

2013

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The crystal structure and magnetic properties of Pr₁₁₇Co_{56.7}Ge₁₁₂

Abstract

The ternary intermetallic compound Pr₁₁₇Co_{56.7}Ge₁₁₂ adopts the cubic Tb₁₁₇Fe₅₂Ge₁₁₂-type related structure with the lattice parameter $a = 29.330(3)$ Å. The compound exhibits one prominent magnetic transition at ~10 K and two additional weak magnetic anomalies are observed at ~26 K and ~46 K in a 1 kOe applied field. At a higher field of 10 kOe, only one broad ferromagnetic-like transition remains at 12 K. The inverse magnetic susceptibility of Pr₁₁₇Co_{56.7}Ge₁₁₂ obeys the Curie-Weiss law with a positive value of the paramagnetic Curie temperature ($\theta_P = 24$ K), indicating that ferromagnetic interactions are dominant. The effective magnetic moment is $3.49 \mu_B/\text{Pr}$, which is close to the theoretical effective paramagnetic moment of $3.58 \mu_B$ for the Pr³⁺ ion.

Disciplines

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The following article appeared in Journal of Applied Physics 113, 17E120 (2013); 1 and may be found at [doi:10.1063/1.4794376](https://doi.org/10.1063/1.4794376).

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Citation: *Journal of Applied Physics* **113**, 17E120 (2013); doi: 10.1063/1.4794376

View online: <http://dx.doi.org/10.1063/1.4794376>

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The crystal structure and magnetic properties of $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$

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(Presented 18 January 2013; received 1 November 2012; accepted 28 November 2012; published online 11 March 2013)

The ternary intermetallic compound $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ adopts the cubic $\text{Tb}_{117}\text{Fe}_{52}\text{Ge}_{112}$ -type related structure with the lattice parameter $a = 29.330(3)$ Å. The compound exhibits one prominent magnetic transition at ~ 10 K and two additional weak magnetic anomalies are observed at ~ 26 K and ~ 46 K in a 1 kOe applied field. At a higher field of 10 kOe, only one broad ferromagnetic-like transition remains at 12 K. The inverse magnetic susceptibility of $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ obeys the Curie-Weiss law with a positive value of the paramagnetic Curie temperature ($\theta_P = 24$ K), indicating that ferromagnetic interactions are dominant. The effective magnetic moment is $3.49 \mu_B/\text{Pr}$, which is close to the theoretical effective paramagnetic moment of $3.58 \mu_B$ for the Pr^{3+} ion. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4794376>]

Rare earth based intermetallics are interesting compounds because they often form extended families of isostructural or nearly isostructural materials, and therefore, exhibit systematic changes of their physical properties. Having identical or nearly identical three-dimensional-arrangements of atoms in these compounds facilitate investigation of the balance between chemistry (crystal and electronic structures) and physical (magnetic, electrical, and thermal) properties. Among numerous isostructural intermetallic families, R-M-X ternary intermetallic systems, where R is a rare earth element, M is a transition metal, and X is a non-metal or a semimetal have been broadly investigated in the past. Unlike many of the common R-M-X ternary compounds that crystallize in conventional, “small” unit cells, the compounds that belong to the $\text{R}_{117}\text{M}_{52+x}\text{X}_{112+y}$ (M = Fe, Co, and Cr, X = Ge, Sn) family are extraordinarily complex because their giant cubic unit cells ($V > 20\,000$ Å³) accommodate in excess of 10^3 atoms. $\text{Tb}_{117}\text{Fe}_{52}\text{Ge}_{112}$ was the first compound of this family to be reported in 1987.¹ Since then, a series of compounds of the $\text{Tb}_{117}\text{Fe}_{52}\text{Ge}_{112}$ -type structure were prepared and characterized. The reported germanides include $\text{R}_{117}\text{Fe}_{52}\text{Ge}_{112}$ (R = Y, Pr, Sm, Gd, Dy, Ho, Er, Tm, and Lu), $\text{R}_{117}\text{Cr}_{52}\text{Ge}_{112}$ (R = Nd and Sm) and $\text{R}_{117}\text{Co}_{52}\text{Ge}_{112}$ (R = Pr and Sm).²⁻⁴ Recently, another series of the isostructural compounds with Sn instead of Ge has been found, namely the $\text{R}_{117}\text{Co}_{52+x}\text{Sn}_{112+y}$ compounds with R = Pr, Sm, Gd, Tb, and Dy.⁵⁻⁷ Their crystal structures are nearly identical to those with Ge, but small differences have been reported.

