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Neutron diffraction studies of $CaMn_2Ge_2$ and $BaMn_2Ge_2$ compounds: first examples of antiferromagnetic Mn planes in $ThCr_2Si_2$-type structure compounds

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Abstract

The magnetic properties of $ThCr_2Si_2$-type structure $CaMn_2Ge_2$ and $BaMn_2Ge_2$ compounds have been investigated by neutron diffraction experiments. In the whole temperature range studied (2–270 K), both compounds are purely collinear antiferromagnets (not detected by bulk magnetometric measurements) characterized by a stacking of antiferromagnetic (001) Mn planes. This peculiar Mn-sublattice magnetic behaviour seems to be related to the valency of the large metal. At 2 K, the total Mn moments are about 2.7 μ_B and 3.6 μ_B for $CaMn_2Ge_2$ and $BaMn_2Ge_2$, respectively. The results are compared with those of closely related RMnSi and RMnGe compounds and the isotypic alkali-metal manganese pnictides. The magnetic properties of the $ThCr_2Si_2$-type structure RMn_2X_2 ($X \equiv$ Si, Ge) compounds are discussed.

1. Introduction

$CaMn_2Ge_2$ and $BaMn_2Ge_2$ crystallize in the tetragonal $ThCr_2Si_2$-type structure (*I4/mmm*) [1]. In spite of the very exciting magnetic behaviour of the Mn sublattice in this class of pseudo-lamellar materials (for a long review, see ref. 2), their magnetic properties have never been studied.

Recently, neutron diffraction studies on rare-earth manganese silicides and germanides RMnSi(Ge) ($R \equiv$ La–Nd) have shown that most of these CeFeSi-type structure compounds are antiferromagnetic and characterized by antiferromagnetic (AF) Mn (001) planes [3, 4]. This result was rather surprising since the closely related $ThCr_2Si_2$ and $TbFeSi_2$-type structure compounds, *i.e.* $RMn_2Si(Ge)_2$ (for a review see ref. 2) and $RMnSi_2$ [5], were characterized by ferromagnetic (F) Mn planes. Furthermore, in these RMnSi(Ge) series, the ferri- or ferro-magnetic behaviour of GdMnSi [6] and YMnSi [7] has led us to point out that the Mn–Mn intralayer distance (d^a_{Mn-Mn}) would control the appearance of AF or F states in the (001) Mn planes. According to the antiferromagnetic behaviour of SmMnSi ($d^a_{Mn-Mn} = 2.86$ Å) and the ferrimagnetic behaviour of GdMnSi ($d^a_{Mn-Mn} = 2.84$ Å), the critical distance in the CeFeSi-type structure compounds seems to be about 2.85 Å. It is noteworthy that this criterion is fulfilled for all the isotypic alkali-metal manganese pnictides [8, 9].

Until now, all the magnetic structures of $ThCr_2Si_2$-type structure manganese silicides and germanides compounds have been said to be characterized by ferromagnetic (001) Mn planes, whatever the intralayer Mn–Mn spacing, *i.e.* $(d^a_{Mn-Mn})_{max.} = 2.97$ Å in $LaMn_2Ge_2$ [2]. In order to check whether a similar criterion would apply in this family (but with a greater value), we decided as a first step to study the magnetic properties of $BaMn_2Ge_2$, *i.e.* the largest unit cell of the family: $d^a_{Mn-Mn} = 3.15$ Å. Since antiferromagnetic (001) Mn–Mn layers were detected in this compound, we decided to complete this work by studying $CaMn_2Ge_2$ ($d^a_{Mn-Mn} = 2.93$ Å; *i.e.* smaller than in the ferromagnetic lanthanum compound) in order to determine whether the Mn–Mn intralayer spacing or the valency of the alkaline-earth element is responsible for this unusual behaviour.

In this paper, we report on a study of the magnetic structures of $BaMn_2Ge_2$ and $CaMn_2Ge_2$ compounds by neutron diffraction experiments.

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2. Experimental procedures

The compounds were prepared from commercially available high-purity elements. Pellets of stoichiometric mixture were compacted into a glove box, using a steel die, and then introduced into silica tubes sealed under argon (100 mmHg). The samples were first heated at 1073 K for preliminary homogenization treatment and then melted in an induction furnace. Purity of the final product was checked by powder X-ray diffraction (Guinier Cu Kα).

The magnetic measurements were carried out on a Faraday balance (between 300 and 800 K) and on a MANICS magneto-susceptometer (between 4.2 and 300 K), in fields up to 1.5 T.

