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Crystal structure of $R_3Ge_{1+x}Se_7$ (R = La, Ce, Pr, Sm, Gd and Tb, x = 0.43–0.49) and magnetic properties of $Ce_3Ge_{1.47}Se_7$

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ABSTRACT

The crystal structures of ternary compounds $R_3Ge_{1+x}Se_7$ ($Dy_3Ge_{1.25}S_7$ structure type, space group $P6_3$, Pearson symbol $hP22+2x$, a = 10.7656(7) Å, c = 6.0801(5) Å, $R1$ = 0.0186 for $La_3Ge_{1.48}Se_7$; a = 10.684(1) Å, c = 6.0611(8) Å, $R1$ = 0.0257 for $Ce_3Ge_{1.47}Se_7$; a = 10.6408(9) Å, c = 6.0548(7) Å, $R1$ = 0.0290 for $Pr_3Ge_{1.49}Se_7$; a = 10.4419(7) Å, c = 6.0283(6) Å, $R1$ = 0.0201 for $Sm_3Ge_{1.48}Se_7$; a = 10.325(7) Å, c = 6.0506(7) Å, $R1$ = 0.0269 for $Gd_3Ge_{1.45}Se_7$; a = 10.2747(7) Å, c = 6.0743(5) Å, $R1$ = 0.0499 for $Tb_3Ge_{1.43}Se_7$) were determined by means of X-ray single-crystal diffraction. The R atoms occupy trigonal prisms capped with two additional atoms. The Ge atoms are located in octahedral and tetrahedral environment. The compound $Ce_3Ge_{1.47}Se_7$ exhibits a Curie–Weiss type paramagnetic behavior due to the presence of fairly stable local magnetic moments on cerium ions. No hint at any magnetic phase transition was observed down to 1.72 K.

1. Introduction

Designing of functional materials with increasingly complex compositions has become a primary direction in modern science and technology. Among such multicomponent systems much attention is put on complex rare earth-based chalcogenides, owing to their specific thermal, electrical, magnetic and optical properties. It is enough to mention here prospective applications of various chalcogenide materials in the field of infrared and nonlinear optics [1,2]. Such application-driven research stimulates intense investigations of complex phases, preferably carried out in a systematic way on extended families of compounds with similar crystal and electronic structures.

The formation of the ternary compounds $La_3Ge_{1.25}Se_7$ and $R_3Ge_{1.5}Se_7$ (R = La, Ce, Pr, Nd, Sm, Gd, Tb and Dy) have been reported in Refs. [3,4], respectively. All these phases have been assumed to crystallize with hexagonal unit cells of the $Dy_3Ge_{1.25}S_7$ type, based on their similar compositions and the values of their lattice parameters determined from X-ray powder diffraction data. In this paper we present the results of our single-crystal structure refinements performed for $R_3Ge_{1+x}Se_7$ (R = La, Ce, Pr, Sm, Gd and Tb, x = 0.43–0.49), which support the previous conjecture. Moreover, we report for the first time on the magnetic behavior of $Ce_3Ge_{1.47}Se_7$, studied on single-crystalline specimens.

2. Experimental details

Powder samples with the nominal compositions $R_4Ge_3Se_7$ (R = La, Ce, Pr, Sm, Gd and Tb) were prepared by sintering the elemental constituents of the purity better than 99.9 wt.% in evacuated quartz tubes. The syntheses were carried out in a tube resistance furnace. The ampoules were first heated with a rate of 30 °C per hour up to 1150 °C, and then kept at this temperature for 3 h. Afterwards, the samples were cooled slowly (10 °C per h) down to 600 °C, and annealed at this temperature for 720 h. Subsequently, the ampoules were quenched in air.

The products were checked by X-ray powder diffraction using a DRON-4-13 powder diffractometer (CuK_α radiation, $10^\circ \le 2\Theta \le 100^\circ$, step scan mode with a step size of 0.05° and counting time of 5 s per data point). In each case, the obtained samples were multiphase, yet contained small single crystals with shapes of hexagonal prisms, suitable for crystal structure investigations. The compositions of these single crystals were determined by microprobe analysis performed using an EDAX PV9800 microanalyzer.

