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## The nature of magnetism in CeScSi and CeScGe

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### Abstract

Conflicting reports on the nature of the magnetic transition in CeScSi and CeScGe have appeared in the literature. We have readdressed this problem in this report by working on well characterized polycrystalline samples. Our data prove conclusively that the two compounds order antiferromagnetically at  $T_N \approx 26$  and 46 K, respectively. An analysis of the x-ray diffraction intensity profile in the polycrystalline samples and a structural refinement of CeScSi by single-crystal work showed that these are crystallographically well ordered intermetallics. It is important to anneal the compounds at the proper temperature to remove parasitic impurity phases which are present in the as-cast materials and are the likely cause of the conflicting reports on these two compounds.

### 1. Introduction

Differing reports on the nature of magnetism in CeScSi and CeScGe have appeared in the literature. Canfield *et al* [1] were the first to investigate the magnetic behaviour of these two compounds, which have the tetragonal, La<sub>2</sub>Sb-type crystal structure. They reported ferromagnetic transitions in both CeScSi and CeScGe occurring at  $T_c = 26$  and 46 K, respectively. In [1], the authors plotted only the low-temperature electrical resistivity of the two compounds, which shows an obvious anomaly at the transition from the paramagnetic to the magnetically ordered state. Evidence for the ferromagnetic transition was concluded by these authors from the presence of substantial hysteresis in magnetization against field measurements below the transition temperature. However, [1] does not show any plots of the magnetization either as a function of field or temperature. On the other hand, Uwatoko *et al* [2] studied the magnetization of a polycrystalline sample of CeScGe up to applied fields of 300 kG at 4.2 K and as a function of temperature up to 300 K. They reported an antiferromagnetic transition at 46 K contrary to the results of [1]. Actually, the susceptibility data (the value of the applied field is not quoted) of Uwatoko *et al* [2] show three peaks marked  $T_1$ ,  $T_2$  and  $T_N$ , respectively, with  $T_N = 46$  K. The magnitudes of  $T_1$  and  $T_2$  ( $T_1 < T_2$ ) are not quoted but they are lower than  $T_N$ .

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Both Canfield *et al* [1] and Uwatoko *et al* [2] made their samples by the standard procedure of arc melting, but they do not mention whether any annealing treatment was given to the samples. More recently, Uwatoko *et al* [3] reported the magnetization results of single crystals of CeScSi and CeScGe. They observe a hysteresis in the magnetization along the *c*-axis in both CeScSi and CeScGe, measured at 5 and 2.5 K respectively, with a remanent magnetization of about  $0.3 \mu_B/\text{Ce}$  (figure 1 of [3]). Surprisingly, these authors record a magnetic transition at 46 K in a single crystal of CeScSi in an applied field of 1 kG. An anomaly at 46 K is observed both along the *a*- and *c*-axes and the behaviour of magnetization below 46 K, according to these authors, indicates a kind of ferromagnetic ordering (figure 2 of [3]). The  $T_c$  for single-crystal CeScSi is thus substantially different from that reported in [1] for the polycrystalline material. This is surprising as typically the properties of a compound in single-crystal and polycrystalline forms are very similar. A slight enhancement of the transition temperature and a sharper transition may be observed in a single crystal due to superior chemical order, lack of randomness and grain boundaries. Uwatoko *et al* [3] also claim that upon annealing their polycrystalline sample of CeScSi at 1300 °C, the magnetic behaviour changed from  $T_N = 28$  K for the as-cast sample to  $T_c = 46$  K for the annealed sample. However, they have not shown any data taken on the 1300 °C annealed sample. For CeScGe, Uwatoko *et al* [3] observe a broad maximum in the magnetization around 27 and 25 K along the *a*- and *c*-axes, respectively. This result is again in contradiction to the earlier results reported in [1, 2]. It may be noted that the transition temperatures reported by Uwatoko *et al* [3] in single-crystal CeScSi and CeScGe are the opposite of what is reported for polycrystalline forms in [1, 2]. Taken altogether, the situation as regards CeScSi and CeScGe is not clear.

Both CeScSi and CeScGe have the La<sub>2</sub>Sb-type, tetragonal structure which has two inequivalent La sites La1 (4c) and La2 (4e), respectively. From their single-crystal data on CeScSi, Mokra and Bodak [4] concluded that the cerium atoms in CeScSi selectively occupy the La2 (4e) site and all cerium atoms are, therefore, crystallographically equivalent. The same conclusion was obtained by Bodak and Kohkan [5] for CeScGe on the basis of powder diffraction data. In [1] the authors also studied Ce<sub>2</sub>Sb, Ce<sub>2</sub>Bi and CeSb<sub>2</sub>. The first two compounds have the La<sub>2</sub>Sb-type structure with both the 4c and 4e sites occupied by cerium and both compounds are antiferromagnetic. CeSb<sub>2</sub> has the LaSb<sub>2</sub>-type structure in which there is only one cerium site which has a somewhat similar environment to the cerium atoms in CeScSi and CeScGe. CeSb<sub>2</sub> undergoes a ferromagnetic transition at 15 K [1]. From these observations it was concluded in [1] that the absence of cerium atoms at the La1 (4c) site favours ferromagnetism in CeScSi and CeScGe.

The question arises of whether the conflicting reports in the literature can be attributed to sample inhomogeneity, atomic disorder or the presence of minor impurity phases. We have, therefore, readdressed this problem by investigating well characterized polycrystalline samples. Our results show that the polycrystalline samples of CeScSi and CeScGe order antiferromagnetically around 26 and 46 K, respectively. Our present work is a part of a larger study in which the magnetic behaviour of Ce<sub>3</sub>Si<sub>2</sub>, La<sub>3</sub>Si<sub>2</sub>, Ce<sub>2</sub>Sc<sub>3</sub>Si<sub>4</sub>, Ce<sub>2</sub>ScSi<sub>2</sub> and Ce<sub>2</sub>YSi<sub>2</sub> was also investigated. The results on these compounds have been published elsewhere [6].