Being one of the most structurally complex ternary solid systems, $\text{R}_{117}\text{M}_{52+x}\text{X}_{112+y}$ compounds are expected to exhibit unique physical properties. However, until now, most reports have been limited to crystallographic studies, lacking the information about the physical properties of these compounds. To date, there are only two papers reporting the basic magnetic properties of $\text{R}_{117}\text{Co}_{52+x}\text{Sn}_{112+y}$ (R = Pr, Sm, Tb, and Dy)^{5,6} and one paper discussing the magnetic, transport properties,

and heat capacity of $\text{Gd}_{117}\text{Co}_{56}\text{Sn}_{112}$.⁷ Magnetic properties of the $\text{Tb}_{117}\text{Fe}_{52}\text{Ge}_{112}$ -type structure family remain unknown. Therefore, in this work, the compound $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ was synthesized and studied in order to gain a deeper insight into this highly complex structure. The crystal structure of the $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ was determined using x-ray single crystal diffraction. The magnetic properties of this compound were investigated in detail by means of temperature- and field-dependent magnetization measurements.

A sample of the compound $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$, weighing about 5 g, was prepared by arc melting the three elements in an argon atmosphere. The Pr metal used to prepare this alloy was obtained from the Materials Preparation Center of the Ames Laboratory,⁸ and it was 99.8+ at. % pure. The Co metal with 99.95 wt. % purity and Ge with 99.999 wt. % purity were purchased from Alfa Aesar, Inc. The phase purity and structural analysis of the sample were evaluated by Rietveld refinement⁹ of the x-ray powder diffraction data, and by single crystal diffraction analysis, respectively. The powder diffraction data reveal that the as cast $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ sample is nearly a single phase compound crystallizing in the $\text{Tb}_{117}\text{Fe}_{52}\text{Ge}_{112}$ -type related structure (space group, $Fm\bar{3}m$) with a lattice parameter $a = 29.330(3)$ Å. A single crystal measuring $60 \times 60 \times 80$ μm was mounted on a Bruker APEX CCD single crystal diffractometer equipped with graphite-monochromatized Mo K α ($\lambda = 0.71069$ Å) radiation. Room temperature intensity data were collected by the ω -scan method over $2\theta = \sim 7^\circ - 57^\circ$ with exposures of 15 s per frame. An empirical absorption correction was performed with the aid of subprogram SADABS.¹⁰ The starting atomic parameters derived via direct methods and the program SIR 97 (Ref. 11) were subsequently refined using the program SHELX-97 (Ref. 12) with anisotropic atomic displacement parameters included for all atoms. The magnetic properties of $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ were investigated by dc magnetic susceptibility measurements from 2 to 300 K in magnetic fields up to 70 kOe using a superconducting quantum interference device magnetometer MPMS XL-7 made by Quantum Design, Inc.

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TABLE I. Details of the crystal structure investigation and refinement for $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$.

Emp. form.	$\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$
Space group	$Fm-3m$
a (Å)	29.330(3)
Absorption coefficient, μ (mm^{-1})	38.779
θ range	1.20° – 28.62°
Index ranges	$-38 \leq h \leq 39$
Reflections collected	55942
Independent reflections	1643
Data/restraints/parameters	1643/0/96
Goodness-of-fit on F^2	1.08
Final R indices [$I > 2\sigma(I)$] ^a	$R_1 = 0.037$, $wR_2 = 0.070$
R indices (all data)	$R_1 = 0.058$, $wR_2 = 0.078$
$R_{\text{int}}/R_{\text{sigma}}$	0.145/0.038

