



High-pressure synthesis and structures of lanthanide germanides of $LnGe_5$ ($Ln = Ce, Pr, Nd, \text{ and } Sm$) isotypic with $LaGe_5$

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ABSTRACT

A series of lanthanide penta-germanides $LnGe_5$ ($Ln = Ce, Pr, Nd \text{ and } Sm$) has been prepared by high-pressure (5–13 GPa) and high-temperature (500–1200 °C) reaction. $CeGe_5$ crystallizes in an orthorhombic unit cell (S.G. *Immm* (71)) with $a = 4.000(5) \text{ \AA}$, $b = 6.192(5) \text{ \AA}$, $c = 9.86(1) \text{ \AA}$, and $V = 244.1(5) \text{ \AA}^3$. The new germanides are isotypic with $LaGe_5$ consisting of a Ge covalent network with tunnels where guest ions Ln^{3+} are situated. The network is composed of sublayers with edge-sharing Ge six-membered rings with only boat conformation. The sublayers are connected by rare eight-coordinated Ge atoms. The cell volume of the compounds systematically decreases from La to Sm compounds, except for $CeGe_5$, owing to the lanthanide contraction. The lattice constants of $CeGe_5$ are smaller than those of the Pr compound because it contains Ce^{4+} ions. $CeGe_5$ is paramagnetic above 2 K, but does not obey the Curie–Weiss law. $PrGe_5$ and $NdGe_5$ are Curie–Weiss type paramagnets with Weiss temperatures of –3.3 and –18.4 K. $SmGe_5$ shows an antiferromagnetic transition at 10.4 K.

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1. Introduction

High-pressure and high-temperature synthesis is getting increasingly common in inorganic material science due to improvements in high-pressure techniques as well as development of good, inexpensive apparatus [1]. Compounds obtained at high pressures are dense and compact, and atoms tend to increase their coordination numbers.

Recently, we prepared a new binary lanthanum germanide $LaGe_5$ with a novel structure at 5 GPa and 1200 °C [2]. It consists of a Ge covalent network having a tunnel structure. La^{3+} ions are guest species and are situated in the tunnels. One of the Ge sites is an unusual eight-coordinated site. This abnormally high coordination number is believed to be an effect of high-pressure, since $LaGe_5$ cannot be prepared under ambient pressure. $LaGe_5$ shows superconductivity at 6.8 K, which is so far the highest transition temperature among La–Ge binary compounds [3]. In the present study, we investigated reactions under high-pressure conditions between Ge and the light rare-earth elements Ce, Pr, Nd, and Sm. We successfully obtained $LaGe_5$ -type compounds in these binary systems.

2. Experimental

$LnGe_5$, where $Ln = Ce, Pr, Nd, \text{ and } Sm$, were prepared by two step reactions as follows: Ce (Furu-uchi Chemical 99.9%), Pr

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(Nilaco 99.9%), Nd (Nilaco 99.9%), and Sm (Nilaco 99.9%) were reacted with Ge (Mitsuwa Pure Chemical 99.999%) in an arc furnace to prepare $LnGe_2$. The obtained $LnGe_2$ and Ge were mixed in various molar ratios from $Ln:Ge = 1:3$ – $1:8$. The mixtures were put in an h-BN cell and reacted at 3–13 GPa and 500–1600 °C. Details of the high-pressure synthesis are published elsewhere [2,4].

Powder X-ray diffraction (XRD) measurement of the products was performed with a MacScience M18XHF diffractometer with graphite-monochromated $CuK\alpha$ radiation and a Bruker AXS D8 Advance diffractometer. Single-crystal X-ray analysis was performed with a Rigaku R-Axis diffractometer equipped with an imaging plate area detector with graphite-monochromated $MoK\alpha$ radiation. Single-crystal structure analysis was performed with the SHELX-97 crystallographic software package [5]. Chemical compositions of the products were determined with an electron probe microanalyzer (EPMA) (JEOL JCM-733). Magnetic susceptibility measurements were performed with a SQUID magnetometer (Quantum Design MPMS-5) in a 5000-Oe field.

