

# Exploring high temperature magnetic order in $\text{CeTi}_{1-x}\text{Sc}_x\text{Ge}$

**J.G. Sereni, P. Pedrazzini, M. Gómez Berisso, A. Chacoma, S. Encina**

Low Temperature Division, CAB-CNEA, IB and CONICET, 8400 S. C. de Bariloche,  
Argentina

**T. Gruner, N. Caroca-Canales, C. Geibel**

Max-Planck Institute for Chemical Physics of Solids, D-01187 Dresden, Germany

E-mail: [jsereni@cab.cnea.gov.ar](mailto:jsereni@cab.cnea.gov.ar)

**Abstract.** We studied the magnetic, transport, and thermodynamic properties of the alloy  $\text{CeTi}_{1-x}\text{Sc}_x\text{Ge}$  in order to shed some light into the origin of the exceptionally large antiferromagnetic (AFM) ordering temperature  $T_N = 47$  K in pure CeScGe. We observed a complex magnetic phase diagram, which present an interesting dichotomy: Despite strong changes in the nature of the ordered state, from ferromagnetic (FM) for  $x < 0.55$  to AFM for  $x > 0.55$ , the ordering temperature increases smoothly and continuously from  $T_C = 7$  K at  $x = 0.25$  to  $T_N = 47$  K at  $x = 1$ . Within the AFM regime we observe a metamagnetic transition at a critical field increasing from  $H = 0$  at  $x \approx 0.55$  to  $\mu_0 * H \approx 6$  Tesla at  $x = 1$ . Furthermore a second transition appears at  $T_L \leq T_N$  for  $x \geq 0.65$ . In contrast to observations in  $\text{CeRh}_2\text{Si}_2$  or  $\text{CeRh}_3\text{B}_2$ , we found no evidence for a strong hybridization of the 4f electrons at large Sc contents. Therefore the exceptionally large  $T_N$  of CeScGe could be attributed to the unusually strong RKKY interaction in this type of compounds.

## 1. Introduction

Most of magnetic transitions in Ce-based compounds showing a local 4f character are found below  $T_{ord} \approx 12$  K [1, 2]. Among the few cases exceeding that temperature, two types of behaviors can be distinguished. One of them is related to the rare cases of Ce binary compounds formed in BCC structures, with a quartet ground state, whose degeneracy ( $N = 4$ ) is reduced by undergoing different types of transitions mostly connected with structural modifications [3]. Those compounds are: CeZn ( $T_N = 30$  K); CeTl ( $T_N = 25.5$  K); CeMg ( $T_C = 20$  K); CeCd ( $T_C = 16.5$  K) and CeAg ( $T_N = 15.6$  K). The other group shows evidences of itinerant character [4] with the outstanding example of  $\text{CeRh}_3\text{B}_2$  which shows the highest ordering temperatures  $T_{ord} = 115$  K [5]. The second highest ordering temperature has been reported for CeScGe with  $T_{ord} = 47$  K [6], but the nature of its magnetic state has not been investigated in detail yet. Within this context, one of the most studied systems is  $\text{CeRh}_2\text{Si}_2$  [7], which shows a  $T_{ord} = 36$  K [8]. Within those studies evidences for both local and itinerant magnetic character are equally claimed by different authors [9, 10, 11]. Such ambiguity has been discussed since long time and recognized as the local-itinerant dilemma of Ce-4f<sup>1</sup> electrons [12].