## 2. Experiment

The elements used were commercial products; the purity of the rare earth metals Ce, Sc and La was 99.99 wt%, while that of Si and Ge was better than 99.99 wt%. Polycrystalline samples were prepared in a high-frequency induction furnace on a water-cooled tantalum support, under a flux of transistor-grade argon. The reactions were highly exothermic. The sample buttons were flipped and remelted three times to ensure homogenization. In the above procedure the

total weight loss was negligible (less than 0.2%). The as-cast alloy buttons were wrapped in Ta foils, sealed in quartz tubes under vacuum and subjected to various heat treatments. The first two alloys, CeScSi and CeScGe, initially prepared and annealed at 750 °C for 25 and 15 days respectively, will be hereafter called CeScSi-I and CeScGe-I. A second series of alloys, CeScSi, CeScGe, LaScSi, Ce<sub>1.1</sub>Sc<sub>0.9</sub>Ge, Ce<sub>0.9</sub>Sc<sub>1.1</sub>Ge and Ce<sub>1.1</sub>Sc<sub>0.9</sub>Si, were prepared and annealed at 1000 °C for 12 days. The first two alloys of this series will be hereafter called CeScSi-II and CeScGe-II, respectively. The purpose of also making the three off-stoichiometric samples was to check whether a solid-solution region exists where homogeneous alloys are formed and how composition and site disorder would affect their magnetic behaviour. To check the stability of CeScSi, different pieces of CeScSi-I and CeScSi-II were subsequently reannealed at 1050 °C for 12 days, 1150 °C for 3 days, 1200 °C for 7 days and 1300 °C for 4 h. The first three were air cooled, the last one water quenched. A differential thermal analysis (DTA) scan was also carried out on three Si samples, CeScSi as-cast, CeScSi-I and CeScSi-II, and three Ge samples, CeScGe as-cast, CeScGe-I and CeScGe-II. For this purpose, a chunk of alloy of approximately 0.6–0.8 g was sealed by welding under argon into an outgassed molybdenum DTA crucible and cycled at 10 °C min<sup>-1</sup> up to about 1450 °C. Optical and scanning electron microscopes equipped with a quantitative microprobe EDX were used in the identification of secondary and trace phases; the standards were pure elements and the equiatomic compounds (accuracy to within 1 at.%). X-ray powder diffraction patterns were taken on a Guinier camera with long exposure times (24–36 h), using Cu K $\alpha$  radiation and Si as an internal standard; the powder intensities were compared to those calculated by means of the Lazy Pulverix program [7]. A single crystal, in the form of a platelet (0.04 × 0.06 × 0.13 mm<sup>3</sup>), was picked out after crushing a piece of the bulk alloy from the specimen CeScSi-II; the single-crystal intensity data were collected in the ( $\omega$ -2 $\theta$ ) mode, (2°–30°)  $\theta$  range by an Enraf–Nonius CAD-4 automatic diffractometer with graphite-monochromated Mo K $\alpha$  radiation. Magnetization was measured on commercial SQUID (Quantum Design) and VSM (Oxford) magnetometers. The heat capacity was measured using a semi-adiabatic, heat pulse method on an automated, home-built set-up. The reliability of the heat capacity data is ensured by occasionally measuring the heat capacity of a copper pellet which is 99.999 wt% pure and comparing the data with those reported in the literature. The ac susceptibility was also measured on a home-built susceptometer.

### 3. Results and discussion

The DTA results show that the CeScSi and CeScGe alloys do not melt when heated up to about 1450 °C. Below 1450 °C the as-cast CeScSi sample shows three peaks on cooling, the first at about 1430 °C (weak and broad) followed by two sharper peaks at 1130 and 1030 °C (that at 1130 °C being stronger, and shifting on heating to about 1170 °C). CeScSi-I and CeScSi-II exhibit on first heating only the peak at 1170 °C, while on cooling all the three peaks are shown. DTA curves of all three Ge samples show a weak peak, both on heating (at about 1330 °C) and on cooling (at about 1310 °C).

The combined x-ray powder patterns and EDX microprobe analyses of all samples showed the formation of the principal phase, which could be indexed on the basis of the La<sub>2</sub>Sb-type tetragonal structure, with or without secondary phases depending on the annealing. The as-cast and the slow-cooled DTA samples of CeScSi contained a mixture of the following phases: equiatomic CeScSi, the binary compounds Ce<sub>5</sub>Si<sub>3</sub> and Sc<sub>5</sub>Si<sub>3</sub> (each one dissolving 1–2 at.% of the other rare earth) and a new ternary compound with a primitive tetragonal cell and stoichiometry Ce<sub>51.5</sub>Sc<sub>11</sub>Si<sub>37.5</sub> (hereafter called 'Ce<sub>4</sub>ScSi<sub>3</sub>'). Similar results were obtained for samples reannealed at 1150, 1200 and 1300 °C. For CeScSi-I, five very weak extra lines present

in the diffraction pattern, which cannot be indexed to the  $\text{La}_2\text{Sb}$ -type structure, were found to pertain to ' $\text{Ce}_4\text{ScSi}_3$ '; we estimate the total amount of this extra phase to be 2–3%. These extra lines disappeared in CeScSi-II. Therefore, with regard to the contamination by parasitic impurity phases, the sample annealed at 1000 °C is superior to the 750 °C annealed sample. As regards any site disorder, we made three different powder pattern calculations using Lazy Pulverix; the first in which there is complete order with Ce in the 4e site and Sc in the 4c site; the second as 'anti-ordered' with cerium in the 4c site and Sc in the 4e site; and the third as completely disordered with 50% Ce and 50% Sc at each site. The results were compared with the experimental diffraction intensity patterns obtained for both CeScSi-I and CeScSi-II samples. The comparison clearly favours an ordered structure. Confirmation was obtained by the single-crystal work. The structural refinement data of CeScSi-II are shown in table 1 and interatomic distances are listed in table 2. We conclude that CeScSi is truly an ordered ternary variant of the  $\text{La}_2\text{Sb}$ -type structure. It may be mentioned here that our single-crystal data obtained from a specimen annealed at 1000 °C are in good agreement with the earlier work of Mokra and Bodak [4].