Neutron diffraction experiments were carried out at the Siloe Reactor of the Centre d'Etude Nucléaire de Grenoble. Several patterns were collected in the temperature range 2–270 K with the one-dimension curved multidetector DN5 ($\lambda = 2.4895$ Å). Long-duration patterns were recorded at 2 K. In order to correct for texture effects, following a procedure described in ref. 10, we used during the refinements a fitted coefficient (r_{cor}) which reflects the importance of preferential orientation. The values of r_{cor} obtained (see below) strongly support the validity of this correction.

Using the scattering lengths $b_{Ge} = 8.185$ fm, $b_{Mn} = -3.73$ fm, $b_{Ba} = 5.07$ fm and $b_{Ca} = 4.70$ fm and the form factor of Mn from ref. 11, the scaling factor, the z_{Ge} atomic positions, r_{cor} and the Mn magnetic moments were refined by the MiXeD crystallographic executive for diffraction (MXD) least-squares fitting procedure [12]. The MXD program allows simultaneous fitting of the calculated nuclear and magnetic intensities to the observed ones.

In the $ThCr_2Si_2$-type structure (space group: *I4/mmm*), the rare-earth and germanium atoms occupy the 2(a) (0, 0, 0) and 4(e) (0, 0, z) with $z \approx 0.38$ sites, respectively. The manganese atoms occupy the special position 4(d) (0, 1/2, 1/4) with an additional *C* translation mode. Thus, it is important to stress that the magnetic contributions to the observed intensities, due to a ferromagnetic ordering of the Mn sublattice, affect only the nuclear lines obeying the limiting reflection condition: (*hkl*) with $h+k=2n$. On the other hand, in each case, attempts made to fit the nuclear lines by interchanging the position of the Mn and Ge atoms always led to a poorer agreement and gave no evidence for

