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Magnetic properties of the ternary RMgSn (R = Pr, Nd, Sm, Gd–Tm): First series of antiferromagnetic CeScSi-type structure compounds

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ABSTRACT

The equiatomic ternary RMgSn compounds crystallize in the CeScSi (Pr, Nd, Sm, Gd–Tm), TiNiSi (Ce, Pr) or ZrNiAl (Yb) type structures. Macroscopic magnetic measurements, performed in the 5–300 K range, show that all the CeScSi-type compounds behave antiferromagnetically ($8 < T_N < 79$ K). They also evidence metamagnetic-like behavior ($H_{crit} < 7$ T). The TiNiSi-type compounds are antiferromagnetic and ferromagnetic below 12 K and 52 K for CeMgSn and PrMgSn, respectively.

1. Introduction

The equiatomic ternary RTX (R = Lanthanide, T = Transition metal, X = p-element) compounds crystallize in numerous types of structure within which the CeFeSi (*P*4/*nmm*), TiNiSi (*Pnma*) and ZrNiAl (*P*–62*m*) are the most represented [1]. These structures are closely related since they are characterized by different arrangements of identical RX_5 and TX_4 polyhedra (Fig. 1). The CeScSi-type structure (*I*4/*mmm*) is an ordered variant of the La_2Sb-type and derives from the CeFeSi-type by a simple [½, ½, 0] translation of one RX_5 slab out of two, inducing a modification of the TX_4 tetrahedral to TX_4 square plane (Fig. 2). The coexistence of these two type structures has been evidenced for the GdTiGe compound [2–4], and derived alloys [5]. Recently, this structural transition has been observed by insertion of carbon or boron atoms in the CeFeSi-type RTiGe compounds [6,7]. The previous studies have evidenced that most of the ternary compounds with CeScSi-type structure are ferromagnets (GdTiGe [2,3], RScSi with R = Ce, Nd, Sm, Gd [8–10], RScGe with R = Ce–Nd, Sm, Gd, Tb [8–11], RZrSb with R = Gd–Tm [12,13]. Only few compounds are antiferromagnetically ordered (PrScSi [8], PrScGe [8,11], and ErZrSb [13]).

Recently, Manfrinetti *et al.* [14] have reported on new RMgSn ternary compounds which crystallize in TiNiSi (R = La–Pr, Eu), CeScSi (R = Y, Nd, Sm, Gd–Tm, Lu) and ZrNiAl (R = Yb) types of structure but, surprisingly, their magnetic behaviors have not been analyzed. This paper deals with the magnetic properties of the RMgSn series through macroscopic magnetic measurements.

2. Experimental methods

The polycrystalline samples were synthesized starting from stoichiometric amounts of high purity (99.9 wt.% for the lanthanides, 99.99 wt.% for magnesium and tin) commercially available elements. As a general precaution, all sample manipulations were undertaken in a purified argon-filled glove box ensuring an oxygen level of less than 2 ppm O_2 and about 3 ppm H_2O. The high volatility of magnesium constrains to place the elements in Mo crucible which was arc-welded. In a first step, the samples were melted in a water-cooled copper crucible using a high frequency induction furnace (CELES), under secondary vacuum, for a preliminary homogenization treatment. In a second step, to prevent their oxidation, the Mo crucibles were subsequently enclosed in a silica tube under purified argon (300 mm Hg) and then placed in a tube furnace during 1 week at 1073 K (*973 K for the low temperature form of the PrMgSn compound*) and water-cooled. No reaction of the samples with the container material was observed.

The crystallographic structure and the presence of impurities in the samples were checked by powder X-ray diffraction (Philips X'Pert Pro Diffractometer, Cu K_α). The analysis of the patterns was performed by Rietveld profile refinement using the software FULLPROF [15]. Profile-matching adjustments were used to refine the cell parameters. It is worth noting that during this stage, it was clearly observed that the samples were not stable in air up to one day. Therefore, in the following, they were always kept under argon or helium atmosphere.

The magnetic measurements were performed using a conventional PPMS-9 system (Quantum Design) in the 5–300 K temperature range and under applied magnetic fields up to 9 T. The thermomagnetic curves were recorded upon heating after zero-field cooling (ZFC).

