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Magnetic properties of $Tb_2Mn_{17}C_x$ compounds studied by magnetic measurements and neutron diffraction

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Abstract

Compounds of the type $Tb_2Mn_{17}C_x$ with $x = 0.9$, 1.8 and 2.7 were prepared by arc melting. The crystal structure of these compounds was studied by means of neutron diffraction. All these compounds were found to have crystallised in the hexagonal Th_2Ni_{17}-type structure. The refinement results of the neutron-powder-diffraction patterns show that the C atoms occupy exclusively the 6h site. Magnetic measurements made on these compounds show that they do not give rise to a well defined magnetic ordering transition at low temperatures. This is interpreted in terms of three different mechanisms that randomise the exchange interactions in these compounds and lead to spin-glass or cluster-glass behaviour.

Keywords: Terbium manganese compounds; Interstitial alloys; Ternary carbides; Crystal structure; Magnetic properties

1. Introduction

It has already been known for many decades that intermetallic compounds of the hexagonal Th_2Ni_{17} or the rhombohedral Th_2Zn_{17} types form when rare-earth elements R are combined with one of the transition metals Ni, Co or Fe. No such compounds form when rare earths are combined with Mn. However, Block and Jeitschko [1] showed that compounds of the 2:17 stoichiometry do form with manganese when comparatively small amounts of carbon are used as a stabilising element. From the structure determination presented by Block and Jeitschko it follows that the stabilising influence of the carbon atoms consists of filling of interstitial holes in the 2:17 structures. These interstitial holes are located close to the rare-earth atoms, giving the carbon an approximately octahedral coordination. Complete filling of these interstitial holes would lead to the formula composition $R_2Mn_{17}C_3$, a composition almost reached in the compound $Tb_2Mn_{17}C_{2.43}$ studied by Block and Jeitschko.

The compounds of the 2:17 type have attracted much attention recently because it also proved possible to realise interstitial-hole filling in the Fe-based compounds, either by normal casting [2] or via gas–solid reactions [3]. The advantage of the interstitially modified materials over the pure compounds is a strong enhancement of their Curie temperature and magnetocrystalline anisotropy. A review of the changes in properties due to interstitial hole filling and of the application of these materials as permanent magnets has been given by Fujii and Sun [4].

The present investigation has been undertaken in order to investigate in how far it is possible to vary the carbon concentration in $R_2Mn_{17}C_x$ compounds and in order to study the corresponding changes in crystal structure and magnetic properties.

2. Experimental

Samples of $Tb_2Mn_{17}C_x$ compounds were prepared by arc melting starting materials of at least 99.9% purity. In order to compensate for losses of Mn during arc melting, an excess of 5% of Mn was used. After arc melting the samples were wrapped into Ta foil, sealed into an evacuated quartz tube and annealed for 3 weeks at 900 °C. The X-ray diffraction diagrams showed that the annealed samples were approximately single phase for $x \geq 0.8$ and that their crystal structure corresponded to the hexagonal Th_2Ni_{17}-structure type. For lower carbon concentrations,

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increasing amounts of other phases were observed, including the $TbMn_{12}$ phase.

Neutron-diffraction data were collected at 16 K on samples of approximately 2 g using the position-sensitive-detector diffractometer at the University of Missouri Research Reactor. The neutron wavelength used in these experiments was 1.4783 Å obtained by means of a pressure-bent perfect silicon (511) monochromator. Data were taken in a 2θ range extending from 5 to 105°.

The magnetic measurements were made on powdered samples of $Tb_2Mn_{17}C_x$ with $x = 0.9$, 1.8 and 2.7 on a SQUID magnetometer in the temperature range 5–300 K in magnetic fields up to 6 T.

3. Results

The powder neutron-diffraction data of the compounds $Tb_2Mn_{17}C_x$ with $x = 0.9$, 1.8 and 2.7 were analysed by the Rietveld method using the FULLPROF program for multiphase material [5]. The following nuclear scattering lengths were employed in the refinement: $b_{Tb} = 0.738 \times 10^{-12}$ cm, $b_{Mn} = -0.373 \times 10^{-12}$ cm, $b_C = 0.665 \times 10^{-12}$ cm. All lines were indexed and refined on the basis of the hexagonal Th_2Ni_{17} structure. The results of the Rietveld refinements are presented in Table 1. During the refinement, the following constraints have been used: (i) The Mn (4e) site occupancy and the Tb (2b) occupancy were constrained in a way that the missing fraction of the latter site led to a statistical occupation of dumb-bell atoms at the former site; (ii) a similar constraint was applied to the occupancies of the Mn (4f) site and the Tb (2c) site; (iii) for the sample with the highest carbon concentration, $Tb_2Mn_{17}C_{2.7}$, the Mn (4e) occupancy was considered as too low to give a meaningful value for the z parameter. The z parameter for this site was therefore constrained to be equal to that of the corresponding Mn (4f) site. The carbon content was refined unconstrained. The formula compositions $Tb_2Mn_{17+\delta}C_x$ listed in the third row of Table 1 were calculated from the corresponding refined site occupancies by normalising the Tb content to the same value.