The X-ray intensities data were collected on a KUMA Diffraction KM-4 four-circle diffractometer equipped with a CCD camera, using graphite-monochromatized MoK_α radiation (λ = 0.071073 nm). The raw data were treated with the CrysAlis Data Reduction program [5] taking into account an absorption correction. The intensities of the reflections were corrected for Lorentz and polarization factors. The crystal structures were solved by Patterson methods [6] and refined by the full-matrix least-squares method using SHELXL-97 [6]. Acentric space group $P6_3$ was checked with the PLATON program, and no additional symmetry elements were found [7].

Magnetic measurements of $Ce_3Ge_{1.47}Se_7$ were performed in the temperature range 1.72–400 K and in magnetic fields up to 5 T using a Quantum Design MPMS-5 SQUID magnetometer. For these studies a collection of several small single crystals was used. The crystals were freely placed in a gelatin capsule that served as a sample holder. The obtained magnetic data were corrected for the signal due to the holder.

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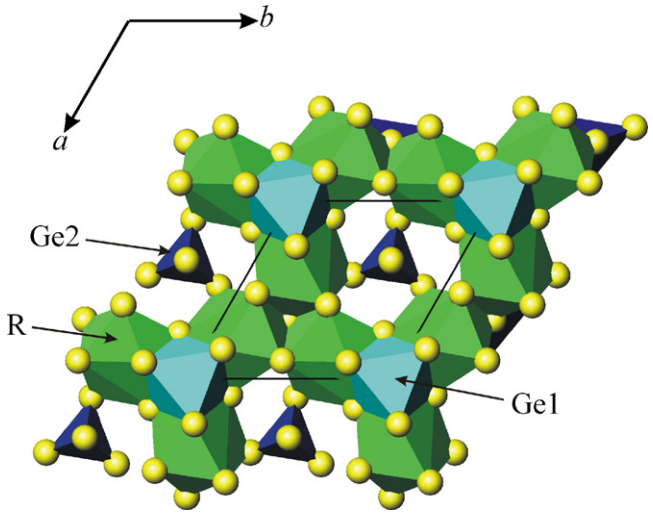

Fig. 1. Coordination polyhedra of the R and Ge atoms in the structures of $R_3Ge_{1+x}Se_7$ (R = La, Ce, Pr, Sm, Gd and Tb, x = 0.43–0.49).

3. Results and discussion

The crystal data and the structure refinement details for $R_3Ge_{1+x}Se_7$ (R = La, Ce, Pr, Sm, Gd and Tb, x = 0.43–0.49) are summarized in Table 1, whereas the refined atomic coordinates and the thermal displacement factors are given in Table 2. The results are generally in good accordance with the $Dy_3Ge_{1.25}S_7$ type of structure reported in Ref. [4]. The R atoms occupy just one crystallographic position in the unit cell, while the Ge and Se atoms are located in two and three inequivalent positions, respectively. Remarkably, for all the compounds studied, the position of Ge1 is only partially occupied. The refinements of the occupancy factor for Ge1 yielded the values close to 0.5. In order to satisfy the charge balance requirements one may presume that the 2*a* position is occupied by Ge(II), whereas the 2*b* positions contain Ge(IV), as initially proposed in Ref. [4]. Similar assignment of the formal oxidation states of Ge ions in $Ho_3Ge_{1.272}S_7$ and $Er_3Ge_{1.33}S_7$ was suggested in Ref. [8].

The relevant interatomic distances and the coordination numbers of the R and Ge atoms are listed in Table 3. All the distances are close to the sums of the respective ionic radii [9]. Generally, the crystal structures of $R_3Ge_{1+x}Se_7$ (R = La, Ce, Pr, Sm, Gd and Tb, x = 0.43–0.49) are built by different coordination polyhedrals, *e.g.* [$RSe1_1Se2_4Se3_3$] bi-capped trigonal prisms, [$Ge1Se2_6$] octahedra and [$Ge2Se1_1Se3_3$] tetrahedra (see Fig. 1) with adjacent corners or faces.