**Table 1.** Atomic coordinates and isotropic equivalent displacement parameters of CeScSi, space group  $I4/mmm$ , Pearson symbol  $tI12$ ,  $a = 4.3231(6)$  Å and  $c = 15.852(2)$  Å. Anisotropic refinement to  $wR2 = 0.059$ ,  $R1 = 0.025$  (both given for all 161 independent reflections).

Atom	Position	$x$	$y$	$z$	$U_{eq}$ (Å <sup>2</sup> )
Ce	4e	0	0	0.32381(3)	0.077(2)
Sc	4c	0	1/2	0	0.0092(4)
Si	4e	0	0	0.1211(2)	0.0083(6)

**Table 2.** Interatomic distances (in Å) in CeScSi.

Ce–	4Si	3.179(1)
	Si	3.214(3)
	4Sc	3.532(1)
	4Ce	3.850(1)
Si–	4Sc	2.890(2)
	4Ce	3.179(1)
	Ce	3.214(3)
Sc–	4Si	2.890(2)
	4Sc	3.057(1)
	4Ce	3.532(1)

The diffraction patterns obtained from single-phase CeScSi samples reannealed at 1150, 1200 and 1300 °C are all similar to that of as-cast CeScSi, and thus show that the samples had dissociated into a mixture of CeScSi,  $\text{Sc}_5\text{Si}_3$ ,  $\text{Ce}_5\text{Si}_3$  and ' $\text{Ce}_4\text{ScSi}_3$ ' phases. The same 1300 °C reannealed multiphase sample, after it was once more annealed at 1000 °C for nine days reverted to the single-phase state. Therefore, the DTA and x-ray diffraction results together indicate that CeScSi decomposes above about 1150 °C, probably peritectoidally, and on cooling reforms at about 1130 °C with undercooling effects of about 40 °C.  $\text{Sc}_5\text{Si}_3$ ,  $\text{Ce}_5\text{Si}_3$  and ' $\text{Ce}_4\text{ScSi}_3$ ' form first at higher temperatures from the liquid. Our results call into question the observations of Uwatoko *et al* [3] mentioned above.

As regards the compound CeScGe, the as-cast sample is already nearly single phase. For the sample annealed at 750 °C (CeScGe-I), the diffraction patterns showed one to two additional

weak lines and these were verified beyond any doubt to belong to  $\text{Sc}_5\text{Ge}_3$  (1% or less) with a Ce content at a trace level as detected by the microprobe. For CeScGe-II we did not detect any extra lines in the powder diffraction profile. CeScGe is likely to be a congruently or nearly congruently melting compound; we have not yet been able to identify the thermal effect detected at 1330 °C (even after some quenching attempts were tried) which apparently is not associated with either melting or formation, but perhaps with a structural transition. Comparison of the experimental spectra with a Lazy Pulverix calculation again favoured a site-ordered structure. As regards  $\text{Ce}_{1.1}\text{Sc}_{0.9}\text{Ge}$  and  $\text{Ce}_{0.9}\text{Sc}_{1.1}\text{Ge}$  annealed at 1000 °C, while the latter is multiphase the former is nearly single phase. There are five weak extra reflections in  $\text{Ce}_{1.1}\text{Sc}_{0.9}\text{Ge}$  due to parasitic impurity phase ' $\text{Ce}_4\text{ScGe}_3$ '; its amount is about 4%. From microprobe analysis we find the Ce content of the main phase (La<sub>2</sub>Sb type) in  $\text{Ce}_{1.1}\text{Sc}_{0.9}\text{Ge}$  is about 34–35 at.%, slightly increased compared to that of the equiatomic composition (33.3 at.%). This indicates that some extra cerium atoms in the off-stoichiometric  $\text{Ce}_{1.1}\text{Sc}_{0.9}\text{Ge}$  are accommodated in the tetragonal La<sub>2</sub>Sb-type structure. However, it seems that the extra cerium atoms take the place of Ge atoms whose content drops to about 32–33 at.% while the Sc content remains nearly the same at 33 at.% in the principal phase. A confirmation would, however, come only from a structural refinement on a single crystal of  $\text{Ce}_{1.1}\text{Sc}_{0.9}\text{Ge}$ .

For  $\text{Ce}_{1.1}\text{Sc}_{0.9}\text{Si}$ , the extra phase was much more than found in the corresponding Ge-based alloy and it was not, therefore, studied further. The results on the off-stoichiometric alloys show that CeScSi and CeScGe are practically line compounds with no or very limited solubility ranges. To summarize, annealing at 1000 °C is very important for preparing good single-phase samples of CeScSi and CeScGe. Lattice constant values of the different samples investigated are reported in table 3.

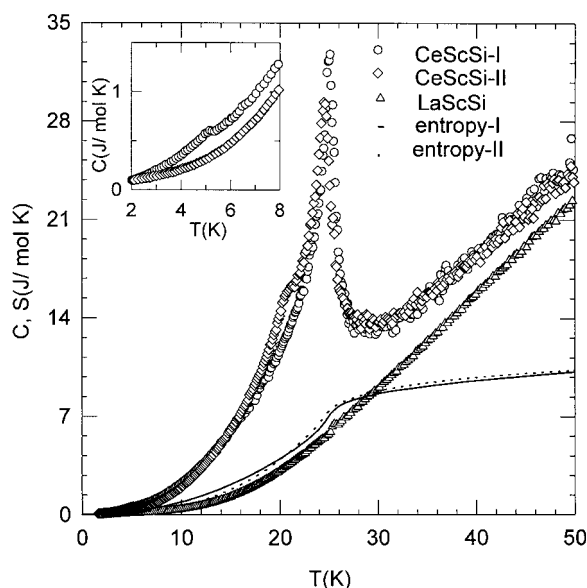
**Table 3.** Lattice parameters of samples utilized for physical measurements (structure; tetragonal La<sub>2</sub>Sb type).

Sample	Lattice parameter (Å)	
	<i>a</i>	<i>c</i>
LaScSi	4.335(2)	15.997(1)
CeScSi-I	4.315(0)	15.864(2)
CeScSi-II	4.323(0)	15.857(2)
CeScGe-I	4.342(1)	15.986(3)
CeScGe-II	4.349(0)	15.979(2)
$\text{Ce}_{1.1}\text{Sc}_{0.9}\text{Ge}^a$	4.348(2)	15.983(4)

<sup>a</sup> Contains about 4% impurity phase.

