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EFFECT OF MANGANESE ON MAGNETIC AND ELECTRICAL PROPERTIES OF THE $\text{RMn}_x\text{T}_{12-x}$ ALLOYS

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Devoted to memory of late E. Leyarovsky

The magnetic and electrical properties of the tetragonal, ThMn_{12} -type $\text{RMn}_x\text{T}_{12-x}$ alloys ($R = \text{Y, Ce, Pr, Nd, Sm}$ and $T = \text{Fe, Co, Ni}$) were studied in broad temperature and magnetic field ranges to elucidate an influence of manganese on the magnetic ordering in these materials. Magnetic properties were examined at $T = 1.7\text{--}300$ K in magnetic field up to 14 T, whereas the electrical properties were examined at $T = 4.2\text{--}300$ K, on the polycrystalline samples. Majority of the samples exhibit ferro- or ferrimagnetic properties. Some samples containing larger concentration of Mn are paramagnetic in the whole temperature range. The electrical resistivity of these alloys shows metallic character.

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1. Introduction

The magnetic properties of the ThMn_{12} -type f -electron tetragonal ternaries containing rare earths and $3d$ transition metals are of special interest because of their potential applications as permanent magnets (for review see [1]). Only very few binary compounds of this type are known but there is plenty of ternaries obtained with the p electron elements (Si, Al), early $3d$ (Ti, V, Cr, Mn), $4d$ (Zr, Nb, Mo) or $5d$ (Ta, W, Re) metals as stabilizing components. However, compounds with Mn reported for Fe as transition element and in principle for heavier rare earths are not very popular [2–5]. A paper concerning RCo_8Mn_4 compounds in

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which besides the heavier rare earths Pr and Y were used as R elements provides unique results for Co as transition element [6]. All these materials crystallize in the tetragonal ThMn_{12} -type structure ($I4/mmm$ space group) in which the 2a site is occupied by rare earth atoms and 3d atoms are located in the 8f, 8i, and 8j positions.

For $\text{YMn}_{12-x}\text{Fe}_x$ alloys the single phase samples were found for $0 \leq x \leq 6.7$, and for $x = 4$ no long-range magnetic order was detected above 77 K [2].

The $\text{RMn}_{12-x}\text{Fe}_x$ alloys with R = Gd, Tb, Dy, and Ho exist as the single phase for $x \leq 8$. It is shown that the Néel temperature is almost independent of R and has a maximum at about $x = 5$ [3] or 6 [4]. For $\text{ErMn}_{12-x}\text{Fe}_x$ alloys [4] at low temperature ferromagnetism is observed on Er atoms and the maximum T_C is detected for $x = 4$. Abad et al. [5] claim that in the $\text{RMn}_{12-x}\text{Fe}_x$ (where R = Tb, Y) there are positive interactions for Fe and negative for Mn sublattices. Wang et al. [6] have reported that among the RCo_8Mn_4 alloys (R = Y, Pr, Gd, Tb, Dy) the compounds of Y, Pr, and Gd are ferromagnetic whereas the compounds of Tb and Dy are considered as the ferrimagnetic with two magnetic sublattices.

At present, the compounds of light rare earths with Fe, Co, and Ni are reported for the first time, except for PrCo_8Mn_4 [6].

The goals of the present paper are as follows: the search for magnetic materials with favourable parameters for application, and the elucidation of the influence of Mn on the magnetic ordering of these materials, particularly, the modification of the two-sublattice model (see e.g. [7]) by the third (Mn) 3d magnetic sublattice. The preliminary results of these investigations have been published recently [8].

2. Experimental

The $\text{RMn}_x\text{T}_{12-x}$ alloys were prepared as it had been described previously [8]. The magnetic measurements were performed on a bulk pieces of polycrystalline material. The magnetic properties were investigated in principle in the temperature range 1.7–300 K using a SQUID magnetometer technique in magnetic field of 0.5 T. Some samples have the magnetic transition temperature above room temperature (see Table). The magnetization was measured at $T = 1.7$ K in magnetic fields up to 5 T and at $T = 4.2$ K up to 14 T. The electrical resistivity was studied at $T = 4.2$ –300 K for polycrystalline samples of Y and Ce.

3. Results and discussion

All the investigated samples are a single phase, tetragonal ThMn_{12} -type, with the lattice parameters presented in [9]. This structure type has only one position for the *f* element (2a) but three positions available (8f, 8i, and 8j) for transition (3d) elements. The investigated samples form a variety of stoichiometric types, as it was also observed previously [2–5]. Most probably the reason for that is the close location of the contributing 3d elements in the periodic table. The absence of La compounds, observed also previously [3, 6], seems to indicate that the La atom is too large to be located in the ThMn_{12} -type crystal lattice. Due to the absence of

TABLE

Magnetic data of the $\text{RMn}_x\text{T}_{12-x}$ alloys.