3. Results and discussions

3.1. The Ce–Ge binary system

In this system, binary compounds Ce_3Ge , Ce_5Ge_3 , Ce_5Ge_4 , $CeGe$, and $CeGe_2$ were already reported [6–18]. The compounds were prepared by simple melting of constituent mixtures of Ce and Ge at normal pressure. $CeGe_2$ has the α - $ThSi_2$ structure composed

only of trigonal-Ge atoms. It is the Ge-richest phase at ambient pressure.

We performed high-pressure reactions by varying temperatures and molar ratios of Ce to Ge. Reaction conditions are summarized in Table 1. Powder XRD patterns of some samples in Table 1 are shown in Fig. 1. Arc-melted samples 1 and 2 were mixtures of CeGe_2 and unreacted Ge. When mixtures with Ge/Ce ratios > 3 were used, no binary compound CeGe_x with $x > 2$ was obtained by arc melting (Fig. 1(a)). In a previous letter, we reported the synthesis and some physical properties of CeGe_3 [19]. The compound was obtained as a main phase by reaction at 5 GPa and 500 °C from a starting mixture of Ce:Ge = 1:3 (Fig. 1(b)). The purest CeGe_3 with good crystallinity was obtained at 1000 °C (Fig. 1(c)). Chemical analysis by EPMA shows that the composition is $\text{CeGe}_{2.99}$.

Fig. 1(b) shows some reflections that are not assignable to CeGe_3 (marked with solid circles). These reflections can be assigned to a new cerium germanide CeGe_5 with the LaGe_5 structure. Chemical analysis by EPMA shows that the composition is $\text{CeGe}_{4.96}$. As Ge content increases from 4 to 5, the amount of CeGe_5 in the products increases as shown in Figs. 1(d) and (e), but samples of pure CeGe_5 are not obtained. The product of reaction at 5 GPa and 1600 °C is not CeGe_5 but a mixture of CeGe_3 and Ge (Fig. 1(f)). For the synthesis of pure CeGe_5 , we should drastically change the reaction conditions especially the reaction pressure. Much higher pressure may work for the preparation of pure CeGe_5 .

In the case of LaGe_5 , single crystals are obtained in reaction from a starting mixture with large excess amount of Ge. We therefore performed a similar reaction and successfully obtained single crystals of CeGe_5 (sample 11) by starting with a 1:8 mixture, decreasing heating temperature from 1300 to 950 °C at 100 °C/h and quenching to room temperature at 5 GPa. The excess Ge probably acts as a flux for the crystal growth of CeGe_5 .

3.2. Structure and properties of CeGe_5

The results of single-crystal analysis are summarized in Tables 2 and 3. CeGe_5 crystallizes in the orthorhombic LaGe_5 type structure with unit cell dimensions $a = 4.000(5) \text{ \AA}$, $b = 6.192(5) \text{ \AA}$, $c = 9.86(1) \text{ \AA}$, and $V = 244.1(5) \text{ \AA}^3$. CeGe_5 consists of a subunit composed of Ge six-membered rings (Fig. 2). The rings share their edges to form sublayers containing Ge1 atoms alone. Adjacent sublayers are connected through Ge2 atoms to form a host network with tunnels running along the a -axis where Ce atoms are situated.

Table 1

Preparation conditions and products of the high-pressure reactions in the Ce–Ge system.

Sample no.	Atomic ratio (Ge/Ce)	Pressure (GPa)	Temperature (°C)	Products
1	3	–	Arc melting	CeGe_2 Ge
2	5	–	Arc melting	CeGe_2 Ge
3	3	5	500	CeGe_3 CeGe_5
4	3	5	1000	CeGe_3
5	3	5	1600	CeGe_3
6	4	5	1200	CeGe_5 CeGe_3
7	5	5	700	CeGe_5 CeGe_3
8	5	5	1200	CeGe_5 CeGe_3
9	5	5	1600	CeGe_3 Ge
10	8	5	1200	CeGe_5 Ge
11	8	5	1300 → 950 (100 °C/h)	Ge CeGe_5 (single crystals)