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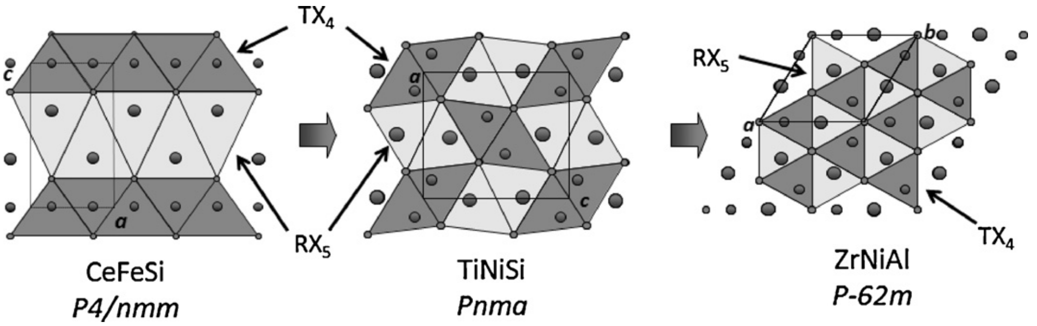

Fig. 1. Representations of the CeFeSi-, TiNiSi- and ZrNiAl-type showing the arrangements of the RX_5 and TX_4 polyhedra.

3. Results and discussion

3.1. Crystallographic analysis

Eleven RMgSn samples have been synthesized and checked with R = Ce–Nd, Sm, Gd–Yb. The indexation of the powder X-ray diagrams confirmed the space group *I*4/*mmm* for all of these compounds except Ce, and Yb. Lattice parameters are gathered in Table 1. Diffraction patterns show unambiguously that R, Sn and Mg atoms occupy 4(e) [$z_R \approx 0.33$, $z_{Sn} \approx 0.13$] and 4(c) crystallographic positions, characteristic of the tetragonal CeScSi-type structure. All these data are in fair agreement with those previously published by Manfrinetti *et al.* [14]. However, it is worth noting that our syntheses allow us to stabilize a new low temperature CeScSi variety for the PrMgSn compound. Its atomic volume is in nice agreement with that which can be deduced from [14]. Attempts to obtain the H.T.-TiNiSi form, signaled for this alloy [14], have systematically led to a mixture of the two types of structure, whatever the thermal treatment and quenching. The occurrence of two structural forms (*i.e. L.T.-CeScSi and H.T.-TiNiSi*) for PrMgSn whereas NdMgSn only crystallizes in the CeScSi-type allows us to conclude that the critical R size value corresponds to the atomic radius of the Pr atom ($R^{3+} \approx 1.03$ Å) in the ternary lanthanide magnesium stannides.

Finally, as previously observed [14], CeMgSn crystallizes in the TiNiSi-type structure (*Pnma*) while YbMgSn crystallizes in the ZrNiAl-type structure (*P*–62*m*). A largely more detailed analysis of the crystallographic data of this family of compounds can be found in Ref. [14].

3.2. Magnetic measurements

The main characteristic magnetic data are gathered in Table 2. The thermal variations of the magnetization are displayed in Figs. 3–5.

The TiNiSi-type CeMgSn compound presents an antiferromagnetic order below 12 K whereas PrMgSn is a ferromagnet below 52 K (Fig. 3). The anomaly detected around 20 K on the thermomagnetic curve of PrMgSn corresponds to the CeScSi form impurity. No magnetic transition is detected in the whole temperature range for YbMgSn compound, in agreement with the divalent state of Yb suggested by Manfrinetti *et al.* [14].

For all the CeScSi-type RMgSn compounds (R = Pr, Nd, Sm, Gd–Tm), the curves are characterized by a typical shape of antiferromagnetic behavior with order temperatures of 20, 31, 79, 48, 34, 27, 17, 8 and <5 K, respectively (Figs. 4 and 5). In some cases (Nd and Gd compounds), the curves present an increase of the magnetization below the Néel temperature, owing to undetected impurities or a modification of the magnetic structure (Fig. 4). A careful analysis of the thermal variation of the susceptibility of SmMgSn compound allows to distinct a small deviation at around 79 K. In spite of its surprisingly high value, this transition has been clearly confirmed by ^{119}Sn Mössbauer spectroscopy (Fig. 6). In the same way, ^{119}Sn Mössbauer spectroscopy shows that TmMgSn orders below 4 K (Fig. 6).

