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## Letter

# $^{155}$Gd Mössbauer effect and magnetic properties of $GdMn_6Ge_6$

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## Abstract

The magnetic properties of $GdMn_6Ge_6$ have been studied by magnetic measurements and $^{155}$Gd Mössbauer spectroscopy. The Mn sublattice orders ferromagnetically in high magnetic fields and at high temperatures but in low fields and low temperatures there is a tendency to antiferromagnetic ordering. Antiferromagnetic order was also found in $YMn_6Ge_6$. The electric field gradient derived from the quadrupolar splitting of the $^{155}$Gd Mössbauer spectra is substantially larger than in the isotypic compound $GdMn_6Sn_6$.

Rare earth compounds of the type $RMn_6Sn_6$ have been reported recently to possess quite interesting magnetic properties owing to the presence of a magnetic moment on the Mn atoms [1, 2]. The magnetic ordering temperatures are well above room temperature but the magneto-crystalline anisotropy is only of moderate magnitude. $^{155}$Gd Mössbauer spectroscopy, used as a probe of the local electric field gradient, has revealed that this may be due to the relatively small size of the second order crystal field parameter $A_2{}^0$ associated with the crystal field induced rare earth sublattice anisotropy [2].

In the present study we have focussed our attention on the properties of the compound $GdMn_6Ge_6$. Several compounds of the series $RMn_6Ge_6$ were prepared by us and found to crystallize in the same structure type as adopted by $RMn_6Sn_6$. This structure type ($HfFe_6Ge_6$) is relatively simple and comprises only a single R site and a single 3d site, the coordination of the R sites being similar but not identical to that found in the $CeCo_3B_2$structure type [3].

The $GdMn_6Ge_6$ sample was prepared by arc melting starting materials with purities of at least 99.9%. After arc melting, the sample was wrapped in Ta foil, sealed in an evacuated quartz tube and then vacuum annealed at 800°C for about 4 weeks. X-ray diffraction showed the sample to be approximately single phase after annealing. The lattice constants are $a$ = 0.52371 nm and $c$ = 0.81828 nm. In order to determine the easy magnetization direction in $GdMn_6Ge_6$ X-ray diagrams were also taken from magnetically aligned powder. Conclusive evidence was obtained that the easy magnetization direction in $GdMn_6Ge_6$ is perpendicular to the $c$ axis.

Results of magnetic measurements, made on a SQUID magnetometer in a field of 0.5 T, are shown in Fig. 1. Magnetic ordering is seen to occur at $T_c$ = 490 K. In the range between 200 and 400 K the magnetization reaches a value of about 30 Am$^2$ g k$^{-1}$ (30 emu g$^{-1}$) which corresponds to about 5 $\mu_B$ per formula unit $GdMn_6Ge_6$. Below about 200 K a dramatic decrease in the magnetization occurs, leading to a magnetic moment of only about 1 $\mu_B$ per formula unit at 4.2 K. These results may be compared with those obtained on $YMn_6Ge_6$. As seen in Fig. 1 this compound gives rise to antiferromagnetic ordering at $T_N$ = 485 K.

The magnetic isotherm of $GdMn_6Ge_6$ at 4.2 K was measured at the Amsterdam high-field installation [4] on fine powder particles that were allowed to orient themselves freely in the applied field. The results are shown in Fig. 2. In the low-field region the magnetization rises very rapidly. Above about 10 T the magnetization varies linearly with the field strength. Extrapolation to $H$ = 0 leads to a saturation moment of 5.0 $\mu_B$ per formula unit. Under the assumption of antiparallel