The heat capacity data of CeScSi-I, CeScSi-II and LaScSi are shown in figure 1. A huge peak in the heat capacity, *C*, of CeScSi with a peak height of nearly 35 J mol<sup>-1</sup> K<sup>-1</sup> and a peak temperature of about 25 K for both specimens is an unambiguous signature of a transition to a magnetically ordered state. The value of the transition temperature is in agreement with [1]. The heat capacity of the corresponding non-magnetic analogue LaScSi does not show any anomaly at 25 K and increases monotonically with temperature. A minor but discernible feature in the heat capacity of CeScSi-I is seen near 5.2 K, as shown in the inset of figure 1, which is absent in the sample annealed at a higher temperature. The magnitude of the low-temperature anomaly is, of course, insignificant compared to that of the main peak near 25 K. We believe that the feature seen near 5.2 K arises due to the impurity phase present in the sample, as inferred from the x-ray powder diffraction and microprobe analyses. A rough estimate of the magnetic entropy associated with the feature at 5.2 K gives a value of about 40 mJ mol<sup>-1</sup> K<sup>-1</sup>, which in our opinion supports the impurity-based explanation. On the

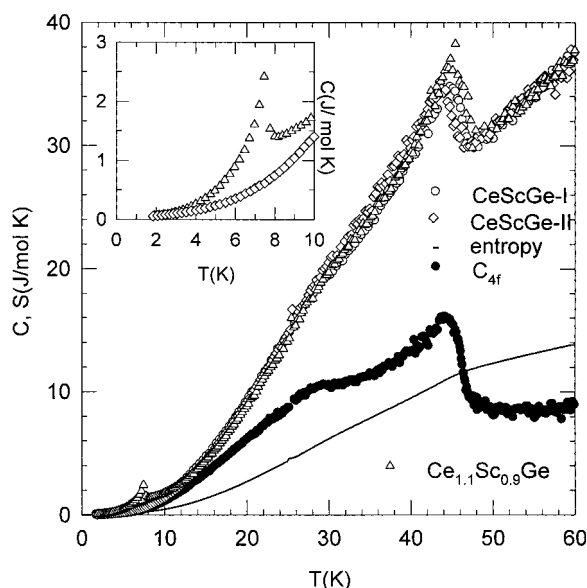
other hand, a shoulder is seen at 21 K in the data of CeScSi-II, but there is no corresponding anomaly in the magnetization (*vide infra*) at that temperature, thereby excluding a magnetic origin of this feature. The heat capacity data were taken twice to confirm this feature which is absent in CeScSi-I. Making the usual assumption that the heat capacity due to lattice vibrations (phonons) and the background conduction band electrons is the same in isotypic LaScSi and CeScSi, the 4f-derived magnetic contribution to the heat capacity of CeScSi is obtained by subtracting from it the heat capacity of LaScSi. The magnetic entropy, shown in figure 1, is nearly  $7 \text{ J mol}^{-1} \text{ K}^{-1}$  at 25 K for both samples, which exceeds the theoretical value of  $5.76 \text{ J mol}^{-1} \text{ K}^{-1}$  for a crystal-field-split doublet ground state with an effective spin  $S = 1/2$ . In the tetragonal crystal symmetry, the  $J = 5/2$ , Hund's rule derived sixfold-degenerate  ${}^2F_{5/2}$  state of the  $\text{Ce}^{3+}$  ion will split into three doublets. Therefore, we conclude from the entropy value at 25 K that at least the first excited crystal-field-split state is not too far above the ground level and makes a sizeable Schottky contribution to the heat capacity below 25 K. For LaScSi, the  $C/T$  against  $T^2$  plot is linear between 1.5 and about 7 K. A least-squares linear fit to the data gives  $\gamma = 14.5 \text{ mJ mol}^{-1} \text{ K}^{-2}$  and  $\beta = 0.22 \text{ mJ mol}^{-1} \text{ K}^{-4}$ , where  $\gamma$  is the coefficient of the linear term in the heat capacity due to the electronic contribution and  $\beta$  is the coefficient of the lattice heat capacity. From  $\beta$  we derive a value of 298 K for the Debye temperature,  $\theta_D$ . It may be noted that the value of  $\gamma$  is fairly large, which points to a high density of electronic states at the Fermi level.



**Figure 1.** The heat capacity of CeScSi-I, CeScSi-II and LaScSi against temperature. The entropy associated with the magnetic ordering is also depicted. The inset shows the heat capacity below 8 K of CeScSi on an expanded scale.

Figure 2 depicts the heat capacity data of CeScGe-I, CeScGe-II and  $\text{Ce}_{1.1}\text{Sc}_{0.9}\text{Ge}$ . The heat capacity shows a sizeable peak with a peak temperature of 45–46 K in the three samples, which we associate with a transition to a magnetically ordered state. The off-stoichiometric sample exhibits a slightly larger jump in the heat capacity at the transition, which appears to occur at a slightly higher temperature compared to that of the stoichiometric compounds. The overall similarity in the data of the three compounds shows that the magnetic transition occurring near 46 K in ‘CeScGe’ is quite robust intrinsically and also with respect to slight