Shown in Fig. 2 is the dependence of the hexagonal lattice parameters (*a* and *c*) and unit cell volume (*V*) of the $R_3Ge_{1+x}Se_7$ (R = La, Ce, Pr, Sm, Gd and Tb, x = 0.43–0.49) compounds on the ionic radius of the rare earth constituent. The lanthanide ion size considerably affects the unit cell dimension in the hexagonal plane, while changes in the parameter *c* are not significant. Nevertheless, the observed systematic variation of the unit cell volume reflects the well-known lanthanide contraction when going from La to Tb.

The magnetic properties of single-crystalline $Ce_3Ge_{1.47}Se_7$ are presented in Fig. 3. Clearly, the compound exhibits localized magnetism with the magnetic susceptibility of the Curie–Weiss type. The effective magnetic moment, derived from the χ(T) data measured above 120 K, amounts to 2.40(8) μ_B per Ce-atom (rather large experimental error is a consequence of small mass of the specimen measured) that is a value fairly close to that expected within the Russell–Saunders coupling scenario for a free trivalent cerium ion (2.54 μ_B). The paramagnetic Curie temperature, extrapolated from the same temperature region, is equal to −12.9(7) K. Its negative sign hints at antiferromagnetic correlations, yet the compound

Table 1
Crystal data and structure refinement details of the $R_3Ge_{1+x}Se_7$ (R = La, Ce, Pr, Sm, Gd and Tb, x = 0.43–0.49) compounds.

Empirical formula	$La_3Ge_{1.48}Se_7$	$Ce_3Ge_{1.47}Se_7$	$Pr_3Ge_{1.49}Se_7$	$Sm_3Ge_{1.48}Se_7$	$Gd_3Ge_{1.45}Se_7$	$Tb_3Ge_{1.43}Se_7$
Formula weight	1072.89	1072.89	1083.25	1111.20	1129.73	1133.28
Space group	$P6_3$ (No. 173)	$P6_3$ (No. 173)	$P6_3$ (No. 173)	$P6_3$ (No. 173)	$P6_3$ (No. 173)	$P6_3$ (No. 173)
Unit cell dimensions	a = 10.7656(7) Å	a = 10.684(1) Å	a = 10.6408(9) Å	a = 10.4419(7) Å	a = 10.325(1) Å	a = 10.2747(7) Å
	c = 6.0801(5) Å	c = 6.0611(8) Å	c = 6.0548(7) Å	c = 6.0283(6) Å	c = 6.0506(7) Å	c = 6.0743(5) Å
Volume	610.26(8) Å^3	599.2(1) Å^3	593.7(1) Å^3	569.23(8) Å^3	558.6(1) Å^3	555.35(7) Å^3
Number of formula units per unit cell	2	2	2	2	2	2
Calculated density	5.839 g/cm^3	5.978 g/cm^3	6.059 g/cm^3	6.483 g/cm^3	6.716 g/cm^3	6.777 g/cm^3
Absorption coefficient	34.571 mm^{-1}	35.982 mm^{-1}	37.199 mm^{-1}	41.422 mm^{-1}	44.165 mm^{-1}	45.565 mm^{-1}
F(0 0 0)	909	917	925	943	953	958
Crystal color	Black	Black	Black	Black	Black	Black
Crystal size	0.06 mm × 0.02 mm × 0.02 mm	0.07 × 0.04 × 0.03 mm	0.07 mm × 0.03 mm × 0.03 mm	0.11 mm × 0.03 mm × 0.02 mm	0.07 × 0.03 × 0.02 mm	0.07 mm × 0.06 mm × 0.06 mm
Θ range for data collection	3.79–27.46	3.81–27.44	3.83–27.38	3.90–27.41	3.95–27.39	3.97–26.71
Index ranges	$-13 \le h \le 13$	$-13 \le h \le 13$	$-13 \le h \le 13$	$-13 \le h \le 13$	$-9 \le h \le 13$	$-12 \le h \le 12$
	$-13 \le k \le 13$	$-13 \le k \le 13$	$-13 \le k \le 13$	$-13 \le k \le 13$	$-13 \le k \le 12$	$-12 \le k \le 12$
	$-6 \le l \le 7$	$-7 \le l \le 6$	$-7 \le l \le 7$	$-7 \le l \le 7$	$-7 \le l \le 7$	$-7 \le l \le 7$
Reflections collected	6184	7508	7508	7005	6543	6178
Independent reflections	813 [R(int.) = 0.0508]	864 [R(int.) = 0.0560]	905 [R(int.) = 0.0884]	863 [R(int.) = 0.0662]	849 [R(int.) = 0.1032]	786 [R(int.) = 0.1042]
Refinement method	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2	Full-matrix least-square on F^2
Absolute structure parameter	0.01(2)	0.00(4)	0.00(5)	0.11(6)	0.0(1)	−0.1(1)
Data/restraints/parameters	813/1/39	864/1/38	905/1/39	863/1/39	849/1/38	786/1/39
Goodness-of-fit on F^2	1.278	1.061	1.075	1.135	0.939	1.064
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0186, $wR2$ = 0.0462	$R1$ = 0.0257, $wR2$ = 0.0501	$R1$ = 0.0290, $wR2$ = 0.0725	$R1$ = 0.0201, $wR2$ = 0.0471	$R1$ = 0.0269, $wR2$ = 0.0525	$R1$ = 0.0499, $wR2$ = 0.1179
R indices (all data)	$R1$ = 0.0192, $wR2$ = 0.0464	$R1$ = 0.0296, $wR2$ = 0.0511	$R1$ = 0.0298, $wR2$ = 0.0731	$R1$ = 0.0210, $wR2$ = 0.0474	$R1$ = 0.0336, $wR2$ = 0.0540	$R1$ = 0.0506, $wR2$ = 0.1186
Extinction coefficient	0.0206(7)	0.0127(7)	0.0127(7)			0.009(1)
Largest diff. peak and hole	1.424 and −1.049 e/Å^3	0.998 and −1.162 e/Å^3	2.427 and −1.435 e/Å^3	1.532 and −1.444 e/Å^3	1.863 and −1.152 e/Å^3	1.569 and −2.022 e/Å^3