The crystal structure of $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ was determined using x-ray single crystal diffraction. Results of the crystal structure refinement are listed in Tables I and II. $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ crystallizes in a structure very close to the $\text{Tb}_{117}\text{Fe}_{52}\text{Ge}_{112}$ structure type.¹ The crystal structure of $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ is very similar to $\text{Gd}_{117}\text{Co}_{56.4}\text{Sn}_{114.3}$.¹³ The crystal structure of $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ belongs to a superstructure modification of the Cu_2MnAl (Ref. 14) type (Figure 1(a)). It can be described starting from the $\text{Pr}(\text{Ge}_6(\text{Co}_{24})_{1/2}(\text{Co}_8)_{1/2})$ clusters, which correspond to the Al positions. $\text{Pr}(\text{Ge}_6(\text{Co}_{24})_{1/2}(\text{Co}_8)_{1/2})$ in analogy with $\text{Gd}(\text{Sn}_6(\text{Co}_{24})_{1/2}(\text{Co}_8)_{1/2})$ is a statistical mixture of a PrGe_6Co_8 cube and a $\text{PrGe}_6(\text{Co}_3)_8$ cuboctahedron. Neither of these two modifications can exist separately resulting in an average polyhedron— $\text{PrGe}_6\text{Co}_4(\text{Co}_3)_4$. Similar, however, well ordered $\text{PrGe}_6(\text{Co}_3)_4(\text{Co})_4$ polyhedra fill the 8c sites, which correspond to the tetrahedral voids of the basic model (Cu positions in Cu_2MnAl). The structural disorder around the 4a position (1/2, 1/2, 1/2) in $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ is slightly different than that in $\text{Gd}_{117}\text{Co}_{55.4}\text{Sn}_{114.4}$. The octahedral voids of the structure (Mn positions) are filled by $[\text{Co}_8]\text{Co}_6\text{Co}_8\text{Pr}_6$ (Figure 1(b)), where the central Co7 cube position is in split with surrounding Co6 octahedron (i.e., when an atom replacing the Co7 position, another atom cannot occupy Co6 position, and vice versa) in contrast to the axially oriented disorder of the Co positions in $\text{Gd}_{117}\text{Co}_{56.4}\text{Sn}_{114.3}$. Such unusual distribution of the electron density in the vicinity of

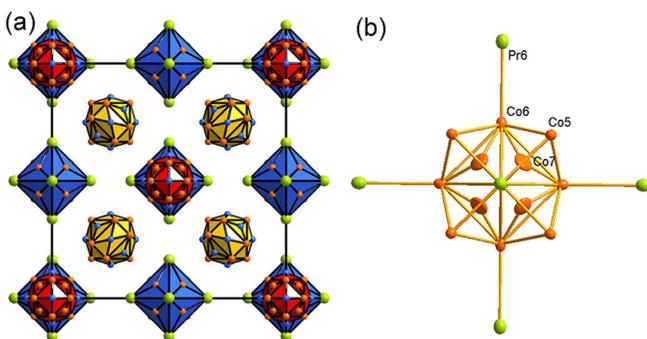


FIG. 1. (a) $\text{Pr}(\text{Ge}_6(\text{Co}_{24})_{1/2}(\text{Co}_8)_{1/2})$ (red), $\text{Pr}(\text{Ge}_6(\text{Co}_3)_4(\text{Ge})_4)$ (yellow), and $\text{Co}_6\text{Co}_8\text{Pr}_6$ fragments in the crystal structure of $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$. (b) Atomic arrangement around the position (0.5 0.5 0.5).

TABLE II. Atomic position, site occupation fraction (SOF), and equivalent thermal displacement (U_{eq}) parameters of $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$.

Atom	Wyck.	x	y	z	SOF	U_{eq} (Å ²)
Pr1	96k	0.06714(2)	0.06714(2)	0.15562(3)	1	0.0121(2)
Pr2	96k	0.18067(2)	0.18067(2)	0.40586(3)	1	0.0089(2)
Pr3	96k	0.19956(2)	0.19956(2)	0.06830(3)	1	0.0081(2)
Pr4	96j	0	0.10401(3)	0.25498(3)	1	0.0086(2)
Pr5	48i	1/2	0.11698(3)	0.11698(3)	1	0.0116(3)
Pr6	24e	0.33703(6)	0	0	1	0.0126(4)
Pr7	8c	1/4	1/4	1/4	1	0.0074(6)
Pr8	4a	0	0	0	1	0.032(1)
Ge1	96k	0.07579(4)	0.07579(4)	0.32241(6)	1	0.0084(3)
Ge2	96k	0.10801(4)	0.10801(4)	0.24255(5)	1	0.0094(3)
Ge3	48i	1/2	0.20928(6)	0.20928(6)	1	0.0123(5)
Ge4	48h	0	0.14436(6)	0.14436(6)	1	0.0099(5)
Ge5	48g	0.14406(8)	1/4	1/4	1	0.0082(4)
Ge6	32f	0.14969(6)	0.14969(6)	0.14969(6)	1	0.0103(6)
Ge7	32f	0.30567(7)	0.30567(7)	0.30567(7)	1	0.0220(7)
Ge8	24e	0.1067(1)	0	0	1	0.0224(8)
Ge9	24e	0.2154(1)	0	0	1	0.0137(7)
Co1	96k	0.16814(5)	0.16814(5)	0.23182(7)	1	0.0088(4)
Co2	32f	0.39493(8)	0.39493(8)	0.39493(8)	1	0.0112(7)
Co3	48h	0	0.0773(1)	0.0773(1)	0.89(1)	0.065(2)
Co4	32f	0.053(1)	0.053(1)	0.053(1)	0.10(1)	0.065(2)
Co5	32f	0.44338(8)	0.44338(8)	0.44338(8)	1	0.0145(8)
Co6	24e	0.4315(3)	1/2	1/2	0.56(2)	0.019(3)
Co7	32f	0.4748(4)	0.4748(4)	0.4748(4)	0.24(2)	0.046(8)