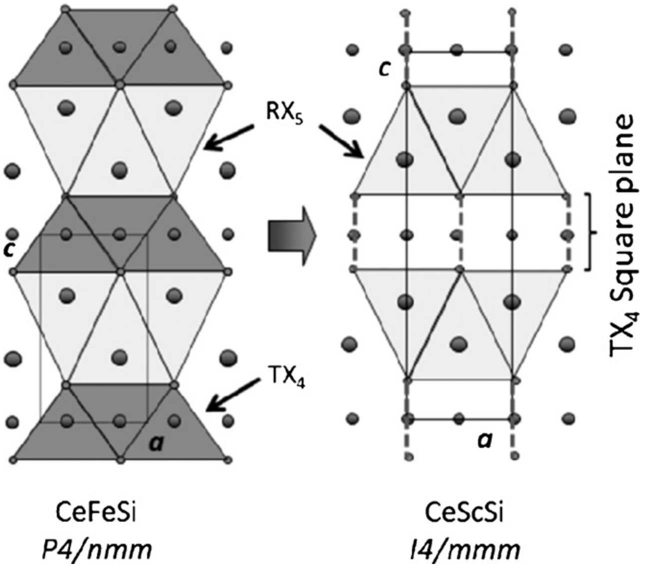

Fig. 2. Representation of the structural modification between CeFeSi- to CeScSi-type transition.

In the paramagnetic range, thermal dependence of the magnetic susceptibility has been fitted by a Curie–Weiss law. The experimental effective values of the R moments are in good agreement with the theoretical R^{3+} free ion values. For CeMgSn, the experi-

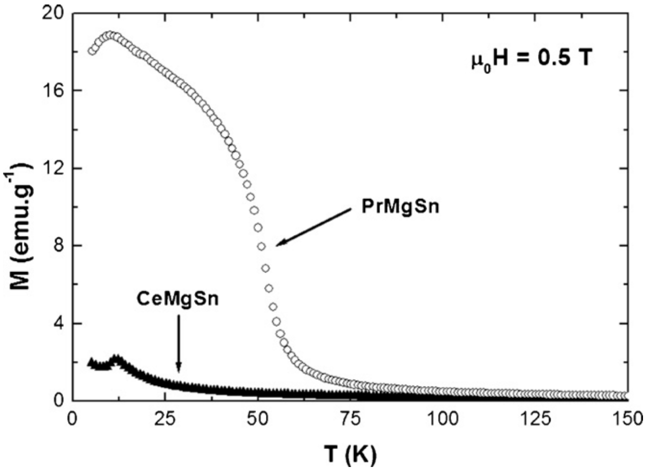

Fig. 3. Thermal variation of the magnetization of TiNiSi-type CeMgSn and PrMgSn compounds.

Table 1
Cell parameters of RMgSn compounds.

RMgSn	Type structure	Space group	*a* (Å)	*b* (Å)	*c* (Å)	*V* (Å^3)	*c*/*a*
CeMgSn	TiNiSi	*Pnma*	7.731 (1)	4.649 (1)	9.083 (1)	326.4 (1)	–
PrMgSn	TiNiSi	*Pnma*	7.690 (1)	4.617 (1)	9.064 (1)	321.8 (1)	–
PrMgSn	CeScSi	*I*4/*mmm*	4.492 (1)	–	16.213 (1)	327.2 (1)	3.61
NdMgSn	CeScSi	*I*4/*mmm*	4.472 (1)	–	16.146 (1)	322.9 (1)	3.61
SmMgSn	CeScSi	*I*4/*mmm*	4.434 (1)	–	16.036 (1)	315.2 (1)	3.62
GdMgSn	CeScSi	*I*4/*mmm*	4.406 (1)	–	15.934 (1)	309.3 (1)	3.62
TbMgSn	CeScSi	*I*4/*mmm*	4.385 (1)	–	15.866 (1)	305.1 (1)	3.62
DyMgSn	CeScSi	*I*4/*mmm*	4.370 (1)	–	15.826 (1)	302.2 (1)	3.62
HoMgSn	CeScSi	*I*4/*mmm*	4.358 (1)	–	15.784 (1)	299.8 (1)	3.62
ErMgSn	CeScSi	*I*4/*mmm*	4.344 (1)	–	15.740 (1)	296.9 (1)	3.62
TmMgSn	CeScSi	*I*4/*mmm*	4.332 (1)	–	15.718 (1)	294.9 (1)	3.63
YbMgSn	ZrNiAl	*P*−62*m*	7.645 (1)	–	4.696 (1)	237.7 (1)	–

