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Tetragonal to triclinic structural transition in the prototypical CeScSi induced by a two-step magnetic ordering: a temperature-dependent neutron diffraction study of CeScSi, CeScGe and LaScSi

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Abstract

An investigation on the ground state magnetism of CeScSi, CeScGe (tetragonal CeScSi-type, *tI*12, space group *I*4/*mmm*) by temperature-dependent powder neutron diffraction has been carried out, as debated and controversial data regarding the low temperature magnetic behaviours of these two compounds were reported.

Our studies reveal that, while cooling, long-range magnetic ordering in CeScSi and CeScGe takes place by a two-step process. A first transition leads to a magnetic structure with the Ce moments aligned ferromagnetically onto two neighbouring tetragonal basal *a*-*b* planes of the CeScSi-type structure; the double layers are then antiferromagnetically coupled to each other along the *c*-axis. The transition temperature associated with the first ordering is $T_N \sim 26$ K and $T_N \sim 48$ K for the silicide and the germanide, respectively. Here the spin directions are rigorously confined to the basal plane, with values of the Ce magnetic moments of $\mu_{Ce} = 0.8$–$1.0\ \mu_B$. A second magnetic transition, which takes place at slightly lower temperatures, results in a canting of the ordered magnetic moments out of the basal plane which is accompanied by an increase of the magnetic moment value of Ce to $\mu_{Ce} = 1.4$–$1.5\ \mu_B$. Interestingly, the second magnetic transition leads to a structural distortion in both compounds from the higher-symmetry tetragonal space group *I*4/*mmm* to the lower-symmetry and triclinic *I*–1 (non-standard triclinic). Magnetic symmetry analysis shows that the canted structure would not be allowed in the *I*4/*mmm* space group; this result further confirms the structural transition. The transition temperatures T_S from *I*4/*mmm* to *I*–1 are about 22 K in CeScSi and 36 K in CeScGe, i.e. well below the temperature of the first onset of antiferromagnetic order observed in this work (or below the ordering temperature, previously reported as either T_C or T_N). This result, along with the synchronism of the magnetic and structural transitions, suggests a magnetostructural origin of this structural distortion.

We have also carried out powder neutron diffraction for LaScSi as a non-magnetically-ordering reference compound and compared the results with those of CeScSi and CeScGe compounds.

Keywords: rare earth ternary compounds, cerium intermetallics, neutron diffraction, magnetic structure, magnetostructural transition

(Some figures may appear in colour only in the online journal)

1. Introduction

Most of the ternary equiatomic compounds with composition RTX, where R = rare earth, T = transition metal and X = p-block element, crystallize in the tetragonal CeScSi structure type (ternary ordered variant of the La_2Sb-type. Pearson symbol *tI*12; space group *I*4/*mmm*, N. 139) [1, 2], where both Ce and Si atoms occupy a Wyckoff site 4*e* (0 0 *z*) while Sc is placed in the 4*c* site (0 ½ 0). A review on the structure-property relationships on equiatomic Ce compounds CeTX has recently been published by Pöttgen *et al* [3]. Our previous work on isostructural RScSb compounds revealed that Sc is slightly shifted from the position 4*c* to the position 8*j* (*x* ½ 0), with $x = 0.04$–0.08 [4], along with a significant reduction of the site occupation [5].

In an earlier work the resistivity and magnetisation of single crystals of Ce_2Sb and Ce_2Bi (La_2Sb-type) were reported and the data compared with those obtained from polycrystalline samples of the ternary CeScSi and CeScGe compounds [6]; the anomalies found at 26 and 46 K for CeScSi and CeScGe, respectively, were associated with ferromagnetic phase transitions which were signified by the presence of substantial magnetic hysteresis below T_C. The authors also highlighted that these were unusually high transition temperatures for Ce intermetallic compounds; mostly CeScGe gained interest on its own. In a first work by Uwatoko *et al* [7] the magnetisation of polycrystalline CeScGe as a function of temperature (up to 300 K) and magnetic field (at 4.2 K, and up to applied fields of 300 kG) was measured; they reported an antiferromagnetic ground state but with three magnetic transition temperatures: the highest being $T_N = 46$ K, followed by T_2 and T_1 (values not reported). However, the presence of spontaneous magnetization and ferromagnetic behaviour in single crystals of CeScGe and CeScSi was again stated in a subsequent work [8]. More recent magnetic data on these two compounds have shown that impurity free CeScSi and CeScGe are not ferromagnetic but have an antiferromagnetic ground state with $T_N = 26$ and 46 K, respectively [2]; heat capacity data also revealed the presence of further anomalies around 21 K for the silicide and 30 K for the germanide.