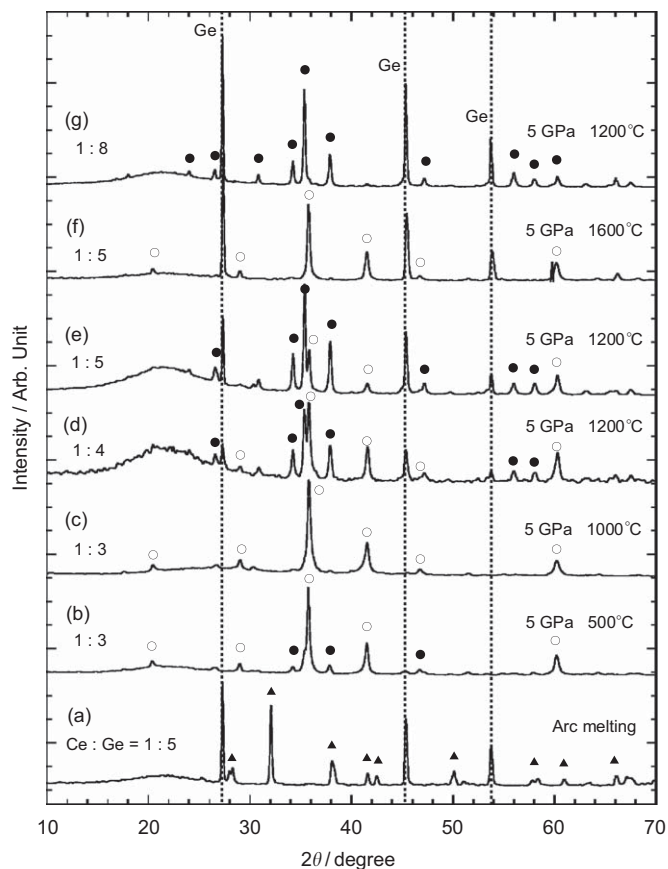


Fig. 1. X-ray powder diffraction patterns of Ce–Ge samples: (a) No. 2, (b) No. 3, (c) No. 4, (d) No. 6, (e) No. 8 (f) No. 9, and (g) No. 10. Filled triangles show diffractions from CeGe_2 . Filled and open circles show patterns for CeGe_5 and CeGe_3 , respectively.

Sublayers consisting of Ge six-membered rings with only chair conformation are often observed in germanides such as EuGe_2 . The cubic diamond structure also contains rings with only chair conformation. The sublayer in the LaGe_5 structure is unique; it is composed of rings with only boat conformation. This type of sublayer can be seen in the hexagonal diamond structure.

The local structure around Ge1 is shown in Fig. 3(a). Each Ge1 atom has three neighboring Ge1 atoms. Bond angles are in the range $100.6(1)^\circ$ – $102.36(4)^\circ$, and the Ge1–Ge1 bond distances are $2.540(3)$ and $2.599(3) \text{ \AA}$. These distances are much longer than in diamond Ge (2.447 \AA) because of electrons doped from Ce atoms to the Ge network as well as the effect of the second nearest neighbors. Two Ge2 and two Ce atoms surround a Ge1 atom with distances of $2.906(2)$ and $3.096(3) \text{ \AA}$, respectively (Fig. 3(a)). These atoms, especially Ge2, have some interaction with Ge1 atoms and reduce the bond order of Ge1–Ge1 bonds, resulting in the long Ge1–Ge1 bond distances.

Moreover, electrons from Ce ions are doped in the conduction band mainly composed of 4p orbitals of Ge, resulting in a negatively charged Ge framework, which causes the Ge1–Ge1 bonds to elongate.

