Magnetic phase transitions in Pr$_5$Ge$_4$

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The magnetic structure and magnetic phase transitions of the Pr$_5$Ge$_4$ compound are investigated by means of neutron powder diffraction (NPD) and small-angle neutron scattering (SANS). Both NPD and SANS indicate the existence of two magnetic phase transitions at 25 K and 42 K. Refinement of the crystal structure based on the high-resolution NPD data shows that from room temperature to 1.6 K the compound maintains the Sm$_5$Ge$_4$-type structure ($Pnma$, $Z=4$), in which Ge atoms occupy two 4$c$ sites and one 8$d$ site and Pr atoms occupy two 8$d$ sites and one 4$c$ site. Refinements of the magnetic structures reveal that the two magnetic transitions essentially correspond to the long-range orderings of the Pr moments on different crystallographic sites. The Pr moments on the 4$c$ site order ferromagnetically with $Pn’ma’$ symmetry at 42 K and induce small ordered Pr moments on the 8$d$ sites. The long-range ordering of the Pr moments on the 8$d$ sites develops at 25 K with $Pnm’a’$ symmetry. The separate ordering of the Pr moments on different crystallographic sites can be readily understood by the salient difference in the rare earth metal environments between the different crystallographic sites. The Pr moments on the 4$c$ site in Pr$_5$Ge$_4$ compound align along the $b$ axis, in contrast to other reported $R_5$Ge$_4$ compounds, and can be attributed to the contribution of higher-order terms of crystal-field to magnetocrystalline anisotropy of the various $R$ atoms in the $R_5$Ge$_4$ compounds.

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1. INTRODUCTION

Interest in the $R_5$(Si,Ge)$_4$ pseudobinary alloys ($R$= rare earth) has been revived recently owing to the discovery of a giant magnetocaloric effect (MCE) in Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ by Pecharsky and Gschneidner,$^{1,2}$ which is attractive for its potential application as magnetic refrigerants. The giant MCE in Gd$_5$(Si$_{1-x}$Ge$_x$)$_4$ shows a maximum at a specific temperature tunable by adjusting the Ge content$^2$ and is essentially due to simultaneous first-order structural/magnetic phase transitions near that temperature.$^{3,4}$ These transitions also lead to a strong magnetoelastic effect$^1$ and giant magnetoresistance$^5$ of the compounds. Similar effects were observed in other $R_5$(Si,Ge)$_4$ alloys$^6,7$ and recently in Gd$_5$Sn$_4$.$^8$ Knowledge of the magnetic structures of these compounds is indispensable for understanding these intriguing field-dependent properties of the compounds. However, such knowledge remains largely unknown, although $R_5$Si$_4$ and $R_5$Ge$_4$ compounds were discovered and their crystal structures were identified over 30 years ago.$^9$

$R_5$Si$_4$ crystallizes in either the tetragonal Zr$_5$Si$_4$-type structure (space group $P4_121$2) or the orthorhombic Gd$_5$Si$_4$-type structure (space group $Pnma$) depending on whether $R$ is a light or a heavy rare earth metal, whereas all $R_5$Ge$_4$ compounds crystallize in the orthorhombic Sm$_5$Ge$_4$-type structure (space group $Pnma$)$^{9,10}$ The structures of Gd$_5$Si$_4$ and Gd$_5$Ge$_4$ as well as their difference were nicely illustrated by Pecharsky and Gschneidner.$^{11}$ Both structures are basically built from equivalent layers (slabs) that are infinite in two dimensions ($a$ and $c$). The Gd atom on the 4$c$ site is coordinated by six Si or Ge atoms forming a distorted octahedron and by eight Gd atoms on two different 8$d$ sites (four on each 8$d$ site) forming a slightly distorted cube that shares edges with each other to form the slab. The Si or Ge atoms inside the slab form partially covalent bonds, and the other Si or Ge atoms locate on the surface of the slab. In Gd$_5$Si$_4$ the slabs are all interconnected via partially covalent interslab Si-Si bonds, while in Gd$_5$Ge$_4$ all the interslab Ge-Ge bonds are broken.$^{12}$ For the purpose of constructing a magnetic structure model, only the magnetic rare earth atoms are considered, and the structure can be viewed as composed of two-dimensional slabs consisting of the edge-shared cubes and interconnected by shorter bonds between $R$ atoms on two different 8$d$ sites. Figure 1 illustrates the crystal structure of Pr$_5$Ge$_4$.