However, information on the low-temperature structural behaviour of the prototypical CeScSi compound is still lacking (as far as we are aware), and understanding its ground-state magnetic and structural behaviour remains unexposed. To the best of our knowledge, neither the size of the ordered Ce^{3+} magnetic moments nor the details of either the magnetic structures or the origin of the above anomalies in both compounds are known.

We present here the results of a neutron powder diffraction study which aims at the determination of crystallographic details and magnetic structure as a function of temperature of the prototypical CeScSi and of the isostructural CeScGe. We have shown that both compounds below T_N adopt first an antiferromagnetic structure with a magnetic propagation vector $\tau = (1\,0\,0)$ with moments lying in the tetragonal basal plane. Below T_N a strong magnetostructural transition, which implies a rotation of the magnetic moments partly into the unit cell *c*-direction and a structural phase transition from the tetragonal *I*4/*mmm* to the triclinic *I*–1, has been observed. These observed data are compared with those of the isostructural LaScSi, which was also studied as a non-magnetically-ordered reference compound.

2. Experimental

Polycrystalline ingots of CeScSi, CeScGe and LaScSi were prepared by arc melting the elements under a pure argon atmosphere on a water-cooled copper hearth; the buttons were re-melted three times, turning them upside-down each time to ensure homogenization (total weight 7–8 g; weight losses between 0.1–0.3 wt.%). The starting materials were high purity elements supplied by commercial vendors (99.9 wt.% for both La and Sc, 99.95 wt.% for Ce (all R from Koch-Light, England)) and 99.9999 wt.% for Si and Ge (from Alfa-Aesar, Germany). The final ingots were placed inside an outgassed Ta tube, sealed under vacuum in silica tubes and annealed at 900 °C for 10 d. Phase analysis was performed by x-ray powder diffraction using a Guinier camera (Cu Kα1 radiation; Si as internal standard). Indexing of the powder patterns was carried out with the help of the Lazy-Pulverix program [9].

Neutron diffraction data were taken at the Institute Laue Langevin (ILL), in Grenoble (France), using the high resolution powder diffractometer D2B ($\lambda = 1.594$ Å) and the high intensity powder diffractometer D20 ($\lambda = 2.4$ Å). The temperature dependence of the patterns (thermodiffractograms) was measured on D20 between 1.7 and 35 K for the Si-compound by taking data over $\Delta T = 0.7$ K intervals and between 1.7 and 74 K over $\Delta T = 1.2$ K intervals for the Ge-compound. High resolution data were taken at 1.5 K, 100 K, 200 K and 300 K for all three compounds and additionally at six different temperatures close to the respective transition temperatures for the Ce-compounds and at 20 K and 50 K for LaScSi. Data analysis was performed using the Rietveld refinement program FULLPROF [10]; magnetic symmetry analysis was performed using the program Basireps [11, 12].

3. Results and discussion

The refinement of the high-resolution powder neutron diffraction data of all the three compounds CeScSi, CeScGe and LaScSi measured at 300 K proceeded smoothly, revealing

Table 1. Results of the Rietveld refinement of the high resolution diffraction data at 300 K for RScX compounds in the tetragonal space group *I*4/*mmm*.

RScX	a (Å)	c (Å)	z_R (4*e*)	z_X (4*e*)	occ_{Sc} (4*c*)	R_{Bragg}
CeScSi	4.320 66(5)	15.8812(2)	0.3233(1)	0.1201(1)	0.912(5)	3.1
CeScGe	4.345 73(7)	15.9822(3)	0.3230(2)	0.1212(1)	0.944(4)	5.6
LaScSi	4.351 40(3)	16.0511(2)	0.3234(1)	0.1184(1)	0.924(4)	3.1

the expected tetragonal structure with space group *I*4/*mmm* and Ce/La and Si/Ge atoms in the Wyckoff position 4*e* (0 0 *z*) and Sc in 4*c* (0 ½ 0)]. Details of the results, with corresponding agreement factors, are presented in table 1. Small amounts of Sc_5Si_3, or Sc_5Ge_3, (Mn_5Si_3-type, *hP*16, *P*6$_3$/*mmc*) were present as an impurity phase in the Ce-containing compounds and were included in the refinements as a LeBail fit. The attempt to liberate the *x*-coordinate of 4*c* by going to position 8*j* (*x* ½ 0), as found in other isostructural RScSb phases [5], did not improve the refinements. However, when refining the occupations a sub-stoichiometry was found on the Sc site varying between 5.5 and 8.5%, as in the RScSb (R = Ce, Pr, Nd) compounds [5] (see table 1).