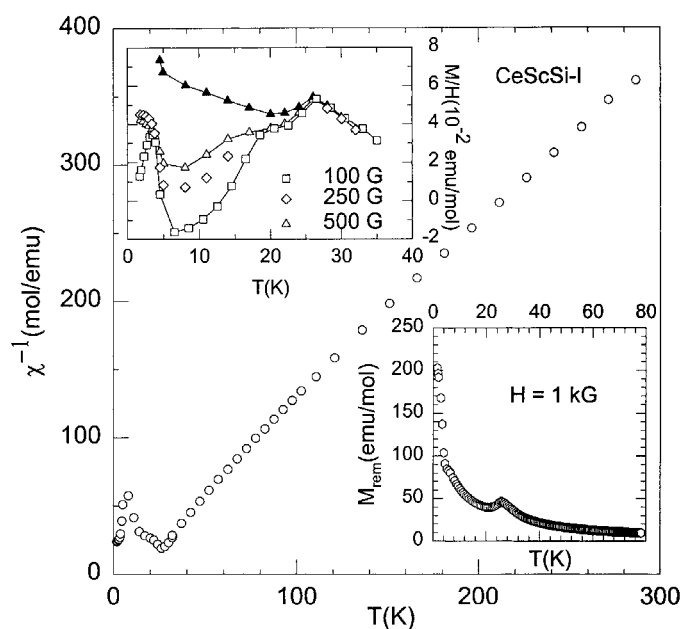
changes in the stoichiometry. A broad hump centred around  $\sim 27$  K is also seen in the plot of total heat capacity in all the three compounds. This feature becomes more prominent after the background lattice and electronic contribution is subtracted from the total heat capacity to obtain the magnetic 4f contribution,  $C_{4f}$ . For this purpose the lattice heat capacity of LaScSi was renormalized to account for the difference in the atomic mass of Si and Ge using the relation  $\theta_D^{\text{CeScGe}} / (\theta_D^{\text{LaScSi}} = (m^{\text{LaScSi}} / m^{\text{CeScGe}})^{1/2}$ , where  $m$  is the molecular weight and  $\theta_D$  is the Debye temperature. The inset shows the heat capacity data on an expanded scale below 10 K. A sharp peak at 7.5 K occurs in  $\text{Ce}_{1.1}\text{Sc}_{0.9}\text{Ge}$ , which is absent in CeScGe. The peak therefore arises due to the impurity 'Ce<sub>4</sub>ScGe<sub>3</sub>' phase. The integrated magnetic entropy of CeScGe up to 48 K is nearly  $12 \text{ J mol}^{-1} \text{ K}^{-1}$  and points to a relatively small crystal-field splitting, which is in conformity with a similar result inferred above for CeScSi. It is thus quite plausible that the broad hump around 27 K arises due to the thermal depopulation of the excited crystal-electric-field levels with temperature. The heat capacity data thus confirm the onset of a magnetic transition at about 25 K and about 46 K in CeScSi and CeScGe, respectively. In order to ascertain the nature of the magnetic ordering, magnetization measurements were carried out, which are described next.



**Figure 2.** The heat capacity of CeScGe-I, CeScGe-II and  $\text{Ce}_{1.1}\text{Sc}_{0.9}\text{Ge}$  against temperature. The 4f-derived magnetic part of the heat capacity for CeScGe and the associated entropy are also plotted. The inset shows the heat capacity of CeScGe and  $\text{Ce}_{1.1}\text{Sc}_{0.9}\text{Ge}$  below 10 K on an expanded scale.

The inverse susceptibility,  $\chi^{-1}$ , of CeScSi-I and CeScGe-I as a function of temperature is plotted in figures 3 and 4, respectively. For CeScSi-I the data above 35 K were taken in an applied field of 1 kG, while a field of 500 G was used below 35 K. In the case of CeScGe-I an applied field of 1 kG was used above 60 K and 100 G at lower temperatures. Figure 4 also depicts  $\chi^{-1}$  above 50 K for CeScGe-II. There is a difference between the values of the susceptibility of the two specimens at higher temperatures. For CeScSi-I, the magnetization shows a peak at 26 K (figure 3 upper inset) which does not change with the applied field, at least up to 1 kG, both in zero-field-cooled (ZFC) and field-cooled (FC) modes. Correlated with the peak in the heat capacity (figure 1), the peak in the magnetization confirms antiferromagnetic ordering of the cerium ions, with Néel temperature  $T_N = 26$  K.

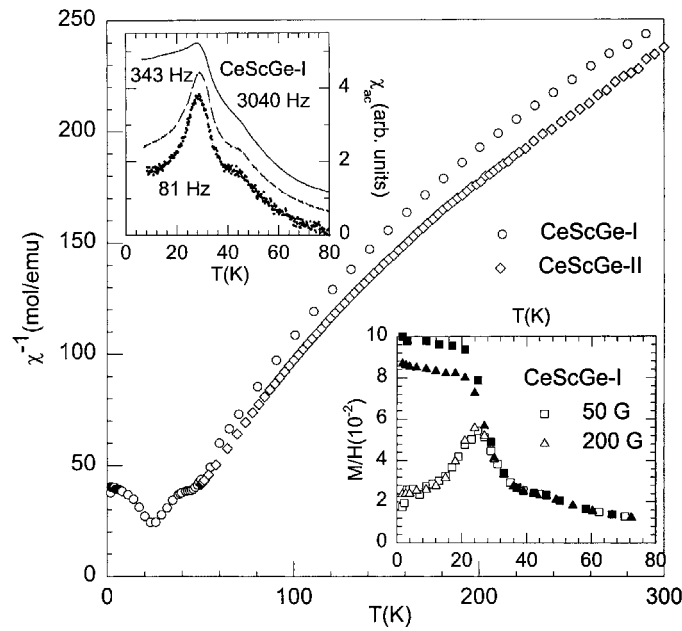




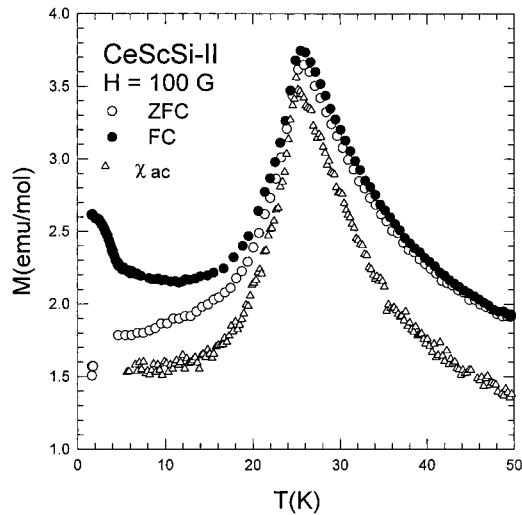
**Figure 3.** The inverse susceptibility,  $\chi^{-1}$ , against temperature for CeScSi-I. The upper inset shows the ZFC (open symbols) and FC (full symbols) data measured in various low fields. The lower inset shows the thermal variation of the remanent magnetization of CeScSi-I in a field of 1 kG. The curves drawn through data points are guides to the eye.

