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Structure and magnetic properties of TbMnGa

M. Bacmann, D. Fruchart and J.L. Soubeyroux

Laboratoire de Cristallographie CNRS, BP 166, 38042 Grenoble Cedex 9 (France)

J.H.V.J. Brabers and F.R. de Boer

van der Waals-Zeeman Laboratory, University of Amsterdam, 1018 XE Amsterdam (Netherlands)

K.H.J. Buschow

Philips Research Laboratories, 5600 JA Eindhoven (Netherlands)

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Abstract

The compound TbMnGa was studied by means of neutron diffraction at various temperatures between 2 and 300 K. From the data obtained in the paramagnetic range it was derived that TbMnGa has the hexagonal Fe₂P crystal structure with Tb on 3g, Mn mainly on 3f, and Ga mainly on 2c and 1b positions. The magnetic structure derived from the data obtained at 2 K consists of an antiferromagnetically ordered Tb sublattice and an equally antiferromagnetically ordered Mn sublattice, the magnetic unit cell in the *a* direction being twice that of the chemical unit cell. The preferred moment direction is along the *c* direction. Diffuse neutron scattering and high field measurements indicate that there may be a magnetic component perpendicular to the *c* axis that does not show long-range magnetic order.

1. Introduction

Previous investigations of rare earth compounds of the type RMnGa have shown that they can generally be obtained in two modifications [1–3]. The cubic modification is the cubic C15 type. It is observed for compounds of light rare earth elements and for compounds of heavy rare earth elements at high temperatures. In these cubic compounds, there is a statistical distribution of the Mn and Ga atoms over the non-rare earth sites in the C15 structure. In the RMnGa compounds formed with heavy rare earth elements, that are annealed at low temperatures after casting, a different structure type is obtained. A structure determination of HoMnGa based on X-ray diffraction showed that this structure is of the hexagonal Fe₂P type in which the Ga and Mn atoms occupy different crystallographic positions. Magnetic measurements made on the RMnGa compounds showed that the rare earth atoms as well as the Mn atoms carry a magnetic moment. However, the result of magnetic measurements did not allow any conclusion to be drawn as to the type of magnetic ordering adopted by these compounds at low temperatures [3]. In fact, the results indicated that the magnetic ordering is of a complex nature in these materials. This prompted us to investigate one of these compounds (TbMnGa) by means of neutron

diffraction in the paramagnetic as well as in the magnetically ordered regime and to study its magnetic isotherm at 4.2 K in high magnetic fields.

2. Experimental details

The compound TbMnGa was prepared by arc melting, using starting materials of at least 99.9% purity. Annealing was performed by wrapping the sample in Ta foil and heating inside an evacuated silica tube at 750 °C for more than 2 weeks. After annealing, the sample was found to be approximately single phase (Fe₂P structure; space group, *P6₃2m* (No. 189). Neutron diffraction patterns of TbMnGa were recorded at various temperatures between 2 and 300 K using the Siloé reactor facilities, Nuclear Center of Grenoble. The diffractometer DN5 used was operated at the wavelength $\lambda = 2.475$ Å. The atomic and magnetic structure refinements have been undertaken using the MXD program [4].

The temperature dependence of the magnetization of the sample was studied on a superconducting quantum interference device magnetometer in the temperature range 5–350 K. For measurements above 300 K we used a home-built magnetometer based on the Faraday method. The magnetic isotherm at 4.2 K was studied

in the Amsterdam high field installation in fields with $\mu_0 H$ up to 35 T. The measurements were made on fine powder particles able to rotate freely into the equilibrium position at each field strength.

3. Experimental results and discussion

The room-temperature neutron diffraction pattern is shown in Fig. 1. At this temperature, TbMnGa is still paramagnetic so that only nuclear contributions need to be considered. Attempts to describe the crystal structure on the basis of the Fe₂P structure proposed earlier [3] with Ga on the 3f site, Mn on the 1b and 2c sites and Tb on the 3g site did not lead to a satisfactory result. The structure model used in the present investigation can be inferred from Table 1 where the refined atomic position parameters are listed. These data confirm the Fe₂P structure type proposed earlier, including the occupation of the 3g position by the rare earth atoms. However, the distribution of the Mn and Ga atoms over the remaining sites is different. The Ga atoms are located primarily at the 2c and 1b sites whereas the Mn atoms occupy mainly the 3f site. Roughly speaking, one could say that the site occupancy of the Mn and Ga atoms obtained in the present investigation corresponds to interchanging the Mn and Ga sites in the structure proposed on the basis of X-ray data. The present result, including the observation of partial site occupancies (Table 1) is considered to be more realistic in view of the large difference in neutron-scattering length between Mn and Ga and the concomitant larger differentiation between Mn and Ga site occupancies. The reliability factor corresponding to the structure model given in Table 1 is $R=0.05$.