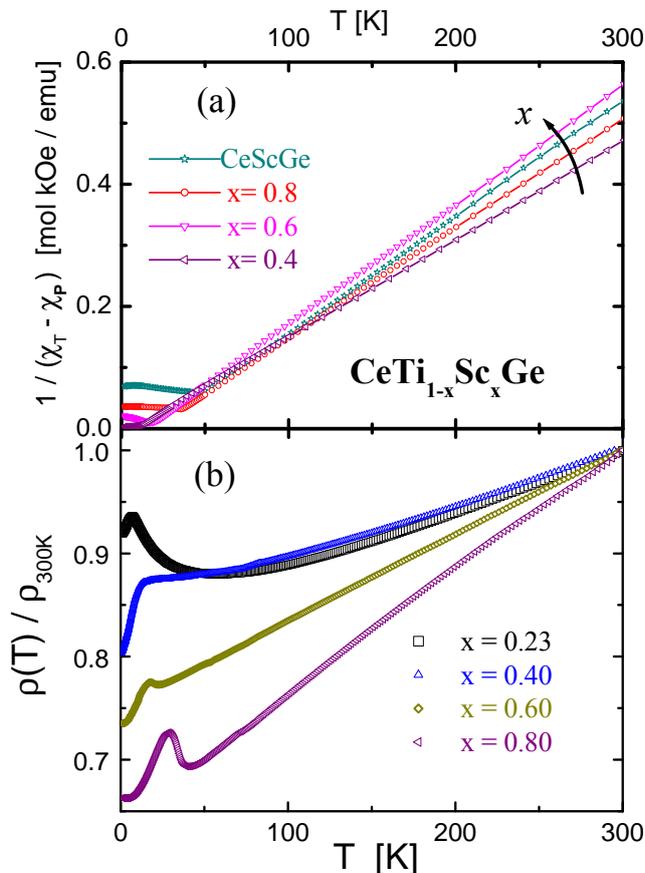
With the aim to contribute with further experimental information to this unsolved problem, we have studied the  $\text{CeTi}_{1-x}\text{Sc}_x\text{Ge}$  series whose magnetic transition temperatures cover an



unusually extended range of temperature from  $T_{ord} \approx 7$  K in  $\text{CeTi}_{0.75}\text{Sc}_{0.25}\text{Ge}$  up to  $\approx 47$  K at the stoichiometric limit  $\text{CeScGe}$  [6]. The lower concentration limit is determined by the range of stability of the  $\text{CeScSi}$ -type structure, since below  $x \approx 0.15$  the related  $\text{CeFeSi}$ -type structure becomes more stable. Due to such a large variation of  $T_{ord}$ , the excited crystal-electric-field (CEF) levels are expected to progressively increase their contribution to the formation of the ordered phase with the consequent modification of the ground state (GS) magnetic properties.

## 2. Experimental results

### 2.1. High temperature measurements



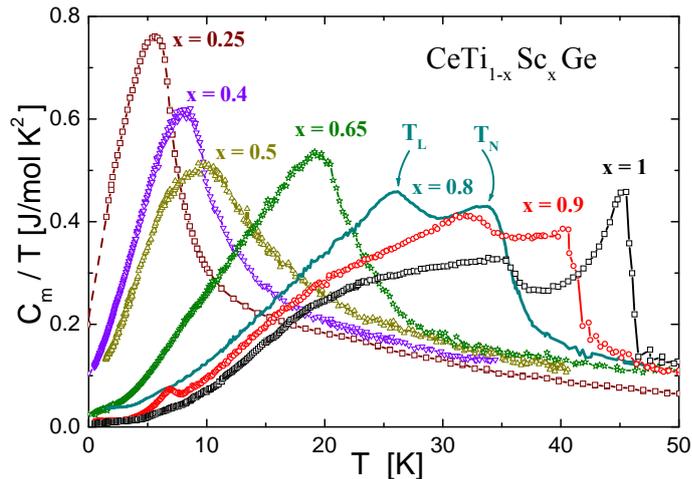
**Figure 1.** a) Inverse of high temperature magnetic susceptibility measured in a field of  $H = 10$  kOe, after subtraction of a Pauli type ( $\chi_P$ ) contribution. b) Electrical resistivity normalized at 300K for samples between  $0.23 \leq x \leq 0.8$ .

