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NEUTRON DIFFRACTION STUDIES OF THE CeFeSi-TYPE CaMnSi AND CaMnGe COMPOUNDS

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The magnetic properties of the tetragonal CeFeSi-type compounds CaMnSi and CaMnGe have been investigated by neutron diffraction. They order antiferromagnetically below T_N~360 and 420 K respectively (this was not detected by macroscopic measurements). Below T_N, the two magnetic structures are characterized by a stacking of purely antiferromagnetic (001) planes with the Mn magnetic moments (~3.3μ_B) along the c-axis in the case of CaMnSi and 30° tilted from this axis in the case of CaMnGe. The results are compared to those of isotypic rare earth manganese silicides and germandes and to the closely related $ThCr_2Si_2$-type RMn_2Si_2 and RMn_2Ge_2 compounds.

1-Introduction

We recently reported on the magnetic properties of RMnX and RMn_2X_2 (X=Si, Ge)[1-7] compounds which crystallize in the closely related CeFeSi (*P4/nmm*) and $ThCr_2Si_2$ (*I4/mmm*) structures respectively. The two structures can be described as alternating (001) square planes containing R, Mn or X atoms with the following sequences : $RXMn_2XRXMn_2XR$ ($ThCr_2Si_2$) and $RXMn_2XRRXMn_2XR$ (CeFeSi). Thus, these structures can be regarded as stacking variants of metal atom planes with the same "XMn_2X" slab, the stacking being more or less anisotropic.

In both families, the Mn sublattice orders at relatively high temperature and the sign of the coupling strongly depends on the Mn-Mn spacings. It was shown that for $d_c(=d_{Mn\text{-}Mn}{}^{intra})<2.86$ Å, the compounds are characterized by ferromagnetic (001) Mn planes while for $d_c>2.86$ Å antiferromagnetic (001) Mn layers are observed. In this latter case, the RMnSi compounds are characterized by antiferromagnetic Mn planes in the whole ordered range while in the RMn_2X_2 series, mixed (001) Mn planes, where ferro- and antiferromagnetic components coexist, occur at lower temperature (*a detailed description of the thermal dependent Mn sublattice magnetic orderings within the RMn_2X_2 (X=Si,Ge) series can be found in ref.8*). In all the cases, the antiferromagnetic transition is not detected by magnetometric measurements.

The distance-dependant oscillatory character of the RKKY interactions may explain the magnetic properties of these compounds. This assumption could be corroborated by the difference in the conduction electron concentration between the two series. Assuming that the electropositive rare earth (R^{3+}) element donates all its valence electrons to the "XMn_2X" slab, it gives twice as many electrons in RMnX than in RMn_2X_2 (i.e. 3e⁻ in RMnX against 1.5e⁻ in RMn_2X_2). As a result, the "XMn_2X" slab in RMn_2X_2 is poorer in electrons than in RMnX. Furthermore in $ThMn_2Si_2$ (d=2.84 Å), where 2e⁻ are given to the slabs under the same assumption, Mn sheets are ferromagnetically coupled[9] while antiferromagnetic Mn planes occur in the whole ordered range in $CaMn_2Ge_2$ and $BaMn_2Ge_2$ (d=2.93/3.15 Å)[5].

For all these reasons, and in order to complete the comparison between these two families, it appears very interesting to examine the magnetic behaviour of the alkaline earth metal ATMnX compounds (AT^{2+}=Ca- Ba).

In this paper, we report on the magnetic properties of the CaMnGe and the new CaMnSi compounds investigated by magnetization measurement and neutron diffraction experiments.

2-Experimental results

a) Synthesis

The compounds were prepared from commercially available high purity elements. Pellets of stoichiometric mixture were compacted using a steel die and then introduced into silica tubes sealed under argon (200 mmHg). Preliminary homogenization treatement was conducted at 1273 K. The samples were then melted in an induction furnace. The resulting ingots were annealed for three days at 1173 K. The single phase nature of both compounds was confirmed by X-ray diffraction technique (Guinier Cu Kα).

