# MAGNETIC ORDER OF GdMn<sub>2</sub>Ge<sub>2</sub> STUDIED BY NEUTRON DIFFRACTION AND X-RAY RESONANT MAGNETIC SCATTERING.

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# Abstract

The magnetic structure of the natural-layered GdMn<sub>2</sub>Ge<sub>2</sub> (tetragonal *I4/mmm*) has been studied by hot neutron powder diffraction and X-ray resonant magnetic scattering techniques. These measurements along with results of bulk experiments confirm the collinear ferrimagnetic structure with moment direction parallel to the *c*-axis below  $T_C = 96$  K and the collinear antiferromagnetic phase in the temperature region  $T_C < T < T_N = 365$  K. In the antiferromagnetic phase the X-ray resonant magnetic scattering has been detected at Mn K and Gd L<sub>2</sub> absorption edges. The Gd contribution is a result of an induced Gd 5*d* electron polarization caused by the antiferromagnetic order of Mn moments.

*Keywords:* Rare earth - transition metal compounds; Magnetization, Resistivity, Magnetic coupling, Neutron diffraction, X-ray resonant magnetic scattering.

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# Introduction.

Among the large variety of magnetic materials containing rare earth and 3*d* elements, the ternary  $RT_2X_2$  compounds (R = rare earth and Y, T = transition metal, X = Ge or Si) are of special interest. These compounds exhibit a wide range of physical phenomena: superconductivity, mixed valence, Kondo and heavy-fermion behavior. Whereas  $RMe_2X_2$  compounds with T = Co, Fe and Ni have non-magnetic 3*d* sublattices, the magnetic properties of manganese containing  $RMn_2X_2$  are determined by two subsystems formed by rare earth and manganese ions. Various magnetic structures and a number of field-, temperature- or pressure-induced magnetic phase transitions were observed in these compounds due to the interplay between the exchange interactions of the different subsystems [1].

RT<sub>2</sub>X<sub>2</sub> compounds crystallize in the ThCr<sub>2</sub>Si<sub>2</sub>-type tetragonal structure (space group I4/mmm) [2]. The R, T = Mn and X layers form a sequence R-X-Mn-X-R along the tetragonal axis. The Mn-atoms occupy a primitive tetragonal sublattice in this structure in which the distance between the Mn-atoms in the layer is approximately half the distance between the adjacent layers. This feature leads to a significant spread of the manganese 3d electrons within the layers, and, as a result, to a significant dependence of the strength and of the sign of magnetic interactions on the Mn-Mn distances [3]. Investigations made on numerous diluted (R<sub>1</sub>,R<sub>2</sub>)Mn<sub>2</sub>X<sub>2</sub> compounds where R<sub>1</sub> and R<sub>2</sub> represent non-magnetic rare-earths showed that in these series an universal temperature dependence of the magnetic order on the distance between Mn ions in a particular layer exists. If the distance between Mn atoms within the layer is less than a critical value  $d_{\rm C} \approx 2.83$  Å and in absence of magnetically ordered R - sublattice, the Mn moments are forced to couple collinearly antiparallel at any temperature below  $T_{\rm N}$ . For distances between 2.83 Å < d < 2.89 Å the ground state is a non-collinear antiferromagnetic order. However, phase transitions to non-collinear ferromagnetic or conical phases occur at higher temperatures. Compounds with d > 2.85 Å exhibit a sequence of phase transitions with increasing temperature first from non-collinear antiferromagnetic to conical and then to an intra-layer antiferromagnetic phases. Samples with d > 2.89 Å have conical magnetic structures at low temperatures [4, 5].

If the rare earth ion R is magnetic, the R-Mn and R-R couplings have to be considered and the competition between Mn-Mn and R-Mn interactions determines the low temperature properties of  $RMn_2X_2$ . As the 4*f* electrons of the rare earths are localized, the R-Mn coupling is established through hybridization of rare earth 5*d* and manganese 3*d* bands [6]. The strength of the R-R exchange in this series of intermetallics is much smaller in comparison to the R-Mn and Mn-Mn couplings [7].