Each Ge2 atom is coordinated by eight Ge1 atoms; this type of coordination is rare in germanides and probably arises due to high pressure (Fig. 3(b)). The Ge1–Ge2 bond ($2.906(1) \text{ \AA}$) is much longer than the Ge1–Ge1 bond, due to the large coordination number of Ge2. Neuhaus proposed a rule about the relationship between coordination number and pressure [20]. This pressure-coordination rule states that the higher the pressure, the larger

Table 2
Crystallographic data and details on the structure determination of CeGe₅, PrGe₅, NdGe₅, and SmGe₅.

Formula	CeGe ₅	PrGe ₅	NdGe ₅	SmGe ₅
Formula weight	503.07	503.86	507.19	513.30
Space group	<i>Immm</i> (No. 71)	<i>Immm</i> (No. 71)	<i>Immm</i> (No. 71)	<i>Immm</i> (No. 71)
<i>a</i> (Å)	4.000(5)	3.998(2)	3.993(2)	3.9876(8)
<i>b</i> (Å)	6.192(5)	6.228(2)	6.200(2)	6.162(1)
<i>c</i> (Å)	9.86(1)	9.887(4)	9.865(4)	9.850(2)
<i>V</i> (Å ³)	244.1(5)	246.2(2)	246.2(2)	242.02(9)
<i>Z</i>	2	2	2	2
Crystal size (mm)	0.05 × 0.04 × 0.05	0.05 × 0.05 × 0.03	0.05 × 0.05 × 0.05	0.1 × 0.1 × 0.05
Diffractometer	Rigaku Raxis-Rapid	Rigaku Raxis-Rapid	Rigaku Raxis-Rapid	Rigaku Raxis-Rapid
Radiation (graphite monochromated)	MoKα	MoKα	MoKα	MoKα
2θ Limit	54.9	54.9	54.9	54.9
No. of observed unique reflections	179	180	181	178
No. of variables	14	14	14	14
<i>R</i> , <i>wR2</i> ^a	0.027, 0.062	0.045, 0.109	0.047, 0.094	0.041, 0.119
Goodness of fit, <i>S</i> ^b	1.08	1.17	1.01	1.21
Residual density (eÅ ⁻³)	1.54/−1.59	2.38/−2.20	2.91/−2.28	2.35/−2.76

$$^a wR2 = \{\sum[(F_o^2 - F_c^2)^2] / \sum w(F_o^2)^2\}^{1/2}$$

$$^b S = [\sum w(|F_o| - |F_c|)^2 / (N_o - N_v)]^{1/2} \text{ where } N_o \text{ is the number of reflections and } N_v \text{ is the total number of parameters refined.}$$

Table 3
Atomic and thermal parameters of CeGe₅, PrGe₅, NdGe₅, and SmGe₅.

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Ce	0	0	0	0.0132(3)
Ge1	1/2	−0.2949(2)	0.1707(1)	0.0155(3)
Ge2	0	1/2	0	0.0184(5)
Pr	0	0	0	0.0215(5)
Ge1	1/2	−0.2958(3)	0.1706(1)	0.0235(5)
Ge2	0	1/2	0	0.0270(8)
Nd	0	0	0	0.0185(5)
Ge1	1/2	−0.2948(2)	0.1702(1)	0.0199(5)
Ge2	0	1/2	0	0.0226(6)
Sm	0	0	0	0.0184(6)
Ge1	1/2	−0.2932(3)	0.1694(2)	0.0190(6)
Ge2	0	1/2	0	0.0214(8)

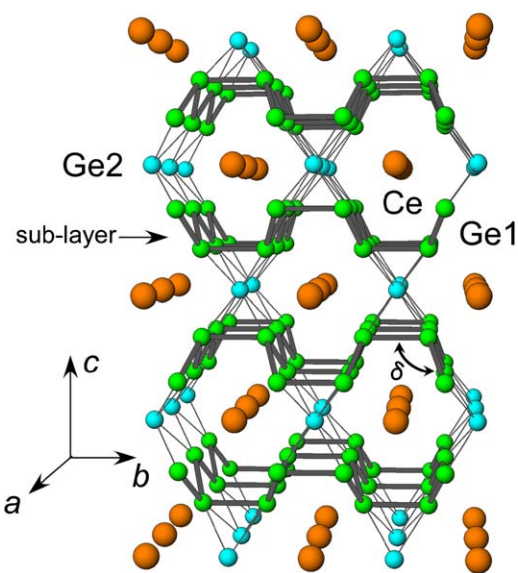


Fig. 2. Crystal structure of CeGe₅. Large orange balls are Ce atoms. Small green and blue balls are Ge1 and Ge2 atoms, respectively. The thick bonds are the Ge1–Ge1 connections to form sublayers. The thin bonds are the Ge1–Ge2 bonds. [For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.]

