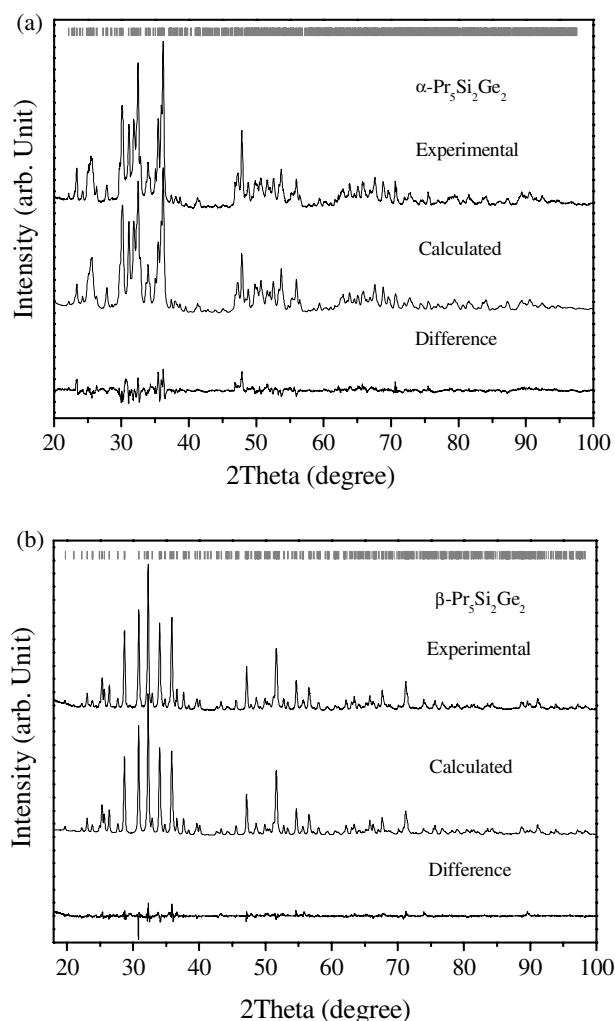


Figure 1. Experimental and calculated XRD patterns and the difference between them for (a) $\alpha\text{-Pr}_5\text{Si}_2\text{Ge}_2$ and (b) $\beta\text{-Pr}_5\text{Si}_2\text{Ge}_2$. The vertical bars indicate the expected Bragg reflection positions.

like behaviour [15, 16], which may indicate that both of these phases undergo spin-glass-like state–ferromagnetic–paramagnetic transitions on warming. In figure 3 we also show the M – T curves measured with decreasing temperature (DT) under 0.05 T for these two phases. There is no hysteresis between the FC and DT curves, which suggests that the transition occurring in these two phases at high temperature is of second order. A freezing temperature T_f is defined at the point where the irreversibility disappears; we get $T_f = 35$ K for $\alpha\text{-Pr}_5\text{Si}_2\text{Ge}_2$ and $T_f = 45$ K for $\beta\text{-Pr}_5\text{Si}_2\text{Ge}_2$. Taking the Curie temperatures T_C to be the temperatures at which dM/dT exhibits maximum values, we get $T_C = 38$ and 50 K for $\alpha\text{-Pr}_5\text{Si}_2\text{Ge}_2$ and $\beta\text{-Pr}_5\text{Si}_2\text{Ge}_2$, respectively. There is a high-temperature anomaly in the M – T curves of $\alpha\text{-Pr}_5\text{Si}_2\text{Ge}_2$, which could be attributed to the contribution of the minority phase ($\beta\text{-Pr}_5\text{Si}_2\text{Ge}_2$).

The Curie temperature of $\beta\text{-Pr}_5\text{Si}_2\text{Ge}_2$ is 12 K higher than that of $\alpha\text{-Pr}_5\text{Si}_2\text{Ge}_2$, which can be understood within the Ruderman–Kittel–Kasuya–Yosida (RKKY) approximation.