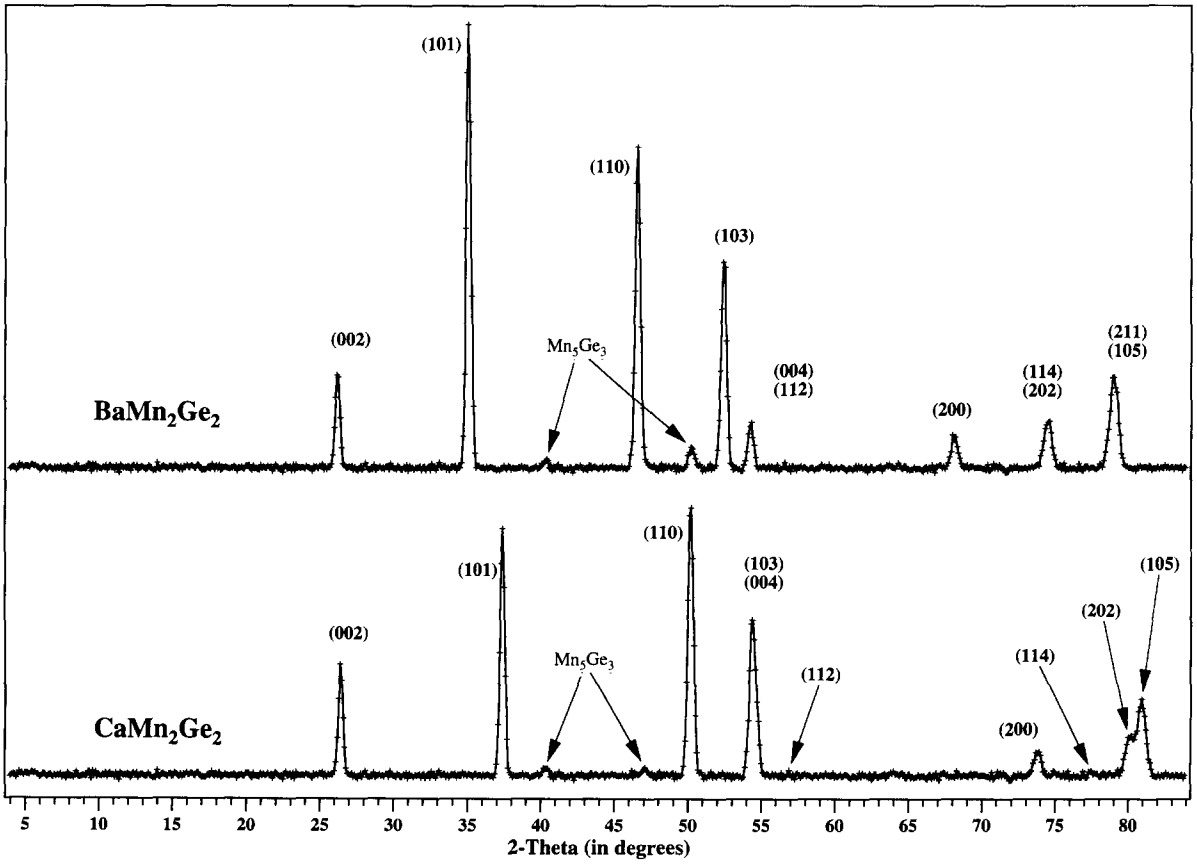

Fig. 1. Neutron diffraction patterns of $CaMn_2Ge_2$ and $BaMn_2Ge_2$ at 2 K.

any mixing between Mn and Ge atoms in 4d and 4e sites.

3. Magnetic measurement

As observed in the previously studied AMnX pnictides [8, 9], the present compounds do not exhibit any magnetic transition in the whole temperature range studied (4.2–800 K). Nevertheless, it is noteworthy that very small anomalies are detected at 465 K and 546 K for the barium and calcium compounds, respectively. The occurrence of small amounts of ferromagnetic Mn_5Ge_3 impurity prevents an accurate study of the paramagnetic state.

4. Neutron diffraction study

The neutron diffraction patterns of both compounds (Fig. 1) are similar over the whole temperature range studied (2–270 K).

They are characterized by an increase of only those nuclear lines which obey the rule (hkl) with $h+k=2n+1$. This is particularly obvious for the (101) line, for which the observed intensity is much greater than the purely nuclear calculated intensity. This result indicates an anti-C ordering, giving evidence of an antiferromagnetic arrangement of the Mn moments within the (001) planes. The best refinements lead to moments aligned along the c-axis and give Mn moment values of 2.67(5) μ_B and 3.66(3) μ_B for $CaMn_2Ge_2$ and $BaMn_2Ge_2$, respectively (Tables 1 and 2). The magnetic structure is drawn in Fig. 2. It consists of a stacking of antiferromagnetic (001) Mn layers, the manganese moments being antiferromagnetically coupled with their direct neighbours situated in each adjacent plane along the c-axis, in agreement with the remaining I translation mode (Tables 1 and 2). It is noteworthy that this magnetic behaviour is not detected in the bulk susceptibility measurements. Therefore, a neutron diffraction study, above room temperature, would be necessary to determine the corresponding Néel temperatures.

Tables 1 and 2 give, in each case, the observed and calculated intensities together with the lattice constants and the various adjustable parameters at 270 and 2 K.

TABLE 1. Calculated and observed intensities, lattice constants and adjustable parameters in $BaMn_2Ge_2$ at 270 and 2 K

$h\ k\ l$	2 K		270 K	
	I_c	I_o	I_c	I_o
0 0 2	19.7	20(1)	19.5	20(1)
1 0 1	143.9	144(2)	146.0	146(2)
1 1 0	200.0	201(4)	210.8	212(4)
1 0 3	157.0	156(3)	159.9	160(4)
0 0 4				
1 1 2	40.4	41(2)	40.5	37(3)
2 0 0	46.2	48(6)	48.7	45(6)
1 1 4				
2 0 2	88.5	78(8)	91.7	87(8)
2 1 1				
1 0 5	311.9	290(3)	321.8	299(12)
a (Å)	4.444(6)		4.473(5)	
c (Å)	10.91(1)		10.98(1)	
z_{Ge}	0.3782(7)		0.3778(8)	
r_{cor}	1.014(6)		1.026(7)	
μ_{Mn}	3.66(3)		3.60(4)	
R (%)	5.7		5.8	

TABLE 2. Calculated and observed intensities, lattice constants and adjustable parameters in $CaMn_2Ge_2$ at 270 and 2 K

$h\ k\ l$	2 K		270 K	
	I_c	I_o	I_c	I_o
0 0 2	131	134(2)	129	131(1)
1 0 1	648	649(4)	597	598(4)
1 1 0	1447	1466(9)	1378	1389(7)
1 0 3				
0 0 4	1071	1051(12)	1189	1117(17)
1 1 2	5		12	
2 0 0	326	285(11)	311	273(15)
1 1 4	47	60(8)	54	56(9)
2 0 2	635	560(14)	553	488(19)
1 0 5	1039	1048(19)	989	907(23)
a (Å)	4.146(2)		4.153(2)	
c (Å)	10.827(5)		10.864(4)	
z_{Ge}	0.382(1)		0.379(2)	
r_{cor}	1.05(1)		1.02(1)	
μ_{Mn}	2.67(5)		2.60(5)	
R (%)	4.0		6.2	

5. Discussion

The occurrence of antiferromagnetic Mn layers in $CaMn_2Ge_2$ and $BaMn_2Ge_2$ compounds indicates that this peculiar Mn-sublattice magnetic ordering previously encountered in the RMnSi [3] series and in the AMnX alkali-metal manganese pnictides [8, 9] is not a particular feature of the CeFeSi type of structure.

