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Ternary compounds $REMSb_2$, RE ≡ La, Ce, Pr, Nd, Sm, Gd; M ≡ Mn, Zn, Cd; compound formation, crystal structure and magnetism

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Abstract

Ternary compounds $REMnSb_2$ (RE ≡ La, Ce, Pr, Nd, Sm), $REZnSb_2$ (RE = La, Ce, Pr, Nd, Sm, Gd) and $RECdSb_2$ (RE = La, Ce, Pr, Nd, Sm) were synthesized. From room temperature X-ray powder diffractometry all compounds were found to crystallize with the $ZrCuSi_2$-type structure. The magnetic behavior of $REMnSb_2$ compounds is characterized by the onset of ferromagnetism of the Mn sublattice in the temperature range between 100 and 520 K. Ordering of the rare-earth sublattice below 50 K is indicated for samples containing Ce, Pr and Nd. $CeZnSb_2$ remains paramagnetic in the temperature range investigated (4.2–550 K).

Keywords: Crystal structure; Compound formation; Magnetism; X-ray powder diffraction

1. Introduction

Since the discovery of the Heusler alloy Cu_2MnAl, interest in ferromagnetic Mn-based alloys has triggered a series of investigations. This is particularly true for crystal structures with interatomic Mn–Mn distances large enough to enable ferromagnetic Mn–Mn interactions. Ternary combinations with p-metal components such as Sb and Bi seem to stabilize phases whose crystal structures are closely related to the Heusler type. Recent investigations of the phase relations in the {Ce, Nd}–Mn–Sb ternary prompted the formation of an $REMSb_2$ phase [1], which seemed to be isotypic with the homologs $LaMn_{1-x}Sb_2$ and $LaZn_{1-x}Sb_2$ found earlier [2] to crystallize with the $ZrCuSi_2$-type structure. However, no information has hitherto been obtained about the magnetic behavior of these compounds. Thus we undertook a detailed inspection of the formation, structural chemistry and magnetism of ternary compounds $REMSb_2$, with M ≡ Mn, Zn, Cd.

2. Experimental

The alloys, each with a total weight of 0.5–1 g, were synthesized in two different ways starting from a nominal composition $RE_{25}M_{25}Sb_{50}$ (in at.%). The starting materials were used in form of freshly prepared fine filings from ingots of the rare earth metals (99.9 mass% from Auer-Remy GmbH, Germany) and platelets of Mn (99.9 mass%, Alfa-Ventron, Karlsruhe, Germany) which were surface cleaned in dilute HNO_3 prior to use. Sb, Zn and Cd were used in the form of fine powders as supplied by Johnson & Matthey, UK (99.9 mass%). Mn-containing samples were prepared by argon arc melting ingots of the elements under an electric current as low as possible to minimize Mn losses by evaporation while melting. To some extent these losses were compensated by adding extra Mn beforehand. For annealing, the buttons were sealed in evacuated silica capsules and treated at 550–800 °C for 350 h. In this way homogeneous specimens were obtained even after repeated melting and maximal deviations by weight were less than 1.5 mass%. Owing to exceedingly high vapor losses, the arc melting technique proved unsuitable for preparation of the Zn and Cd containing compounds. These materials were therefore obtained via powder metallurgical reaction sintering of blends of Zn(Cd), Sb-powders and fine filings of the rare earth metals. The thoroughly mixed blends were cold compacted in steel dies without the use of lubricants and were then sealed in evacuated silica capsules. After slowly heating to about 600 °C for a first reaction, the hard sintered pellets were reground under C_6H_{12} and recompacted for final heat treatment in a thyristor controlled wire wound furnace at 550–600 °C for 350 h and finally quenched by submerging the silica tubes in cold water.

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Table 1
Crystallographic and magnetic data of ternary compounds $REMSb_2$ ($M \equiv Mn, Zn, Cd$); structure type $ZrCuSi_2$; space group $P4/nmm$, No. 129, origin at centre, $Z=2$