Results of magnetic measurements are shown in Fig. 1 Fig. 2. The values of the magnetisation obtained at various temperatures in a field of 1 T have been used to plot the temperature dependence of the reciprocal susceptibility as displayed in Fig. 1. It is seen that indications of a magnetic ordering transition are absent in the curves of all three compounds investigated. For the compound with $x = 2.7$ the reciprocal susceptibility is almost linear, reflecting Curie–Weiss behaviour. This linear behaviour is gradually lost when going to lower carbon concentrations. This behaviour has been interpreted as an increasing antiferromagnetic interaction between the Mn moments with de-

Table 1
Results of the refinement of the neutron data obtained on $Tb_2Mn_{17}C_x$ compounds at 16 K

Parameter		$x = 0.9$	$x = 1.8$	$x = 2.7$
x, refined		0.91(5)	1.93(5)	2.76(5)
Composition		$Tb_2Mn_{17.54}C_{0.93}$	$Tb_2Mn_{17.43}C_{1.97}$	$Tb_2Mn_{17.21}C_{2.79}$
a (Å)		8.6073(4)	8.6741(3)	8.7027(4)
c (Å)		8.4581(5)	8.4878(4)	8.5138(5)
c/a		0.9827	0.9785	0.9783
V (Å^3)		542.673	553.065	558.423
Tb(2b),	n(%)	73(1)	88(1)	93(1)
Tb(2d),	n(%)	100	100	100
Tb(2c),	n(%)	22(1)	8(1)	5(1)
Mn(12k),	x	0.1688(12)	0.1672(8)	0.1679(11)
	z	0.9806(5)	0.9762(4)	0.9789(5)
Mn(12j),	x	0.3216(10)	0.3241(8)	0.3318(10)
	$-y$	0.0531(7)	0.0542(6)	0.0519(8)
Mn(4f),	z	0.1073(13)	0.1065(10)	0.1021(11)*
	n(%)	78(1)	92(1)	95(1)
Mn(4e),	z	0.1079(73)	0.1049(95)	0.1021(11)*
	n(%)	27(1)	12(1)	7(1)
C(6h),	x	0.8359(38)	0.8359(11)	0.8360(9)
	n(%)	28.8	66.0	91.6
χ^2		2.80	2.55	4.47
R-factor		5.56	5.85	6.73
Rw-factor		7.02	7.39	8.81

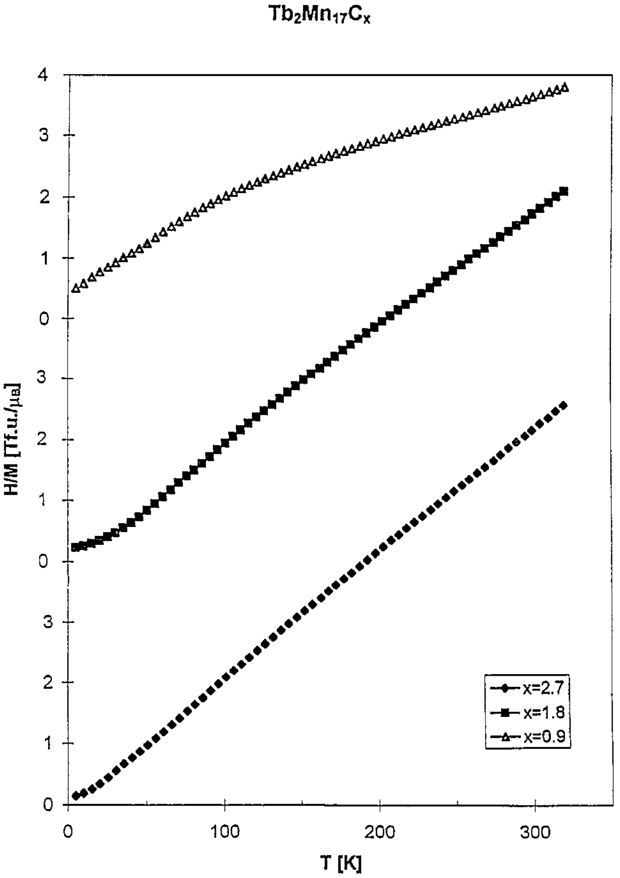

Fig. 1. Temperature dependence of the reciprocal susceptibility for $Tb_2Mn_{17}C_x$ compounds measured in a field of 1 T.