the coordination number and the longer the bond distance. The unusually large coordination number and bond distances of Ge2 can be understood by this rule.

The local structure around Ce is shown in Fig. 3(c). Each Ce atom has two Ge2 atoms as nearest neighbors and eight Ge1 atoms with distances of 3.096(3) and 3.188(2) Å, respectively. These 10 atoms surround the Ce atom isotropically. We note that the coordination of Ge2 atoms is topologically the same as that of the Ce atoms. This probably indicates a metallic character for the Ge2 atoms, but further experimental and theoretical approaches should be necessary to prove it.

Although isotypic LaGe₅ is a superconductor, CeGe₅ does not exhibit superconductivity to 2 K. This is presumably due to the *f* electrons on the Ce atoms.

3.3. Structure and properties of binary Pr, Nd, and Sm germanide systems

LnGe_x compounds with *x* > 2 have not been reported in these systems. In the present work, LaGe₅-type compounds were successfully obtained by high-pressure reaction as for the La and Ce binary systems. We tried to prepare GdGe₅ by a similar way but it was unsuccessful. Single crystals of PrGe₅ and NdGe₅ were obtained by starting with 1:8 mixtures, decreasing the heating temperatures from 1300 to 950 °C (for Pr) and from 1200 to 900 °C (for Nd) at 100 °C/h, and quenching to room temperature at 5 GPa. Single crystals of SmGe₅ were obtained by reaction of Sm:Ge = 1:5 mixtures at 10 GPa and 1000 °C. Chemical analysis by EPMA shows that the compositions are PrGe_{5.00}, NdGe_{4.94}, and SmGe_{4.85}.

The results of single-crystal structure analysis are summarized in Tables 2 and 3. The crystal structures are much the same as those of La and Ce compounds but some details differ, reflecting the difference in size of the guest ion. Fig. 4 shows plots of lattice parameter against effective ionic radii of eight-coordinated *Ln*³⁺ ions for all LaGe₅-type compounds [21]. Lattice parameters of *LnGe₅* compounds decrease with decreasing effective ionic radii of the guest ion due to the lanthanide contraction. Selected bond lengths and angles are listed in Table 4. *Ln*–Ge1 distances monotonically decrease from 3.199 to 3.166 Å for Pr to Sm compounds. This causes the distances between adjacent sublayers to shrink and then the length *c* to decrease.

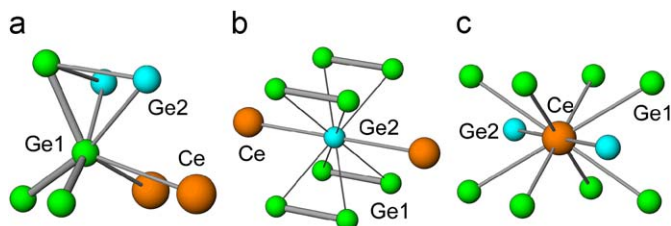


Fig. 3. Local structure of CeGe_5 around: (a) Ge1, (b) Ge2, and (c) Ce.