Our syntheses confirm the occurrence of the CaMnGe compound and allow us to prepare the new silicide CaMnSi. Powder X-ray diffraction patterns show that both compounds cristallize in the tetragonal CeFeSi-type structure (space group P4/nmm). Refinements using silicon as internal standard give the following parameters :

CaMnSi : a=4.194(3); c=7.149(6); c/a=1.704(3)
CaMnGe : a=4.242(3); c=7.23(1); c/a=1.704(4)

in good accordance, in the latter case, with those obtained by Dörrscheidt et al.[10]. It is noteworthy that despite a calcium atomic radius close to that of Nd, the Ca compounds exhibit the largest a and the smallest c lattice parameters with a c/a ratio of 1.70 against 1.74 for the other members of the RMnX series (Table I).

Unfortunatly, up to now, attempts to synthetize the corresponding barium compounds have always failed.

TABLE I : Lattice parameters, c/a ratio and Néel temperatures in RMnSi and RMnGe (R = Ca, La-Nd[1,2]) compounds.

Compounds	a(Å)	c(Å)	c/a	T_N(K)
CaMnSi	4.194	7.149	1.704	360
LaMnSi	4.181	7.388	1.767	310
CeMnSi	4.125	7.285	1.766	240
PrMnSi	4.124	7.307	1.772	265
NdMnSi	4.103	7.284	1.775	280
CaMnGe	4.242	7.23	1.704	420
LaMnGe	4.254	7.425	1.745	415
CeMnGe	4.235	7.386	1.744	410
PrMnGe	4.182	7.308	1.747	410
NdMnGe	4.173	7.349	1.761	410

b) Magnetometric measurements

The magnetic measurements were carried out using a Faraday balance (above 300K) and a MANICS magneto-susceptometer (between 4.2 and 300K), in field up to 1.7T.

For both CaMnSi and CaMnGe samples, these measurements gave no evidences of any magnetic ordering in the whole temperature range investigated (4K-700K).

c) Neutron diffraction study

experimental procedures

Neutron diffraction experiments were carried out at the Siloe Reactor of the Centres d'Etudes Nucléaires de Grenoble. Several patterns have been collected in a temperature range 2-500K for both compounds with the

TABLE II : Observed and calculated intensities and refined parameters at 300 and 2 K in CaMnSi.

	300K		2K	
h k l	I_c	I_o	I_c	I_o
0 0 1	13.4	13.7(4)	15.1	15.1(4)
1 0 0	21.7	21.8(5)	54.2	54(2)
1 0 1	29.7	30(1)	87.6	88(3)
0 0 2	48.3	48(1)	60.5	59(3)
1 1 0	157.2	157(3)	149.0	148(4)
1 0 2	85.3	84(4)		
1 1 1	11.1	15(3)	123.1	128(7)
0 0 3	1.6	-	0.9	-
1 1 2	10.1	13(3)	16.4	23(5)
2 0 0	25.5	29(4)	24.1	27(4)
2 0 1	50.2	53(5)	48.9	54(6)
1 0 3	24.0	19(4)	46.9	43(7)
a(Å)	4.194(3)		4.172(3)	
c(Å)	7.149(6)		7.121(8)	
f_{cor}	0.985(4)		0.95(1)	
z_{Si}	0.211(1)		0.213(3)	
z_{Ca}	0.666(1)		0.669(2)	
μ_{Mn} (μ_B)	1.96(1)		3.27(4)	
θ(°)	0		0	
R(%)	4.3		4.6	

one-dimension curved multidetector DN5, at a wavelength λ=2.496 Å. In order to correct texture effect, following a procedure largely described in ref.11, we used during the refinement a fitted coefficient f_{cor} which reflect the importance of preferential orientation. The value of f_{cor} obtained (see table 1 and 2), strongly support the validity of this correction.

