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Crystal structure and magnetic properties of the $R_6Si_4Se_{17}$ (R = La and Ce) compounds

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ABSTRACT

The crystal structure of the $R_6Si_4Se_{17}$ (R = La and Ce) selenides was studied by means of X-ray powder and single crystal diffraction. The magnetic behaviour of the Ce-based compound was determined through SQUID magnetometry. The two materials crystallize with the $Ce_6Si_4S_{17}$ structure type (space group $P\bar{1}$, Pearson symbol *aP*54). Their unit cells comprise as many as six inequivalent positions of the rare-earth atoms. The compound $Ce_6Si_4Se_{17}$ exhibits Curie–Weiss paramagnetism with no hint at any magnetic ordering down to 1.72 K. The magnetic susceptibility data indicates that the Ce ions in this compound may have fluctuating valence character.

1. Introduction

Designing of compounds with increasingly complex compositions, such as ternary and quaternary, has become a principle direction in modern materials science. In particular, numerous rare-earth chalcogenides have been intensively studied over recent years owing to their specific thermal, electrical and optical properties, which for example make them prospective materials in the field of infrared and nonlinear optics. For this purpose, the synthesis and the investigation of structural and physical properties of new complex chalcogenides are commonly considered as an essential challenge in the development of various novel technologies [1,2].

In the course of our study on the R_2Se_3–$SiSe_2$ system, we previously identified the series of ternaries $R_3Si_{1.25}Se_7$ with R = Pr, Nd and Sm, which crystallize with the $Dy_3Ge_{1.25}S_7$ structure type (space group $P6_3$) [3]. Here, we report on the formation of other compounds within this system, namely $R_6Si_4Se_{17}$ phases with R = La and Ce. The new materials have been characterized as regards their crystal structure and low-temperature magnetic properties.

2. Experimental details

The samples with the overall nominal composition $R_6Si_4Se_{17}$ (R = La and Ce) 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/h up to 1150 °C, and then kept at this temperature for 3 h. Afterwards, the samples were cooled slowly (10 °C/h) down to 500 °C, and annealed at this temperature for 720 h. Finally, the ampoules were quenched in air. The so-obtained materials were dark red and black powders for $Ce_6Si_4Se_{17}$ and $La_6Si_4Se_{17}$, respectively. The samples contained small crystalline grains of the average size of about 0.2 mm for the former and smaller than 0.05 mm for the latter compound.

The products were checked by X-ray powder diffraction using a DRON-4-13 powder diffractometer (Cu K_α radiation, $10^\circ \leq 2\Theta \leq 100^\circ$, step scan mode with a step size of 0.05° and counting time of 20 s per data point). The collected data were analyzed using the CSD software package [4].

Small single crystal suitable for crystal structure investigations was selected from the sample of $Ce_6Si_4Se_{17}$. Its quality was examined on a Phillips 515 scanning electron microscope equipped with an EDAX PV 9800 spectrometer. Our attempts to find well-defined single crystal from the $La_6Si_4Se_{17}$ sample were not successful.

The single-crystal X-ray diffraction intensities were collected on a KUMA Diffraction KM-4 four-circle diffractometer equipped with a CCD camera, using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.071073$ nm). The raw data were treated with the CrysAlis Data Reduction program [5] taking into account an absorption correction. The intensities of the Bragg reflections were corrected for Lorentz and polarization factors. The crystal structure was solved by Patterson methods and refined by the full-matrix least-squares method using SHELXL-97 [6]. The space group $P\bar{1}$ was checked with the PLATON program [7], and no additional symmetry elements were found.

Magnetic measurements were performed in the temperature range 1.72–400 K in applied magnetic fields up to 50 kOe using a Quantum Design MPMS-5 SQUID magnetometer.

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Table 1
Crystal data and structure refinement details of $Ce_6Si_4Se_{17}$.

Empirical formula	$Ce_6Si_4Se_{17}$
Formula weight	2295.40
Space group	$P\bar{1}$ (No. 2)
Unit cell dimensions	$a = 9.383(1)$ Å
	$b = 10.356(2)$ Å
	$c = 14.884(3)$ Å
	$\alpha = 81.94(3)^\circ$
	$\beta = 87.66(3)^\circ$
	$\gamma = 89.25(3)^\circ$
Volume	1430.9(5) Å^3
Number of formula units per unit cell	2
Calculated density	5.328 g/cm^3
Absorption coefficient	31.129 mm^{-1}
$F(000)$	1964
Θ Range for data collection	2.93–27.10
Index ranges	$-12 \le h \le 11$
	$-13 \le k \le 13$
	$-15 \le l \le 19$
Reflections collected	14,416
Independent reflections	6228 [R(int.) = 0.1193]
Refinement method	Full-matrix least-square on F^2
Data/restraints/parameters	6228/0/244
Goodness-of-fit on F^2	0.977
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0480$, $wR2 = 0.0973$
R indices (all data)	$R1 = 0.0617$, $wR2 = 0.1028$
Largest diff. peak and hole	2.224 and −2.509 e/Å^3

3. Results and discussion

The very close similarity of the X-ray powder diffraction patterns obtained for $La_6Si_4Se_{17}$ and $Ce_6Si_4Se_{17}$ suggested that the two compounds are isostructural. The key structure refinement results are summarized in Table 1. In turn, Table 2 presents the refined atomic coordinates and the anisotropic displacement parameters, while Table 3 gives the shortest interatomic distances in the unit cell for the Ce and Si atoms. All these interatomic distances agree well with the sums of the respective ionic radii [8]. Table 4 lists the shortest distances between the Ce atoms. Clearly, they are much larger than the Hill limit for direct magnetic exchange interactions.