The magnitude of the magnetization is in conformity with the occurrence of the Néel state at 26 K. For a ferromagnet the susceptibility diverges at the transition and is much larger in magnitude. However, below about 20 K the magnetization is field dependent, exhibits some structure and has thermo-magnetic irreversibility. We associate the various features seen in the magnetization of CeScSi-I below  $T_N$  with the presence of parasitic phases such as 'Ce<sub>4</sub>ScSi<sub>3</sub>' and Ce<sub>5</sub>Si<sub>3</sub>. The latter compound has a solid-solution range with two inequivalent cerium sites, one of which orders magnetically at 12 K while the other remains paramagnetic down to at least 1.3 K [8]. The lower inset of figure 3 shows the temperature dependence of the magnetization of CeScSi-I after it was first measured up to 120 kG at 1.6 K and the field then decreased to 1 kG. A fairly substantial remanent magnetization is observed below  $T_N$  arising due to the contribution from the parasitic impurity phases. On the other hand, a relatively simple response of the magnetization is observed in CeScSi-II, which from the point of view of phase purity is superior to CeScSi-I. The ZFC and FC data taken in 100 G on CeScSi-II are shown in figure 5. A peak at 26 K confirms the antiferromagnetic ordering. The magnetization decreases smoothly below  $T_N$  and does not show the various anomalies recorded in CeScSi-I. (Due to some technical problem in this particular run, we could not take the full data between 1.6 and 4.2 K in the ZFC run.) A slight thermomagnetic irreversibility develops below about 20 K, which increases with the decrease of temperature.

In the case of CeScGe-I, the ZFC and FC runs show a broad kink in the magnetization at 46 K which is independent of applied field (see the lower inset figure 4). Surprisingly, a much larger feature in the magnetization in the ZFC runs occurs in the form of a peak at about 24 K. The position of this peak is field independent at least up to 1 kG. While pronounced thermomagnetic irreversibility is observed below about 28 K, magnetization above this temperature is practically the same in ZFC and FC runs. In [2] the main peak in the



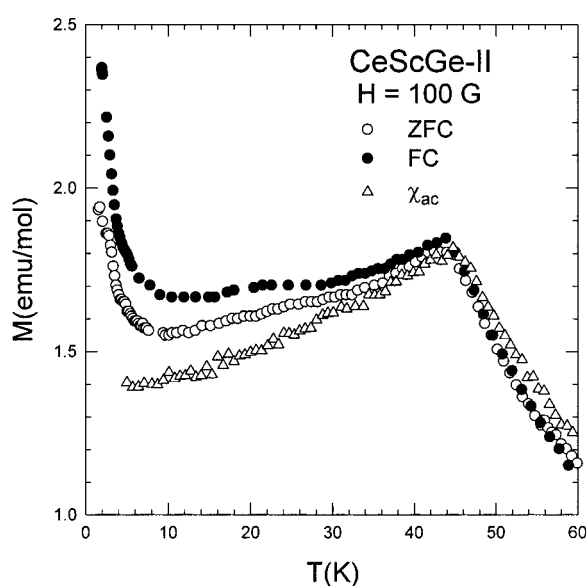
**Figure 4.** The inverse susceptibility,  $\chi^{-1}$ , against temperature for CeScGe-I and CeScGe-II. The upper inset shows the ac susceptibility of CeScGe-I at three frequencies in an ac field of 1 G. The lower inset shows the ZFC (open symbols) and FC (full symbols) data measured on CeScGe-I in various low fields.



**Figure 5.** ZFC and FC magnetization of CeScSi-II in 100 G. The ac susceptibility in arbitrary units is also plotted.

susceptibility occurs at 46 K and the other two peaks  $T_1$  and  $T_2$ , which occur below 46 K, are less pronounced. In this respect the present magnetization data differ qualitatively from those of [2]. However, the broad kink in our magnetization data at about 46 K correlates nicely with the peak in the heat capacity at the same temperature, and taken together with

the magnitude of the magnetization it marks the onset of the antiferromagnetic transition in CeScGe. On the other hand, in CeScGe-II the broad peak at 24 K has completely disappeared and we observe only one peak near 46 K characteristic of antiferromagnetic transition, as shown in figure 6. A slight thermomagnetic irreversibility below about 28 K still persists in this sample as well. Thus the peak seen near 24 K in CeScGe-I is not intrinsic to the pure CeScGe phase and originates from some impurity phase. Figure 7 shows the magnetization of  $\text{Ce}_{1.1}\text{Sc}_{0.9}\text{Ge}$  measured in 100 G in ZFC and FC modes. The peak at 46 K corroborates the peak in the heat capacity and is a signature of the antiferromagnetic transition. Below the transition the magnetization increases and exhibits a peak at 7.6 K, in tune with the anomaly seen in the heat capacity data at around the same temperature. A large irreversibility is seen below the lower transition which falls sharply in the ZFC mode. We attribute the peak at 7.6 K to 'Ce<sub>4</sub>ScGe<sub>3</sub>', which is the main impurity phase in this compound. It may be mentioned here that the compound Ce<sub>5</sub>Ge<sub>3</sub> is reported to be antiferromagnetic or ferrimagnetic below 6.4 K [9]. The increase in the magnetization below 46 K in  $\text{Ce}_{1.1}\text{Sc}_{0.9}\text{Ge}$  may thus be attributed to the presence of impurity phase(s).



**Figure 6.** ZFC and FC magnetization of CeScGe-II in 100 G. The ac susceptibility in arbitrary units is also plotted.

AC susceptibility data were also taken on CeScSi and CeScGe samples. The data basically reflect the behaviour observed in the low-field, ZFC, dc magnetization. For CeScGe-I, data taken at three different frequencies are shown in the upper inset of figure 4 while for CeScSi-II and CeScGe-II the data are shown in figures 5 and 6, respectively.