In GdMn<sub>2</sub>Ge<sub>2</sub> the intralayer Mn-Mn distance is slightly smaller than  $d_{\rm C}$  at room temperature ( $d_{\rm C}^{300\rm K}$  = 2.8453 Å) [8]. According to results of magnetization, resistivity and thermal expansion experiments, a collinear ferrimagnetic structure, in which Gd-moments are coupled in *c*-direction antiparallel to Mn moments, is formed below  $T_{\rm C}$  = 96 K [9,10]. With increasing temperature the strength of the 4*f*-3*d* exchange is decreasing and at  $T_{\rm C}$  magnetic moments rearrange to an antiferomagnetic structure. The transition ferrimagnetism-antiferromagnetism is of first-order type and is accompanied by a significant lattice expansion ( $\Delta V/V \approx 3 \cdot 10^{-3}$ ) and an anomaly of the temperature-dependent electrical resistivity. The molecular field of the neighboring Mn atoms in the high temperature phase above  $T_{\rm C}$  is compensated at the Gd sites. Therefore, the Gd moments does not order in the antiferromagnetic phase and an independent magnetic order of Mn-moments is established in this temperature region up to the Néel temperature  $T_{\rm N}$  = 365 K.

As for most compounds containing strongly neutron absorbing elements, conclusions about the type of magnetic order in GdMn<sub>2</sub>Ge<sub>2</sub> has been deduced from bulk data. However, there is a controversy in the results published by different authors. In Ref. [11] a non-collinear antiferromagnetic structure with a moment component perpendicular to the *c*-axis is proposed for the temperature region between  $T_{\rm C}$  and  $T_{\rm N}$  while other authors claim a collinear antiferomagnetic state. There is still an open question about the existence of a high-temperature weakly ferromagnetic phase above  $T_{\rm N}$ . Dilatometry data on GdMn<sub>2</sub>Ge<sub>2</sub> show that this compound may overcome the critical value  $d_{\rm C}$  at high temperatures due to thermal expansion [12]. In this case an additional magnetic phase transition may take place. The observation of this transition was reported in Ref. [8,13] - an additional kink in the thermal dependence of magnetization and resistivity was detected at  $T^* \approx 480$  K. X-ray thermal expansion measurements were also performed, however, the accuracy of this experiment was not enough to prove or to decline the existence of this high-temperature phase [12]. Therefore, microscopic experiments are of particular importance to clarify the magnetic properties of GdMn<sub>2</sub>Ge<sub>2</sub>. High-intensity hot neutron and synchrotron radiation sources allow to investigate magnetic structures of neutron-absorbing materials using the combination of hot neutron powder diffraction and X-ray resonant magnetic scattering (XRMS). Thus, the well quantifiable magnetic scattering in a neutron experiment can be combined with the good angular resolution of the XRMS technique. In this contribution the

study of the magnetic structure in GdMn<sub>2</sub>Ge<sub>2</sub> obtained by these two complementary methods is reported.

# **Experimental.**

The 8 gram polycrystalline sample of GdMn<sub>2</sub>Ge<sub>2</sub> was synthesized from elements with at least 99.9% purity in an induction furnace using a quasi-levitation copper crucible. A 2 wt. % excess of Mn was added to the stoichiometric mixture in order to compensate the preferential Mn evaporation during the melting procedure. To insure the homogeneity the ingot was remelted three times in high-purity Ar atmosphere and then annealed in dynamic vacuum at 850 °C for 120 hours. X-ray powder diffraction analysis showed the ThCr<sub>2</sub>Si<sub>2</sub> phase to be present as main phase (not less than 95 vol. %). For the XRMS experiment we used a single crystal of GdMn<sub>2</sub>Ge<sub>2</sub> out of the same batch used in Ref. [14] grown by the flux method as described in [15]. Both samples were made from a natural isotope-mixture of Gd.