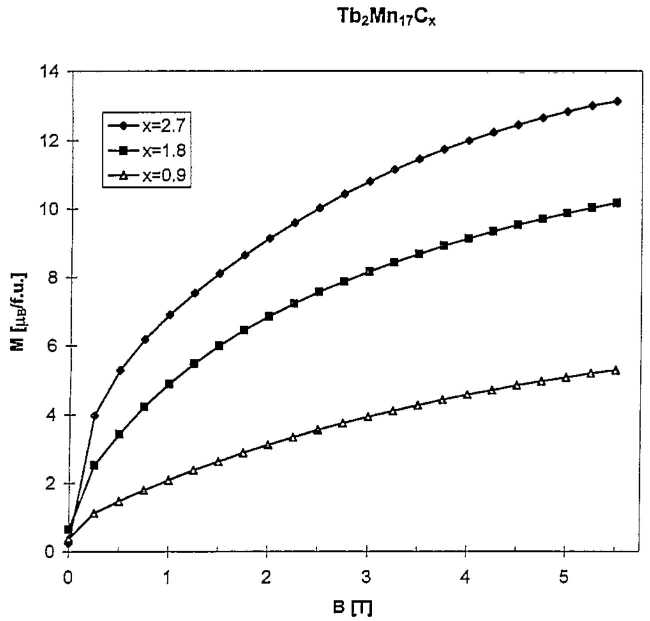

Fig. 2. Field dependence of the magnetic moment of $Tb_2Mn_{17}C_x$ compounds measured at 5 K with decreasing field on samples cooled to 5 K in a field of 2 T.

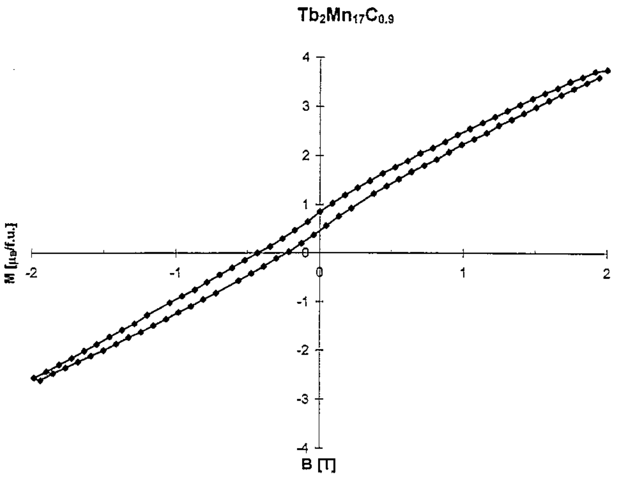

Fig. 3. Hysteresis loop of $Tb_2Mn_{17}C_{0.9}$ measured at 5 K after field-cooling.

creasing carbon content and a correspondingly larger negative Curie–Weiss intercept. The contribution of the Mn sublattice to the susceptibility will therefore become more dominant in the lower temperature range, causing a break in the temperature dependence of the reciprocal susceptibility.

The field dependence of the magnetisation at 5 K is shown for all three compounds in Fig. 2. All data displayed were obtained on samples cooled to 5 K in a field of 2 T and the measurements were made with decreasing field strength. These results show that a spontaneous moment is practically absent in all three materials. The curve shown for the $x = 2.7$ compound is reminiscent of a paramagnetic system tending to saturation in the applied field. This behaviour is gradually lost when going to lower carbon concentrations, reflecting again the increasing tendency to antiferromagnetic coupling mentioned above. However, even the curve for the $x = 2.7$ compound is difficult to reconcile with a paramagnetic system tending to saturation in the highest fields because the moment value in the highest field strength is much lower than the Tb free ion moment value. The most likely interpretation of our data is one in terms of a spin glass or cluster glass. In order to check this, we have measured the hysteresis loop of the $x = 0.9$ sample at 5 K after field cooling. This resulted in a strongly asymmetric hysteresis loop, as can be seen in Fig. 3. Such behaviour is generally regarded as a signature of a spin- or cluster-glass. We have also measured the temperature dependence of the a.c. susceptibility for the three $Tb_2Mn_{17}C_x$ compounds in the temperature range 5–300 K. Contrary to the results obtained on the corresponding Gd samples [6], we did not observe susceptibility maxima, as would have been expected for a cluster glass. We ascribe this different behaviour of the Tb samples to the strong random single site anisotropies associated with the Tb moments, as will be discussed further below.

