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Magnetic properties of the $RMn_{12-x}T_x$ alloys in high magnetic field*

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The structure and magnetic properties of the tetragonal $ThMn_{12}$-type $RMn_{12-x}T_x$ alloys (R = Nd, Sm; T = Co, Ni) have been studied over a broad range of magnetic fields (up to 35 T). A high-pulsed magnetic field is applied at T = 4.2 K with the pulse duration of 10 ms. The $NdMn_{12-x}Ni_x$ system has been additionally investigated in the temperature range extended up to about 750 K. The ternaries exist in, approximately, the $4 \leq x \leq 8$ composition range. The alloys with $x \sim 4$ are frequently paramagnetic in a broad temperature range, whereas for other compositions, complex magnetic properties are observed. The results are discussed in relation to the free-ion values of the Nd and Sm ions.

Key words: *rare-earth intermetallics; magnetic properties; high magnetic field*

1. Introduction

Considerable attention has recently been paid to intermetallic compounds of rare-earth elements R and 3d magnetic transition metals T. because of a possibility of their application, e.g. due to their favourable magnetic properties, or as hydrogen accumulators. Compounds with the $ThMn_{12}$-type tetragonal structure (space group *I*4/*mmm*) belong to such materials. Alloys with nominal composition RNi_{12} or RCo_{12} do not exist, but can be stabilized by a partial substitution of Ni or Co by a transition metal with a lower valence-electron density, or the p-elements such as Si or Al (for review see Ref. [1]). In these ternary compounds, the R atoms occupy the 2a sites, whereas the 3d-transition elements occupy remaining 8f, 8i and 8j positions. In contrast to the mostly paramagnetic character

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of nickel-rich compounds, cobalt-rich compounds are usually ferro- or ferrimagnetic, whereas the parent RMn_{12} compounds exhibit non-collinear antiferromagnetic ordering at low temperature [2] if R is non-magnetic Y. The transition temperature of YMn_{12} has been confirmed by electrical measurements [3]. It is remarkable that different Mn sites with their different Mn moments, as reported in neutron diffraction (ND) experiments [2], do not appear in μSR spectra [4]. However, if R is a heavy rare-earth atom, ferrimagnetic properties are observed [5–7]. Consequently, a complex magnetic behaviour is expected to occur in $RMn_{12-x}T_x$ solid solutions as a result of competing ferro- and antiferromagnetic interactions. The magnetic and electrical properties of compounds with Fe as a transition element and with heavier rare earths or with Y and Nd are reported in Ref. [8–17] (and in references herein).

Brief information about selected Co compounds has been presented in [12, 14, 18], whereas a more systematic study of those intermetallics has been reported (for Nd and Sm) in [19]. In all the materials mentioned above, within a limited composition range, three magnetic sublattices exist (R, Mn and Co), while in the whole concentration range x, a magnetic ordering is observed at least in two sublattices (R and Co). Until now, only few papers have been published on ternaries containing Ni, which turned out to be non-magnetic in these alloys [20]. Particularly interesting is the case of $SmMn_{12-x}Ni_x$ compounds [21] for which the temperature dependence of the magnetic susceptibility exhibits a maximum at T ~60 K. The field dependence of magnetisation at low temperature and at relatively low field is in principle linear. These results suggest that the maximum corresponds to the onset of an antiferromagnetic ordering at the Sm sublattice, because it is not sensitive to the composition change, while both the Mn and Ni sublattices seem to be nonmagnetic. Our preliminary investigations of the $NdMn_{12-x}Ni_x$ system seemed to suggest that these materials are nonmagnetic [22]; however, in the light of present results, this conclusion is not quite correct.

For getting a better insight into properties of these interesting alloys, we report at present on high magnetic field measurements of the $(Nd, Sm)Mn_{12-x}(Co, Ni)_x$ systems.