Figure 1 gives plots of the temperature dependence of the lattice parameters for LaScSi from 300 down to 1.5 K, which shows a usual thermal contraction behaviour for the La compound where the *I*4/*mmm* symmetry is preserved down to the lowest temperature. Unlike in LaScSi, CeScSi and CeScGe show a strong change on their respective diffraction pattern on cooling. In both cases new peaks appear at low 2Θ values and a broadening/splitting of nearly all the peaks becomes visible. Figure 2(a) displays the thermal dependence of the low angle region of the thermodiffractogram of CeScSi as measured on the instrument D20.

The transition temperatures of 26 K and 48 K were determined by fitting the intensity of the strongest new peaks for CeScSi and CeScGe, respectively. These values are consistent with the magnetic transition temperatures reported in the literature [2, 6]; the new peaks are identified as being of magnetic origin. The temperature dependence of two new peaks of CeScGe is shown in figure 2(b) with the intensities normalized to the values found at the lowest temperature. A different behaviour is found for the two reflections between T_N and about 20 K, indicating that the magnetic structure adopted could change in this temperature range. For both compounds a magnetic propagation vector of $\tau = (1\ 0\ 0)$ was determined from the position of the magnetic peaks using the program K-search which is part of the FULLPROF suite of programs [10].

Figure 3 shows a portion of the high resolution patterns obtained at 52 K and 1.5 K for CeScGe where the splitting of the Bragg peaks at low temperatures can be seen at high *Q*-values (where $Q = 2\pi\ (\sin\theta)/\lambda$). Changes in the diffraction patterns at high *Q* values are more likely associated with a structural transition, as the intensity of magnetic scattering depends on the magnetic form factor which decreases rapidly with increasing *Q*. The lowering of symmetry, which leads to the splitting of the Bragg peaks, clearly removes the tetragonal symmetry but could neither be explained by a transition to an orthorhombic nor to a monoclinic subgroup of the space

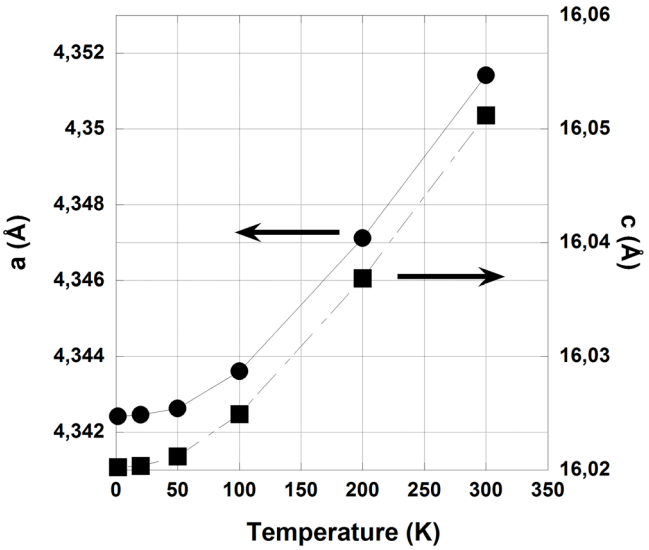

Figure 1. Temperature dependence of the tetragonal lattice parameters, *a* and *c*, of LaScSi. The thin solid line is a guide to eyes.

group *I*4/*mmm*. LeBail fits of the data in *Pmmm* and *P*2/*m* did not work but showed that at least two of the unit cell angles deviate significantly from 90° and therefore the symmetry was reduced to triclinic. The highest triclinic symmetry in our case corresponds to the non-standard space group *I*–1, where the transformation from *I*4/*mmm* to *I*–1 leads simply to Ce and Ge occupying general positions (*x y z*) while the Sc site gets split into two different positions at special sites[5]. The number of positional parameters for the atoms increases only from two to six. In order to verify this hypothesis a full Rietveld refinement is needed, however, as the low temperature distorted structure is magnetically ordered the contribution of the magnetic scattering has to be included in the fit. Magnetic symmetry analysis using the program BASIREPS [11, 12] was performed for the space group *I*–1 and the magnetic propagation vector $\tau = (1\,0\,0)$.

The left side of table 2 lists the resulting allowed irreducible representations (IR) and their basis vectors (BV) for the magnetic Ce atom in the *I*–1 space group. There are only two IRs, each one having three BVs corresponding to a fully ferromagnetic or antiferromagnetic ordering of the two Ce positions related by symmetry. There is no mixing of ferromagnetically and antiferromagnetically coupled BVs. A refinement of the high resolution data taken at 1.5 K for CeScGe, using the antiferromagnetic model (IR2), converged immediately with the

[5] The description in *I*–1 is chosen so as to keep a strong resemblance to the high temperature *I*4/*mmm* symmetry and in order to limit the number of refinable atomic coordinates. Synchrotron x-ray data are needed to determine the exact atomic positions in the standard description using *P*-1.