Using the scattering length :b_{Si}=4.149 fm, b_{Ge}=8.185 fm, b_{Mn}=-3.73 fm, b_{Ca}=4.70 fm, and the form factor of Mn from ref.12, the scaling factor, the z_{Si}, z_{Ge} and z_{Ca} atomic positions, f_{cor} and the Mn magnetic moment were refined by the MiXeD crystallographic executive for diffraction (MXD) least-square-fitting procedure[13]. The MXD program allows simultaneous fitting of nuclear and magnetic intensities to the observed ones.

Results

The neutron diffraction patterns of both compounds are similar over the whole temperature range studied (500-2 K).

At 500 K, the patterns are purely nuclear (fig. 1). The extinction rules of the space group P4/nmm are fulfilled and confirm unambiguously the CeFeSi-type structure for both CaMnSi and CaMnGe. According to our refinements, any possible interchange of Mn and Si on their crystallographic sites is excluded.

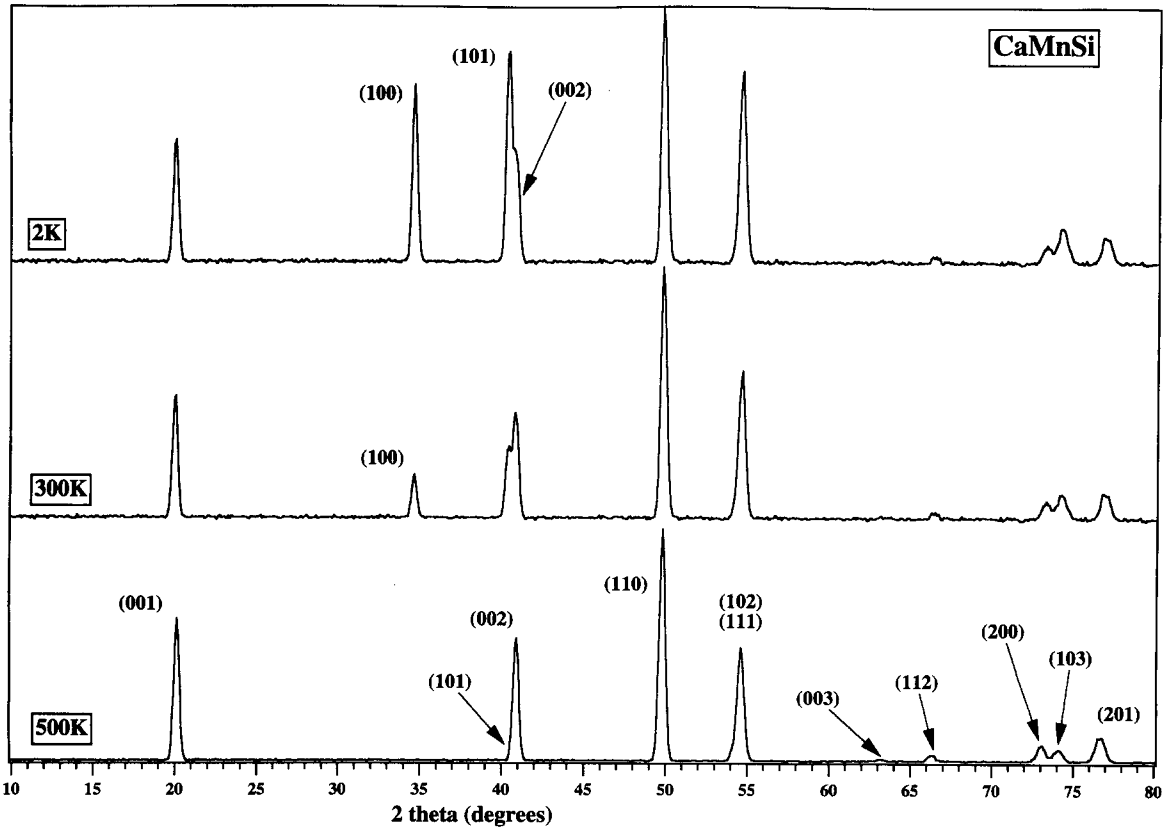
Below ~350 K, an additional line, which can indexed in the crystal unit cell as (100) (*forbidden by the nuclear space group P4/nmm*), appears. This result is characteristic of an antiferromagnetic ordering, which was not detected in the bulk susceptibility measurement. Futhermore, magnetic contributions occur under nuclear (*hkl*) lines with *h+k=2n+1*, as indicated by the increase of their intensities together with the one of the (100) line when the temperature decreases down to 2 K (fig.1).