2. Experimental

All the $RMn_{12-x}T_x$ alloys investigated have been prepared as has been described previously [23]. The magnetic susceptibility of $NdMn_{12-x}Ni_x$ has been investigated in the temperature range of 300–750 K, in the magnetic field of 0.5 T, using a SQUID magnetometer. The magnetisation has been measured in a pulsed magnetic field up to 35 T at T = 4.2 K, with a pulse duration of 10 ms.

3. Results and discussion

All the samples investigated, stable for R = Nd in the $4 \leq x \leq 6$ range and for R = Sm in the $4 \leq x \leq 8$ range, have been found to be in principle single-phase. Their

unit cell volumes decrease as the concentration of the transition metal x increases (see Fig. 1). Only $NdMn_6Ni_6$ is an exception from this trend.

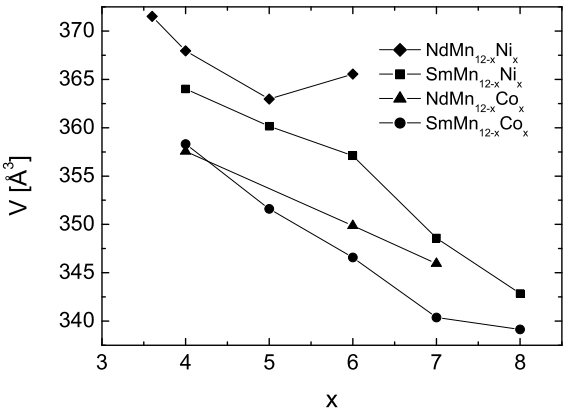

Fig. 1. Unit-cell volume V versus Co [19] and Ni [21, 22] concentration x for $NdMn_{12-x}Co_x$ (triangles), $SmMn_{12}$–Co_x (full circles), $NdMn_{12-x}Ni_x$ (diamonds) and $SmMn_{12-x}Ni_x$ (full squares)

Figure 2 shows the results of the high-field measurements of the magnetization M at $T = 4.2$ K for the $NdMn_{12-x}Co_x$ alloys. It is seen that the character of the $M(H)$ plots for all the samples is ferromagnetic, however, without a clear saturation, even for the highest magnetic fields. The result for the sample $x = 4$ suggests that the ferromagnetic contribution is field-induced (see Fig. 10 in [19]) and rather weak.

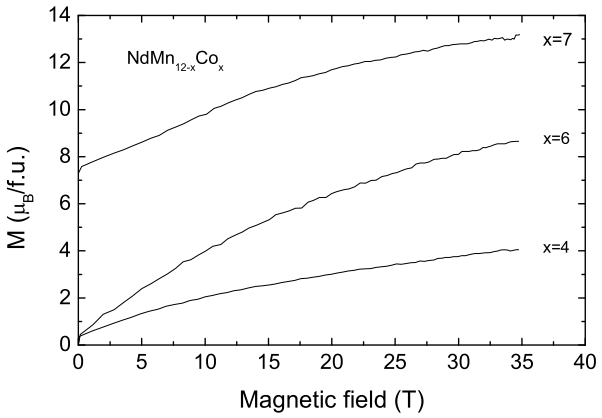

Fig. 2. Magnetization M versus magnetic field up to 35 T at 4.2 K for $NdMn_{12-x}Co_x$

As can be seen from Fig. 3, at $T = 4.2$ K and under high magnetic fields the $SmMn_{12-x}Co_x$ compounds have a character slightly different from those of the Nd compounds. The sample $x = 4$ is antiferromagnetic up to the highest field, but the

compound $x = 6$ exhibits some ferromagnetic contribution which is also seen in lower fields [19]. However, the values of magnetization are clearly lower than for the sample $x = 4$. The sample $x = 7$ is apparently strongly ferromagnetic, however, also without a saturation and, in turn, with a lower value of the saturation magnetic moment than the corresponding Nd sample. The lack of saturation may result from a considerable anisotropy which is indicated by a difference in the magnetization of powdered and bulk samples (see [19]).