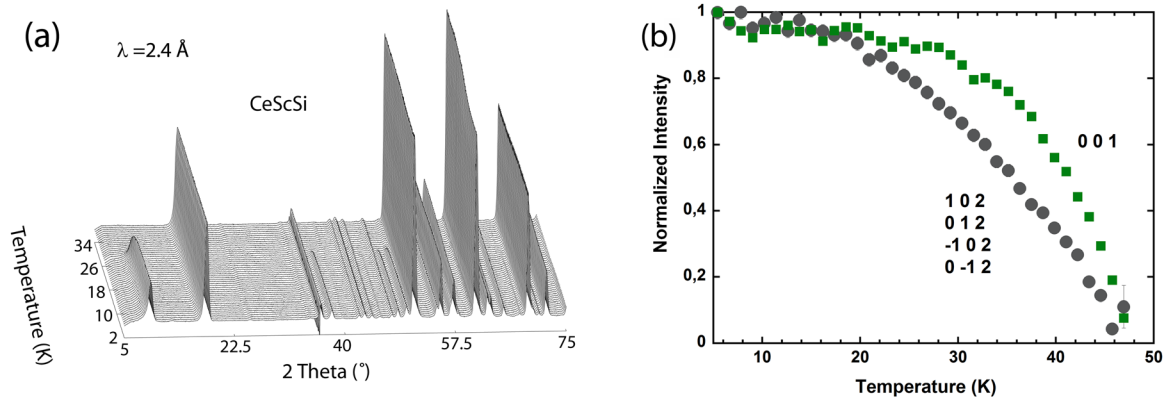

Figure 2. (a) Thermodiffractogram of CeScSi; (b) normalized intensity of two magnetic peaks of CeScGe.

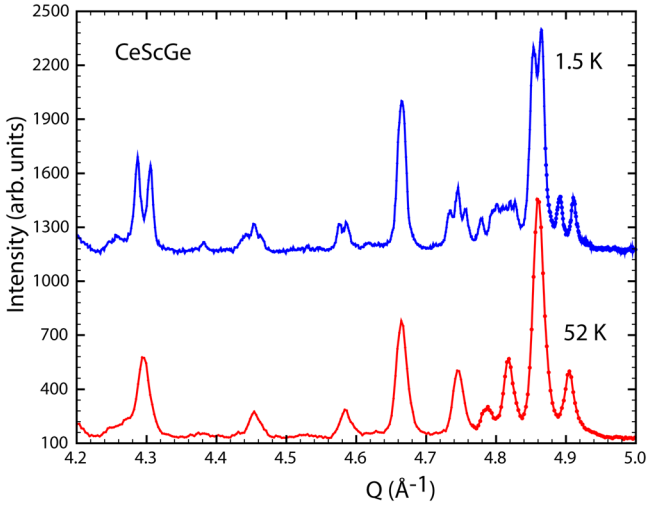

Figure 3. Comparison at large Q-values ($Q = 2\pi\,(\sin\theta)/\lambda$) of the high resolution diffraction patterns of CeScGe, measured at 52 K and 1.5 K, showing the splitting of structural Bragg peaks.

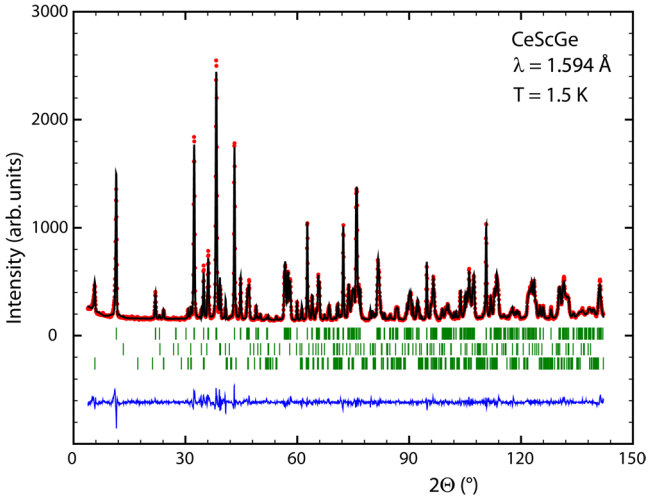

Figure 4. Observed (dots, red), calculated (line, black) and difference pattern of CeScGe at 1.5 K. The tick marks indicate the calculated position of the nuclear (upper row) and magnetic (lower row) Bragg peaks of the main phase and of a small amount of the impurity phase Sc_5Ge_3 (middle row).

Table 2. Basis vectors (BV) of the allowed irreducible representations (IR) for $\tau = (100)$ for the Wyckoff position 4*e* of the space group *I*4/*mmm* and 4*i* of the space group *I*–1.