Fig. 1. Neutron diffraction diagram of TbMnGa observed at 300 K. The peaks labelled with asterisks correspond to an unidentified impurity. Indexation is done in the hexagonal cell.

TABLE 1. Atomic position parameters derived after refinement of the neutron data obtained for TbMnGa at 300 K (Fe₂P type; hP9; $P\bar{6}2m$, $a=0.7079$ nm and $c=0.4314$ nm; $R=0.05$)

Site	x	Occupation
3g (x 0 $\frac{1}{2}$)	0.5792(29)	Tb
3f (x 0 0)	0.2749(75)	0.91Mn + 0.09Ga
2c ($\frac{1}{3}$ $\frac{1}{3}$ 0)	$\frac{1}{3}$	0.05Mn + 0.95Ga
1b (0 0 $\frac{1}{2}$)	0	0.18Mn + 0.82Ga

Fig. 2. Neutron diffraction diagram of TbMnGa observed at 2 K. The peaks labelled with asterisks correspond to an unidentified impurity. Indexation is done in the hexagonal cell.

Fig. 3. Basal plane projection of the magnetic structure of TbMnGa. The $\uparrow$ and $\downarrow$ signs indicate a moment direction in the positive and negative c directions respectively. $\bullet$, Tb_{pyr}, $Z=1/2$; $\circ$, Mn_{tet}, $Z=0$.

The neutron diffraction diagrams recorded at low temperatures in the long-range magnetic order regime show additional peaks. This may be illustrated by means of the diagram taken at 2 K shown in Fig. 2, where one sees strong peaks of magnetic origin in addition to the nuclear peaks. Analysis of this diffraction pattern shows that the magnetic ordering has led to a magnetic

Fig. 4. Three-dimensional plot of neutron diffraction patterns of TbMnGa recorded at various temperatures.

Fig. 5. Temperature dependence of the magnetization of TbMnGa measured in a field of $\mu_0 H = 3$ T. The inset shows the temperature dependence of $\chi^{-1} = \mu_0 H / M$ obtained with $\mu_0 H = 1.25$ T.

unit cell twice as long in the a direction as the chemical unit cell. The magnetic structure is most conveniently described in terms of the propagation vector $\mathbf{q} = [\frac{1}{2} \ 0 \ 0]$ with respect to the chemical cell. Then the magnetic periodicity can be described in the orthohexagonal cell $3^{1/2} a, b, c$.

The moment arrangement in the magnetic unit cell was determined by means of group theoretical consid-

Fig. 6. Magnetic isotherm of TbMnGa at 4.2 K.

erations applied to the magnetic symmetry group $G_q \equiv Cm2m$. This led to a model for the magnetic structure in which the easy-magnetization direction of the Mn and Tb moments is along the c axis and for which the individual moment orientation ($\uparrow$ or $\downarrow$) are schematically represented in Fig. 3, corresponding to the magnetic space group $C_p m' 2' m$. It may be inferred from the structural model shown in Fig. 3 that, owing to symmetry reduction, the original $3g$ site in the space group $P\bar{6}2m$ has become split into two sites denoted by M(1) and M(3) on the one hand, and by M(2) on the other hand. Also the original $3f$ site occupied by Mn atoms has become split into two sites denoted by

Mn(4) and Mn(6), and by Mn(5). The basis vectors corresponding to the magnetic space group $C_p m' 2' m$ are as follows: $M_z(1) + M_z(3) - M_z(1') - M_z(3')$, $M_z(2) - M_z(2')$ for Tb; $M_z(4) + M_z(6) - M_z(4') - M_z(6')$, $M_z(5) - M_z(5')$ for Mn; the primed numbers are deduced from the corresponding unprimed numbers by the C translation.