The inverse of the high temperature magnetic susceptibility is presented in Fig. 1a, after subtracting a Pauli type  $\chi_P$  paramagnetic contribution. At high temperature,  $\chi(T)$  is characterized by a small decrease of the effective magnetic moment  $\mu_{eff}(x)$  from  $\approx 2.25\mu_B$  at  $x = 0.4$  to  $\approx 2\mu_B$  at  $x = 0.5$  and remains nearly unchanged for higher Sc content. The paramagnetic temperature  $\theta_P(x)$  is always positive, reflecting ferromagnetic interactions, and increases with Sc concentration from  $\theta_P \approx 8$  K at  $x = 0.4$  up to 19 K at  $x = 0.8$ , where it starts a slight decrease. The Pauli-type  $\chi_P(x)$  contribution is observed all along the concentration range, decreasing from  $\chi_P = 0.9 \times 10^{-3}$  at  $x = 0.4$  down to  $0.47 \times 10^{-3}$  emu/Oe mol at  $x = 1$ . This type of contribution was already reported for  $\text{CeScGe}$  [13].

The electrical resistivity measurements on some representative concentrations between  $0.23 \leq x \leq 0.8$  are presented in Fig. 1b after being normalized at 300K. One can see in sample  $x = 0.23$  an increase of  $\rho(T)$  when approaching the ordering temperature from the paramagnetic phase as reminiscence of Kondo scattering. This increase progressively disappears and a pronounced

drop appears at the ordering temperature at  $x = 0.4$  reflecting the suppression of the spin flip scattering. For higher Sc concentrations, an upward is observed which may indicate a superzone gap opening. Interestingly this anomaly is most pronounced for  $x = 0.8$  and almost disappears for  $x = 1$ .

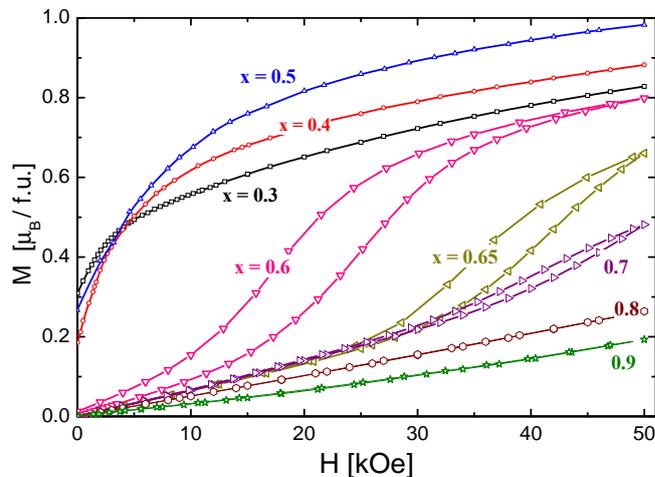
## 2.2. Low temperature specific heat



**Figure 2.** Magnetic contribution to the specific heat throughout the entire range of concentration, shown as  $C_m/T$  vs  $T$ .  $T_L$  and  $T_N$  indicate lower and upper transitions respectively.

Several peculiar features are observed in the specific heat results along the concentration variation in coincidence with the different regimes detected in the  $M(T)$  measurements (not shown). The results are presented in Fig. 2 as  $C_m/T$  vs  $T$  after phonon subtraction, taking the isotopic  $\text{LaTi}_{0.5}\text{Sc}_{0.5}\text{Ge}$  alloy as a reference. The lowest concentration  $x = 0.25$  presents a rather large, but broadened transition at  $T_C \approx 7\text{K}$ . Increasing  $x$  leads to a continuous shift of  $T_C$  to higher temperatures with the anomaly broadening up to  $x = 0.5$ , where the  $C_m/T(T)$  tail above  $T_C$  increases significantly. The decrease in the size of the maximum in this concentration range is a consequence of plotting  $C_m(T)/T$  instead of  $C_m(T)$ , whose maximum value slightly changes with concentration. In coincidence with  $\text{Ce}_2(\text{Ni}_{1-y}\text{Pd}_y)_2\text{Sn}$  [14], this nearly constant maximum of  $C_m(T)$  behavior differs from the usually observed in systems with ordering temperatures approaching zero temperature. Beyond  $x = 0.5$ , the maximum of  $C_m/T$  stop dropping and slightly increases at  $x = 0.65$ . Another characteristic of this concentration range is the decrease of  $C_m/T|_{T \rightarrow 0} = \gamma_0$  from  $\gamma_0 \approx 0.22\text{J mol}^{-1}\text{K}^{-2}$  down to  $\approx 0.02\text{J mol}^{-1}\text{K}^{-2}$  between  $x = 0.25$  and  $0.65$ .

