EPJ Web of Conferences **185**, 04009 (2018) https://doi.org/10.1051/epjconf/201818504009
MISM 2017

Magnetic structures of $(Gd_{1-x}Y_x)Mn_2Ge_2$ and $(Tb_{1-x}Y_x)Mn_2Ge_2$ studied by neutron powder diffraction

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Abstract. Magnetic structures and magnetic phase transitions in "naturaly-layered" $(Gd_{1-x}Y_x)Mn_2Ge_2$ and $(Tb_{1-x}Y_x)Mn_2Ge_2$ compounds have been studied by electrical resistivity and neutron powder diffraction experiments. Hot neutrons were used to probe the magnetic structures of Gd-containing materials. The variable R-Mn exchange forces Gd moments to realign from the tetragonal axis into the plane and back to this axis, whereas canted and tripled structures were detected in the series of compounds containing the highly anisotropic Tb-ion.

1 Introduction

Recent achievements in spintronics require better understanding and classification of antiferro- and ferrimagnetic materials. In the range of hundreds of such materials, tetragonal RT_2X_2 (R- rare earth or Y, T – transition metal, X- Ge or Si, $ThCr_2Si_2$-type structure, space group $I4/mmm$) receives a special interest: superconductivity, mixed valence, Kondo effects have been investigated during last decades. The long-range magnetic order in 3*d*-sublattice is established only in Mn-containing compounds while in those with Fe, Co and Ni only the rare earth sublattice is magnetic. The magnetic transition in Mn sublattice occurs in RMn_2T_2 at 350-500K; all compounds with heavy rare earths exhibit the separate transition to ferrimagnetic phase at T less than 100K while for light rare earths the "separate ordering" takes place in a number of cases too, with transition temperatures ranging from 100K to 250K.

The manganese atoms form a primitive tetragonal sublattice in the $ThCr_2Si_2$-type structure; the distance between Mn atoms in the layer is approximately half of the distance between the adjacent Mn-layers. This feature leads to a significant spread of the 3*d* electrons within the layers and this structure could be considered as "naturally layered" in that sense. Consequently, the magnetic structure of such a compound is determined by the interplay of four types of magnetic exchange: Mn-Mn exchange in one particular layer $J^{L}_{Mn\text{-}Mn}$, interlayer exchange $J^{IL}_{Mn\text{-}Mn}$, R-Mn exchange $J_{R\text{-}Mn}$ and R-R interaction $J_{R\text{-}R}$.

Magnetic structures of $GdMn_2Ge_2$ and $TbMn_2Ge_2$ were widely studied by macroscopic as well as microscopic methods. In both compounds the interplanar Mn-Mn exchange has approximately the same value as the R-Mn interaction and the competition between these two types of couplings determines the low temperature properties of these compounds. The Mn-sublattice orders collinearly and antiferromagnetically (*AFil* structure, here and below we follow the classification given in Ref. [1]) at $T_N = 363$ K in the Gd-based compound and at $T_N = 414$ K in $TbMn_2Ge_2$. Another transition from *AFil* to collinear ferrimagnetic *F* structure where the R-sublattice is now aligned antiparallel to the Mn-sublattice occurs in both compounds at $T_C = 95$K. This transition is of the first-order type and is accompanied by a significant change of the lattice constants and temperature-dependent resistivity.

The substitution of magnetic rare earth element to non-magnetic Y, La or Lu should, generally, decrease the R-Mn interaction and also the magnetic anisotropy of the R ion. As in- and interlayer interactions between Mn ions depend mostly on Mn-Mn separations, these will be not affected by substitution when the ionic radii of substitutional and replaceable elements are close to each other. Thus, pseudo-ternary $(Gd_{1-x}Y_x)Mn_2Ge_2$ and $(Tb_{1-x}Y_x)Mn_2Ge_2$ are good objects to investigate magnetic structures and phase transitions caused by the interplay of R-Mn and interlayer Mn-Mn interactions.

Macroscopic properties of $(Gd_{1-x}Y_x)Mn_2Ge_2$ were studied in [2, 3]. Following [2], the collinear low-temperature phase should be replaced by a canted *Fmc* structure with increasing of Y-content while the sample with composition $(Gd_{0.6}Y_{0.4})Mn_2Ge_2$ undergoes two transitions *AFil-Fmc-F*. According to calculations and experimental data in the ref. [3], the specific canted ferrimagnetic structure with Gd-moment in the *c*-plane is expected to be a low-temperature phase for compounds with $x \sim 0.4$.