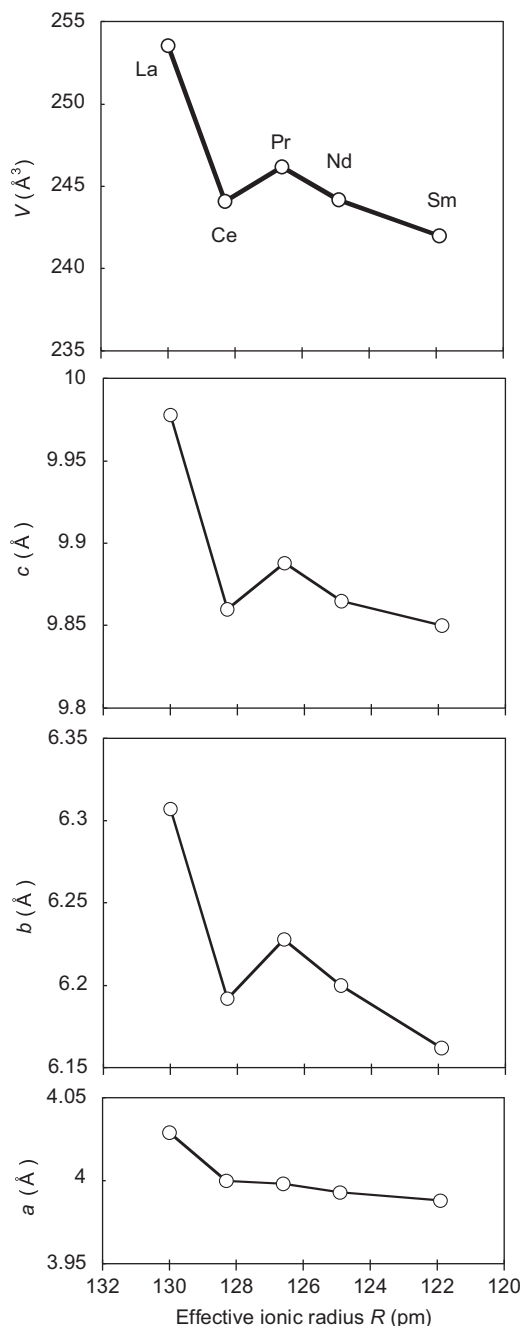


Fig. 4. Variations in lattice parameters for LnGe_5 series plotted against the effective ionic radii of eight-coordinated Ln^{3+} ions.

Contraction in the size of the guest ion also reduces the Ln-Ge_2 distance. As the $\text{Ge}_1\text{-Ge}_1$ distance does not change much with changing guest ions, the lattice constant b is determined mainly

Table 4
Selected bond lengths (Å) and angles (deg) for LaGe_5 -type compounds.

	Ln-Ge_1	Ln-Ge_2	$\text{Ge}_1\text{-Ge}_1$	$\text{Ge}_1\text{-Ge}_2$	Ang. δ
La	3.250(1)	3.1535(5)	2.534(3)	2.621(2)	103.68(6)
Ce	3.188(2)	3.096(3)	2.540(3)	2.599(3)	102.36(4)
Pr	3.199(1)	3.1141(9)	2.544(3)	2.605(2)	102.64(7)
Nd	3.185(1)	3.100(1)	2.544(3)	2.603(2)	102.32(6)
Sm	3.166(1)	3.0809(7)	2.549(3)	2.604(2)	101.79(7)

by the angle δ (Fig. 4). The δ value of each compound is listed in Table 4. The angle decreases with decreasing guest ion size, and the lattice constant b shrinks monotonically from Pr to Sm compounds.

Contrasting situations are observed for lattice constant a ; it is almost independent of the size of the guest ion. The tunnels in LnGe_5 run along the a axis and adjacent Ln ions are well separated along this direction (about 4 Å). The lattice constant a is, therefore, determined by the $\text{Ge}_1\text{-Ge}_1$ bond length and the angle of $\text{Ge}_1\text{-Ge}_1\text{-Ge}_1$ along the a axis in the sublayer. The bond length and angle are almost identical for all the compounds. For this reason, the lattice constant a of LaGe_5 -type compounds is not affected by the guest ion size.

Only CeGe_5 does not obey this trend. The cell volume of CeGe_5 is smaller than that of the Pr compound. This anomaly is sometimes observed for lanthanide compounds having isotopic structures [22], probably due to the very small ionic radius of Ce^{4+} . Not all the Ce ions in CeGe_5 are in a 3+ oxidation state; some of them are in a 4+ oxidation state. The ionic state of guest ions is discussed in the next section.