The low-field AC magnetic susceptibility,  $\chi_{AC}$ , was measured by an induction method in a magnetic field of  $H_{AC} = 15$  Oe. The electrical resistivity,  $\rho$ , measurements were carried out by a standard 4-probe method using silver paint to fix the contacts.  $\rho(T)$  measurements were limited to the stability range of the conducting paint  $T \le 420$  K. Magnetization versus temperature was measured in the temperature range 5 K < T < 600 K in an Oxford vibrating sample magnetometer equipped with the high-temperature furnace insert.

Neutron diffraction experiments were performed at ILL, Grenoble. Diffractograms were collected at the hot source powder and liquid diffractometer D4. The neutron wavelength was set to  $\lambda = 0.4972$  Å using a Ge monochromator. Diffraction patterns were collected at different temperatures with a counting time of 2 hours per pattern. To cover the whole temperature range of magnetic phase transitions an orange-type cryostat (5 K< T < 300 K) was used together with a resistance furnace (300 K < T < 600 K). For both sample environments the background scattering was determined by measuring an empty sample container and the same container filled with strongly absorbing enriched <sup>10</sup>B powder. A linear combination of both measured backgrounds was then subtracted from the measured scattering intensity in order to give the purely sample determined scattering. The so corrected neutron diffraction patterns were analyzed by a modified Rietveld method using the FULLPROF software [16]. The effective coherent cross-section of the natural Gd was set to 9.3 fm in the refinements [17].

The XRMS experiment was performed at the MAGS beamline at BESSY, Berlin. The sample with its surface perpendicular to the (001) direction was mounted on the cooper head of the closed-cycle displex refrigerator. Scans were performed in the vertical ( $\sigma$ - $\pi$ ) scattering geometry using a graphite analyzer.

#### **Results and discussion.**

In Fig.1 some of the results of the macroscopic experiments performed to characterize the polycrystalline GdMn<sub>2</sub>Ge<sub>2</sub> sample are presented. The ac-susceptibility data (not shown) manifest characteristic anomalies at  $T_{\rm C} = 96$  K and  $T_{\rm N} = 365$  K. The magnetization M(T) versus temperature dependence indicates the ferrimagnetic behavior below  $T_{\rm C}$ . Reaching  $T_{\rm C}$  the magnetization sharply decreases and a jump-like increase in the electrical resistivity  $\rho(T)$  is observed indicating a first-order magnetic phase transition. The Néel transformation corresponds to a small kink in M(T) and a negative turn of the  $\rho(T)$  dependence. The results of the bulk experiments are in good agreement with previously reported data [8 - 13].

The XRMS technique was recently employed by J.W.Kim *et. al.* [14] to study the ferrimagnetic phase of GdMn<sub>2</sub>Ge<sub>2</sub>. Analyzing the resonance at the Gd L<sub>2</sub> edge it was proven that Gd moments are ferromagnetically aligned in the [001] direction below  $T_{\rm C}$ . The present study focuses on XRMS measurements above  $T_{\rm C}$ . Figure 2 (plots a and b) shows the energy dependencies close to Gd L<sub>2</sub> and Mn K absorption edges for the fluorescence signal and for the intensity of the magnetic (007) reflection obtained at T = 200 K. Element-specific resonance enhancements were detected for both Gd and Mn magnetic scattering cross sections.