The $(Tb_{1-x}Y_x)Mn_2Ge_2$ system is more complicated with regard to the anisotropy of Tb ions. The magnetisation and X-ray thermal expansion experiments

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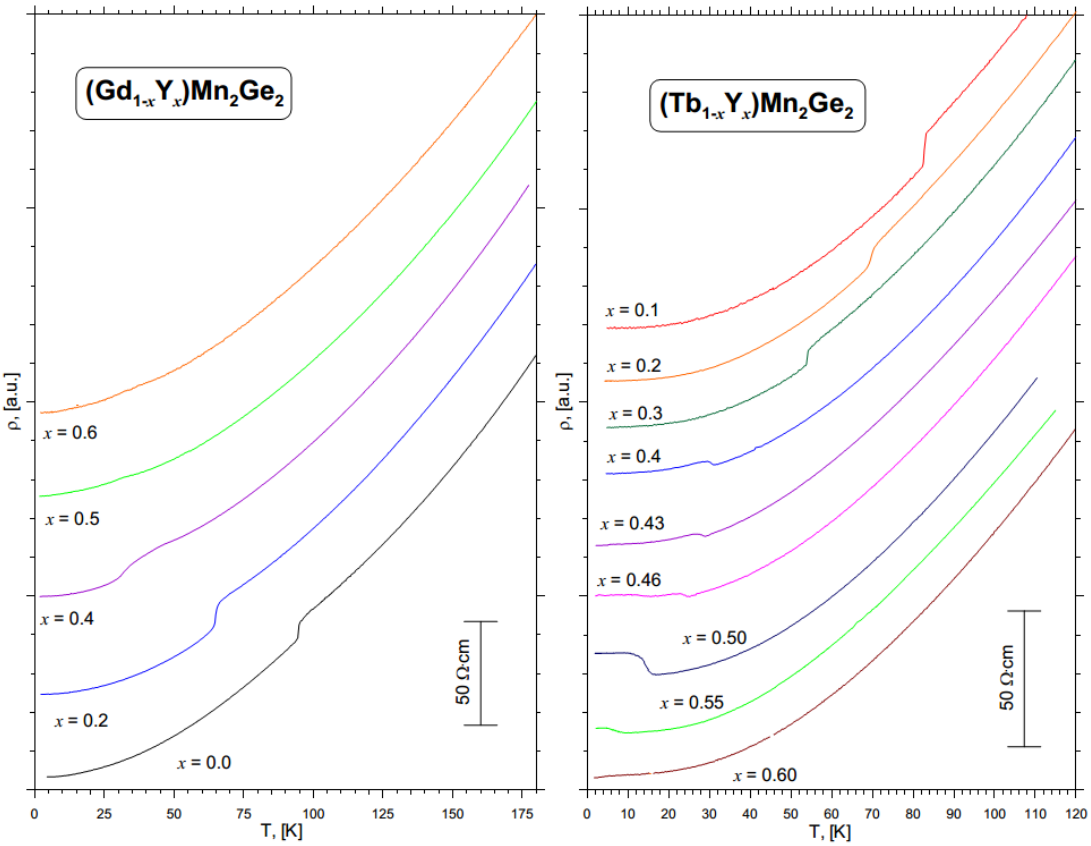

Fig. 1. Resistivity thermal dependencies for $(Gd_{1-x}Y_x)Mn_2Ge_2$ and $(Tb_{1-x}Y_x)Mn_2Ge_2$ series.

are presented in [4]. Following this work, the magnetic structure changes in the consequence *AFil-F-Fmc* in all diluted compounds. At the same time, the volume effect, characteristic of the first-order type *AFil-F* transition was seen only in $TbMn_2Ge_2$ and $(Tb_{0.9}Y_{0.1})Mn_2Ge_2$.

The aim of the current work was to probe directly the magnetic structures in pseudo-ternary systems $(Gd_{1-x}Y_x)Mn_2Ge_2$ and $(Tb_{1-x}Y_x)Mn_2Ge_2$.

2 Experiments

Large 7-8 g polycrystalline samples $(Gd_{1-x}Y_x)Mn_2Ge_2$ $x = 0,2, 0,4, 0.5, 0.6$ and $(Tb_{1-x}Y_x)Mn_2Ge_2$ $x = 0.1, 0.2, 0.3, 0.4, 0.43, 0.46, 0.50, 0.55, 0.6$ were synthesised using the induction melting technique in a quasi-levitation cooper crucible of a special design which provided the minimum contact of the melted elements with the crucible. Preferential Mn evaporation was taken into account; therefore, weights of the components were calculated in accordance to the results of a number of test meltings. After the melting procedure, samples were annealed in dynamic or static vacuum for 7 days.