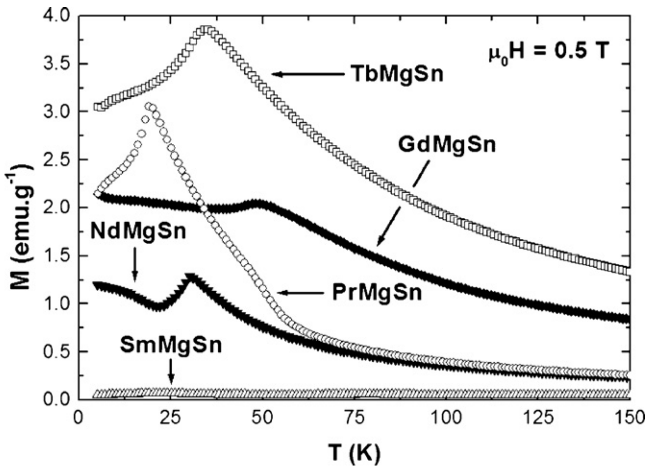

Fig. 4. Thermal variation of the magnetization of (Pr, Nd, Sm, Gd, Tb)MgSn CeScSi-type compounds.

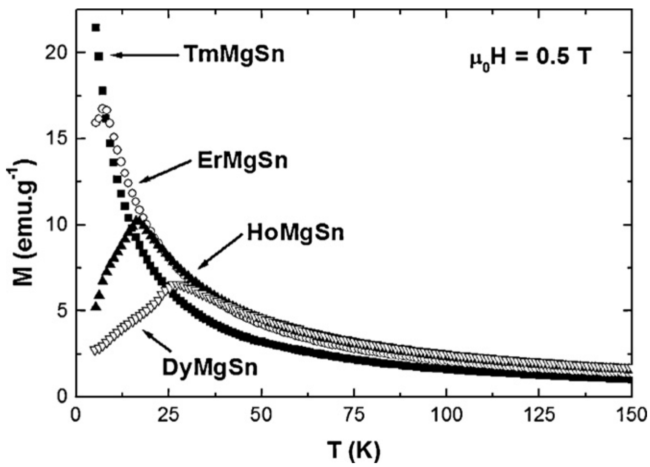

Fig. 5. Thermal variation of the magnetization of (Dy–Tm)MgSn CeScSi-type compounds.

mental effective moment (2.9(2) μ_B) is close to the free Ce^{3+} ion value (2.54 μ_B), in agreement with the conclusions derived from the lattice parameter variations observed in this series [14].

The paramagnetic Curie temperatures (θ_P) are close to zero (sometimes slightly positives: Ce, Pr, Er, Tm) indicating non-negligible ferromagnetic interactions in these compounds. Indeed, the antiferromagnetic structures observed in such intermetallic materials, generally characterized by two dimensional ferromagnetic layers coupled antiferromagnetically in the third direction induce a competition between ferro- and antiferromagnetic interactions [16].

The magnetic orders temperatures predict by the de Gennes law are compared with the ones obtained experimentally in Fig. 7. For the heavy lanthanide compounds (Gd–Er), the Néel points well obey the de Gennes scaling which predicts a magnetic ordering temperature for TmMgSn around 4 K (Fig. 7) in good agreement with the Mössbauer result (Fig. 6). It means that their magnetic properties may be considered in terms of RKKY model of indirect interactions, the crystal electric field playing an important role. By contrast, the variation of the ordering temperature across the light lanthanide compounds (Pr–Sm) shows a strong deviation to the de Gennes law and should probably not be explained by crystal field effects alone. The origin of these anomalies should also be found either in the modification of the band structure along the series or in the presence of orbital effects in the bilinear couplings. Such behavior is currently observed in RTX and RT$_2$X$_2$ related compounds [16].

The isotherm curves, measured at 5 K in fields up to 9 T, are plotted in Figs. 8 and 9. For the CeScSi-type compounds (Fig. 8), the curves exhibit a linear part at low magnetic field and metamagnetic-like transition what confirms the antiferromagnetic

Table 2
Magnetic data of RMgSn compounds.