The magnetic structures of only a few $R_5$Ge$_4$ compounds were studied by neutron diffraction—i.e., Tb$_5$Ge$_4$,$^{13}$ Ho$_5$Ge$_4$,$^{14}$ and Nd$_5$Ge$_4$.$^{15}$ Recently the magnetic structures of Tb$_x$(Si$_{1-x}$Ge$_x$)$_4$ were investigated by Ritter et al.$^{16}$ and those of Nd$_5$Si$_4$ and Nd$_5$Ge$_4$ by Cadogan et al.$^{17}$ It is intriguing to notice that, unlike the crystal structure, the magnetic structures of $R_5$Ge$_4$ belong to different magnetic space groups depending on the rare earth—e.g., $Pnm’a’$ for Tb$_5$Ge$_4$, $Pn’ma’$ for Ho$_5$Ge$_4$, and $Pnm’a’$ for Nd$_5$Ge$_4$. In addition, neutron diffraction studies reveal that there are two magnetic phase transitions in Ho$_5$Ge$_4$ and Tb$_5$Ge$_4$. Two magnetic phase transitions are also evident in Pr$_5$Ge$_4$ in the temperature dependence of the magnetization in a field of 500 Oe.$^{18}$ As temperature increases, the magnetization curve exhibits two sudden drops at $T_C^{\text{L}}=25$ K and $T_C^{\text{H}}=41$ K, respectively. A large magnetoresistance ($\Delta \rho/\rho$) was observed (about 25% at 24 K and 15% at 40 K) in the presence of a magnetic field of 5 T.

Pr$_5$Ge$_4$ crystallizes in the Sm$_5$Ge$_4$ structure. Detailed crystallographic data, including lattice parameters, atomic positions, and bond lengths derived from x-ray powder dif-

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fraction (XRD) data, were reported by Yang et al. In the present work we focus on the investigation of the magnetic structure of Pr₅Ge₄ by means of temperature-dependent small-angle neutron scattering (SANS) and neutron powder diffraction (NPD).

II. EXPERIMENT

The sample of polycrystalline Pr₅Ge₄ was prepared by arc-melting the mixture of pure metal components (with purity better than 99.9% for Pr and 99.9999% for Ge) from General Research Institute for Nonferrous Metals, China) in a water-cooled copper hearth under an argon atmosphere as described previously. All the neutron experiments were performed at the NIST Center for Neutron Research (NCNR). SANS measurements over the q range from 0.008 Å⁻¹ to 0.132 Å⁻¹ were carried out using the NG-1 8-m SANS instrument with an incident neutron wavelength of λ = 8 Å and resolution of Δλ/λ = 0.14. The magnetic order parameter and coarse-resolution magnetic diffraction patterns were determined on the BT-7 spectrometer with a wavelength of 2.4649 Å. NPD data for refinement of the magnetic structures were collected on the high-resolution, 32-counter BT-1 diffractometer. A Cu(311) monochromator was used to produce a monochromatic neutron beam of wavelength 1.5402(1) Å. Collimators with horizontal divergence of 15°, 20°, and 7° full width at half maximum of arc were used before and after the monochromator and after the sample, respectively. Data were collected in the 2θ range of 3°–168° with a step of 0.05°. The structure refinements were carried out using the program GSAS.

III. RESULTS AND DISCUSSION

Neutron diffraction at room temperature confirms the investigated Pr₅Ge₄ to be paramagnetic and to crystallize in the Sm₃Ge₄-type structure (Pnma, Z = 4). The derived lattice constants from the structure refinement are a = 7.9172(4) Å, b = 15.1916(7) Å, and c = 8.0112(4) Å, in good agreement with the XRD results. No structural transitions were detected between 9 and 295 K.

Figure 2 shows the experimental and calculated NPD patterns of the Pr₅Ge₄ compound at room temperature. The refined structural parameters and R factors of the refinement for Pr₅Ge₄ are listed in Table I.

Figure 3 shows the magnetic diffraction patterns obtained by subtracting the data at 26 and 9 K, respectively, from the data taken at 60 K, well above the magnetic ordering temperature. The magnetic Bragg peaks can be indexed on the nuclear unit cell. The temperature dependence of the peak intensity of the overlapping (131) and (040) peaks and the integrated intensity of the (010) peak measured on BT-7 during warming are shown in Fig. 4(a). The temperature dependence of the peak intensity of the (131) overlapping the (040) peak is very similar to the low-field magnetization curve reported in Ref. 18. Two steps are evident: one occurs at ~25 K and the other at ~42 K. Both temperatures coincide well with the magnetic transition temperatures derived from the magnetization measurements. The (010) peak is a purely magnetic one, and on warming its integrated intensity starts to decrease prominently. The intensity increases rapidly, reaches a maximum at about 32 K where the lower step of the (131) and (040) peak intensities obviously decline. The (010) peak then disappears at the magnetic transition temperature TᵢC = 41 K. The evolution of the magnetic (010) peak strongly suggests a change of symmetry of the magnetic structure.