Table 2
Atomic coordinates and thermal displacement factors for $R_3Ge_{1+x}Se_7$ (R = La, Ce, Pr, Sm, Gd and Tb, x = 0.43–0.49).

Atom	Position	x/a	y/b	z/c	Occupancy	$U_{eq.}\times10^2$, Å^2	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
$La_3Ge_{1.48}Se_7$												
La	6*c*	0.12815(3)	0.35786(3)	0.22403(8)	1	0.0100(1)	0.0093(1)	0.0087(1)	0.0124(2)	−0.0011(1)	−0.0011(1)	0.0048(1)
Ge1	2*a*	0	0	0.4827(7)	0.481(7)	0.0152(9)	0.0108(9)	0.0108(9)	0.024(1)	0	0	0.0054(5)
Ge2	2*b*	1/3	2/3	0.6394(2)	1	0.0093(2)	0.0095(3)	0.0095(3)	0.0088(5)	0	0	0.0047(1)
Se1	2*b*	1/3	2/3	0.0192(1)	1	0.0114(3)	0.0125(3)	0.0125(3)	0.0094(6)	0	0	0.0062(1)
Se2	6*c*	0.25628(6)	0.16451(6)	0.2387(1)	1	0.0117(1)	0.0137(3)	0.0108(3)	0.0133(3)	−0.0015(3)	−0.0005(3)	0.0081(2)
Se3	6*c*	0.41618(7)	0.51888(6)	0.4870(1)	1	0.0098(1)	0.0097(3)	0.0074(3)	0.0126(3)	0.0015(3)	0.0013(3)	0.0044(2)
$Ce_3Ge_{1.47}Se_7$												
Ce	6*c*	0.12870(5)	0.35794(5)	0.2760(1)	1	0.0089(1)	0.0090(3)	0.0080(2)	0.0100(2)	0.0016(3)	0.0013(3)	0.0044(2)
Ge1	2*a*	0	0	0.516(1)	0.473(8)	0.012(1)	0.007(1)	0.007(1)	0.023(2)	0	0	0.0036(7)
Ge2	2*b*	1/3	2/3	0.8607(3)	1	0.0071(4)	0.0082(6)	0.0082(6)	0.0050(9)	0	0	0.0041(3)
Se1	2*b*	1/3	2/3	0.4785(3)	1	0.0099(4)	0.0115(5)	0.0115(5)	0.006(1)	0	0	0.0058(3)
Se2	6*c*	0.2567(1)	0.16425(9)	0.2596(2)	1	0.0103(2)	0.0125(4)	0.0097(4)	0.0110(5)	0.0015(6)	0.0009(6)	0.0073(4)
Se3	6*c*	0.1010(1)	0.5830(1)	0.0150(1)	1	0.0082(2)	0.0074(5)	0.0086(5)	0.0094(5)	0.0009(5)	0.0000(4)	0.0046(4)
$Pr_3Ge_{1.49}Se_7$												
Pr	6*c*	0.12955(5)	0.35793(5)	0.2239(1)	1	0.0094(1)	0.0082(3)	0.0073(3)	0.0132(3)	−0.0011(3)	−0.0009(3)	0.0040(2)
Ge1	2*a*	0	0	0.485(1)	0.48(1)	0.013(1)	0.008(1)	0.008(1)	0.024(2)	0	0	0.0043(7)
Ge2	2*b*	1/3	2/3	0.6392(3)	1	0.0083(4)	0.0081(6)	0.0081(6)	0.0087(8)	0	0	0.0040(3)
Se1	2*b*	1/3	2/3	0.0213(3)	1	0.0104(4)	0.0109(6)	0.0109(6)	0.009(1)	0	0	0.0054(3)
Se2	6*c*	0.2578(1)	0.1639(1)	0.2416(2)	1	0.0104(3)	0.0115(5)	0.0079(5)	0.0138(5)	−0.0016(5)	−0.0011(5)	0.0064(4)