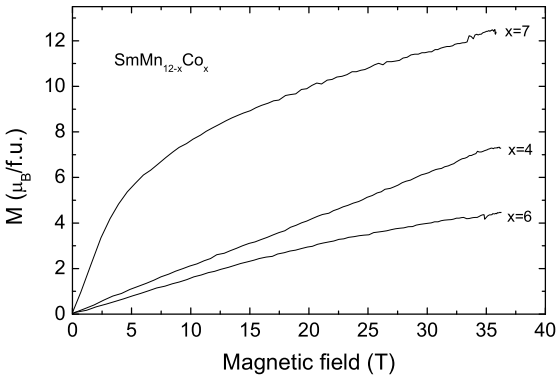

Fig. 3. Magnetization M versus magnetic field up to 35 T at 4.2 K for $SmMn_{12-x}Co_x$

Our previous results [22] indicate, as mentioned above, that the $NdMn_{12-x}Ni_x$ alloys are most probably paramagnetic below 300 K. To support this hypothesis, at present we extend the susceptibility measurements up to about 750 K. It is seen from Fig. 4 that the compounds with $x = 4$ and $x = 5$ exhibit weakly temperature-dependent paramagnetism, whereas $NdMn_6Ni_6$ shows a maximum of magnetic susceptibility at about 590 K, which can correspond to the Néel point.

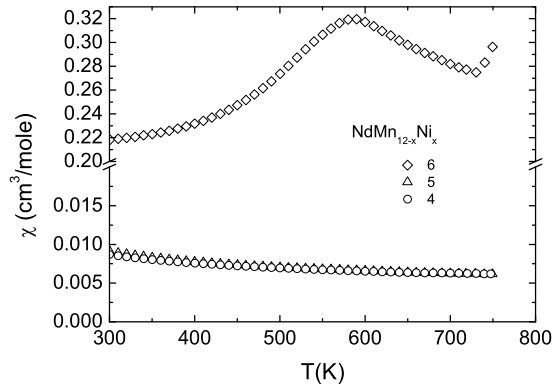

Fig. 4. Magnetic susceptibility χ versus temperature T from 300 to 750 K for $NdMn_6Ni_6$

Such a high ordering temperature is often observed in other Mn ternaries [24]. The increase of magnetic susceptibility above 720 K most probably follows the thermal decomposition of the material. In Figure 5, the magnetic field dependence of the magnetization is presented at $T = 4.2$ K for the latter material. For the sake of simplicity, only the results obtained for the polycrystalline sample are shown, because the results for the powder sample are very close to those shown in Fig. 5. This behaviour proves that there is a very small anisotropy in this material. It is seen that the $M(H)$ dependence exhibits an apparent approach to saturation which could be an indication of a metamagnetic transition, although it is difficult to determine precisely the critical field. One can estimate it to occur below about 15 T for both polycrystalline and powder samples. Therefore, we believe that magnetic ordering (AF) is responsible for the high-temperature anomaly.

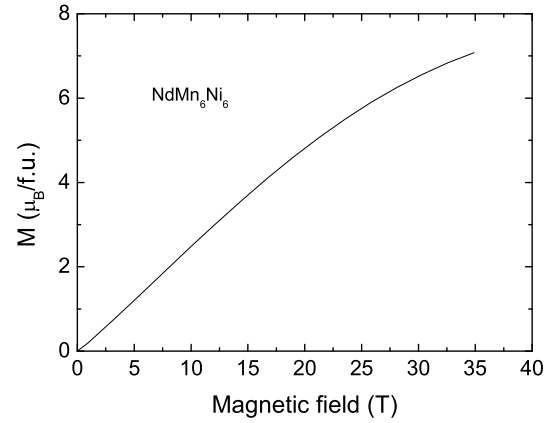

Fig. 5. Magnetization M versus magnetic field up to 35 T at 4.2 K for $NdMn_6Ni_6$