The refined parameters of the triclinic crystal lattice of $Ce_6Si_4Se_{17}$ are: $a = 9.383(1)$ Å, $b = 10.356(2)$ Å, $c = 14.884(3)$ Å, $\alpha = 81.94(3)^\circ$, $\beta = 87.66(3)^\circ$, $\gamma = 89.25(3)^\circ$. The lattice parameters found for $La_6Si_4Se_{17}$ from the X-ray powder diffraction data are: $a = 9.4333(4)$ Å, $b = 10.4482(4)$ Å, $c = 14.9866(6)$ Å, $\alpha = 81.906(2)^\circ$, $\beta = 87.475(3)^\circ$, $\gamma = 89.499(3)^\circ$. Both compounds were found to adopt the $Ce_6Si_4S_{17}$ unit cell reported recently for the sulphides $R_6Si_4S_{17}$ (R = Ce, Pr, Nd and Sm) [9,10].

Fig. 1 displays the crystal structure of $Ce_6Si_4Se_{17}$ and the selected coordination polyhedra. In total, there are in the unit cell six symmetry independent sites of Ce atoms, four positions of Si atoms, and 17 sites of Se atoms. All these positions are fully occupied. The Ce1, Ce2, Ce3 and Ce6 atoms are surrounded by distorted trigonal prisms with two additional atoms, whereas the Ce5 atoms are located in distorted trigonal prisms with three additional atoms. In turn, the Ce4 atoms are located in octahedra with one additional atom. All the Si atoms have tetrahedral surrounding. For more details on the crystal structure of the $Ce_6Si_4S_{17}$ type the interested reader is referred to Refs. [9,10].

The magnetic behaviour of $Ce_6Si_4Se_{17}$ is presented in Fig. 2. Above about 50 K, the reciprocal magnetic susceptibility can be approximated by the modified Curie–Weiss (MCW) formula $\chi(T) = \chi_0 + (C/(T - \theta_p))$ with the parameters (the values are given per Ce atom): $\chi_0 = 1.8(2) \times 10^{-3}$ emu/mol, $C = 0.698(4)$ (emu K)/mol and $\theta_p = -20.6(9)$ K. At lower temperatures, $\chi^{-1}(T)$ deviates from the MCW law, likely due to crystal field effect. As shown in the upper inset to Fig. 2, down to 1.72 K the compound remains paramagnetic (little hump seen near 6 K presumably arises because of tiny amount of cerium oxide impurity). The paramagnetic ground state is corroborated by the characteristic behaviour of the isothermal magnetization, displayed in the lower inset to Fig. 2.

The Curie constant C derived from the MCW analysis implies the effective magnetic moment $\mu_{\text{eff}} = \sqrt{8C} = 2.36(2)\mu_B$. This value is considerably smaller than that predicted within the Russell–Saunders coupling scenario for a free Ce^{3+} ion ($g\sqrt{J(J+1)} = 2.54$). The origin of this reduction is not clear. Taking into account that there are as many as six independent Ce atom

Table 2
Atomic coordinates and anisotropic displacement parameters refined for $Ce_6Si_4Se_{17}$.