Small-angle neutron scattering is particularly sensitive to the ferromagnetic component of a magnetic structure, and
Table I. Crystallographic data and magnetic moments of Pr₅Ge₄ at room temperature, 50 K, 30 K, and 9 K derived from refinements of the high-resolution neutron diffraction data. x, y, z are fractional coordinates of the atoms in a unit cell, U_iso is the isotropic temperature factor, and μₓ, μᵧ, μz, are components of the magnetic moment along the a, b, c directions, respectively. R_p and R_wp are residuals of fitting to the pattern and weighted pattern, respectively. χ² is a “goodness of fit” indicator (Ref. 20).

<table>
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<tr>
<th></th>
<th>9 K</th>
<th>9 K</th>
<th>30 K</th>
<th>50 K</th>
<th>Room temperature</th>
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<tr>
<td>a (Å)</td>
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<td>7.9105(2)</td>
<td>7.9114(2)</td>
<td>7.9117(3)</td>
<td>7.9172(4)</td>
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<tr>
<td>b (Å)</td>
<td>15.144(5)</td>
<td>15.1455(3)</td>
<td>15.1404(3)</td>
<td>15.1409(7)</td>
<td>15.1916(7)</td>
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<tr>
<td>c (Å)</td>
<td>7.9968(3)</td>
<td>7.9973(3)</td>
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<td>7.9943(3)</td>
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<td>V (Å³)</td>
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<td>958.15(4)</td>
<td>957.84(3)</td>
<td>956.74(9)</td>
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<td>0.9098(4)</td>
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<td>μₓ (μB)</td>
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<td>μᵧ (μB)</td>
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<td>0.40(5)</td>
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<td>0.1158(4)</td>
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<tr>
<td>μᵧ (μB)</td>
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<td>μz (μB)</td>
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<tr>
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<td>0.286(7)</td>
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<td>0.00(7)</td>
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<tr>
<td>μᵧ (μB)</td>
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<td>2.66(7)</td>
<td>2.71(7)</td>
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<tr>
<td>μz (μB)</td>
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<td>2.66(7)</td>
<td>2.71(7)</td>
<td>0.00(7)</td>
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</table>

Refinement results of the magnetic structural model with symmetry P112₁/a', in which the Pr atoms on the 8d site (x, y, z) in Pnma are split into two 4e sites in P112₁/a: (x, y, z) and (x, -y + 1/2, z) with moments (μₓ, μᵧ, μz) and (μₓ, -μₓ, μz), respectively, whereas the Pr on the 4c site in Pnma occupy the 4e site in P112₁/a with fixed y = 1/4 and its moment follows the P112₁/a' symmetry (see text). For the sake of comparison, the site symbol 8d is retained in the table.

Fig. 4(b) shows the temperature dependence of the SANS intensity at two selected wave vectors of q = 0.0102 Å⁻¹ and q = 0.0875 Å⁻¹. The data for q = 0.0102 Å⁻¹ exhibit two steps in agreement with the magnetization data18 as well as the results from the (131) and (040) peak intensities [Fig. 4(a)]. Two peaks are evident for the q = 0.0875 Å⁻¹ data at ~25 K and ~42 K, respectively, suggestive of a spin fluctuation at the magnetic phase transitions. A sharp increase of
the ferromagnetic intensity below 25 K observed in the $q = 0.0102 \, \text{Å}^{-1}$ curve likely originates from domain or domain wall scattering.\textsuperscript{21}

The magnetic structures of Pr$_5$Ge$_4$ at 30 K and 9 K were modeled successfully based on an analysis of the high-resolution NPD data. The lower-angle portions of the observed and calculated NPD patterns at 50, 30, and 9 K are shown in Fig. 5. The crystallographic data and magnetic moments of the Pr atoms are listed in Table I.