these positions (expressed in the flattened and elongated ellipsoids) is the result of the low local atomic density and is typical for all of the reported compounds of this family.^{5–7}

Figure 2(a) shows the temperature variation of the magnetization of $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ measured in a 1 kOe applied field under zero-field-cooled heating (ZFC) and field-cooled-cooling (FCC) conditions. The results show that there is one prominent magnetic transition at ~ 10 K (T_{f1}) and two weak magnetic anomalies at ~ 26 K (T_{f2}) and ~ 46 K (T_{f3}) under both ZFC and FCC conditions, which can be clearly seen from the temperature derivatives of the ZFC and FCC data. All of the transitions have ferromagnetic characteristic. A significant thermal irreversibility between the ZFC and FCC branches is clearly observed below T_{f1} . Considering the eight atomic positions of Pr atoms, the arrangement of the magnetic moments in this compound can be very complex. The three transitions may be associated with the reorientations of Pr moments among the different magnetic structures.

Figure 2(b) shows the ZFC and FCC magnetization curves measured in an applied field of 10 kOe. The anomaly at T_{f2} observed in a low field of 1 kOe has disappeared. The anomaly at T_{f3} becomes nearly indistinguishable, but a broad ferromagnetic-like transition at 12 K remains clearly visible. In addition, the bifurcation between the ZFC and FCC data is suppressed by the high field. The magnetocrystalline anisotropy of the Pr ions and the nonzero coercivity (see below) are the reasons for the observed thermomagnetic irreversibility.¹⁵ The inset in Figure 2(b) shows the temperature dependence of the inverse susceptibility (H/M) of $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ measured in 10 kOe applied field and the Curie-Weiss fit to the experimental data. The paramagnetic Curie temperature and the effective