Se3	6*c*	0.4179(1)	0.5177(1)	0.4834(2)	1	0.0089(2)	0.0088(5)	0.0060(5)	0.0124(5)	0.0011(4)	0.0016(4)	0.0039(4)
$Sm_3Ge_{1.48}Se_7$												
Sm	6*c*	0.13211(3)	0.35831(3)	0.27675(8)	1	0.0115(1)	0.0116(1)	0.0109(1)	0.0122(1)	0.0016(1)	0.0013(1)	0.0058(1)
Ge1	2*a*	0	0	0.5094(7)	0.479(6)	0.0138(9)	0.010(1)	0.010(1)	0.020(1)	0	0	0.0051(5)
Ge2	2*b*	1/3	2/3	0.8608(1)	1	0.0089(2)	0.0103(4)	0.0103(4)	0.0061(5)	0	0	0.0051(1)
Se1	2*b*	1/3	2/3	0.4770(1)	1	0.0103(2)	0.0122(4)	0.0122(4)	0.0064(5)	0	0	0.0061(1)
Se2	6*c*	0.25904(7)	0.16236(7)	0.2524(1)	1	0.0113(1)	0.0133(3)	0.0109(3)	0.0116(3)	0.0020(3)	0.0012(3)	0.0074(2)
Se3	6*c*	0.09692(8)	0.57959(8)	0.0197(1)	1	0.0094(1)	0.0095(3)	0.0115(3)	0.0085(3)	0.0009(3)	0.0000(3)	0.0061(3)
$Gd_3Ge_{1.45}Se_7$												
Gd	6*c*	0.13568(5)	0.35873(6)	0.2213(1)	1	0.0151(1)	0.0116(3)	0.0123(3)	0.0219(3)	−0.0018(4)	−0.0017(3)	0.0063(2)
Ge1	2*a*	0	0	0.489(1)	0.449(8)	0.019(1)	0.012(1)	0.012(1)	0.034(3)	0	0	0.0061(9)
Ge2	2*b*	1/3	2/3	0.6392(3)	1	0.0104(5)	0.0104(7)	0.0104(7)	0.010(1)	0	0	0.0052(3)
Se1	2*b*	1/3	2/3	0.0214(3)	1	0.0112(5)	0.0123(7)	0.0123(7)	0.008(1)	0	0	0.0062(3)
Se2	6*c*	0.2594(1)	0.1594(1)	0.2540(1)	1	0.0148(3)	0.0142(6)	0.0110(6)	0.0212(7)	−0.0021(5)	−0.0017(6)	0.0077(5)
Se3	6*c*	0.4233(1)	0.5182(1)	0.4782(1)	1	0.0108(2)	0.0113(6)	0.0099(6)	0.0122(5)	0.0008(5)	0.0009(5)	0.0061(5)
$Tb_3Ge_{1.43}Se_7$												
Tb	6*c*	0.22121(8)	0.35921(7)	0.6262(2)	1	0.0156(3)	0.0115(4)	0.0121(5)	0.0231(5)	0.0018(4)	0.0003(3)	0.0059(3)
Ge1	2*a*	0	0	0.347(1)	0.43(1)	0.013(2)	0.006(2)	0.006(2)	0.027(4)	0	0	0.003(1)
Ge2	2*b*	1/3	2/3	0.2081(5)	1	0.0097(6)	0.0105(8)	0.0105(8)	0.008(1)	0	0	0.0053(4)
Se1	2*b*	1/3	2/3	0.8255(4)	1	0.0113(6)	0.0122(8)	0.0122(8)	0.009(1)	0	0	0.0061(4)
Se2	6*c*	0.2605(1)	0.1026(1)	0.5872(3)	1	0.0146(4)	0.0134(7)	0.0099(7)	0.0210(9)	−0.0014(6)	0.0018(6)	0.0061(6)
Se3	6*c*	0.4811(1)	0.5748(1)	0.3696(3)	1	0.0111(4)	0.0096(7)	0.0126(7)	0.0119(7)	0.0008(6)	0.0009(6)	0.0061(6)