	I–1				*I*4/*mmm*	
	BV1	BV2	BV3		BV1	BV2
IR1				IR1		
x, y, z	100	010	001	x, y, z	001	
$-x, -y, -z$	100	010	001	$-x, -y, -z$	00 −1	
IR2				IR2		
x, y, z	100	010	001	x, y, z	001	
$-x, -y, -z$	−100	0 −10	00 −1	$-x, -y, -z$	00 −1	
				IR3		
				x, y, z	100	0 −10
				$-x, -y, -z$	−100	010
				IR4		
				x, y, z	010	100
				$-x, -y, -z$	010	100

Table 3. Results of the structural and magnetic refinement for CeScSi and CeScGe at $T = 1.5$ K in the space group *I*–1; Sc is positioned on sites (0½0) and (½00). Values of the coefficients of the BVs of the magnetic refinement using IR2.

	CeScSi	CeScGe
Ce; x	0.994(3)	0.989(2)
y	0.004(3)	0.010(2)
z	0.3233(1)	0.3233(1)
Ge; x	0.012(2)	0.007(1)
y	0.995(2)	0.996 [1]
z	0.1198(1)	0.1207(8)
a (Å)	4.3131(4)	4.3359(3)
b (Å)	4.3122(4)	4.3347(3)
c (Å)	15.8565(3)	15.9628(3)
α (°)	90.21(1)	90.22(1)
β (°)	90.20(1)	90.26(4)
γ (°)	89.954(2)	89.992(2)
R_{Bragg}	2.5%	3.1%
BV1 = BV2	0.82(1)	0.60(1)
BV3	0.96(3)	1.15(4)
μ_{Ce}^{3+} (μ_{B})	1.51(4)	1.42(4)
R_{Mag}	8.2%	12.2%

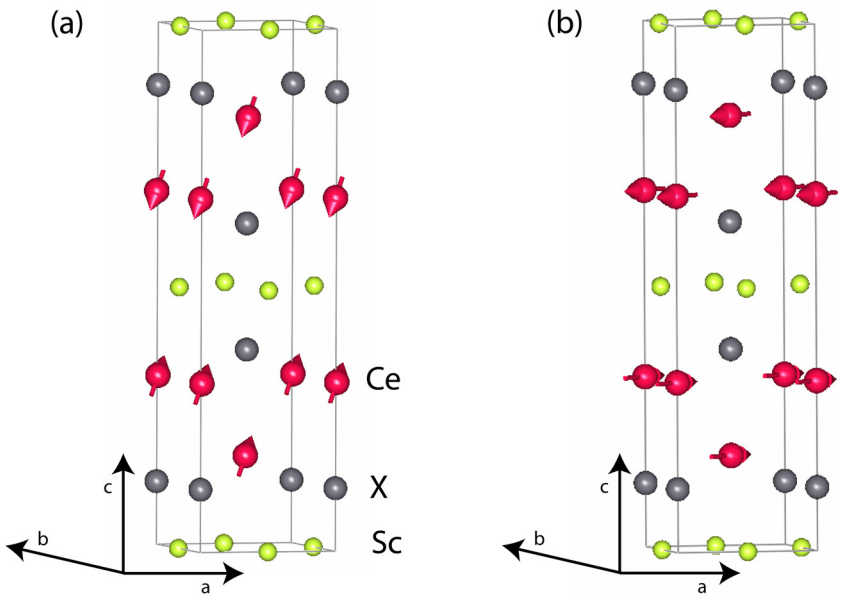

Figure 5. Magnetic structure of the CeScX compounds (X = Si, Ge). (a); at 1.5 K: below the structural transition temperature T_S, within the triclinic phase; (b) below T_N: within the tetragonal phase.