Beyond  $x = 0.65$  the anomaly exhibits further changes in its morphology and becomes more step like, particularly for  $x \geq 0.8$ . Simultaneously, the anomaly splits into two maxima with  $T_L < T_N$ . This is a first evidence for a change in the magnetic ordered state between  $x = 0.25$  and  $x = 0.65$ , lying the higher concentration at a critical point. In fact, the shape of the anomaly at  $T = T_L$  suggests the presence of a first order transition which is broadened by a slightly inhomogeneous Sc/Ti distribution in the poly-crystalline sample. The transition temperatures deduced from  $C_m(T)/T$  maxima coincide with the temperatures obtained from susceptibility data (not shown). Notice that the  $\Delta C_m(T_N)$  jump observed at  $x = 1$  is  $\approx 16\text{J mol}^{-1}\text{K}^{-1}$ , which is in between the respective values expected for a doublet ( $\Delta C_m = 1.5R$ ) and a quartet ( $\Delta C_m = 2.2R$ ) within the mean field approximation [15]. The small anomaly observed in  $x = 0.9$  at  $T \approx 7\text{K}$  can be attributed to an extrinsic contribution of a small amount of Ce-oxide.



**Figure 3.** Field dependence of the magnetization at  $T = 1.8\text{K}$  up to  $H = 50\text{kOe}$ , showing a ferromagnetic GS for  $x < 0.6$  and an antiferromagnetic one with a metamagnetic transition for  $x \geq 0.6$ .

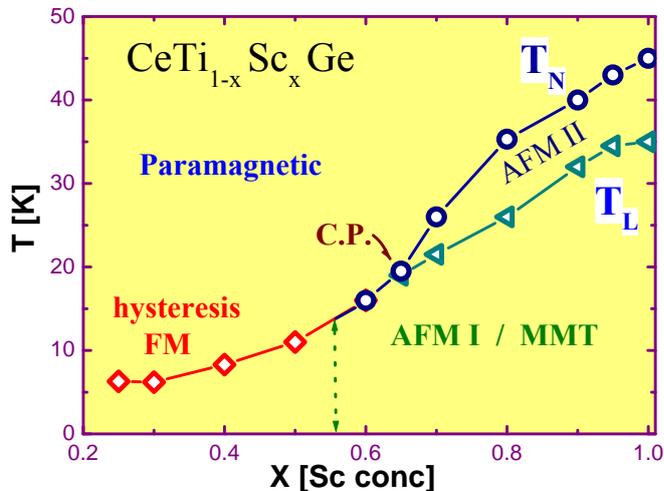
### 3. Discussion

The field dependence of the magnetization,  $M(H)$ , measured at  $T = 1.8\text{K}$  up to  $H = 50\text{kOe}$ , is presented in Fig. 3. The alloys with  $x \leq 0.5$  reveal the FM character of their ordered phase. The saturation magnetization ( $M_{sat}$ , extracted from Fig. 3 as  $M(x, H) = M_{sat} \times (1 - a/H)$ ), increases from  $1.04\mu_B/f.u.$  for  $x = 0.3$  up to  $1.15\mu_B/f.u.$  for  $x = 0.5$  and then decreases again to  $1\mu_B/f.u.$  for  $x = 0.6$ , but the latter value is not reliable because of the limited fitting range. At that concentration ( $x = 0.6$ ) the FM spontaneous magnetization disappears and gets replaced by a small susceptibility at low fields, proving the transition from a FM ground state to an AFM one. Furthermore, a metamagnetic (MMT) transition appears with the critical field  $H_{cr}$  increasing with Sc content up to the our maximum applied field  $H = 50\text{kOe}$ , with an initial slope of  $\partial H_{cr}/\partial x = 2.2\text{kOe/Sc}\%$ .  $M(H)$  measurements performed on CeScGe [13, 16] report a MMT transition at  $H_{cr} \approx 60\text{kOe}$  with a weak associated hysteresis. Notably, the area of the hysteresis loops decrease with increasing  $x$  and increasing  $H_{cr}(x)$ , including the mentioned for stoichiometric CeScGe.