Atom	Position	x/a	y/b	z/c	$U_{\text{eq.}}$ (Å^2)	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ce1	2i	0.95152(8)	0.23861(6)	0.00153(4)	0.0132(1)	0.0195(4)	0.0112(3)	0.0094(3)	−0.0021(2)	−0.0051(3)	0.0046(3)
Ce2	2i	0.39622(8)	0.11543(6)	0.18639(4)	0.0140(1)	0.0203(4)	0.0105(3)	0.0112(3)	−0.0001(2)	−0.0047(3)	0.0045(3)
Ce3	2i	0.48874(8)	0.73613(6)	0.53361(4)	0.0152(1)	0.0215(4)	0.0122(3)	0.0131(3)	−0.0042(2)	−0.0083(3)	0.0057(3)
Ce4	2i	0.13486(8)	0.43970(6)	0.32294(4)	0.0157(1)	0.0193(4)	0.0157(3)	0.0135(3)	−0.0056(2)	−0.0073(3)	0.0067(3)
Ce5	2i	0.58622(8)	0.58076(6)	0.16417(4)	0.0140(1)	0.0199(4)	0.0128(3)	0.0094(3)	−0.0011(2)	−0.0036(3)	0.0042(3)
Ce6	2i	0.16754(8)	0.08766(6)	0.65789(4)	0.0161(1)	0.0260(4)	0.0118(3)	0.0108(3)	−0.0019(2)	−0.0030(3)	0.0033(3)
Si1	2i	0.2502(4)	0.4415(3)	0.0793(2)	0.0127(7)	0.015(1)	0.013(1)	0.009(1)	−0.001(1)	−0.003(1)	0.003(1)
Si2	2i	0.2224(4)	0.4451(3)	0.6080(2)	0.0137(7)	0.018(2)	0.012(1)	0.011(1)	−0.000(1)	−0.005(1)	0.003(1)
Si3	2i	0.2498(4)	0.9941(3)	0.4155(2)	0.0128(7)	0.016(1)	0.013(1)	0.009(1)	−0.001(1)	−0.007(1)	−0.000(1)
Si4	2i	0.7322(4)	0.9410(3)	0.0992(2)	0.0152(7)	0.023(2)	0.012(1)	0.010(1)	−0.001(1)	−0.006(1)	0.004(1)
Se1	2i	0.1781(1)	0.0157(1)	0.04611(7)	0.0145(3)	0.0205(7)	0.0138(5)	0.0097(5)	−0.0022(4)	−0.0057(5)	0.0044(5)
Se2	2i	0.3179(1)	0.5223(1)	0.46775(7)	0.0137(3)	0.0178(7)	0.0140(5)	0.0094(5)	−0.0014(4)	−0.0051(5)	0.0025(5)
Se3	2i	0.8436(1)	0.5003(1)	0.05842(7)	0.0147(3)	0.0193(7)	0.0153(5)	0.0095(5)	−0.0017(4)	−0.0037(5)	0.0060(5)
Se4	2i	0.4373(1)	0.3581(1)	0.28075(7)	0.0146(3)	0.0204(7)	0.0133(5)	0.0099(5)	−0.0005(4)	−0.0040(5)	0.0037(5)
Se5	2i	0.4638(1)	0.3495(1)	0.04865(7)	0.0153(3)	0.0206(7)	0.0136(5)	0.0106(5)	0.0020(4)	−0.0016(5)	0.0055(5)
Se6	2i	0.3943(1)	0.2975(1)	0.65852(7)	0.0144(3)	0.0209(7)	0.0133(5)	0.0095(5)	−0.0022(4)	−0.0050(5)	0.0061(5)
Se7	2i	0.1963(1)	0.1911(1)	0.45782(7)	0.0161(3)	0.0245(8)	0.0118(5)	0.0120(6)	−0.0014(4)	−0.0037(5)	0.0045(5)
Se8	2i	0.1179(1)	0.2835(1)	0.16544(7)	0.0135(3)	0.0188(7)	0.0122(5)	0.0104(5)	−0.0030(4)	−0.0063(5)	0.0030(5)
Se9	2i	0.7502(1)	0.1212(1)	0.17043(7)	0.0160(3)	0.0241(8)	0.0112(5)	0.0134(6)	−0.0031(4)	−0.0027(5)	0.0024(5)
Se10	2i	0.1272(1)	0.2199(1)	0.83081(7)	0.0160(3)	0.0231(7)	0.0152(5)	0.0092(5)	−0.0003(4)	−0.0032(5)	0.0075(5)
Se11	2i	0.4900(1)	0.0048(1)	0.37910(7)	0.0154(3)	0.0210(7)	0.0130(5)	0.0121(6)	−0.0011(4)	−0.0053(5)	0.0062(5)
Se12	2i	0.5069(1)	0.8739(1)	0.11300(8)	0.0176(3)	0.0198(7)	0.0119(5)	0.0217(6)	−0.0034(4)	−0.0044(5)	0.0038(5)
Se13	2i	0.1926(1)	0.8579(1)	0.54182(7)	0.0159(3)	0.0213(7)	0.0125(5)	0.0137(6)	−0.0010(4)	−0.0026(5)	0.0019(5)
Se14	2i	0.2452(1)	0.6240(1)	0.14964(7)	0.0151(3)	0.0229(7)	0.0107(5)	0.0124(6)	−0.0026(4)	−0.0063(5)	0.0052(5)
Se15	2i	0.8135(1)	0.4113(1)	0.29415(8)	0.0181(3)	0.0251(8)	0.0159(6)	0.0148(6)	−0.0060(4)	−0.0082(5)	0.0069(5)
Se16	2i	0.1472(1)	0.9578(1)	0.28841(8)	0.0204(3)	0.0240(8)	0.0265(6)	0.0109(6)	−0.0015(5)	−0.0057(5)	−0.0058(6)
Se17	2i	0.0121(1)	0.3454(1)	0.59810(8)	0.0184(3)	0.0179(7)	0.0128(5)	0.0259(7)	−0.0069(5)	−0.0054(5)	0.0031(5)

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