RMgSn	Type structure	T_N (K) (±2 K)	T_C (K) (±2 K)	θ_p (K) (±2 K)	m_{eff} (μ_B)	M_{MAX} (μ_B/f.u.) at 5 K	H_{crit} (T) (±0.2 T)
CeMgSn	TiNiSi	12	–	12	2.9 (2)	1.4	2.0
PrMgSn	TiNiSi	–	52	50	3.4 (2)	–	–
PrMgSn	CeScSi	20	–	14	3.9 (2)	1.9	3.0
NdMgSn	CeScSi	31	–	2	4.0 (2)	1.3	6.0
SmMgSn	CeScSi	79	–	–	–	0.02	–
GdMgSn	CeScSi	48	–	−16	8.2 (2)	1.6	7.0
TbMgSn	CeScSi	34	–	−11	10.2 (2)	4.4	6.4
DyMgSn	CeScSi	27	–	−6	11.4 (2)	7.5	2.6
HoMgSn	CeScSi	17	–	−2	10.9 (2)	8.9	1.8
ErMgSn	CeScSi	8	–	7	9.8 (2)	7.2	1.4
TmMgSn	CeScSi	<5	–	19	8.1 (2)	5.8	–
YbMgSn	ZrNiAl	–	–	–	–	–	–

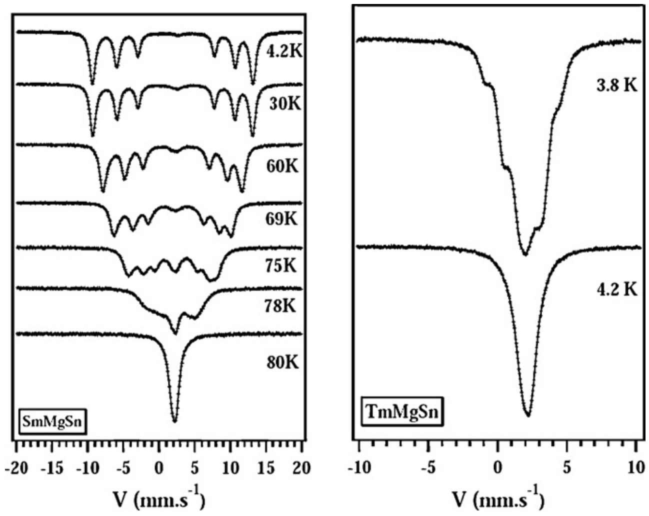

Fig. 6. ^{119}Sn Mössbauer spectra of the SmMgSn and TmMgSn compounds.

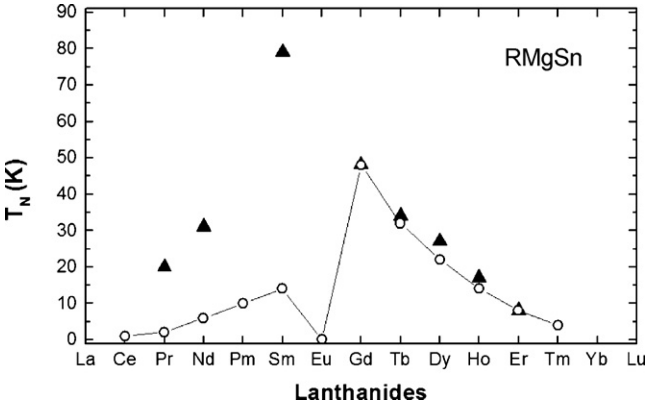

Fig. 7. Observed Néel temperatures in the CeScSi-type RMgSn compounds (▲) and their relation to the de Gennes function (○, normalized to R = Gd).

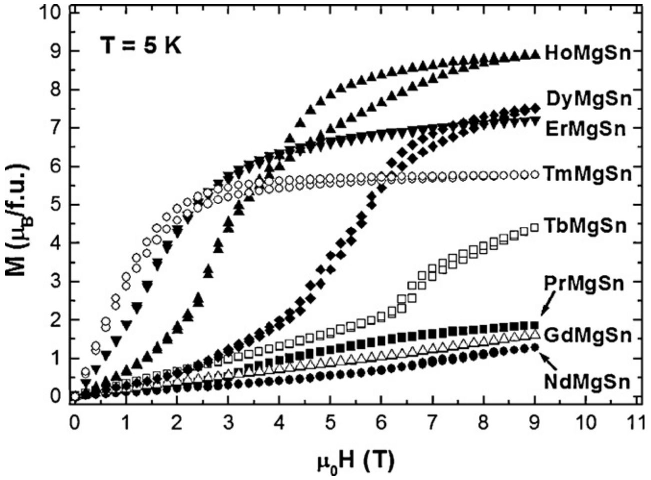

Fig. 8. Field dependence of the magnetization of the CeScSi-type RMgSn compounds at 5 K.