Compound	Heat treatment (°C)	Lattice parameters (nm) a	c	c/a	V (nm^3)	T_C (K)	σ (μ_a)	θ_p (K)	$\mu_{eff/f.u}$ (μ_B)	$\mu_{eff/Mn}$ (μ_B)	Ref.
$LaMnSb_2$**	600	0.42587(9)	1.0960(4)	2.5144	0.2082(1)						*
$LaMn_{0.87}Sb_2$	800	0.43657(4)	1.0924(3)	2.5024	0.2082(1)	~310	0.8 [a]	228	4.6	4.6	*
$LaMn_{0.76}Sb_2$		0.4372(3)	1.0933(5)	2.501	0.2090						[2]
$LaMn_{0.65}Sb_2$		0.4387(3)	1.0780(5)	2.457	0.2075						[2]
$CeMnSb_2$**	600	0.43371(4)	1.0799(3)	2.4898	0.2031(1)						*
$CeMn_{0.85}Sb_2$	800	0.43439(5)	1.0756(3)	2.4761	0.2029(1)	~130	1.2 [b]	104	4.8	4.3	*
$CeMn_{0.7}Sb_2$**	600	0.43564(5)	1.0675(5)	2.4505	0.2026(1)						*
$PrMn_{0.82}Sb_2$**	800	0.43362(5)	1.0628(3)	2.4512	0.1998(1)	~390	1.0 [b]				*
$NdMn_{0.83}Sb_2$	800	0.43097(4)	1.0672(2)	2.4764	0.1982(1)	~250	0.6 [b]	225	5.5	4.5	*
$SmMn_{0.90}Sb_2$**	800	0.42899(4)	1.0569(2)	2.4637	0.1945(1)	~520	0.4 [a]				*
$LaZn_{0.52}Sb_2$		0.4380(3)	1.0488(5)	2.395	0.2012						[2]
$CeZn_{1-x}Sb_2$	600	0.43605(5)	1.0409(3)	2.3871	0.1979(1)	–		−11	2.6	–	*
$PrZn_{1-x}Sb_2$**	600	0.43398(5)	1.0373(2)	2.3902	0.1953(1)						*
$NdZn_{1-x}Sb_2$**	600	0.43296(6)	1.0330(3)	2.3859	0.1936(1)						*
$SmZn_{1-x}Sb_2$**	600	0.42997(3)	1.0272(2)	2.3889	0.1899(1)						*
$GdZn_{1-x}Sb_2$**	600	0.42838(7)	1.0242(3)	2.3908	0.1879(1)						*
$LaCdSb_2$**	600	0.44048(7)	1.0991(5)	2.4953	0.2132(1)						*
$CeCdSb_2$**	600	0.43751(7)	1.0900(2)	2.4913	0.2086(1)						*
$PrCdSb_2$**	550	0.43574(7)	1.0864(6)	2.4932	0.2063(1)						*
$NdCdSb_2$**	600	0.43454(10)	1.0827(5)	2.4918	0.2044(1)						*
$SmCdSb_2$**	600	0.43301(9)	1.0782(5)	2.4900	0.2021(1)						*

* This work.
** Multiphase samples.
[a] $T=5$ K, $H=2$ Tesla.
[b] $T=5$ K, $H=3$ Tesla.

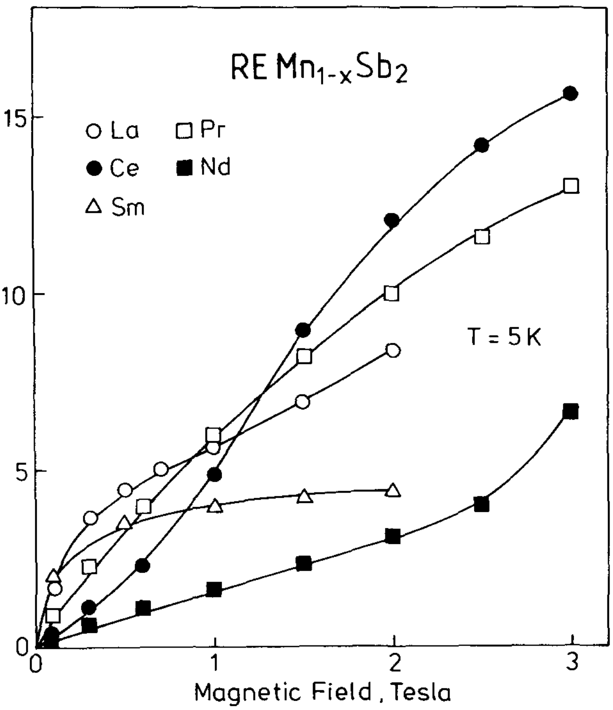

Fig. 1. Magnetization vs. magnetic field for $REMnSb_2$ at $T = 5$ K.

Some technical details on the duration and temperature of the homogenizing anneal of the alloys prior to quenching the capsules in water are given in Table 1. For further details on sample preparation, on the X-ray powder techniques employed for structural characterization as well as on the equipment and type of magnetic measurements performed, the reader is kindly referred to our recent publications on these or related series of compounds [3,4]. Owing to the sensitivity of the samples with respect to moisture, handling of the specimens is recommended in argon-controlled glove box systems.

The magnetic susceptibilities were measured using a Faraday-pendulum magnetometer SUS-10 above liquid nitrogen temperature up to 550 K and in external fields varying from 0.1 to 1.3 T. For temperatures below 100 K down to liquid He temperature a Lakeshore a.c. susceptometer (a.c. field 1 mT, 133.3 Hz) and a SQUID (SHE) magnetometer in fields up to 3 T were employed.