According to the special position of the Mn atoms [*2(a) (3/4, 1/4, 0) i.e. with an additionnal C translation mode*] in the CeFeSi-type structure, these observations give evidence of an antiferromagnetic arrangement of the Mn moments within the (001) planes. Such magnetic structure is identical to that determined previously in LaMnSi[1] and in the alkali metal manganese pnictides by Bronger et al.[14] and Muller et al.[15] .

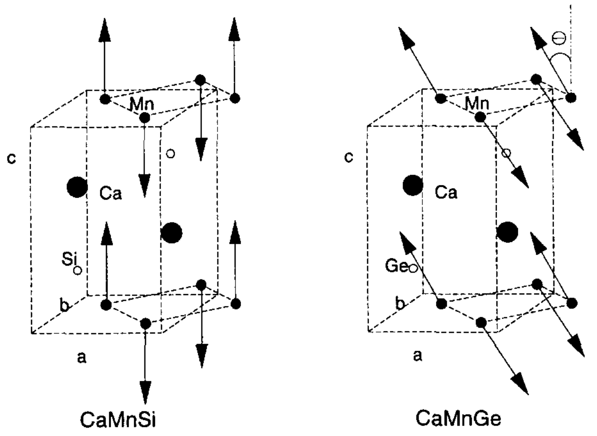
For CaMnSi, the best refinement lead to Mn moments aligned along the c-axis with a magnitude of 1.96(1) and 3.27(4) μ_B at 300 and 2K respectively, while in CaMnGe, they make an angle of about 30° with the stacking axis, the moment values being 2.43(5) and 3.34(3) μ_B at 300 and 2K. The magnetic structures are drawn on figure 2. They consist of stacked antiferromagnetic (001) Mn layers, the manganese moment being ferromagnetically coupled with their direct neighbours located in adjacent planes along the c-axis.

The thermal variation of the intensity of the (100) line gives Néel temperatures of 360(5) and 420(5) K for CaMnSi and CaMnGe, respectively (Fig.3).

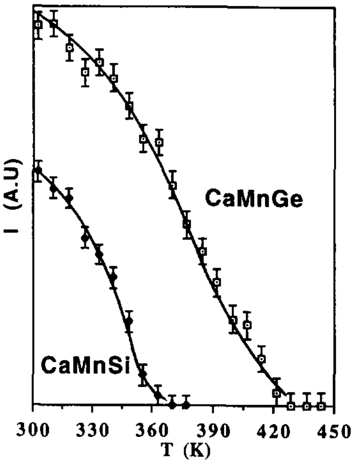
Tables II and III give the observed and calculated intensities together with the lattice constants and the various adjustable parameters at 300 and 2 K.



1- Neutron diffraction patterns of CaMnSi at 400, 300 and 2 K.



2- Magnetic structures of CaMnSi and CaMnGe.



3- Temperature dependence of the (100) line integrated intensity in CaMnSi and CaMnGe.

TABLE III : Observed and calculated intensities and refined parameters at 300 and 2 K in CaMnGe.