Figure 6 shows the magnetic structure models for Pr$_5$Ge$_4$ at 30 and 9 K. For the sake of clarity only the Pr atoms are depicted. At 30 K, the proposed magnetic structure complies with the Shubnikov space group $Pnma$. The magnetic moments of Pr on the 4$c$ site \(\text{Pr}^3\) are arranged ferromagnetically along the $b$ direction with an atomic moment of \(2.71(7) \, \mu_B\), a little smaller than the theoretical value for a free trivalent ion \((3.2 \mu_B)\). The reduced moment is probably due to crystal field effects \(\text{CFE's}\). The three components of the moment \(m_x, m_y, m_z\) of the Pr on each 8$d$ site (Pr1 and Pr2) are comparable. The sublattice of the 8$d$ site Pr1 (or Pr2) exhibits a canted magnetic structure in the $ac$ plane and couples antiferromagnetically (AFM) with the nearest Pr1 (or Pr2) atoms along the $b$ direction, which makes a significant contribution to the (010) Bragg peak as
The long-range ordering of the Pr moments on the 4c sites are probably indicative of moments that are induced by the Pr site and on the 8d sites at 42 K and 25 K. The SANS data shown in Figs. 3(b) and 5(c). In comparison to the magnetic structure model at 30 K, the ordering of the Pr moments on the 4c site does not change—i.e., ferromagnetically along the b direction—and the atomic moment of Pr3 [2.66(7) \( \mu_B \)] is almost the same as that at 30 K. However, the ordering on the (Pr1, Pr2) sublattice is considerably different at low temperature: the symmetry changes from \( Pn' ma' \) to \( Pn'm a' \), the ordered moments of Pr increase to a value comparable to that of Pr3—i.e., 2.58(5) \( \mu_B \) for Pr1 and 2.63(5) \( \mu_B \) for Pr2—and the principal components of the Pr1 and Pr2 moments align ferromagnetically along the a direction.

The change of symmetry of the magnetic structure at low temperature was also observed in the Tb3Si4 compound. The magnetic structure of Tb3Si4 at 2 K was interpreted as a mixing of two magnetic modes belonging to different space groups (\( Pnm'a' \) and \( Pn'm'a' \)). Using the combined subgroup \( P112_1/a' \) of \( Pn'm'a' \) and \( Pnm'a' \), the refinement of the magnetic structure of Pr5Ge4 at 9 K was performed with constraints on the symmetric and magnetic moment to enforce pairs of Pr on the 4e sites to comply with the symmetry \( Pnm'a' \). The Pr atoms on the 8d site \( (x,y,z) \) in \( Pnma \) are split into two 4e sites in \( P112_1/a \): \( (x,y,z) \) and \( (x,-y+1/2,z) \) with moments \( (\mu_x, \mu_y, \mu_z) \) and \( (\mu_x, -\mu_y, \mu_z) \), respectively, whereas the Pr on the 4c site in \( Pnma \) occupy the 4e site in \( P112_1/a \) with fixed \( y=1/4 \) and its moment follows the \( P112_1/a' \) symmetry. A good fit to the NPD data was achieved as shown in Fig. 5(d). The resulting magnetic structure is basically the same as the above two-sublattice model (see Table I). The main component of the Pr3 moment aligns ferromagnetically along the b direction with very small components on the ac plane. The atomic moment of Pr3 is 2.75(7) \( \mu_B \) and slightly deviates from the b axis with an angle of 12°. The atomic moments of Pr1 and Pr2 are 2.64(6) \( \mu_B \) and 2.69(6) \( \mu_B \), respectively, and the largest components of the Pr1 and Pr2 moments align ferromagnetically along the a direction.

The two-sublattice model proposed for the magnetic structure of Pr5Ge4 at low temperature implies that the two magnetic transitions observed in the magnetization data and the temperature dependence of the intensity of magnetic Bragg peak correspond to long-range magnetic orderings of the Pr moments on the 4c site and on the 8d sites, respectively. The Pr moments on the 4c site order at \( \sim 42 \) K and those on the 8d sites at \( \sim 25 \) K. The SANS data shown in