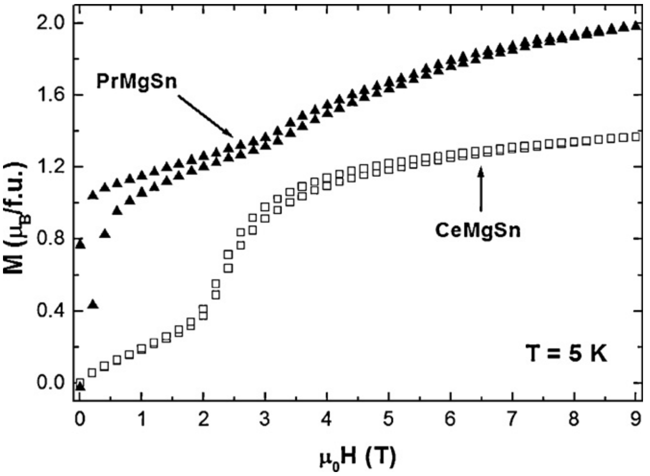

Fig. 9. Field dependence of the magnetization of the TiNiSi-type RMgSn compounds at 5 K.

behavior of these compounds. In the case of TmMgSn, these characteristics are not present but the field dependence magnetization measured is not therefore in contradiction with an antiferromagnetic order in so far as the magnetic order appears just one kelvin below the temperature of measurement. For all the other compounds, the threshold fields increase from 2 T to 7 T between Pr and Gd and then decrease down to 1.4 T between Tb and Er (Table 2). These weak values well follow the evolution of T_N and θ_P all along the series and support the existence of competition between close ferro- and antiferromagnetic interactions. In all cases, the maximum values of the magnetization ($\mu_0 H = 9$ T) are far away the theoretical free ion values (Table 2). We can also notice that only HoMgSn clearly presents rather large magnetic hysteresis at high field (Fig. 8).

In the case of TiNiSi-type compounds (Fig. 9), CeMgSn shows both linear part at low field and metamagnetic-like transition at 2 T. PrMgSn is singular with a curve showing remanent magnetization ($M_R \approx 1.3\,\mu_B$, $H_c \approx 0.5$ T, Fig. 9). Unfortunately, the presence of the both phases (TiNiSi- and CeScSi-types) prevents a quantitative interpretation of this curve.

4. Conclusion

Investigations performed on the RMgSn compounds confirm the crystallographic data of Manfrinetti *et al.* [14] *i.e.* CeScSi-type structure with R = Y, Nd, Sm, Gd–Tm, TiNiSi-type structure for R = La–Pr and ZrNiAl-type for the YbMgSn compound. The present work has also allowed us to evidence a new CeScSi-type L.T. form for the PrMgSn compound. In the equiatomic RTX ternary series, structural transitions are often observed [1]. It has been shown that these transitions are generally dependent on the R^{3+} ionic radius of the lanthanide [17,18]. To our knowledge, it is the first time that a structural transition between TiNiSi and CeScSi forms has been evidenced for a ternary compound. The occurrence of the two structural types for PrMgSn yields the critical *R* size value around 1.03 Å. As regards the structural stability, the RMgSn series appears very interesting and requires an extensive study with X-ray single crystal refinements and electronic structure calculations. Such works are in progress.

For a magnetic point of view, the RMgX (X = Ga, In) compounds exhibit a low temperature antiferromagnetic order but they crystallize in the ZrNiAl-type [19–22], while the CeScSi-type compounds were generally ferromagnets [2,3,8–13]. Consequently, the RMgSn compounds (R = Pr, Nd, Sm, Gd–Tm) represent the first CeScSi-type series with antiferromagnetic behavior. This remarkable feature induces unusual magnetic behaviors in particular for the light lanthanide materials. Further investigations by neutron diffraction experiments and ^{119}Sn Mössbauer spectroscopy are now necessary to complete the understanding of the magnetic ordering of the lanthanide sublattice in the RMgSn series and the comparison with isotypic compounds. Such experiments are in progress.

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