The thermal variation of the (007) magnetic reflections ( $\varphi$ -scans) in the high-temperature phase measured at  $E_{Gd}^{L2} = 7921.5$  eV and  $E_{Mn}^{K} = 6532$  eV is shown in Figure 2 (plots c and d respectively). In order to allow a comparison the relative height of the XRMS peaks is normalized by the maximum intensity of the nuclear (008) reflection registered under the respective experimental conditions. It can be clearly seen that the intensities of the Gd L<sub>2</sub> and the Mn K resonances correlate to each other at all temperatures with at each particular temperature the Gd resonance being roughly two orders of magnitude weaker than the Mn resonance. The (007) reflections vanish above T = 370 K at both absorption edges. This temperature dependence proves that both resonances are related to the antiferromagnetic ordering of Mn moments in this temperature range. Numerous other reciprocal lattice points were also examined in order to find magnetic signals, revealing the absence of magnetic scattering elsewhere than at the (00 2n+1) positions. The XRMS study confirms independently from the results of the bulk experiments that the magnetic moments in GdMn<sub>2</sub>Ge<sub>2</sub> are oriented also in the high-temperature phase along the *c*-direction based on the polarization condition ( $\sigma-\pi$ ) for the measured magnetic reflections and the intensity ratios for different *n*.

Figure 3 shows hot neutron powder diffraction patterns along with results of the Rietveld refinements obtained for GdMn<sub>2</sub>Ge<sub>2</sub> at 573 K, 105 K and 4 K respectively. First the crystal structure was refined in the paramagnetic phase at 573 K. Difference spectra were then used to gain the needed information on the possible adopted magnetic structures by displaying typical magnetic Bragg peaks. Comparison with the from literature known high-resolution data for non-absorbing isostructural TbMn<sub>2</sub>Ge<sub>2</sub>, (Tb,Nd)Mn<sub>2</sub>Ge<sub>2</sub> and TbMn<sub>2</sub>Si<sub>2</sub> compounds [18, 19] was used to recognize and construct the specific models used for the magnetic structure refinements. Using the selected model the values of magnetic moments at Gd and Mn sites were determined.

No evidence of qualitative magnetic structure changes were observed in the temperature range 393K < T < 573 K. The difference spectrum of diffractograms obtained at 300 K and 393 K reveals a weak magnetic contribution to the diffraction peak at  $2\theta \approx 10.5$  deg associated to the (111) magnetic reflection and the upcome of the magnetic (113) reflection at about  $2\theta \approx 12.8$  deg (Figure 3b). At the same time no magnetic contribution to  $(00 \ 2n)$  reflections is present over the whole temperature range. These observations, together with results of the XRMS experiment lead us to the selection of the collinear antiferromagnetic *AFil* phase model for the temperature range 96 K < T < 365 K (here and below we use the notation given in Ref. [5]). Below  $T_{\rm C} = 96$  K the significant increase of intensity of the (101) and (211) peaks (Figure 3c) and the constant intensity of the (002) peak give evidence for the presence of the collinear ferrimagnetic *F* model at low temperatures.

The temperature dependencies of the Gd and Mn magnetic moments obtained from the Rietveld refinements are shown in Fig.4 along with the integrated magnetic intensity of the (007) reflection measured at Gd  $L_2$  and Mn K resonances. Normalized Data from Ref. [14] are also included for the ferrimagnetic phase.

According to the Rietveld refinement, at 5 K the magnetic moments on the Gd sites,  $M_{Gd} = 7.0 \pm 0.2 \ \mu_B$ , are aligned along the tetragonal *c*-axis and are opposite in direction to the Mn-moments,  $M_{Mn} = 2.1 \pm 0.2 \ \mu_B$  so that the collinear ferrimagnetic *F* structure is established. With increasing temperature,  $M_{Gd}$  decreases gradually down to  $4.9 \pm 0.2 \ \mu_B$  at 90 K while  $M_{Mn}$  exhibits no visible change. The magnetic structure corresponds to the one found in TbMn<sub>2</sub>Ge<sub>2</sub> and in the mixed system Tb<sub>1-x</sub>Nd<sub>x</sub>Mn<sub>2</sub>Ge<sub>2</sub> up to about x = 0.3 [19]. This is not surprising as the chemical pressure effect induced by replacing the Tb<sup>3+</sup> ion by the smaller Gd<sup>3+</sup> ion corresponds to the one when substituting about 18% of Tb<sup>3+</sup> by Nd<sup>3+</sup>. The relatively low value of the Mn magnetic moment found at 5 K ( $M_{Mn} = 2.1 \pm 0.2 \ \mu_B$ ) compares well to those found in TbMn<sub>2</sub>Ge<sub>2</sub> ( $M_{Mn} = 1.7 \pm 0.1 \ \mu_B$ ) and Tb<sub>0.8</sub>Nd<sub>0.2</sub>Mn<sub>2</sub>Ge<sub>2</sub> ( $M_{Mn} = 1.8 \pm 0.1 \ \mu_B$ ) where the Mn sublattice adopts the same ferromagnetic *F* structure [19].