3. Results and discussion

3.1. Compound formation and structural chemistry

Room temperature X-ray powder patterns of the alloy specimens of RE{Mn,Zn,Cd}Sb_2 which had been annealed for 300 h revealed close resemblance to the X-ray intensity patterns of the homologous Sb-containing compounds RE{Fe,Co,Ni,Cu,Pd,Ag,Au}Sb_2 [2–5] and were indexed completely on the basis of a primitive tetragonal unit cell (Table 1). Using the atom parameter set obtained from a single-crystal X-ray intensity refinement of $CeAgSb_2$ [5], excellent agreement is found between the experimentally observed and calculated X-ray powder intensities, confirming isotypism with the crystal structure of $ZrCuSi_2$. Metal deficiencies were found in the Mn and Zn containing alloys $REM_{1-x}Sb_2$, which were usually around $0.15 \leqslant x \leqslant 0.4$ (see Table 1).

3.2. Magnetism

The magnetic behavior of the ternary compounds $REMnSb_2$ (RE ≡ La, Ce, Pr, Nd, Sm) as well as $CeZnSb_2$ is

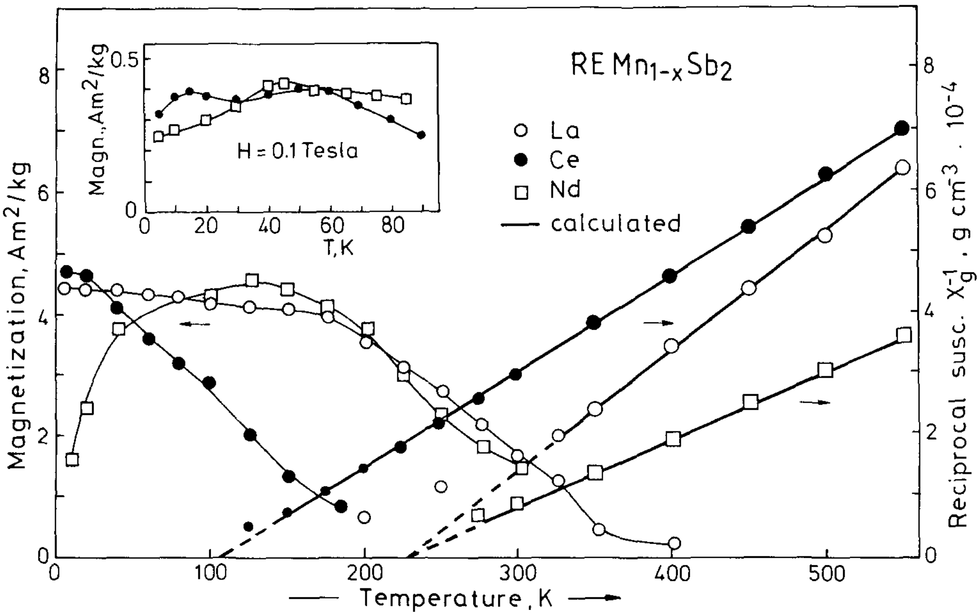

Fig. 2. Inverse susceptibility and magnetization vs. temperature of $LaMnSb_2$ ($H = 0.5$ T) and (Ce,Nd)$MnSb_2$ ($H = 1$ T). The inset shows mangetization vs. temperature of (Ce,Nd) $MnSb_2$ at $H = 0.1$ T.

summarized in Figs. 1, 2 and Table 1. The Mn-containing compounds in general exhibit a weak ferromagnetic ordering of the Mn sublattice at various temperatures between 100 K and 520 K respectively. From isothermal magnetization data at 5 K (see Fig. 1) the magnetic structure of the series of compounds is concluded to be rather complex (metamagnetism). Furthermore, for the Ce and Nd ternaries we observe additional peaks at $T \approx 15$ K and $T \approx 45$ K (inset Fig. 2) in the magnetization vs. temperature curve under an external field $H = 0.1$ T, indicating a second magnetic transition owing to a spin alignment within the rare-earth sublattices. In the paramagnetic region an effective paramagnetic moment per formula unit was calculated using the modified Curie–Weiss law

$$\chi = \frac{c}{T - \Theta_P} + \chi_0$$

For $LaMn_{0.87}Sb_2$ an Mn moment of 4.6 μ_B was calculated. Similar values were obtained for the magnetic rare-earth atoms (Ce, Nd) assuming a tripositive groundstate and applying the formula $\mu_{eff/fu} = (\mu^2_{RE} + p_i \mu^2_{Mn})^{1/2}$. Thus the groundstate configuration for the Mn atom is Mn^{3+}. Analyses of magnetic data of the compounds $(Pr,Sm)Mn_{1-x}Sb_2$ are considered less reliable owing to their multiphase composition.

Although a negative paramagnetic Curie temperature was revealed for $CeZn_{1-x}Sb_2$ no onset of magnetic order of the rare-earth sublattice was found as observed earlier in related compounds $REMSb_2$, where M ≡ Ni, Pd, Cu, Au [4]. The value of the paramagnetic moment agrees well with the theoretical free ion moment $Ce^{3+} - {}^2F_{5/2}$.

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