Alloy	Magnetic order ?	Transition temp. T [K]	Saturation moment [μ_B /f.u.]	Effective moment [μ_B /f.u.]	θ [K]
$\text{YMn}_{5.1}\text{Fe}_{6.9}$	C	$T_{\max} \approx 48$	2.36	7.3	186.9
$\text{Y}_{1.3}\text{Mn}_{7.9}\text{Fe}_{3.8}$	C	$T_{\max} \approx 36$			
$\text{CeMn}_{4.96}\text{Fe}_{7.04}$	F	≈ 230	16.81		
CeMn_7Fe_5	C	$T_{\max} \approx 36$ $T_C \approx 100$		8.16	-43.1
$\text{CeMn}_{9.65}\text{Fe}_{2.35}$	P				
$\text{CeMn}_{4.16}\text{Co}_{7.84}$	C	$T_{\max} \approx 110$	4.08		
CeMn_5Co_7	AF	41			
$\text{CeMn}_{6.24}\text{Co}_{5.76}$	AF	4.5 $T_{\max} \approx 200$			
$\text{PrMn}_{5.6}\text{Fe}_{6.4}$	P			5.26	-3.7
$\text{PrMn}_{5.2}\text{Co}_{6.8}$	C	$T_{\max} = 53$	3.0	10	140
NdMn_4Co_8	F	≈ 400	6.87		
$\text{NdMn}_{8.4}\text{Co}_{3.6}$	P			3.44	7.5
$\text{SmMn}_{3.77}\text{Co}_{8.23}$	F	≈ 500	10.02		
$\text{SmMn}_{8.71}\text{Co}_{3.29}$	F	≈ 18	0.59		
$\text{SmMn}_{3.9}\text{Ni}_{8.1}$	F	$\approx 550-600$	9.1		

F — ferromagnetic, C — complex, AF — antiferromagnetic, P — paramagnetic.

La compounds, Y compounds provide the reference system for the compounds of the magnetic lanthanides. However, the Y-Mn ternaries have been obtained for Fe only, and the compound richest in Mn exhibits a complicated stoichiometry. It is a surprising result because a binary YMn_{12} compound was reported to exist with the interesting magnetic structure below $T_N = 120$ K [10]. Magnetic data of the $\text{RMn}_x\text{T}_{12-x}$ alloys are collected in Table and their temperature and field characteristics are shown in Figs. 1-7. One can see that the magnetic properties allow to classify these materials into a few groups. As it is seen from Table and Figs. 1, 2 and 3, $\text{CeMn}_{4.96}\text{Fe}_{7.04}$, NdMn_4Co_8 , $\text{SmMn}_{3.77}\text{Co}_{8.23}$, $\text{SmMn}_{8.71}\text{Co}_{3.29}$ and $\text{SmMn}_{3.9}\text{Ni}_{8.1}$ can be considered as ferromagnetic. Their common feature is the apparent saturation at low temperature (Fig. 1), however, with different values of saturation moment, the lowest one is for $\text{SmMn}_{8.71}\text{Co}_{3.29}$. This low saturation moment corresponds to the lowest Curie point, $T_C \approx 18$ K. Other Sm compounds and NdMn_4Co_8 exhibit the Curie point above room temperature but small remanence and not a very high saturation moment does not allow to consider them as magnetic materials for application. Moreover, the Ce and Nd compounds show

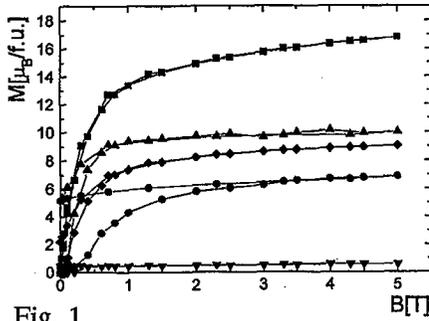


Fig. 1

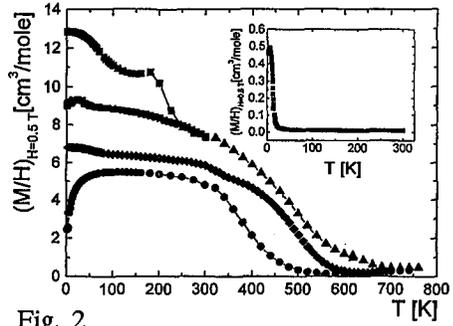


Fig. 2

Fig. 1. Magnetization, M , versus magnetic field B at $T = 1.7$ K for $\text{CeMn}_{4.96}\text{Fe}_{7.04}$ (squares), NdMn_4Co_8 (circles), $\text{SmMn}_{3.77}\text{Co}_{8.23}$ (triangles up), $\text{SmMn}_{8.71}\text{Co}_{3.29}$ (triangles down), and $\text{SmMn}_{3.9}\text{Ni}_{8.1}$ (diamonds).