The thermal evolution of the magnetic contribution to the entropy,  $S_m(T)$ , provides relevant information to understand this complex system. The alloy  $x = 0.25$  with the lowest ordering temperature  $T_C = 7\text{K}$  reaches  $S_m = R \ln 2$  at  $T \approx 11\text{K}$ , suggesting that only the GS doublet contributes to the magnetic order. In the paramagnetic phase  $S_m(T)$  keeps growing continuously with temperature (i.e. without showing any plateau around  $R \ln 2$ ), revealing a small crystal electric field (CEF) splitting.

Although the contribution of the excited CEF levels seems to be marginal in the alloys with low Sc content, it becomes significant at higher concentrations. In fact, for  $x > 0.5$  alloys,  $S_m(T_{ord})$  clearly exceeds  $R \ln 2$  and for larger concentrations it practically reaches the value expected for the two low-lying doublets, i.e.  $S_m = R \ln 4$ . The entropy at  $T = 50\text{K}$  does not change significantly with Sc concentration as an indication that the CEF splitting is practically not modified with Sc content. Thus, the increase of  $T_N(x)$  cannot be attributed to a decrease of the CEF splitting but rather to an increase of the RKKY interaction enhanced by the increasing contribution of the moderately broadened excited CEF levels.

The magnetic evolution of this system with Sc content is resumed in the phase diagram presented in Fig. 4. The transition temperature into the ordered state increases continuously from  $T_C = 7\text{K}$  at the lower limit of CeScSi structure type  $x = 0.25$ , to  $T_N = 47\text{K}$  at  $x = 1$ . Magnetization and susceptibility measurements clearly demonstrate the change from a FM GS for  $x \leq 0.5$  to an AFM GS for  $\geq 0.6$ . However, close to  $x = 0.6$  the FM state can be easily restored by a magnetic field as evidenced by the MMT at low fields. The critical field of this



**Figure 4.** Magnetic phase diagram as a function of Sc concentration showing the transition temperatures extracted from specific heat measurements. C.P.: Critical Point.

MMT increases with further increasing  $x$ , indicating a progressive stabilization of the AFM state relative to the FM one. Beyond a tricritical point, at  $x_{cr} = 0.65$ , a second transition appears in  $C_m(T)$  and  $\chi(T)$  at  $T_L < T_N$ , both increasing continuously with Sc concentration. The onset of AFM order is connected with the appearance of an upturn in  $\rho(T)$  indicating the opening of a gap in a fraction of the Fermi surface.

We did not observe any clear indication for increasing hybridization effects between  $4f$  and conduction electrons at high Sc content. Instead, some evidence for Kondo effect, e.g. the increase in  $\rho(T)$  towards low temperature and an enhanced  $\gamma_0$ , are observed at low Sc contents despite the FM behavior. Thus the high  $T_N$  observed in CeScGe is very unlikely to originate from a strong hybridization, in contrast to itinerant cases like CeRh<sub>2</sub>Si<sub>2</sub> and CeRh<sub>3</sub>B<sub>2</sub> [5, 8]. In this context one should notice that all RScGe and RTiGe compounds (R = magnetic rare earth) present very high ordering temperatures, independently of the structure type, with  $T_C = 350$  K in GdScGe (CeScSi type) [17] and  $T_N = 412$  K in GdTlGe (CeFeSi type) [18]. This ordering temperature is a factor 7 higher than in CeScGe. In contrast, the  $T_N$  ratio between GdRh<sub>2</sub>Si<sub>2</sub> and CeRh<sub>2</sub>Si<sub>2</sub> is only a factor 3. Thus, the high  $T_N$  of CeScGe seems to be connected with an intrinsically very large RKKY interaction in the RTX series of compounds with T = Sc, Ti and X = Si, Ge crystallizing in the CeFeSi or CeScSi structure types.