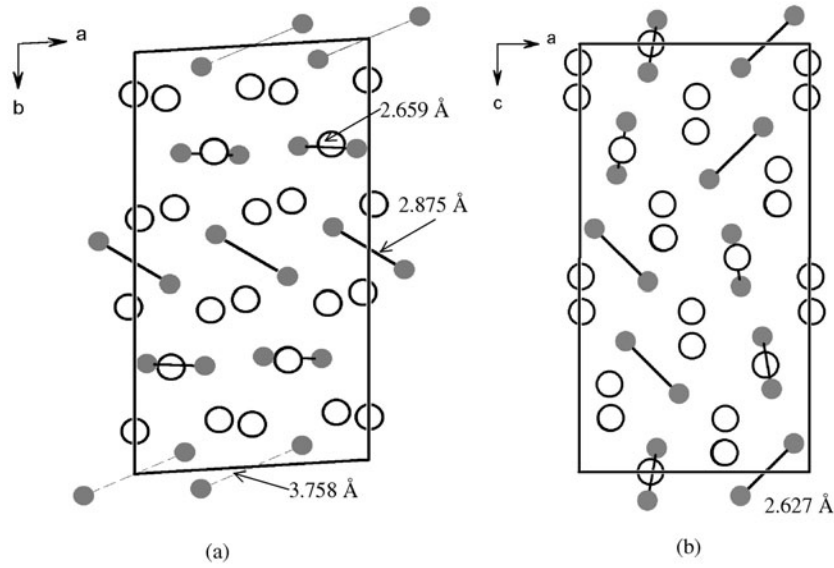


Figure 2. The projections of the crystal structures of (a) α -Pr₅Si₂Ge₂ along the *c*-axis and (b) β -Pr₅Si₂Ge₂ along the *b*-axis. The small and large circles represent M (0.5Si + 0.5Ge) and Pr atoms respectively. The solid lines indicate the covalently bonded pairs. The typical distances of M–M pairs are given in this figure.

According to Callaway [17], the effective exchange interaction is of relatively long range, decreasing as R^{-3} (R is the interatomic distance of magnetic atoms). The average interatomic distance R between magnetic Pr atoms in β -Pr₅Si₂Ge₂ is 3.883 Å, which is smaller than that in α -Pr₅Si₂Ge₂ (3.939 Å). Therefore, the exchange interaction in β -Pr₅Si₂Ge₂ should be stronger than that in α -Pr₅Si₂Ge₂, which will make the β -Pr₅Si₂Ge₂ phase have a higher magnetic ordering temperature than the α -Pr₅Si₂Ge₂ phase. In addition, according to Bleaney and Bleaney [18], within the molecular field approximation the Curie temperature can be expressed as

$$T_C = \frac{3\pi n^2}{kE_F} J_{sf}^2 (g-1)^2 J(J+1) \sum_{i \neq j} F(2k_F R_{ij}) \quad (1)$$

where E_F and k_F are the Fermi energy and Fermi wavevector of the *s* conduction electrons, k is Boltzmann's constant, n is the average number of conduction electrons per atom, J_{sf} is the *s*–*f* exchange integral and $F(2k_F R_{ij})$ is a spherical oscillating function of R_{ij} . The summation extends over all distances R_{ij} between the localized moments. Equation (1) tells us that T_C would increase with increase of the conduction electron concentration. According to the Zintl–Klemm formalism [19], the formal charges for isolated Si or Ge (M) atoms and (Si, Ge)–(Si, Ge) covalently bonded pairs (M₂ dimer) are 4– and 6–, to satisfy closed-shell configurations for Si or Ge, assuming a single bond in a (Si, Ge)–(Si, Ge) covalently bonded pair. Therefore, the corresponding charge-balanced formula is [(Pr³⁺)₅(M₂^{6–})_{1.5}(M^{4–})(2e[–])] for α -Pr₅Si₂Ge₂, which indicates two electrons assigned to the conduction band. In the same way, the charge-balanced formula of β -Pr₅Si₂Ge₂ is [(Pr³⁺)₅(M₂^{6–})₂(3e[–])], which indicates three electrons assigned to the conduction band. The higher conduction band electron concentration will also make a contribution to the higher Curie temperature of the β -Pr₅Si₂Ge₂ phase.