From figures 3 and 4 it is found that  $\chi^{-1}$  against  $T$  in the paramagnetic region has a curvature, which is more pronounced in CeScGe. Normally, in rare-earth intermetallic compounds  $\chi^{-1}$  shows Curie–Weiss behaviour in the paramagnetic state due to the well localized, 4f-derived magnetic moments. Typically, in cerium compounds that order at low temperatures, the deviation from Curie–Weiss linear behaviour is seen below about 100 K, which is ascribed to the combined effects of exchange and crystal fields. However, sometimes an appreciable temperature-independent contribution to the Pauli susceptibility,  $\chi_0$ , can be the cause of deviation from Curie–Weiss behaviour at temperatures above 100 K. The presence

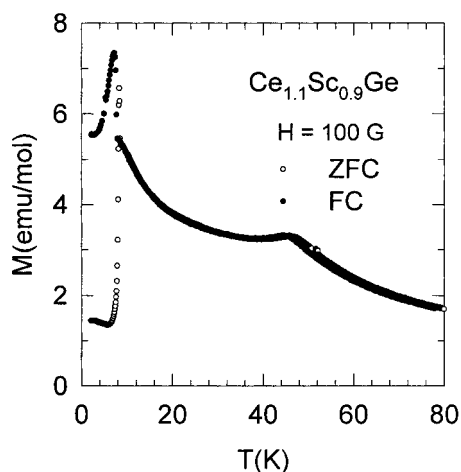
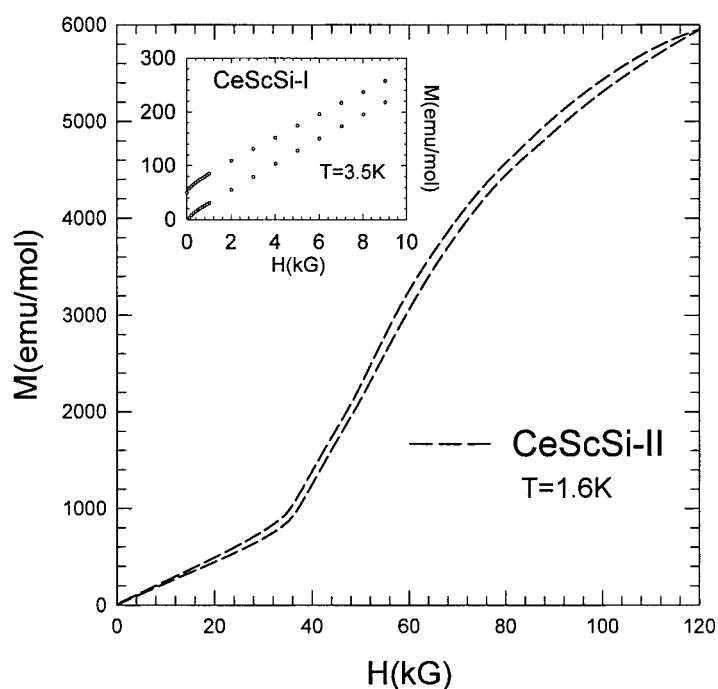


Figure 7. ZFC and FC magnetization of  $\text{Ce}_{1.1}\text{Sc}_{0.9}\text{Ge}$  in 100 G.

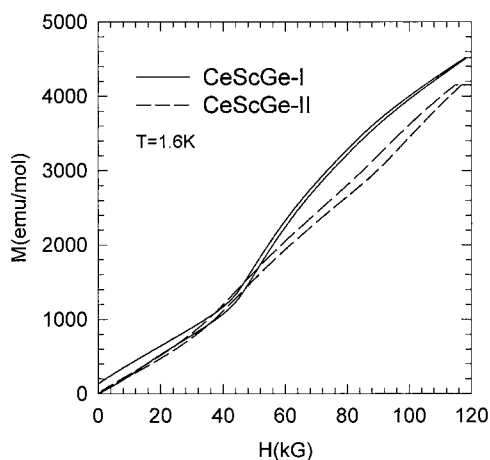
of magnetic anisotropy, which leads to an easy direction of magnetization that shows Curie–Weiss behaviour and a hard direction in which the susceptibility is temperature independent or slightly dependent on temperature, can also give rise to a curved inverse susceptibility against temperature curve in polycrystalline samples, such as is seen for CeScGe. Substantial anisotropy is indeed observed in isostructural  $\text{Ce}_2\text{Bi}$  [1],  $\text{Ce}_2\text{Sb}$  and CeLaBi [10]. It may, however, be noted that the curvature of  $\chi^{-1}$  against  $T$  in CeScSi-I (figure 3) is much less pronounced above 150 K, and we have fitted the data in the 160–300 K range to the expression  $\chi = C/(T + \theta_p)$  where  $C$  is the Curie constant. We obtain  $\mu_{eff} = 2.59 \mu_B$  and  $\theta_p = 15.7 \text{ K}$ . The value of  $\mu_{eff}$  is found to be nearly the same as that for the Hund’s rule derived ground state  $^2F_{5/2}$  for the free  $\text{Ce}^{3+}$ , which has an effective moment of  $2.54 \mu_B$ . The magnitude of  $\theta_p$  is comparable to  $T_N$  and it is positive, which arises from the antiferromagnetic exchange between cerium ions.

The isothermal magnetization of CeScSi and CeScGe was measured at selected temperatures in both SQUID and VSM magnetometers and some of the data are shown in figures 8 and 9. These data clearly show the antiferromagnetic nature of the ground state in both CeScSi and CeScGe. Magnetization at 1.6 K is linear up to about 40 kG in both compounds and exhibits a spin-flop behaviour at higher fields. No signature of saturation is observed up to the highest applied field of 120 kG. Samples annealed at 1000 °C show a practically negligible remanent magnetization when the field is decreased to zero: about 7 and 10  $\text{emu mol}^{-1}$  ( $\sim 0.001 \mu_B/\text{Ce}$ ) for CeScSi-II and CeScGe-II respectively, in contrast to the value of  $0.3 \mu_B/\text{Ce}$  reported in [3] for single crystals. The corresponding values for CeScSi-I and CeScGe-I are 50 and 132  $\text{emu mol}^{-1}$ , respectively. For CeScSi-I the field was applied up to 55 kG in the SQUID magnetometer and decreased to zero at 3.5 K. The magnetization is completely reversible at 23 and 30 K even in the relatively inferior samples of CeScSi-I and CeScGe-I. Irreversibility sets in at lower temperatures.