Fig. 2. Initial susceptibility (M/H) measured at $B = 0.5$ T versus temperature for $\text{CeMn}_{4.96}\text{Fe}_{7.04}$ (squares), NdMn_4Co_8 (circles), $\text{SmMn}_{3.77}\text{Co}_{8.23}$ (triangles up), and $\text{SmMn}_{3.9}\text{Ni}_{8.1}$ (diamonds). Inset shows the results for $\text{SmMn}_{8.71}\text{Co}_{3.29}$.

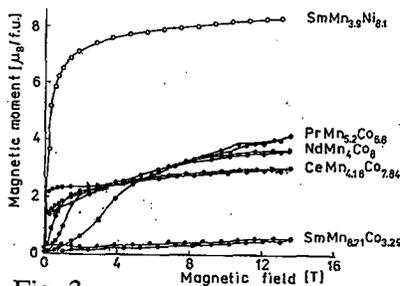


Fig. 3

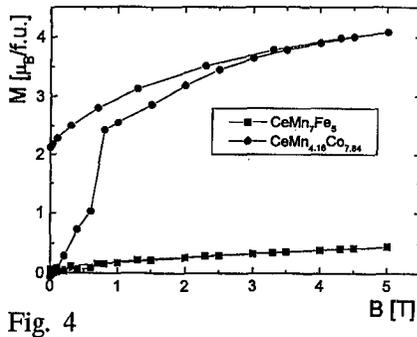


Fig. 4

Fig. 3. Magnetic moment per formula unit, M , versus magnetic field up to 14 T at $T = 4.2$ K.

Fig. 4. Magnetic moment per formula unit, M , versus magnetic field at $T = 1.7$ K.

complicated temperature dependence of the initial susceptibility (Fig. 2): the first compound exhibits two diffuse drops of the susceptibility, whereas the second one shows the initial increase in susceptibility at low temperature and then the decrease corresponding most probably to the Curie point. The initial increase can be related to the domain effects but also can result from the magnetic ordering more complex than simple ferromagnetic one. The similar (M/H) vs. T characteristics has been reported for the Pr compound [6]. The increase in the magnetic field up to 14 T at 4.2 K does not change substantially the data obtained for ferromagnetic NdMn_4Co_8 , $\text{SmMn}_{8.71}\text{Co}_{3.29}$ and $\text{SmMn}_{3.9}\text{Ni}_{8.1}$ at 1.7 K. For compounds with complex behavior (Fig. 3): $\text{CeMn}_{4.16}\text{Co}_{7.84}$ and $\text{PrMn}_{5.2}\text{Co}_{6.8}$ the ferromagnetic character of those materials is confirmed (see Fig. 4) in agreement with the results reported for PrMn_4Co_8 [6]. The temperature dependence of the

inverse susceptibility of $\text{PrMn}_{5.2}\text{Co}_{6.8}$ follows the Curie–Weiss law above about 150 K and for CeMn_7Fe_5 above 50 K (Fig. 5) whereas the magnetization of the last compound is very weakly field dependent at $T = 1.7$ K (Fig. 4). Both yttrium compounds $\text{YMn}_{5.1}\text{Fe}_{6.9}$ and $\text{Y}_{1.3}\text{Mn}_{7.9}\text{Fe}_{3.8}$ exhibit also complex magnetic behavior with maxima in temperature dependence of the magnetic susceptibility at low temperature (Table) and this observation does not contradict the result of [2]. The inverse magnetic susceptibility of $\text{YMn}_{5.1}\text{Fe}_{6.9}$ follows the Curie–Weiss law above 250 K but for three antiferromagnetic Ce compounds the Curie–Weiss law is not fulfilled (Table, Fig. 6). As it is seen from Fig. 7 their magnetization at 1.7 K is linear, weakly field dependent. Paramagnetic $\text{CeMn}_{9.65}\text{Fe}_{2.35}$ does not follow the Curie–Weiss law (Fig. 6) but $\text{PrMn}_{5.6}\text{Fe}_{6.4}$ exhibits such a behavior (Table, Fig. 5).