3.4. Magnetic properties of LaGe_5 -type compounds

It is difficult to prepare single phases of LnGe_5 , $\text{Ln} = \text{Ce}, \text{Pr}, \text{Nd}$, and Sm. To avoid the influence of other binary germanides in magnetic susceptibility measurements, we used samples containing only LnGe_5 and Ge, because Ge does not show any magnetic transitions. Corrections were made on all data considering the content of Ge in each sample. The results are summarized in Table 5. Though LaGe_5 shows superconductivity with a critical temperature T_c of 6.8 K, other LnGe_5 compounds do not show superconductivity at 2 K. PrGe_5 and NdGe_5 obey the Curie–Weiss law with Weiss temperatures of $\theta = -3.3$ and -18.4 K, respectively, as shown in Fig. 5. Effective magnetic moments μ_{eff} of 3.50 and $3.64\mu_B$ were observed for the Pr and Nd compounds, respectively, which correspond well to the theoretical values of 3.58 (Pr^{3+}) and 3.62 (Nd^{3+}) μ_B . Fig. 6(a) shows the temperature dependence of the magnetic susceptibility for SmGe_5 . It does not obey the Curie–Weiss law, due to contributions from first- and second-Zeeman effects of Sm ions [23]. SmGe_5 shows an antiferromagnetic transition at 10.4 K.

The temperature dependence of magnetic susceptibility for CeGe_5 is shown in Fig. 6(b). It does not follow the Curie–Weiss law. An anomaly is observed at 14 K. We applied the modified Curie–Weiss equation $\chi_{\text{mol}} = \chi_0 + C/(T - \theta)$, where χ_0 : constant, C : Curie constant, and θ : Weiss temperature, separately to the data from 300 to 15 K and from 14 to 2 K. The resulted fitting curves are displayed in Fig. 6(b). Deduced fit parameters are $\chi_0 = 0.0052$ emu/mol, $C = 0.0121$ emu K/mol, and $\theta = -0.04$ K for the lower temperature region, and $\chi_0 = 0.0040$ emu/mol, $C = 0.0308$ emu K/mol, and $\theta = -1.48$ K for the higher. The effective magnetic moment $\mu_{\text{eff}} = 0.31$ and $0.50\mu_B$ for lower and higher regions, respectively. These values are too small for Ce^{3+} compounds because the theoretical moment for Ce^{3+} is $2.54\mu_B$. Therefore,

Table 5
Magnetic properties of LaGe₅-type compounds.

LaGe ₅	Superconductor	$T_c = 6.8$ K
CeGe ₅	Paramagnetic ^a	
PrGe ₅	Paramagnetic	$\theta = -3.3$ K
NdGe ₅	Paramagnetic	$\theta = -18.4$ K
SmGe ₅	Antiferromagnetic	$T_N = 10.4$ K

^a Not the Curie–Weiss type.