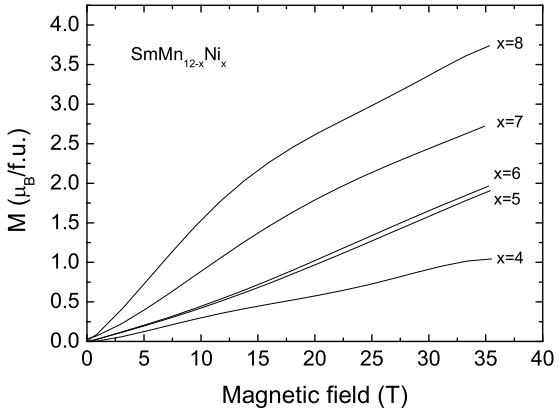

Fig. 6. Magnetization M versus magnetic field up to 35 T at 4.2 K for $SmMn_{12-x}Ni_x$

Previously reported linear character of the field dependence of the magnetization up to 5 T [21] for he $SmMn_{12-x}Ni_x$ system is in principle preserved in higher fields for the samples with x between 4 and 6 (see Fig. 6). However, for the sample $x = 7$ some tendency to saturation is observed above about 20 T, while for the sample $x = 8$, the same behaviour is seen, but the critical field seems to be lower, whereas the values of magnetization are larger. This observation does not contradict the conclusion of Ref. [21] that the magnetic ordering is due to the Sm sublattice only. For the samples with higher concentration of Ni ($x = 7$ and $x = 8$) magnetic field can induce a magnetic ordering in the transition metal sublattice even of a band metamagnetic type (see e.g., [25]). One should notice that for these two samples in magnetic field below about 10 T a tiny hysteresis is observed (see Figs. 3 and 4 [21]).

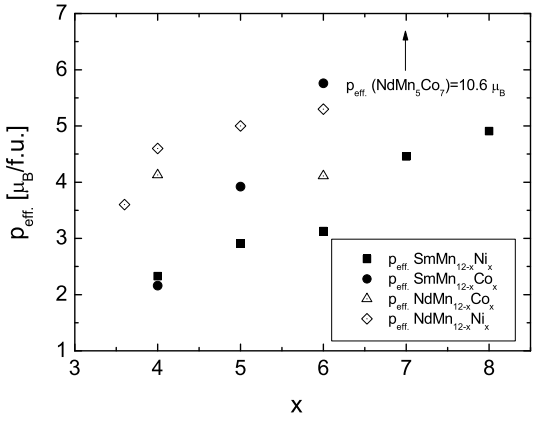

Fig. 7. Effective magnetic moments p_{eff}, versus concentration of transition element x. Note that effective magnetic moment for the $NdMn_5Co_7$ alloy is out of scale

As was mentioned above, we expected the high-field magnetization measurements performed on powdered samples to provide a basis for the consideration of the contribution of the transition elements to the magnetism. Unfortunately, the saturation moments cannot be determined in a direct way, because hardly any saturation is approached in the compounds investigated, even in rather high magnetic fields. In Fig. 7, the values of the effective magnetic moments p_{eff} are collected. Since a modified Curie–Weiss law is fulfilled in a rather narrow temperature range for all systems investigated, the values provided are rough estimates of the effective magnetic moments. For the comparison, we should recollect the values of the magnetic moment for free ions. For Nd they amount to 3.27 and $3.62\mu_B$ and for Sm to 0.71 and $0.85\mu_B$ for the saturation and effective magnetic moment, respectively. One can see that all experimental values are higher than those of free ions. Therefore, a contribution of the transition metal sublattices is expected. However, at present we are not able to say which transition element has a more substantial effect. These systems are

rather complex and hopefully a neutron diffraction experiment will provide the final explanation of their magnetic properties.

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