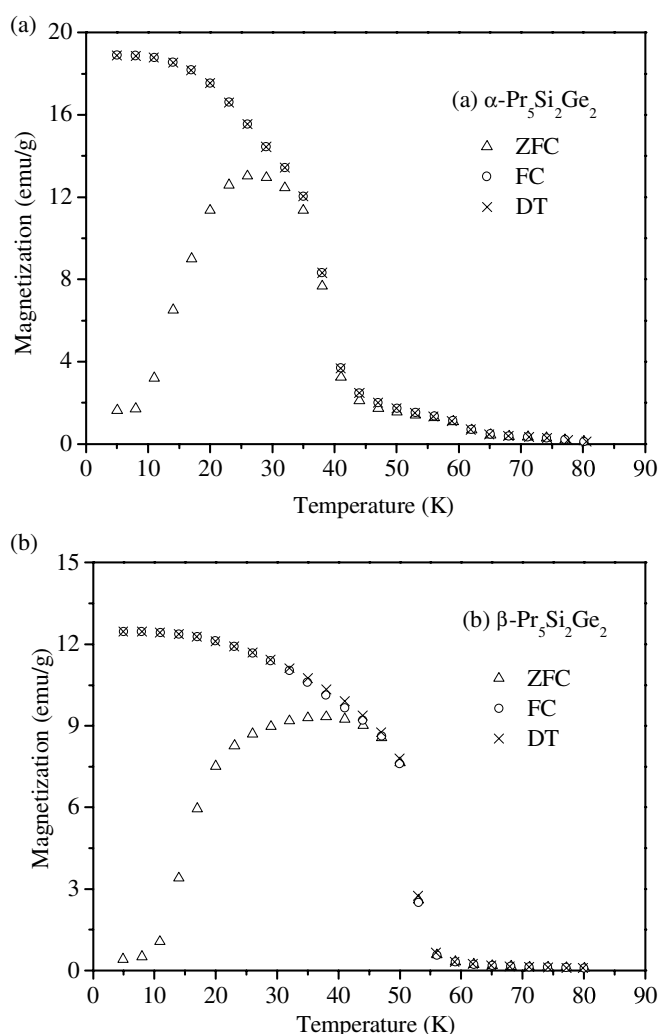


Figure 3. The temperature dependence of the magnetization in a field of 0.05 T for (a) $\alpha\text{-Pr}_5\text{Si}_2\text{Ge}_2$ and (b) $\beta\text{-Pr}_5\text{Si}_2\text{Ge}_2$. ZFC and FC indicate zero-field cooling and field cooling, respectively. DT indicates the DT measurement.

Figure 4 shows the field dependence of the magnetization at 5 K, which was measured after ZFC. S-shaped M - H curves are observed, which may be attributed to a metamagnetic transition at low field or as a characteristic of a spin-glass-like state [20]. The M - H curves reveal that the $\beta\text{-Pr}_5\text{Si}_2\text{Ge}_2$ phase is more difficult to magnetize and has lower magnetization than the $\alpha\text{-Pr}_5\text{Si}_2\text{Ge}_2$ phase. From the M - H curves we get the magnetic moments of these two phases at $H = 5$ T: $1.72 \mu_B$ per Pr for $\alpha\text{-Pr}_5\text{Si}_2\text{Ge}_2$ and $1.33 \mu_B$ per Pr for $\beta\text{-Pr}_5\text{Si}_2\text{Ge}_2$, which is much lower than the saturation value ($gJ = 3.50 \mu_B$) of a free Pr^{3+} ion. The reduced magnetization of these two phases may be related to a canted magnetic structure just like those of other 5 : 4 lanthanide silicides and germanides [21, 22] or be due to the magnetocrystalline anisotropy of Pr ions.

The temperature dependences of the electrical resistances of the $\alpha\text{-Pr}_5\text{Si}_2\text{Ge}_2$ and $\beta\text{-Pr}_5\text{Si}_2\text{Ge}_2$ phases were measured on heating from 5 to 100 K in zero magnetic field and