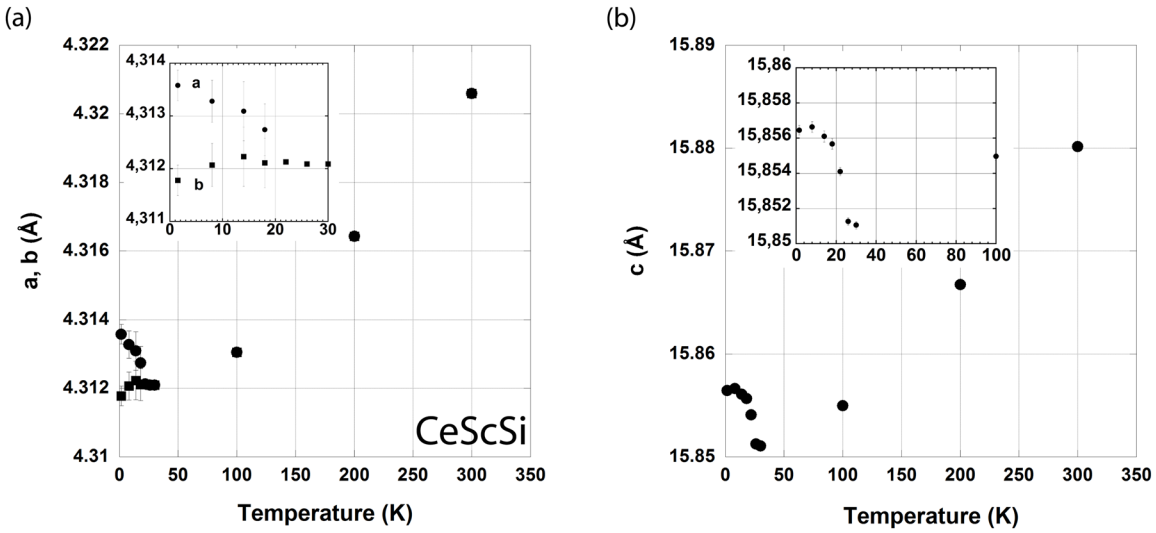

Figure 6. Thermal dependence of the unit cell parameters of CeScSi. (a) Trend of the tetragonal a or triclinic a and b lattice parameters; the inset shows the data below 30 K, on enlarged scale, revealing the change to the triclinic structure below 22 K (T_S). (b) Trend of the c lattice parameter; the inset shows an enlarged scale of the low temperature region, with an expansion starting below about 26 K followed by a sudden increase at about 22 K.

structural part being described in I–1. The values of the coefficients of BV1 and BV2 pointing in direction of the unit-cell a- and b-parameters adopt similar values with, however, large error bars. This can be related to the fact that the resolution of the data at low 2Θ values where the magnetic peaks appear is not sufficiently good to resolve the triclinic distortion. The magnetic peaks could be well described using the original tetragonal unit cell, so the limitations of powder diffraction technique in determining the magnetic moment directions in high symmetries apply. In a tetragonal symmetry, e.g. it is not possible to determine the moment direction within the tetragonal basal plane; we therefore constrained the two BVs corresponding to this plane to be equal in size. This led to a stable refinement as well for the magnetic part of the fit. Figure 4 shows a plot of the refinement of the data at 1.5 K for CeScGe; table 3 summarizes the structural and magnetic parameters obtained from the refinement.

The resulting magnetic structure of CeScGe is shown in figure 5(a); it essentially consists of collinear double layers of ferromagnetically ordered Ce atoms extending in the a-b plane which are antiferromagnetically coupled to the neighbouring double layers along the direction of the unit cell c-axis. The Ce magnetic moments are canted by about 54° towards the c-direction of the triclinic cell, with the magnetic moment reaching a value of about 1.42(4) μ_B.

The data of CeScSi taken at 1.5 K were refined in the same way in space group $I-1$ and using for the magnetic structure the same model of CeScGe. The value of the magnetic moment