Magnetisation, ac-susceptibility and resistivity temperature dependencies were measured on synthesized samples for their characterisation.

The neutron diffraction experiments were performed at ILL, Grenoble. Diffractograms for Gd-contained samples were collected at the two-axis diffractometer D4 which is situated at a hot neutron source. The neutron wavelength was set to $\lambda = 0.4972$ Å using the Ge monochromator. Diffraction patterns were collected at different temperatures with a counting time of 2 hours per pattern. The background scattering was measured with an empty sample container and the same container filled with highly absorbing enriched ^{10}B powder. Then the linear combination of both measured backgrounds was subtracted from the measured scattering intensity. Thermodiffractograms for the Tb-containing series were collected with the high intensity powder diffractometer D1B (dynamic temperature sweep: between 5 - 130 K, 2θ range: 10 - 90 deg., total counting time: approx. 10 hours per sample).

3 Results and discussion

Figure 1 shows the thermal dependence of the electrical resistivity $\rho(T)$ for synthesized samples of both series. As can be seen from these dependencies, the low temperature behaviour of studied samples is significantly different. One first order transition likely from *AFil* to *F* structures accompanied by jump-like decrease in resistivity could be seen in $Gd_{0.8}Y_{0.2}Mn_2Ge_2$ and in Tb-series with $x \leq 0.3$. $Gd_{0.6}Y_{0.4}Mn_2Ge_2$ sample shows two consequent magnetic transitions, which is in agreement with the data from the Ref.[2]. Only one phase transition is detected for Tb-based compounds, however, the $\rho(T)$ dependence for $0.4 \leq x \leq 0.46$ is different from those for $0.5 \leq x \leq 0.55$. Samples with yttrium content of 60% show no transitions and should stay in *AFil* phase down to lowest temperatures.