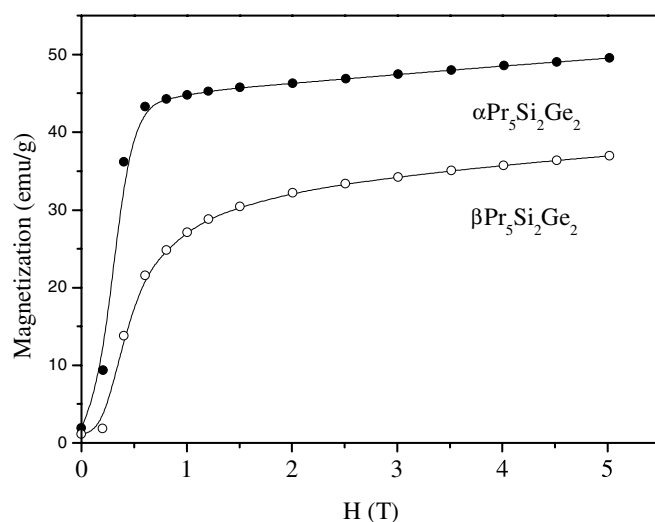


Figure 4. The field dependence of the magnetization of α - $\text{Pr}_5\text{Si}_2\text{Ge}_2$ and β - $\text{Pr}_5\text{Si}_2\text{Ge}_2$.

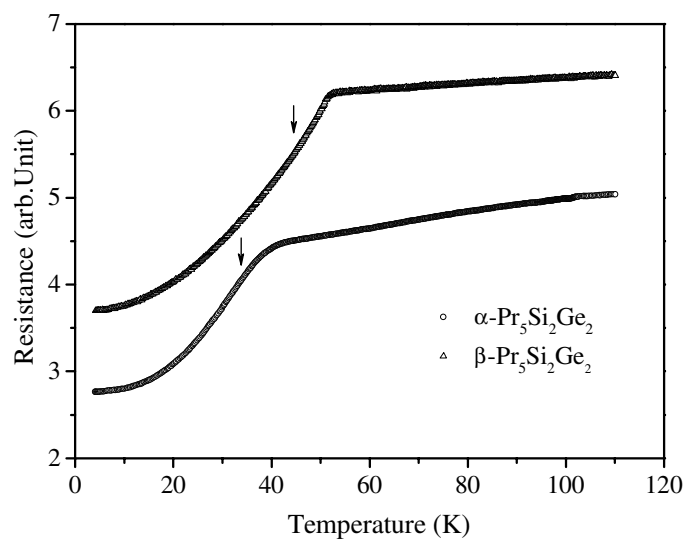


Figure 5. The temperature dependence of the electrical resistance at zero magnetic field, for α - $\text{Pr}_5\text{Si}_2\text{Ge}_2$ and β - $\text{Pr}_5\text{Si}_2\text{Ge}_2$. The arrows indicate the freezing temperatures.

the results are shown in figure 5. The $\rho(T, H = 0)$ curves exhibit a distinct kink at 39 K for α - $\text{Pr}_5\text{Si}_2\text{Ge}_2$ and at 51 K for β - $\text{Pr}_5\text{Si}_2\text{Ge}_2$. The positions of these anomalies agree well with the magnetic transition temperature T_C . No anomaly in $\rho(T, H = 0)$ is observed near the freezing temperature; this is reminiscent of the transport properties of many spin-glass-like systems [20, 23]. Thus the anomaly of the ZFC temperature dependence magnetization curve near T_f could be explained as a spin-glass-like behaviour.

The spin-glass-like state of these two phases may arise from a competition between nearest-neighbour Pr–Pr FM and Pr–Pr antiferromagnetic (AFM) exchange interactions. Within the scenario of RKKY interaction between Pr–Pr atoms, a coexistence of FM and AFM interactions

could result from a broad distribution of the nearest-neighbour Pr–Pr interatomic distance, which ranges from 3.416 to 4.301 Å in α -Pr₅Si₂Ge₂ and from 3.4852 to 4.357 Å in β -Pr₅Si₂Ge₂.

In conclusion, we have reported the crystal structure and magnetic properties of the novel ternary intermediate compound Pr₅Si₂Ge₂. The compound has two polymorphs: α -Pr₅Si₂Ge₂ crystallizing in a monoclinic structure with space group $P112_1/a$, for the as-cast sample, and β -Pr₅Si₂Ge₂ crystallizing in a tetragonal structure with space group $P4_12_12$, for the sample annealed at 1273 K. The Curie temperature of the β -Pr₅Si₂Ge₂ phase is 12 K higher than that of the α -Pr₅Si₂Ge₂ phase and both phases exhibit spin-glass-like behaviour.

Acknowledgments

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