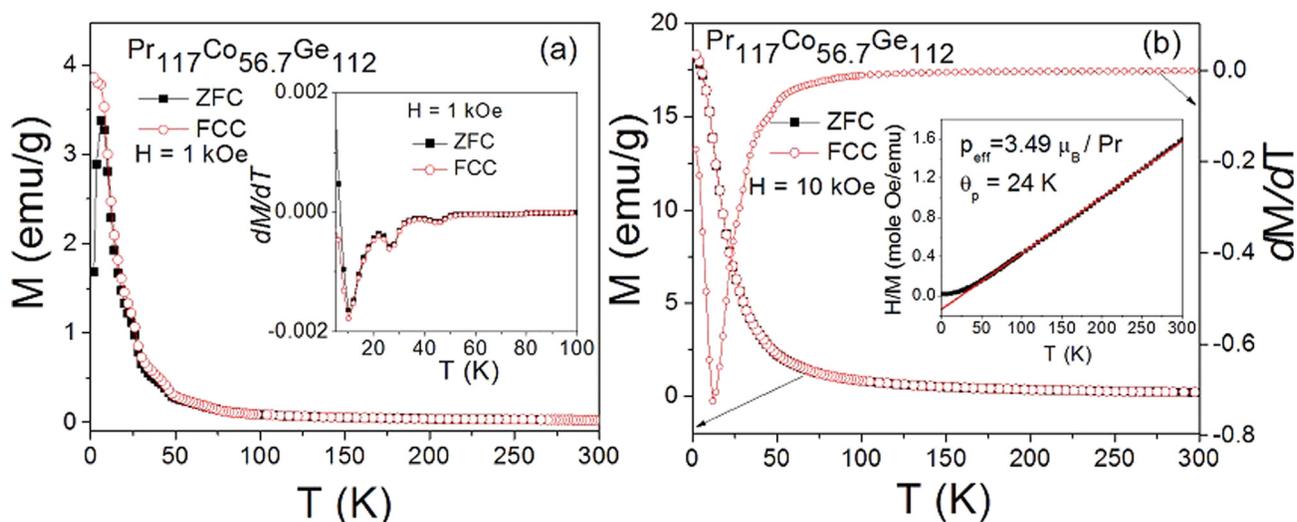


FIG. 2. (a) Temperature (T) dependence of the magnetization (M) of $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ measured in magnetic field (H) of 1 kOe under ZFC and FCC conditions. The inset shows the temperature derivatives of the ZFC and FCC data. (b) M vs. T and the temperature derivative of the FCC data of $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ measured in 10 kOe magnetic field. The inset shows Curie-Weiss fit to the inverse magnetic susceptibility.

magnetic moment, obtained from the Curie-Weiss fit, are 24 K and $3.49 \mu_{\text{B}}/\text{Pr}$, respectively. The value of μ_{eff} is close to the theoretical effective moment for Pr^{3+} ion $(g_J[J(J+1)])^{1/2} = 3.58 \mu_{\text{B}}$. Assuming that the crystalline electric field effects in $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ are weak, the Co sublattice here is not magnetic, the same as in the $\text{Tb}_{117}\text{Co}_{59}\text{Sn}_{111}$ and $\text{Dy}_{117}\text{Co}_{58}\text{Sn}_{111}$ compounds.⁶ The positive value of Weiss constant θ_{p} indicates that the ferromagnetic interactions are dominant.

Figure 3 shows the $M(H)$ isotherms of $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ collected at 2 and 40 K. At 2 K, the magnetization initially increases nearly linearly with field and then shows a trend toward saturation at high field. Coercivity of ~ 800 Oe and ~ 2.7 emu/g remanence are observed. The magnetization measured at 2 K in a field of 70 kOe is $1.46 \mu_{\text{B}}/\text{Pr}$, which is much lower than the saturation value ($gJ = 3.20 \mu_{\text{B}}$) of Pr^{3+} . The magnetization isotherm measured at 40 K shows a minor deviation from paramagnetic behavior. Most likely reasons for the moment reduction are that the arrangement of Pr spin

moments may be noncollinear, or only a fraction of the total of eight inequivalent Pr atoms may order magnetically, which remains to be established. Unfortunately, the complexity of the structure makes neutron scattering studies of the material extremely difficult, if at all possible.

In summary, the crystal structure and bulk magnetic properties of the ternary intermetallic compound $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ have been studied. The structure of this germanide is closely related to $\text{Tb}_{117}\text{Fe}_{52}\text{Ge}_{112}$ -type structure with a giant unit cell. The compound orders magnetically in several steps between 46 and 10 K. The inverse susceptibility follows the Curie-Weiss law and the effective magnetic moment suggests that the magnetic moments are localized on the rare earth atoms.

This work was supported by the U.S. Department of Energy, Office of Basic Energy Science, Division of Materials Sciences and Engineering under Contract No. DE-AC02-07CH11358 with Iowa State University.

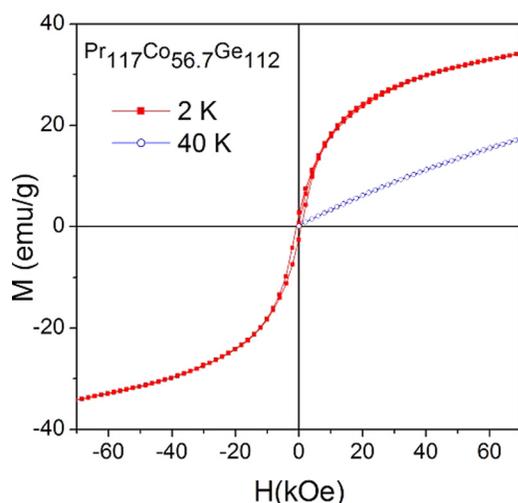


FIG. 3. Field (H) dependence of magnetization (M) of $\text{Pr}_{117}\text{Co}_{56.7}\text{Ge}_{112}$ measured at 2 and 40 K.

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