In the narrow temperature range 91 K < T < 97 K,  $M_{Gd}$  drops to zero and, simultaneously, the magnetic Mn moments re-align from a parallel to an antiparallel arrangement, so that the resulting magnetic structure of GdMn<sub>2</sub>Ge<sub>2</sub> at higher temperatures is collinear and antiferromagnetic as in TbMn<sub>2</sub>Ge<sub>2</sub>. There is no sign of an additional antiferromagnetic coupling along the *a*-axis (magnetic contribution to the (101) peak) as found in  $Tb_{0.8}Nd_{0.2}Mn_2Ge_2$  which would be indicative of the *AFmc* type magnetic structure. Our X-ray thermal expansion data [12] had determined the intra-layer distance at 96 K to  $d_{\text{Mn-Mn}} = 2.833 \pm 0.1$  Å and therefore just below the limit of  $d_{\text{Mn-Mn}} = 2.84$  Å for which Venturini et al. [20] determined the onset of an additional antiferromagnetic coupling along the a-axis leading to the AFmc type magnetic structure. The best fit gives value  $M_{\rm Mn} = 1.9 \pm 0.2 \ \mu_{\rm B}$  at 105 K.  $M_{\rm Mn}$  stays nearly constant up to T = 300 K before it gradually decreases. Our magnetization and diffraction experiments show that above  $T_{\rm N} = 365 \text{ K}$  GdMn<sub>2</sub>Ge<sub>2</sub> has no long-range magnetic ordering. Magnetic phase transitions observed near  $T^* \approx 480$  K in Refs. [8, 13] may originate from ferro- or ferrimagnetic binary or ternary impurities with close composition (for example,  $Gd_6Mn_{23}$  is a ferrimagnet with  $T_{\rm C}$  = 468 K [21]). Thus, the magnetic behavior of GdMn<sub>2</sub>Ge<sub>2</sub> is in good agreement with a modified Yaffet-Kittel model for a two-sublattice ferrimagnet stated in [22] and with the intralayer Mn-Mn coupling scheme proposed in Refs. [5 and 20].

One possible reason for the absence of the additional ferromagnetic phase might be that  $GdMn_2Ge_2$  does not overcome the critical distance  $d_C$ . Our current results on hot neutron powder diffraction do not have sufficient resolution to enable us to refine the temperature dependence of the lattice parameters. Following the X-ray thermal expansion data [12] the intra-layer distance is  $d_{Mn-Mn}^{96K} = 2.833 \pm 0.1$  Å just above  $T_C$  and  $d_{Mn-Mn}^{365K} = 2.849 \pm 0.1$  Å at the Néel point. Both these spacings lie within the range for the collinear antiferromagnetic *AFil* structure (One has to recall here that  $d_c$  is temperature dependent and varies between about 2.83 Å at 0 K and 2.85 Å at

350 K [5]). Another explanation could be the influence of the Gd ions on the interlayer Mn-Mn interactions at high temperatures.