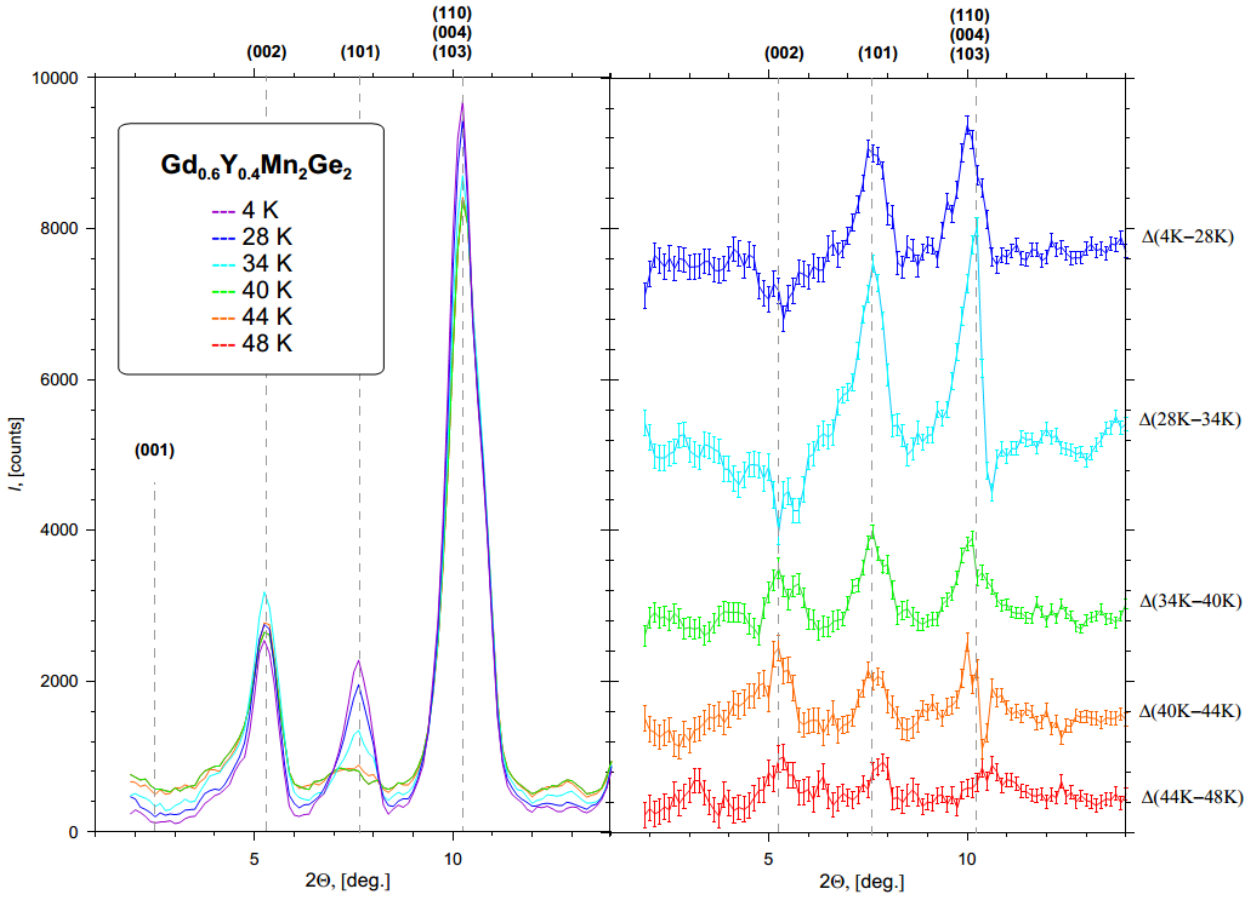

Fig. 2. Hot neutron diffraction patterns for $Gd_{0.6}Y_{0.4}Mn_2Ge_2$ for different temperatures (left) and their difference plots (right). Bragg indexes are indicated above.

The interpretation of hot-source diffractograms obtained for $(Gd_{1-x}Y_x)Mn_2Ge_2$ series is complicated as the short wavelength of the hot neutrons leads to overlapping of reflections. Nevertheless, several conclusions about the magnetic structure could be drawn from the analysis of the first diffraction peaks and the differences of diffraction patterns for different temperatures. The diffraction patterns for $Gd_{0.2}Y_{0.8}Mn_2Ge_2$ are similar to those of non-diluted $GdMn_2Ge_2$ where collinear *F* low temperature phase was confirmed [5].

Two magnetic transitions are expected for $Gd_{0.6}Y_{0.4}Mn_2Ge_2$ [2,3]. Neglecting the thermal expansion in this temperature and angle range, the differences between diffraction patterns are caused only by different magnetic contributions. The difference plots are shown in the Fig.2. One can see that the (001) magnetic reflection, characteristic of the *Fmc* phase is not observed at any temperature. At the same time, the magnetic contribution to the (002) peak related to the in-plane magnetic component is strongly temperature dependent: it increases down to 34 K before it decreases again when cooling to the base temperature of 4 K. Then, comparing the high-temperature *AFil* phase and the low-temperature phase, there is no change in (002) intensity. Thus, our hot source diffraction experiments give the following scenario, which is different from both [2] and [3]. Gd ions order within the tetragonal basis plane first at $T \sim 47$ K. The negative R-Mn interaction force the Mn moments to rearrange from antiparallel *AFil* orientation into the tetragonal basis plane too (*T*' phase in the ref. [3]). The second magnetic transition directs Gd and Mn moments back to the *c*-axis and the resulting structure is collinear *F*.

The Neutron data for the sample with composition $Gd_{0.5}Y_{0.5}Mn_2Ge_2$ show only one magnetic transition from *AFil* to *T*' magnetic phases.

Figure 3 shows diffraction angle-temperature-intensity 3D-plots for selected compounds of $(Tb_{1-x}Y_x)Mn_2Ge_2$. The collinear ferrimagnetic *F* low temperature phase is confirmed for compounds with high terbium content. The low temperature phase for samples with Tb-content $0.4 \le x \le 0.46$ must be different from *F* following our $\rho(T)$ experiments. Diffraction data show the presence of intense (0,0,2*n*+1) peaks, which are the indication of antiferromagnetic component in *a*-direction, below the Curie temperature. The Rietveld analyse clearly proves the canted *Fmc* low temperature phase for these concentrations.