In the $ThCr_2Si_2$-type manganese compounds, the rare-earth compounds are always characterized by ferromagnetic Mn planes [2] whereas with alkaline-earth compounds (this work), antiferromagnetic planes occur. According to the closer Mn–Mn spacing in $CaMn_2Ge_2$ than in $LaMn_2Ge_2$, which was claimed to be purely ferromagnetic [2, 13–17], we have to conclude that, within the $ThCr_2Si_2$-type compounds, the sign of the in-plane Mn–Mn exchange integral seems to be related

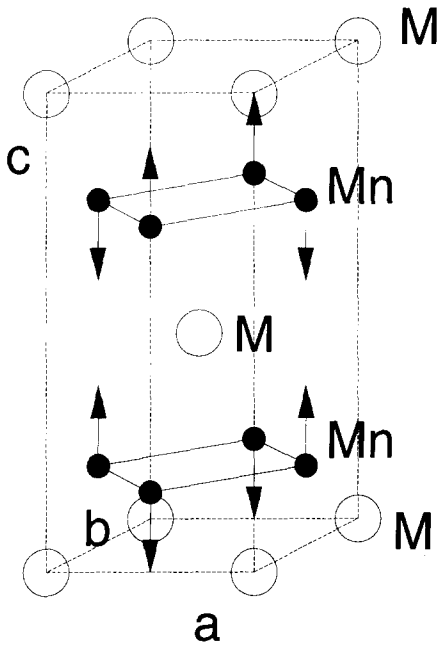

Fig. 2. Magnetic structure of MMn_2Ge_2 at 2 K (M≡Ca, Ba).

to the valency of the large metal (alkaline-earth metal, rare-earth metal or actinide). Under these conditions, it is noteworthy that in $EuMn_2Ge_2$ the europium is in the +2 valency state according to ^{151}Eu Mössbauer spectroscopy [18], and only small magnetization (2 emu g^{-1}) was observed by Felner and Nowik [18]. This fact is then consistent with a possible occurrence of antiferromagnetic (001) Mn layers in this +2 compound.

The second result concerns the values of the Mn moments in $CaMn_2Ge_2$ (2.67(5) μ_B) and $BaMn_2Ge_2$ (3.66(3) μ_B). These values are significantly higher than normally observed in the $ThCr_2Si_2$-type compounds (1.5 μ_B in $LaMn_2Si(Ge)_2$ to 2.1 μ_B in $NdMn_2Si_2$). Similar effects are observed in the equiatomic RMnX (R = alkaline and rare earths, X = elements of groups 15 and 16) [3, 4, 8, 9]. This behaviour has been discussed at length in refs. 3 and 9. It was shown that the values of the moments have to be correlated with the Mn–X distances and with the nature of this bond. It is noteworthy that the same explanation [3] holds in both $CaMn_2Ge_2$ and $BaMn_2Ge_2$.

6. Conclusion

The determination of the magnetic properties of $CaMn_2Ge_2$ and $BaMn_2Ge_2$ provides new information on the magnetic interactions in rare-earth manganese silicides and germanides and enables comparisons to be made with the closely related CeFeSi-type RMnX compounds. Both compounds are purely antiferromagnet down to 2 K. They are characterized by strongly coupled antiferromagnetic (001) Mn layers since no magnetic transitions are detected by magnetometric measurement. Comparison with the previously published magnetic properties of the isotypic rare-earth manganese germanides and silicides indicates that valency effects influence the Mn–Mn exchange.

However, in view of the unusual reduced Mn moments (1.5 μ_B), deduced from magnetization measurements in the ferromagnetic RMn_2Ge_2 and $LaMn_2Si_2$ compounds, it clearly appeared necessary to check the magnetic structures of these compounds by neutron diffraction experiments. Such a study has been done and the surprising conclusions will be reported elsewhere [19].

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