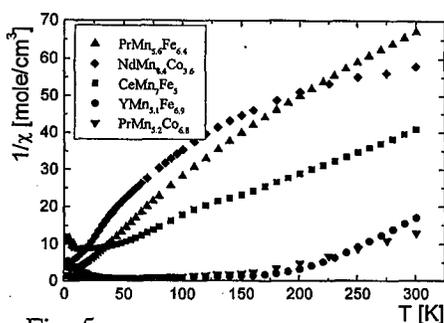


Fig. 5

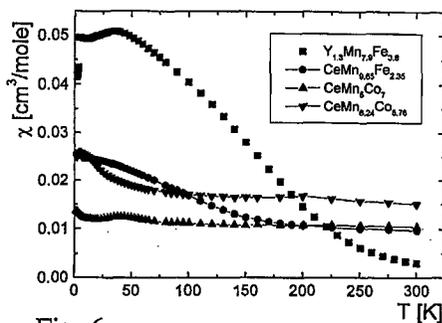
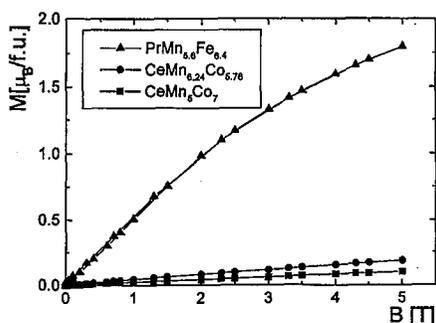


Fig. 6

Fig. 5. Inverse molar magnetic susceptibility, $1/\chi$, versus temperature, measured at $B = 0.5$ T.

Fig. 6. Molar magnetic susceptibility, χ , versus temperature, $T = 1.7$ –300 K, at $B = 0.5$ T.


 Fig. 7. Magnetic moment per formula unit, M , versus magnetic field at $T = 1.7$ K.

It is clear that an interpretation of these complex magnetic properties of $\text{RMn}_x\text{T}_{12-x}$ alloys is very difficult. The problem of the f – d interaction is under extensive investigation by theoreticians (see e.g. [11]). The magnetization depen-

dence on magnetic field for the $f-d$ materials has got satisfactory explanation in terms of the molecular field approximation but these models are set up for the two sublattice models [12], and in the $\text{RMn}_x\text{T}_{12-x}$ alloys there could be three magnetic sublattices. Probably, one can propose the following sequence of the magnitude of the exchange interactions J_{ij} : $J_{\text{TT}} > J_{\text{RT}} > J_{\text{RR}} > \pm J_{\text{RMn}} \sim J_{\text{MnMn}}$. However, to prove this statement, further experiments should be done, particularly neutron diffraction. This last experiment can provide also the answer concerning the transition element distribution on the individual crystallographic sites. For example, Abad et al. [5] propose, as mentioned above, competing interactions in $\text{TbMn}_x\text{Fe}_{12-x}$: positive for Fe (F) and negative for Mn (AF). They claim that when increasing the Fe content one observes an increase in ferromagnetic (F) interaction affecting strongly the $3d$ and $4f$ moments. The magnetic interactions between the $3d$ and Tb ions are considerably stronger than those between Tb ions, according to the scheme presented above. This feature is responsible for the gradual polarisation of the Tb magnetic moments when the temperature is lowered. As far as the distribution of the transition elements is concerned, a clear preference for the Fe atoms to populate the $8f$ sites is observed along the series, whereas Mn shows a very strong tendency towards the $8i$ sites. However, these conclusions can be justified for $\text{TbMn}_x\text{Fe}_{12-x}$ alloys only. There is also a question if magnetic ordering is set up in the Mn sublattice. It seems that the existence and a type of magnetic ordering in this sublattice depends critically on the Mn-Mn separation. Unfortunately, this question cannot be answered properly without neutron diffraction studies.

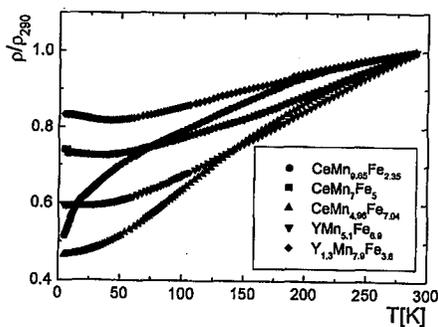


Fig. 8. Electrical resistivity normalized to room temperature value ρ/ρ_{290} versus temperature.

The electrical resistivity normalized to the room temperature value versus temperature for the Y and Ce alloys is shown in Fig. 8. Generally, the resistivity has a metallic character but except for $\text{CeMn}_{9.65}\text{Fe}_{2.35}$ (paramagnetic) other alloys at low temperature exhibit Kondo-like behavior.

4. Conclusions

1. Some of the $\text{RMn}_x\text{T}_{12-x}$ compounds exhibit the high Curie point and magnetization but rather minute remanence.

2. The presence of two magnetic 3d transition elements makes an interpretation very difficult.

3. Without the knowledge of the transition elements distribution in three crystallographic positions no conclusive interpretation of magnetic and electrical properties is possible.

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