$U_{eq.}$ is defined as one third of the trace of the orthogonalized U_{ij} tensor. The anisotropic temperature factor exponent takes the form: $-2\pi^2[h^2a\times{}^2U_{11}+\ldots+2hka\times b\times U_{12}]$.

Table 3
Interatomic distances (δ, Å) and coordination numbers (C.N.) of the R and Ge atoms in $R_3Ge_{1+x}Se_7$ (R = La, Ce, Pr, Sm, Gd and Tb, x = 0.43–0.49).

Atoms		δ, Å						C.N.
		$La_3Ge_{1.48}Se_7$	$Ce_3Ge_{1.47}Se_7$	$Pr_3Ge_{1.49}Se_7$	$Sm_3Ge_{1.48}Se_7$	$Gd_3Ge_{1.45}Se_7$	$Tb_3Ge_{1.43}Se_7$	
R	1Se2	3.0191(7)	2.995(1)	2.980(1)	2.9222(7)	2.885(1)	2.869(1)	8
	1Se2	3.0191(7)	2.999(1)	2.992(1)	2.9456(7)	2.921(1)	2.919(1)	
	1Se3	3.0357(7)	3.013(1)	3.001(1)	2.9534(8)	2.933(1)	2.924(1)	
	1Se2	3.1026(9)	3.080(1)	3.066(1)	3.0084(9)	2.967(1)	2.938(2)	
	1Se3	3.1307(8)	3.105(1)	3.091(1)	3.0366(8)	3.009(1)	2.997(1)	
	1Se1	3.1840(6)	3.1551(9)	3.1426(9)	3.0782(6)	3.041(1)	3.022(1)	
	1Se3	3.1949(7)	3.173(1)	3.168(1)	3.1363(8)	3.140(1)	3.150(1)	
	1Se2	3.273(1)	3.270(1)	3.271(1)	3.2892(9)	3.346(1)	3.393(2)	
Ge1	3Se2	2.839(2)	2.821(4)	2.822(4)	2.784(2)	2.739(5)	2.752(5)	
	3Se2	2.879(3)	2.867(5)	2.862(4)	2.829(2)	2.837(5)	2.820(5)	6
Ge2	1Se1	2.309(1)	2.317(2)	2.313(2)	2.313(1)	2.312(3)	2.324(3)	4
	3Se3	2.3674(8)	2.369(1)	2.375(1)	2.3653(8)	2.363(1)	2.364(1)	