It is clear from the magnetization data presented above that an antiferromagnetic transition takes place in polycrystalline samples of CeScSi and CeScGe near 26 and 46 K, respectively, and that there is no ferromagnetic realignment of spins at lower temperatures. The antiferromagnetic transition in CeScGe is quite robust in the sense that it even occurs in  $\text{Ce}_{1.1}\text{Sc}_{0.9}\text{Ge}$  at nearly the same temperature. Slight off-stoichiometry does not alter the nature of the magnetic ground state; in particular it does not induce any ferromagnetic interaction in the



**Figure 8.** The isothermal magnetization of CeScSi-II at 1.6 K up to 120 kG. The inset shows a portion of the magnetization data taken up to 55 kG at 3.5 K in CeScSi-I.



**Figure 9.** The isothermal magnetization of CeScGe-I and CeScGe-II at 1.6 K. For CeScGe-II the response became saturated near the higher-field end due to the instrument setting for that run.

system. It is important to have well characterized samples as the contribution of minor impurity phases to the magnetization below  $T_N$  may lead one to erroneous conclusions. Thus pronounced thermomagnetic irreversibility and remanent magnetization in CeScSi-I arise mainly from the presence of parasitic phases of  $Ce_5Si_3$  and ' $Ce_4ScSi_3$ ' which may be present in even larger amounts in the as-cast sample. Such a conclusion is justified by the observation of a nearly negligible remanent magnetization ( $\sim 7 \text{ emu mol}^{-1}$ ) in CeScSi-II at 1.6 K compared to its

value of about  $50 \text{ emu mol}^{-1}$  (at 3.5 K) in CeScSi-I. A similar reduction in the remanent magnetization on increasing the annealing temperature is also observed in CeScGe. A slight difference in the ZFC and FC runs seen in both CeScSi-II and CeScGe-II indicates that perhaps we still have some trace amounts of parasitic phase(s) which we do not detect in our x-ray diffraction and microprobe analyses. As already mentioned above, there is no feature in the magnetization of CeScSi-II corresponding to the shoulder in the heat capacity near 21 K. If the latter is attributed to the Schottky heat capacity as proposed for CeScGe (see above), then it should occur in CeScSi-I as well. Although this minor feature still remains to be understood, it does not have a magnetic origin and thus it does not affect the basic conclusion of this work. It is possible that it arises from a structural transition in the 'cleaner' CeScSi-II sample associated with the antiferromagnetic ordering of cerium moments. Detailed thermal expansion and magnetostriction measurements are required to verify our conjecture. Based on our detailed work described above, we would like to make some comments on the single-crystal results reported by Uwatoko *et al* [3]. The transition temperatures reported in [1, 2] and the present work on polycrystalline samples are in good agreement, while those of single-crystal specimens are opposite to those of the polycrystal specimens. We wonder whether it is a case of mistaken identification of the samples in [3]. Typically, single crystals are considered superior to the polycrystalline form, but since our DTA analysis indicates that CeScSi forms peritectoidally the formation of good single crystals free of impurity phases may be difficult. A peritectoid reaction takes place between two solid phases to form the product phase. It is quite likely that the single crystals used in [3] contain secondary phases giving rise to the observed behaviour. Similarly, the claim that polycrystalline CeScSi when annealed at  $1300^\circ\text{C}$  turns into a ferromagnet with  $T_c = 46 \text{ K}$  [3] is questionable because we find from x-ray diffraction and microprobe analyses that the compound is unstable and dissociates into a number of phases when heated to that temperature.

Recently, Shigeoka *et al* [11] carried out band-structure calculations on CeScGe using the LMTO method with the exchange–correlation potential in the framework of the local spin-density approximation. They claim that the minimum total energies for non-magnetic, ferromagnetic and antiferromagnetic states of CeScGe are equal within the calculated error and hence they conclude that there is an inherent magnetic instability in CeScGe. There are some features in their work that we feel need comment. For example, in their calculation the 4f states of Ce are treated as band states. Keeping in mind our data we feel it would be more appropriate to treat the 4f states in CeScGe and CeScSi as core states. Their spin-projected density of states is found to lie just above the Fermi level. In view of the fact that the local spin-density approximation does not predict the location of the f states properly, one becomes sceptical about the values of the magnetic moment,  $0.62 \mu_B$  for the ferromagnetic state and  $0.37 \mu_B$  for the antiferromagnetic state, that the authors have calculated from the tails of the f states. In their calculation the ratio  $c/a$  was fixed and the value of  $a$  determined theoretically from the energy minimum was found to be 4.228, 4.232 and 4.230 Å for the non-magnetic, ferromagnetic and antiferromagnetic states, respectively. The 0.05% differences in the lattice parameters corresponding to the three magnetic states of CeScGe as found by these authors do not seem to be meaningful. Experimentally, we find a larger variation in both the  $a$  and  $c$  lattice parameters between CeScGe-I and CeScGe-II and yet both of them exhibit the antiferromagnetic transition at 46 K. We believe the accuracy of the total-energy calculations reported by these authors is clearly inadequate for distinguishing between the para-, ferro- and antiferromagnetic states and, therefore, they have not substantiated their conclusion that the magnetic states for this compound compete. More careful calculations are required to confirm theoretically the true magnetic ground state of these two compounds.

#### 4. Conclusions

To conclude, we have shown that the exchange interaction between cerium ions in polycrystalline CeScSi and CeScGe is antiferromagnetic. These are basically line compounds with a practically negligible solubility range. We do not find any evidence of site disorder in these alloys. Even if such a disorder is marginally present, our results on off-stoichiometric  $\text{Ce}_{1.1}\text{Sc}_{0.9}\text{Ge}$ , which orders antiferromagnetically at nearly the same temperature as the stoichiometric CeScGe, show that disorder does not induce additional ferromagnetic interactions. In order to obtain good single-phase compounds, annealing at the proper temperature is essential. Failure to do so results in the presence of parasitic impurity phases, which we believe are the root cause of the various conflicting reports in the literature on these two compounds.

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