The combination of hot neutron diffraction with XRMS proved to be efficient and complimentary to study the complex magnetic order in GdMn<sub>2</sub>Ge<sub>2</sub>. The current work is also of methodical importance. We demonstrated that the XRMS is not exactly "element-specific" as it is usually considered. Indeed, the appearance of resonance scattering at Gd edges should not be interpreted as a scattering concerned with an ordering of the local Gd (4f) magnetic moments in this particular case but as resulting from the polarization of the 5d electrons induced by the Mn order. The temperature dependence of the Gd L<sub>2</sub> resonance clearly shows the correlation with the antiferromagnetic ordering of the Mn sublattice vanishing at  $T_{\rm N} = 365$  K while the neutron diffraction data revealed the absence of Gd magnetic ordering. We can interpret the observed resonance magnetic scattering at the Gd L<sub>2</sub> edge therefore in the following way: the interaction between the band magnetism and the almost localized 4f moments of the rare-earth establishes through hybridization of the 3d states of the transition metal with the 5d states of the lanthanide and then, through the local exchange, with the 4f moment [6]. Therefore, the long-range magnetic ordering in the Mn sublattice in GdMn<sub>2</sub>Ge<sub>2</sub> should affect the Gd moments. As a result, the spin polarization of the Gd 5d band follows the antiferromagnetic ordering of the Mn sublattice although the strength of R-Mn interaction is insufficient to establish a Gd long-range ordering of the local 4f Gd-moments. Thus measured resonant enhancements at the Gd L<sub>2</sub> edge results from the spin polarization of the Gd 5d band induced by antiferromagnetic ordering of Mn sublattice. This is consistent with the fact that the induced scattering signal at the Gd L<sub>2</sub> edge is roughly two orders of magnitude weaker than the Mn K signal.

Summarizing, the magnetic structure of GdMn<sub>2</sub>Ge<sub>2</sub> was determined by combination of hot neutron powder diffraction and XRMS. Below  $T_{\rm C}$  = 96 K the magnetic moments of Gd are aligned along the *c*-axis antiparallel to the Mn moments so that the collinear ferrimagnetic *F* structure is established. In the temperature range 95 K < *T* < 365 K the Gd sublattice has no long range magnetic order and the Mn moments are aligned collinear antiparallel to each other (*AFil* structure). XRMS experiment shows that the antiferromagnetic ordering of the Mn moments induces enhancements not solely for the Mn K resonance, but, by means of 3*d*-5*d* hybridization, for the resonances at the Gd absorption edges.

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# **Figure Captions.**

**Fig.1.** (Colour online). Temperature dependence of the magnetisation for polycrystalline  $GdMn_2Ge_2$  measured in a magnetic field B = 0.7 T. Temperature dependence of the (zero field) electrical resistivity for  $GdMn_2Ge_2$ .

**Fig.2.** (Colour online). Energy scans through Gd L<sub>2</sub> (a) and Mn K (b) absorption edges. Scans done at T = 200 K for the fluorescence (upper parts) and (007) reflection. Rocking scans through the (007) diffraction peak measured at Gd L<sub>2</sub> (c) and Mn K (d) absorption edges for selected temperatures.

**Fig.3.** (Colour online). Neutron diffraction patterns of  $GdMn_2Ge_2$  at T = 573 K (paramagnetic phase) (a), T = 105 K (antiferromagnetic phase) (b) and T = 5 K (ferrimagnetic phase) (c). Points represent the experimental data, lines – the result of the Rietveld refinement and the difference function. Bars indicate the reflection positions for the structural and magnetic phases. The schemes illustrate the magnetic structure model used for refinement.

**Fig.4.** (Colour online). Temperature dependence of Gd and Mn magnetic moments in the ferrimagnetic and antiferromagnetic phases – results of Rietveld refinements of neutron data. Normalized thermal variation of square root of the measured XRMS intensities – magnetic contribution to (00 10) peak at Gd L<sub>2</sub> edge [taken from Ref. 14], temperature dependence of the (007) magnetic peak measured at the Gd L<sub>2</sub> and Mn K absorption edges.