FIG. 6. Magnetic structure models for Pr5Ge4 at 30 and 9 K. (a) Arrangements of the b components (arrows) of the Pr magnetic moments. (b) and (c) Arrangements of the Pr magnetic components in the ac plane (arrows) and b components (+ and −).
likely via the indirect Ruderman-Kittel-Kasuya-Yosida (RKKY) mechanism. A Pr(3) on the 4c site is coordinated by four Pr(1) and four Pr(2) atoms on the 8d sites, forming a distorted body-centered cube. The interatomic distance from the center atom Pr(3) to Pr(1) and Pr(2) ranges from 3.574 to 3.713 Å at 9 K. Figure 7 shows the Pr-Pr interatomic distances (<4.3 Å only) as a function of temperature. The distances of three ligand Pr atoms—two on the 4c site [Pr(3)] and one on the 8d site [Pr(2) or Pr(1)]—to the center Pr atom on the 8d site [Pr(1) or Pr(2)] are obviously shorter than those of other ligand Pr atoms [Pr(1) or Pr(2)], leading to a much longer average Pr-Pr distance for the Pr atoms on the 8d sites. The shortest Pr(1)-Pr(2) distance corresponds to the one interconnecting two Pr slabs as indicated in Fig. 1. It seems the ordering of Pr3 increases the Pr3-Pr1 and Pr3-Pr2 distances due to the magnetostriiction and reduces the Pr1-Pr2 distance accordingly. The salient difference in the coordination environment of the Pr atoms on the 4c site and on the 8d sites should be responsible for the different ordering temperatures of the Pr moments on the two sublattices.

It is noteworthy that the easy magnetization direction of the Pr moments on the 4c site is along the b axis and is different from that in other reported $R_x$Ge$_4$ compounds,\cite{13-17} in which the easy magnetization direction of the R moments on the 4c site is perpendicular to the b axis. Considering that the reported $R_x$Ge$_4$ compounds crystallize in different magnetic space groups depending on the nature of the rare earth, it is speculated that the electron configuration of the rare earth metals may play a critical role for the $R_x$Ge$_4$ compounds to adopt the specific magnetic structures (Pr: [Xe]$[4f^36s^2]$; Nd: [Xe]$[4f^46s^2]$; Tb: [Xe]$[4f^86s^2]$; Ho: [Xe]$[4f^{11}6s^2]$). Phenomenologically, the anisotropy of the rare earth metal sublattice is essentially determined by the first-order anisotropy constant $K_1$, which is derived as

$$K_1 = -\frac{3}{2}A_{20}\alpha_J\langle r^2\rangle\langle O_{20}\rangle - 5A_{40}\beta_J\langle r^4\rangle\langle O_{40}\rangle - \frac{21}{2}A_{60}\gamma_J\langle r^6\rangle\langle O_{60}\rangle,$$

where $A_{20}$, $A_{40}$, and $A_{60}$ are crystal-field coefficients determined only by the crystallographic type, $\alpha_J$, $\beta_J$, and $\gamma_J$ are Stevens factors independent of the crystal structure, and the terms $\alpha_J\langle r^2\rangle\langle O_{20}\rangle$, etc., are characteristics of the rare earth ions. The second- and fourth-order Stevens factors $\alpha_J$ and $\beta_J$ are comparable negative values for Pr$^{3+}$, Nd$^{3+}$, Tb$^{3+}$, and Ho$^{3+}$, whereas the sixth-order Stevens factors $\gamma_J$ for these rare earth ions are distinctly different: 60.99 × 10$^6$, −37.99 × 10$^6$, −1.212 × 10$^6$, and −1.294 × 10$^6$ for Pr$^{3+}$, Nd$^{3+}$, Tb$^{3+}$, and Ho$^{3+}$, respectively.\cite{21} Therefore, higher-order terms of the crystal field could be responsible for the observed magnetic structures of the $R_x$Ge$_4$ compounds for different rare earth elements.

**IV. CONCLUSIONS**

Small-angle neutron scattering and neutron powder diffraction experiments reveal that there are two magnetic phase transitions in the Pr$_x$Ge$_4$ compound at $-25$ K and $-42$ K, respectively, consistent with low-field magnetization measurements.\cite{18} Refinements of the magnetic structures based on high-resolution neutron diffraction data indicate that the magnetic phase transitions originate from the long-range orderings of the Pr moments on the 4c site and on the 8d sites, respectively. Between these two transitions the...
magnetic structure belongs to the space group $Pn' ma'$ with small induced Pr moments on the $8d$ sites. Below 25 K, the magnetic structure consists of two magnetic sublattices: one on the $4c$ sites with $Pn' ma'$ symmetry, the other on the $8d$ sites with $Pnm'a'$ symmetry. However, the crystal structure retains the $Pnma$ symmetry over the investigated temperature regime ($1.5$–$300$ K). The separate ordering of the Pr moments on different crystallographic sites can be readily understood by the salient difference in the rare earth metal environments around different crystallographic sites. In contrast to other reported $R_5 Ge_4$ compounds, the Pr moments on the $4c$ site in $Pr_5 Ge_4$ align along the $b$ axis, which can be attributed to the contribution of higher-order terms of the crystal field to the magnetocrystalline anisotropy of $R_5 Ge_4$ compounds.

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