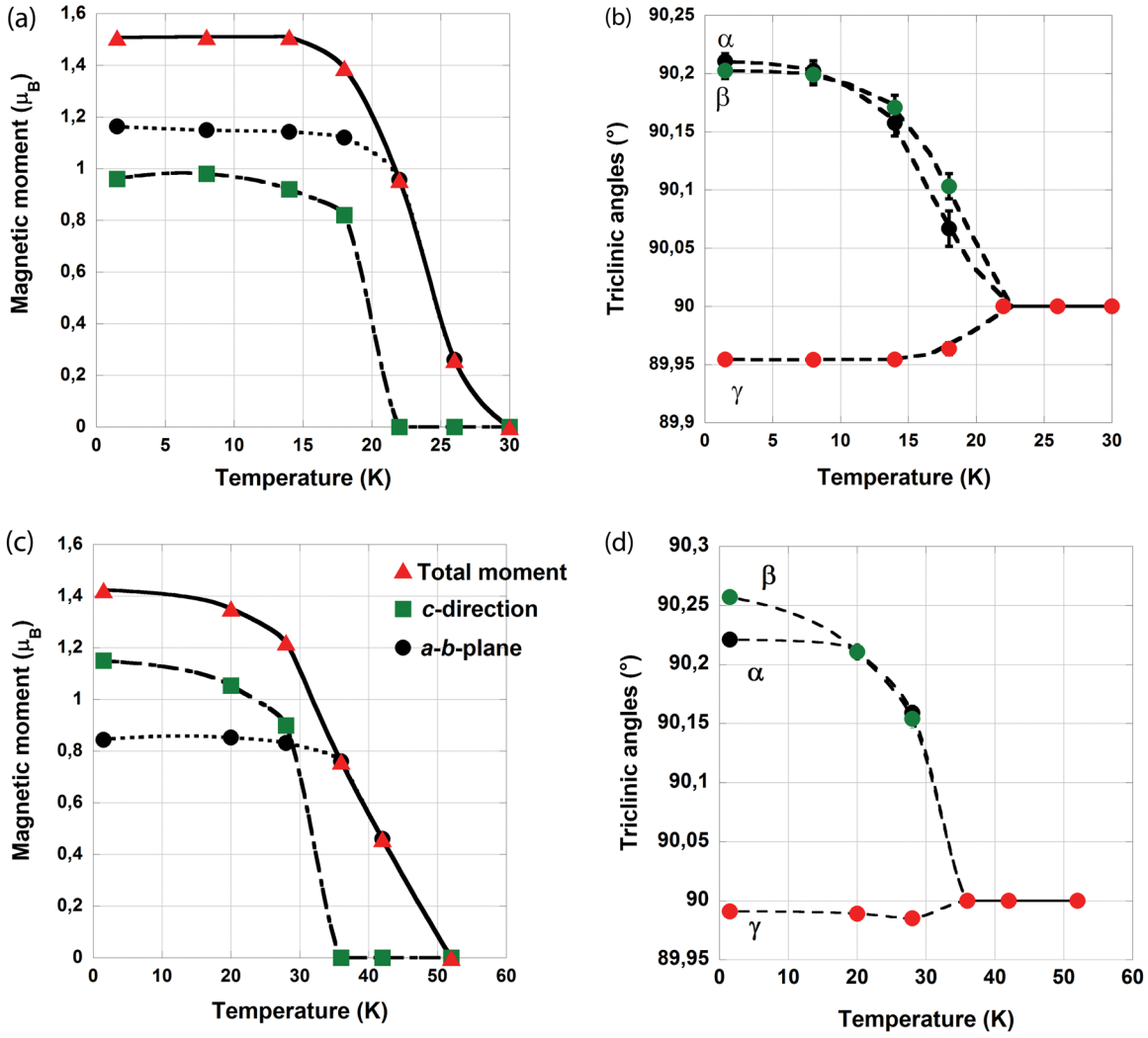

Figure 7. Thermal dependence of the magnetic moment components and of the angles of the triclinic unit-cell in CeScSi ((a) and (b)) and CeScGe ((c) and (d) (Error bars in (a), (c) and (d) are smaller than the symbols). The lines are guides to eyes.

of $\mu_{Ce}^{3+} = 1.51\ (4)\ \mu_B$ is slightly higher than that of the germanide, while the canting angle of about 40° is somewhat lower (table 3). With increasing the temperature a slight decrease of this canting angle can be found for both compounds. It decreases from 54° at 1.5 K to 47° at 30 K in CeScGe and from 40° at 1.5 K to 36° at 18 K in CeScSi. At the same time the difference between the unit cell *a*- and *b*-parameters decreases and the triclinic angles approach 90°.

Figures 6(a) and (b) display the temperature dependencies of the lattice parameters of CeScSi which should be compared with those of the non-magnetic LaScSi (shown in figure 1). It can be seen that when coming from high temperatures an expansion of the *c*-axis starts at the magnetic transition temperature T_N ~ 26 K (figure 6(b)), while the anomalous thermal expansion of the *a*-axis becomes only visible below 22 K (figure 6(a)) where the distortion to the triclinic symmetry takes place. A very similar behaviour is found for CeScGe, with the *c*-axis expanding below T_N ~ 48 K and the anomaly in the basal plane appearing only below 36 K. The temperature at which the structural transition, T_S, from the high temperature symmetry *I*4/*mmm* to the low temperature symmetry *I*–1is observed is ~22 K in CeScSi and ~36 K in CeScGe: in both compounds the structural transition takes place below the first antiferromagnetic ordering (here determined at T_N ~ 26 K for CeScSi and T_N ~ 48 K for CeScGe (see figure 2(b)).

Above T_S, where the crystal structure has the *I*4/*mmm* symmetry the magnetic structure is different as well. The magnetic propagation vector is the same as at lowest temperatures, $\tau = (1\,0\,0)$; however, magnetic symmetry shows that in *I*4/*mmm* the allowed IRs and their BVs are different (see table 2). The refinement shows that the magnetic structure follows IR3 where the magnetic moments of Ce atoms are again ordered antiferromagnetically but confined within the tetragonal *a*-*b* plane. This is in agreement with the symmetry analysis (see table 2), which shows that no single IR can exist within the space group *I*4/*mmm* that has simultaneous components in the tetragonal basal plane and along the *c*-axis. Figures 7(a) and (c) show the temperature dependence of the magnetic moment components of CeScSi and CeScGe within the *a*-*b* plane and along the *c*-axis together with the temperature dependence of the unit-cell angles (Figures 7(b) and (d)). Just above the respective T_S the magnetic moment values amount to 0.76(2) μ_B for CeScGe and to 0.97(2) μ_B for CeScSi.