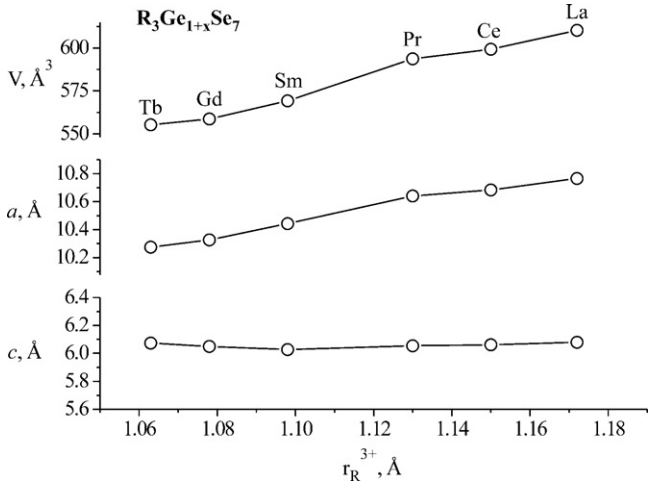

Fig. 2. Unit cell volume (V) and lattice parameters (a and c) of the $R_3Ge_{1+x}Se_7$ (R = La, Ce, Pr, Sm, Gd and Tb, x = 0.43–0.49) compounds versus the ionic radius of the rare earth element.

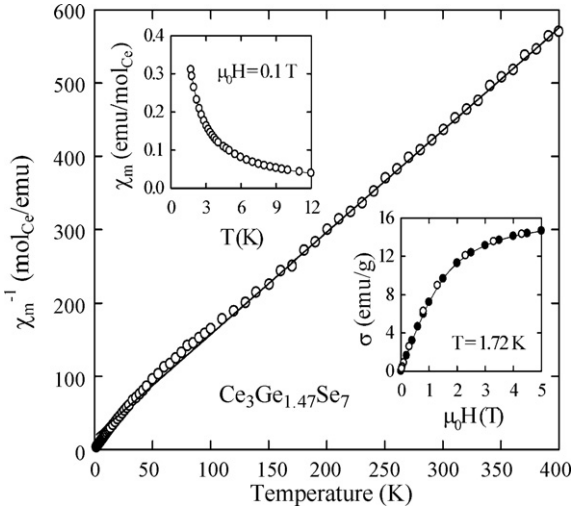

Fig. 3. Temperature dependence of the inverse molar magnetic susceptibility of $Ce_3Ge_{1.47}Se_7$ measured in a field of 0.1 T. The solid line represents the Curie–Weiss fit discussed in the text. Upper inset: the magnetic susceptibility at low temperatures. Lower inset: magnetic field variation of the magnetization taken at 1.72 K with increasing (full symbols) and decreasing (open symbols) field.

does not order magnetically down to 1.72 K (see the upper inset to Fig. 3). The absence of any magnetic phase transition down to very low temperatures, accompanied by relatively large absolute value of θ_p, might give rise to some speculations on possible Kondo-type screening of the cerium magnetic moments in $Ce_3Ge_{1.47}Se_7$ [10]. In order to examine this tempting scenario, we have tried to measure the electrical resistivity on a few selected single crystals. However, all our attempts failed because of problems in making good ohmic contacts to the specimens (epoxy-gluing, metal-soldering and spot-welding techniques were attempted). From this aspect it seems likely that the compound may exhibit nonmetallic (semiconducting/insulating) character of the electrical conduction.

The low temperature paramagnetic behavior in $Ce_3Ge_{1.47}Se_7$ is further reflected in the magnetic field dependence of the isothermal magnetization measured at 1.72 K (see the lower inset to Fig. 3). The magnetization curve has a Brillouin-type shape, and in strong fields it shows a tendency to saturate. The magnetization measured at 5 T is 14.3(4) emu/g that corresponds to the magnetic moment of about 0.9 μ_B per Ce-atom. The latter value is much smaller than the free Ce^{3+} ion value and should be associated with a Kramers doublet ground state that results from the splitting of the $^2F_{5/2}$ multiplet in a hexagonal crystal field potential. Strong crystalline electric field effect in $Ce_3Ge_{1.47}Se_7$ manifests itself also in a distinct deviation of the inverse magnetic susceptibility from the straight-line behavior, observed below 120 K (cf. the main panel in Fig. 3).

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