4. Discussion

Our results have shown that terbium manganese compounds with 2:17 structure can be stabilised with considerably lower carbon concentrations than would correspond to complete filling of the octahedral hole sites. Our refinement results for the compound $Tb_2Mn_{17}C_{2.7}$ in which the octahedral hole sites are almost completely filled ($x = 2.7$) are in good agreement with the refinement results reported for an X-ray study on a single crystal extracted from a strongly Mn-deficient arc-cast sample [1]. It is interesting to note that our refined composition for $x = 2.7$ is fairly close to the ideal 2:17 composition even though we used an excess of Mn.

Closer inspection of the data presented in Table 1 shows that the refined composition tends to higher Mn content when decreasing the carbon concentration. Rare-earth transition-metal compounds of the composition R_2T_{17} can be regarded as ($CaCu_5$ type) RT_5 compounds in which one-third of all R atoms are replaced by an ordered substitution of pairs of T atoms. Depending on the manner of how the ordering of these pair-atoms in the R_2T_{17} lattice is realised, this leads to either the hexagonal Th_2Ni_{17} or the rhombohedral Th_2Zn_{17} types. Of these, only the former type offers the possibility of a larger number of substitutions than corresponds to the 2:17 stoichiometry. Inspection of the data listed in Table 1 shows that the higher Mn content is realised via such a substitution of pairs of dumb-bell-type Mn atoms for part of the Tb atoms. This effect is stronger the lower is the degree of interstitial hole filling. The simultaneous occurrence of increasing interstitial hole filling and decreasing concentration of dumb-bell atoms is most likely the reason for the unsystematic variation of the atomic-position parameters of Mn across the series of compounds investigated.

It has already been mentioned that full octahedral hole site occupation corresponds to the formula composition $Tb_2Mn_{17}C_3$. In this case, each Tb atom would be surrounded by three nearest-neighbour carbon atoms. For lower carbon contents, one has to take account of the presence of a distribution of Tb atoms with either 0, 1, 2 or 3 nearest neighbour carbon atoms. Similar arguments can also be presented to show that for the Mn atoms one has to consider a distribution of nearest-neighbour configurations. A further structural feature leading to short-range atomic disorder in these materials is the presence of the excess Mn dumb-bells. Also, these dumb-bell atoms will lead to a distribution of neighbour configurations. It can be envisaged that both types of distribution will completely randomise the exchange interactions between the magnetic moments, explaining why these systems are reluctant to show sharp magnetic ordering transitions and long-range magnetic ordering. This situation is different from that encountered in the related carbides and nitrides of Fe compounds, because here the magnetic properties are determined by a dominating strongly ferromagnetic Fe–Fe interaction. The interstitial hole filling and the concomitant occurrence of a distribution of ferromagnetic exchange interactions will not suppress long-range magnetic ordering. By contrast, the Mn–Mn interaction is primarily antiferromagnetic so that the occurrence of distributions of the exchange interactions implies the occurrence of frustration.

There is one more mechanism that contributes to the strong magnetic disorder in the $Tb_2Mn_{17}C_x$ compounds. It is well known that the presence of carbon atoms as nearest neighbours of the rare-earth atoms leads to strong changes in the local crystalline fields (see for instance Ref. [4]). The second-order crystal-field parameter A_2^0 was shown to vary from about $-300\,\mathrm{K}/a_0^2$ for rare-earth atoms without C neighbour atoms to about $-1300\,\mathrm{K}/a_0^2$ for rare earth-atoms with three C neighbours in the $R_2Mn_{17}C_x$ compounds [6]. This means that the distribution of interstitial hole filling causes a corresponding distribution in crystal-field splittings. Unlike the situation in the Fe compounds, where strong exchange fields due to the ferromagnetic Fe sublattice lead to level purification, one has in the Mn compounds a situation where the crystal-field ground state can be different from that corresponding to $|\pm J\rangle$ with the maximum J value. In fact, if the second-order parameter is dominant, and if the exchange fields at a given Tb site are negligibly small, one expects $|\pm 1/2\rangle$ to be the zero-field ground state. This may, at least partially, explain the too low moment value found from the field dependence of the magnetisation of the compound with $x = 2.7$.

Concluding, we have shown that when combining Tb and Mn, hexagonal Th_2Ni_{17}-type compounds can become stabilised over a fairly extended range of carbon concentrations. Based on the refinement results of our neutron-diffraction data, we have identified three mechanisms that simultaneously lead to randomisation of the magnetic interactions in the $Tb_2Mn_{17}C_x$ compounds, preventing long-range magnetic ordering and giving them a spin-glass-like behaviour.

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