Summarizing the results displayed in figures 6 and 7, it can be stated that at the magnetic transition temperature of 26 K for CeScSi and 48 K for CeScGe the tetragonal symmetry of the two compounds is preserved, with a magnetic structure confined to the tetragonal *a*-*b* plane; lowering the temperature leads to an expansion of the *c*-axes through magnetostriction. Well separated in temperature from the temperature of the magnetic order onset, a spin reorientation takes place which leads to a concomitant symmetry change to a triclinic unit cell. The existence of this 2-step magnetic transition agrees well and explains the anomalies in the heat capacity plots presented in [2], seen as a shoulder at about 21 K for the silicide and 30 K for the germanide.

The coincidence of the magnetic ordering temperature with that of the crystal structural distortion confirms the magneto-structural origin of this second phase transition. By comparing the unit cell parameters and the unit cell volumes of the three measured compounds with those of the isostructural *R*ScSb [5] and *R*MgSn [13] phases, which maintain the CeScSi-type structure down to lowest temperatures, it can be argued that the smaller size of the tetragonal unit cell is the reason for the structural change in CeScSi and CeScGe. This supposition however does not explain yet the fact that the transition to the triclinic structure is appearing at higher temperature in the Ge-compound (which has a larger cell volume) than in the Si-compound (table 1). None of the isostructural *R*ScSb [5] and *R*MgSn [13] compounds adopts a magnetic structure where the magnetic moment of the R^{3+} ion sees simultaneously components within the tetragonal basal plane and along the *c*-axis direction which would contradict magnetic symmetry analysis. Similar results were found for the isostructural NdScGe [14], and TbScGe [15], which both have a smaller unit cell volume than the CeScX compounds. Highly interesting in this context is however the case of the isostructural compounds PrScSi and PrScGe. Like the Ce compounds, both adopt the same spin-canted magnetic structure: PrScGe in a limited temperature range between about 140 K and 90 K [14], while PrScSi below $T_N \sim 145$ K down to lowest temperatures [16]. However, and contrarily to the case of the Ce compounds, this magnetic structure which is not conforming to magnetic symmetry analysis for the space group *I*4/*mmm* does not lead to a structural transition in the two Pr compounds [15].

The only two Ce-based ternary compounds, adopting the CeScSi prototype, for which the magnetic structures are known are CeMgPb [17] which sees an antiferromagnetic order within the tetragonal basal plane and CeScSb [5] which adopts a purely ferromagnetic structure within the tetragonal basal plane with a much reduced magnetic moment of about 0.9 μ_B. The larger moment values found for CeScSi ($\mu_{Ce}^{3+} = 1.5\ \mu_B$) and CeScGe ($\mu_{Ce}^{3+} = 1.4\ \mu_B$) suggest a stronger localisation of the 4*f* electrons in the latter compounds which could lead to a stronger contribution of the 4*f* electrons to the magnetocrystalline anisotropy and trigger the magnetostructural transition towards a lower symmetry. Further work has to be done, especially on the theoretical side, to explain the exceptional effect brought about by the relatively small Ce moment to give rise to such a strong structural distortion.

5. Summary

Temperature dependent powder neutron diffraction data on CeScSi and CeScGe reveal that the appearance of long range ordered magnetism is a two-step process. On lowering the temperature, a first transition leads to a magnetic structure with Ce magnetic moments of two neighbouring layers ferromagnetically aligned within the tetragonal basal plane of the *I*4/*mmm* structure; the ferromagnetic 'bilayers' are then coupled antiferromagnetically each other in direction of the *c*-axis of the unit cell. In this configuration, overall antiferromagnetic (with T_N of 26 and 48 K, for CeScSi and CeScGe, respectively), the spin directions are rigorously confined to the *a*-*b* plane and the Ce moment μ_{Ce} is of the order of about 0.8–1.0 μ_B. A second magnetic transition, which takes place at slightly lower temperatures, leads to a canting of the magnetic moments out of the basal plane and to an increase of the ordered moment to $\mu_{Ce} = 1.4$–$1.5\ \mu_B$ (Ge and Si compound, respectively). In both compounds the second magnetic transition leads to a structural distortion, with a symmetry reduction from the tetragonal space group *I*4/*mmm* to the triclinic *I*–1; the structural transition temperatures T_S are about 22 K in CeScSi and 36 K in CeScGe. Magnetic symmetry analysis shows that the canted structure would not be allowed in the space group *I*4/*mmm*. These results along with the synchronism of magnetic reordering and structural distortion indicate a magnetostructural origin of the structural transition. The results reported here resolved the issue regarding the ground state magnetism of CeScSi and CeScGe that has been debated for long time.

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