	300K		2K	
h k l	I_c	I_o	I_c	I_o
0 0 1	28.9	28.2(6)	27.8	27.6(4)
1 0 0	86.0	86(2)	156.6	157(2)
1 0 1	205.0	205(3)	309.7	310(3)
0 0 2	289.8	289(3)	287.0	287(3)
1 1 0	778.0	777(5)	801.1	800(5)
1 0 2 1 1 1	267.8	240(7)	277.8	310(11)
0 0 3	5.7	-	3.6	-
1 1 2	294.1	297(8)	321.3	321(11)
2 0 0	231.0	251(11)	237.9	234(10)
2 0 1	118.8	106(9)	123.3	132(9)
1 0 3	227.7	220(14)	234.2	247(15)
a(Å)	4.242(3)		4.227(2)	
c(Å)	7.23(1)		7.201(6)	
f_{cor}	1.02(1)		1.04(1)	
z_{Ge}	0.231(2)		0.235(1)	
z_{Ca}	0.684(2)		0.690(1)	
μ_{Mn} (μ_B)	2.43(5)		3.34(3)	
θ(°)	26(7)		34(3)	
R(%)	3.8		3.3	

3-Discussion

The main result of this study is the occurrence in both compounds of an antiferromagnetic ordering on the Mn sublattice, which was not detetcted by magnetization measurements. As previously emphasized for the isotypic rare earth RMnX and RMn_2X_2 compounds, this study clearly confirms that a better understanding of the magnetic properties in this class of materials imperatively requires the use of the neutron diffraction technique.

The analysis of the magnetic properties of both CaMnSi and CaMnGe compounds nicely completes the conclusions drawn about the magnetic anisotropy and exchange interactions in the RMnX series.

With Mn-Mn intraspacings larger than 2.96 Å, these compounds clearly confirm that the sign of the Mn-Mn intralayer exchange parameter is sensitive to the Mn-Mn intralayer separation. Moreover, one observes purely antiferromagnetic (001) Mn planes in the whole ordered range and we have to conclude that, in contrast with the RMn_2X_2 compounds, the in-plane Mn-Mn exchange does not seem to be related to the valency of large metal (alkaline earth metal, rare earth metal) in the CeFeSi-type RMnX compounds. It should be noted that, according to their high values of Néel and (negative) Curie-Weiss temperatures, the CaMnGe and CaMnSi compounds exhibit the strongest antiferromagnetic interaction among the Mn spins in the basal plane, in each series. This could be related to peculiar c/a ratio observed in both compounds (Table 1). Lastly, the Mn moment value (greater in CaMnGe than in CaMnSi) is correlated with the Mn-X distance, a shorter value of the distance yielding a smaller value of the Mn moment, whereas the magnetic interactions between the Mn sublattices are stonger in the germanide than in the silicide, in spite of the larger unit cell of the former (Table I). These magnetic behaviours have been already observed in both RMnX and RMn_2X_2 families, and are largely discussed in ref. 1-2, 6-7.

Nevertheless, some differences between CaMnX and RMnX compounds have to be emphasized. Firstly, the interlayer interactions between nearest neighbours in adjacent Mn planes are antiferromagnetic in all the rare earth germanides, as well as in the PrMnSi and NdMnSi compounds (*yielding a doubling of the c-axis*)[1,2], whereas they are ferromagnetic in both Ca compounds. The distance-dependant oscillatory character of the RKKY interaction may probably explain the various types of interlayer coupling (Table I).

Secondly, the Mn sublattice exhibits an easy-axis character in the rare earth germanides while an easy plane prevails in the corresponding silicides. This result reflects the significant influence of the nature of the X atoms on the constant of anisotropy. The easy direction observed in the CaMnX compounds (along the c-axis or at 30° from this direction in CaMnSi and CaMnGe, respectively) appears therefore surprising. This phenomenon could be related to the valency of the calcium yielding a difference in the value of the conduction electron concentration between RMnX and CaMnX as described in section 1 (i.e. the electrostatic potentiel due to the environment of the Mn atom site).

Further investigations are now necessary to complete this study. The influence of the R valency will be checked by magnetization measurements and neutron diffraction experiments on solid solutions such as $La_xCa_{1-x}MnX$ or $La_xCa_yY_{1-x-y}MnX$, where y is related to the mean valency and x is chosen to keep the Mn-Mn spacings constant. Mn nuclear magnetic resonance experiments are also in progress.

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