#### 4. Conclusions

The present results on CeTi<sub>1-x</sub>Sc<sub>x</sub>Ge reveal a surprising dichotomy: on the one hand one observes a pronounced change in the type of magnetic order from FM to AFM at  $x \approx 0.55$ , but on the other hand the transition temperature from the paramagnetic to the ordered state increases continuously with  $x$ , from  $T_C = 7$  K to  $T_N = 47$  K, without reflecting the change in the type of ordering. This smooth increase of the ordering temperature across the change from FM to AFM indicates that no strong discontinuity occurs in the order parameter. The appearance of a MMT at the onset of AFM order, which continuously shifts from zero to higher field with increasing  $x$ , also reveals a weak energy difference between both states. Therefore, these results suggest a smooth evolution from a FM-stacking to an AFM-stacking of FM layers, with a strong FM coupling within the layers which dominates the ordering process. Because of a rather small CEF splitting, the increase of  $T_N$  up to 47 K at  $x = 1$  results in an evolution from an effective doublet system at  $x = 0.25$  to an effective quartet system at  $x = 1$ . However, this is not at the origin of the increase in  $T_N$  since CEF splitting does not change on its own and neither evidences for a strong hybridization of the  $4f$  electrons on the Sc rich side were observed. Therefore, the high  $T_N$  of CeScGe has to be attributed to unusual large RKKY interactions mediated by an

increasing role of Sc atoms as evidenced by very high ordering temperatures in homologues RTX compounds.

## References

- [1] see for example Bauer E 1991 *Adv. Phys.* **40** 417
- [2] Sereni J G 1998 *J. Phys. Soc. Japan* **67** 1767
- [3] see for example: Sereni J G 1991 *Low temperature behavior of Cerium compounds* (Handbook Phys Chem of Rare Earths Vol 15) ed Gschneidner K and Eyring L (Amsterdam: Elsevier Science Pub.) chapter 98 pp 1-59
- [4] De Long L E, Huber J F, Bedell K S 1991 *J. Magn. Magn. Mater* **99** 171.
- [5] Malik S K, Vijayaraghavan R, Wallace W E 1983 *J. Magn. Magn. Mater* **37** 303
- [6] Canfield P C, Thompson J D and Fisk Z 1991 *J. Appl. Phys.* **70** 5992.
- [7] see for example Kawarazaki S, Sato M, Miyako Y, Chigusa N, Watanabe K, Metoki N, Koike Y, Nishi M 2000 *Phys. Rev. B* **61** 4167
- [8] Godard C, Gupta L C, Ravet-Krill L C 1983 *J. Less-Common Met.* **94** 187
- [9] Kawarazaki S, Kobashi Y, Fernandez-Baca J A, Murayama S, Önuke Y and Miyako Y 1995 *Physica B* **206-207** 298
- [10] Settai R, Misawa A, Araki S, Koski M, Sigiyama K, Takeuchi T, Kindo K, Haga Y, Yamamoto Y, Önuke Y 1997 *J Phys. Soc. Japan* **66** 2260
- [11] Gómez Berisso M, Pedrazzini P, Sereni J G, Trovarelli O, Geibel C and Steglich F 2002 *Eur. Phys. J. B* **30** 343
- [12] Mackintosh A R 1985 *Physica B* **130** 112
- [13] Uwatoko Y, Ishii T, Oomi G, Takahashi H, Mōri N, Nimori S, Kido G, Serrao J L, Mandrus D, Fisk Z, Thompson J D 1997 *Physica B* **237-238** 207
- [14] Sereni J G 2013 *Phil. Mag.* **93** 409
- [15] See for example: Meijer P H, Colwell J H, Shah B P 1973 *Am. Jour. Phys.* **41** 332
- [16] Singh S, Dhar S K, Mitra C, Paulose P, Mainfrinetti P, Palenzona A 2001 *J. Phys.: Condens. Matter* **13** 3753
- [17] Couillaud S, Gaudin E, Franco V, Conde A, Pttgen R, Heying B, Rodewald U, Chevalier B et al. 2011 *Intermetallics* **19** 1573
- [18] Nikitin S A, Tskhadadze I A, Telegina I V, Morozkin A V, Seropegin Y 1998 *J. Mag. Mag. Mater* **182** 375