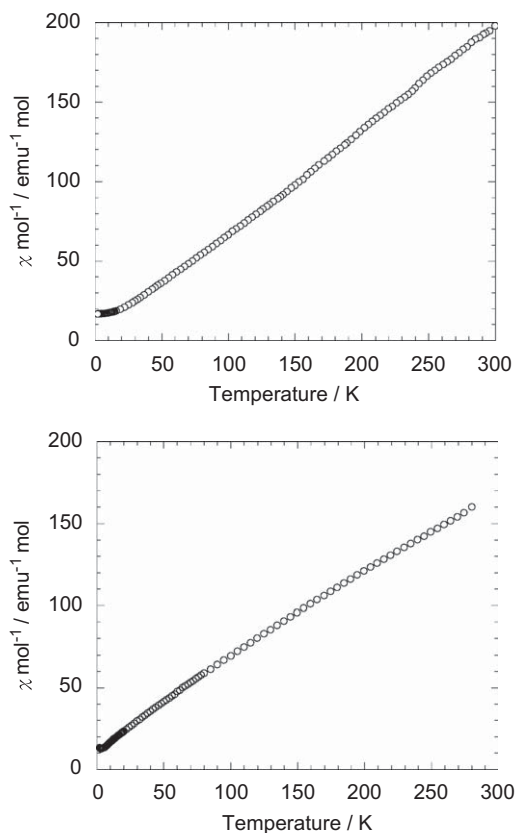


Fig. 5. Temperature dependence of magnetic susceptibility for: (a) PrGe₅ and (b) NdGe₅. The inverted molar susceptibility χ_{mol}^{-1} is plotted against temperature.

some Ce ions are possibly in a 4+ oxidation state. More detailed study is necessary to determine the valence of Ce in CeGe₅.

4. Conclusions

Isotypic compounds with the LaGe₅ structure were prepared for Ce, Pr, Nd, and Sm. Single-crystal structure analysis shows a systematic shrinking of lattice constant by changing guest ion from Pr to Sm. The Ce compound has a smaller cell volume than does PrGe₅, due to the presence of Ce⁴⁺ ions. Although LaGe₅ is a superconductor having $T_c = 6.8$ K, other isotypic compounds do not show superconductivity at 2 K. PrGe₅ and NdGe₅ are Curie–Weiss type paramagnetic compounds, whereas SmGe₅ shows an antiferromagnetic transition with $T_N = 10.4$ K.

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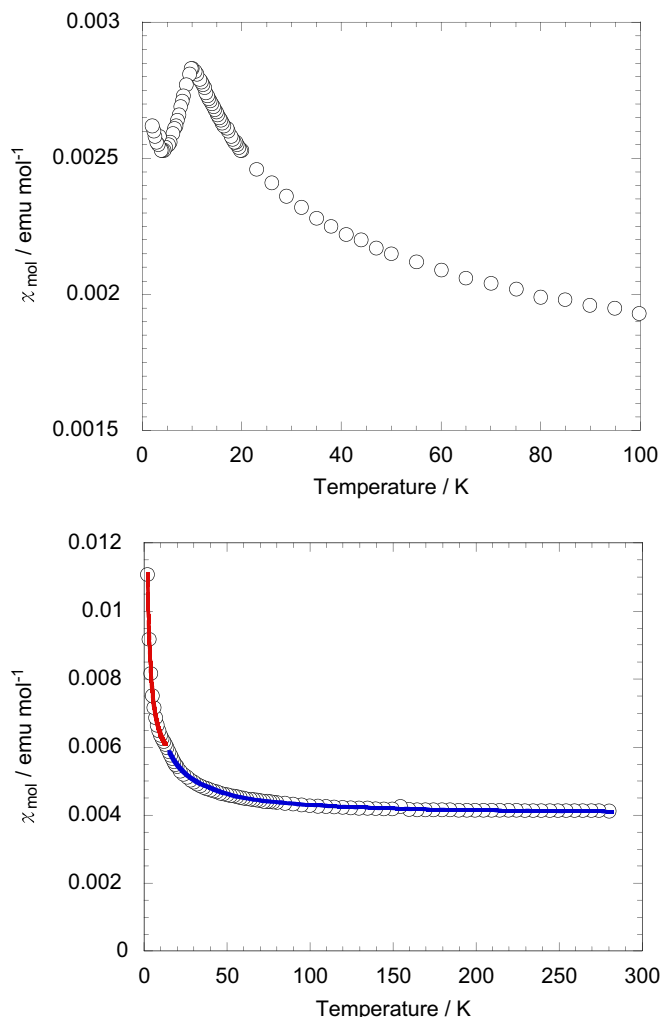


Fig. 6. (a) Temperature dependence of the magnetic susceptibility χ_{mol} for SmGe₅. (b) The magnetic susceptibility of CeGe₅. The fitting curves for lower and higher temperature regions are represented in red and blue. [For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.]

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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2009.05.018](https://doi.org/10.1016/j.jssc.2009.05.018).

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