As Tb content decreases the diffraction patterns change again. The low temperature plot for $Tb_{0.5}Y_{0.5}Mn_2Ge_2$ and $Tb_{0.55}Y_{0.45}Mn_2Ge_2$ reveals magnetic peaks of (*h*,*k*,*l*/3)-type together with (0,0,2*n*+1) reflections, characteristic of *Fmc* structure. The magnetic state is then a mixture of the *Fmc* phase and the "triplet" collinear phase, whose magnetic cell is three time larger in the tetragonal direction. One third of Mn ions ordered antiparallel to another 2/3 in this cell, then one third of Tb ions, located between different Mn orientations, are non-magnetic. This magnetic structure has been previously observed in $DyMn_2Ge_2$ and $TbMn_2Si_2$ and could be interpreted using additional interlayer J^{IL-3}_{Mn-Mn}

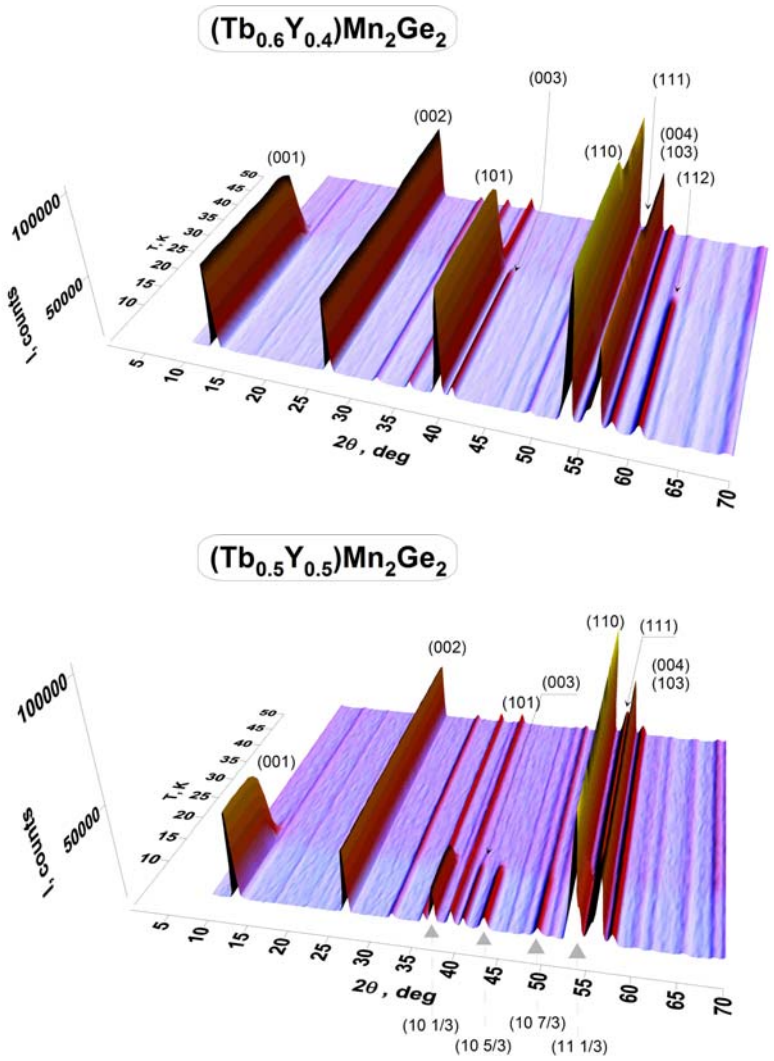

Fig. 3. Neutron powder diffraction patterns for $Tb_{0.6}Y_{0.4}Mn_2Ge_2$ and $Tb_{0.6}Y_{0.4}Mn_2Ge_2$. Bragg indexes are indicated.

term [6,7]. This long-periodic magnetic structure creates a band gap in the first Brillouin zone in tetragonal direction, explaining the significant increase of electrical resistivity in comparison to antiferromagnetic *AFil* phase.

As a summary, magnetic structures, realized in RMn_2Ge_2 with tuneable R-Mn exchange were directly probed in this work. Results of neutron diffraction experiments found to be in good agreement with bulk measurements and partly in agreement with theory expectations. Although the hot neutron diffraction data could not be used for quantitative refinements, it was possible to use the information to select between relatively simple magnetic structures. Thus, we demonstrated that variable R-Mn exchange leads Gd moments to realign from the tetragonal axis into the plane and back to this axis in low-anisotropic Gd-series. In contrast, high-anisotropic Tb holds itself to the *c*-axis and forces reorientation of Mn moments. *Ab-initio* calculations with known CEF-parameters for rare earth ions could provide the quantitative data on magnetic structures and phase transitions in these series.

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