The reliability factor obtained after refinement equals $R=0.09$. The refined moment values are, for Tb, $M_z(1) = M_z(3) = 4.2(1) \mu_B$ and $M_z(2) = 2.6(2) \mu_B$ and, for Mn, $M_z(4) = M_z(6) = -0.2(2) \mu_B$ and $M_z(5) = 1.6(1) \mu_B$. The magnetic structure shown in Fig. 3 can be characterized as follows. The single Tb and Mn positions (Tb(2) and Mn(5)) give rise to ferromagnetic (100) planes containing mutually parallel moments of Tb(2) and Mn(5) located at $z = \frac{1}{2}$ and $z = 0$ respectively. These planes are stacked antiferromagnetically along the [100] direction (orthorhombic notation). They are indicated by horizontal bars in Fig. 3. Closer inspection of Fig. 3 shows that also the twofold Tb positions (Tb(1)) and Mn(6)) give rise to (puckered) sheets in which the Tb moments and Mn moments are mutually parallel. These puckered sheets are indicated in Fig. 3 by puckered bars. Considering the planar ferromagnetic layers and the puckered ferromagnetic layers together, it can be seen in Fig. 3 that they are stacked antiferromagnetically in the [100] direction in an alternating manner.

The values for the Tb moments derived from the refinement of the neutron data obtained at 2 K are substantially lower than the free-ion value of Tb^{3+} ($9 \mu_B Tb^{-1}$). While this may originate from crystal field interaction, one cannot exclude the possibility that there is a magnetic component also perpendicular to the c axis. This magnetic component may not give rise to long-range magnetic order but varies from site to site. Such a situation may occur if there is a strong magnetic anisotropy in the basal plane, varying from site to site as a consequence of differences in the nearest-neighbour configuration. Such differences may be expected on the basis of the partial site occupation listed in Table 1. This partial site occupation may also affect the local Mn moments. The presence of a magnetic basal plane component without long-range order would be in agreement with the comparatively large diffuse scattering superimposed on the background scattering in the low temperature patterns. The three-dimensional data plot shown in Fig. 4 reveals this most clearly. For completeness we note that group theory does not allow to construct any magnetic structure for basal plane components of Tb and Mn moments within the representation considered here. It would require further lowering of the crystal symmetry, which is difficult to detect in the neutron powder data at present available.

The results of the neutron diffraction measurements may be compared with the results of magnetic measurements presented in Figs. 5 and 6. The temperature dependence of the magnetization of TbMnGa is shown in Fig. 5. No clear indication of magnetic ordering is observed in the $M(T)$ plot. The low value of the magnetization indicates antiferromagnetic ordering. The absence of a sharp Néel transition and the sluggish decrease in $M(T)$ with increasing temperature may be interpreted as being due to considerable short-range ordering, in agreement with the large diffuse scattering observed in the neutron diffraction data. However, it may be concluded from the neutron data (Fig. 4) that the z components M_z of the moments order at $T_N \approx 80$ K.

The values of $M(T)$ obtained in a field with $\mu_0 H = 1.25$ T have been used to plot the temperature dependence of the quantity $\chi^{-1} = \mu_0 H / M$, which is shown in the inset of Fig. 5. The effective moment derived from the slope of this plot is larger than the free-ion value of Tb^{3+} . In fact, when assuming the free-ion value for Tb, one finds an additional effective moment due to Mn equal to $2[S(S+1)]^{1/2} = 3.3 \mu_B Mn^{-1}$. From this $2S$ value of $2.46 \mu_B$ can be derived, as expected for the average Mn moment in the magnetically ordered state. Comparison with the much lower neutron value shows that the disordered basal plane component may be quite substantial.

The results of high field measurements made on TbMnGa are shown in Fig. 6. The results are in agreement with the magnetic structure proposed, the zero net magnetic moment in zero field strength indicating a zero Tb sublattice moment and a zero Mn sublattice moment. It is interesting to discuss the possibility that the field applied is able to align all Tb and Mn moments parallel eventually. Using the refined moment values listed above, this would lead to a total moment, averaged over all sites, equal to $4.3 \mu_B$ per formula unit TbMnGa. This value is much lower than the moment value ($5.5 \mu_B$) reached at 35 T in Fig. 6. This again is an indication of the presence of a substantial moment component perpendicular to the c axis, as was discussed above.

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