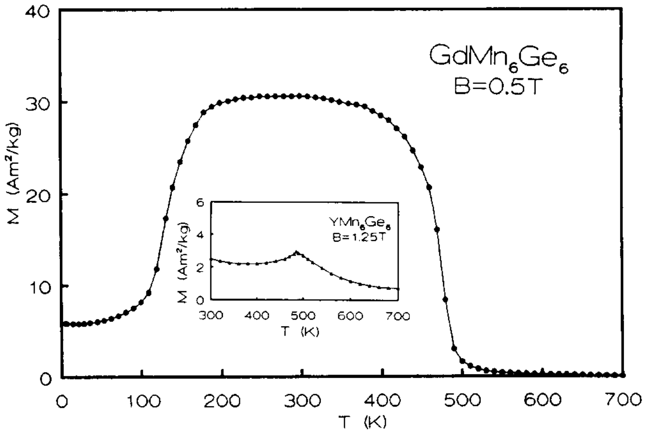

Fig. 1. Temperature dependence of the magnetization in $GdMn_6Ge_6$ and $YMn_6Ge_6$ (inset) measured in fields of 0.5 T and 1.25 T respectively.

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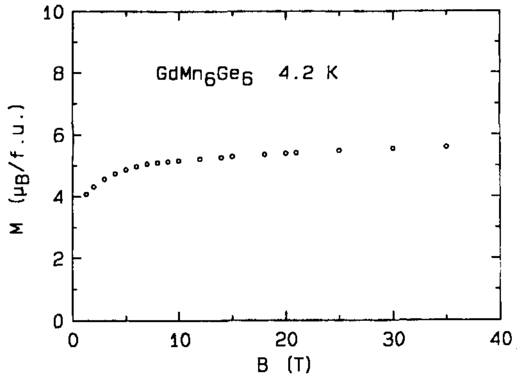

Fig. 2. Field dependence of the magnetization of $GdMn_6Ge_6$ at 4.2 K.

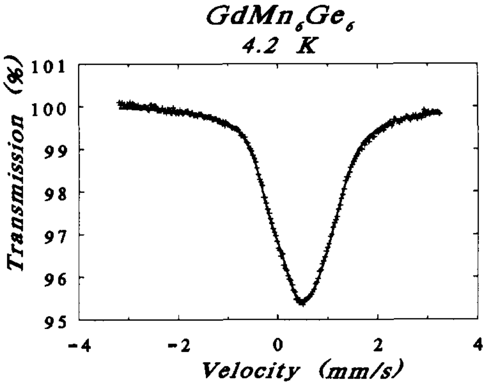

Fig. 3. $^{155}$Gd Mössbauer spectrum of $GdMn_6Ge_6$ at 4.2 K. The solid curve through the data points represents a fit.

coupled Gd and Mn sublattice magnetizations the saturation moment of 5.0 $\mu_B$ may be interpreted as being the result of an Mn sublattice moment of 12.0 $\mu_B$ and a Gd sublattice moment of 7.0 $\mu_B$ (free ion value). The shape of the magnetic isotherm suggests that the situation is different in low fields since one would have expected that the magnetization has a linear field dependence in fields much lower than 10 T for ferromagnetic particles able to rotate freely in the sample holder. Most likely the Mn sublattice is no longer ferromagnetic in zero field but rather antiferromagnetic, leaving only a relatively small net Mn sublattice moment induced by the molecular field of the Gd sublattice. As may be seen from Fig. 1 this situation is present only up to about 100 K. The strong rise in the magnetization between 100 and 200 K suggests that with increasing temperature there is a transition from an antiferromagnetic Mn sublattice to a ferromagnetic Mn sublattice. This transition is most likely driven by thermal expansion. This hypothesis is based on the fact that Mn atoms have a tendency to couple antiparallel for small Mn–Mn distances but to couple parallel for sufficiently large Mn–Mn distances. It agrees with preliminary observations on $TbMn_6Ge_6$ where the corresponding transition occurs at substantially higher temperatures, only slightly below $T_c$. More experiments are currently being undertaken to study the origin of this interesting behaviour in more detail.

The Mössbauer spectrum of $GdMn_6Ge_6$ was obtained by means of the 86.5 keV resonance of $^{155}$Gd. The source consisted of neutron-irradiated $SmPd_3$ prepared with samarium enriched to 98% in $^{154}$Sm. Details of the spectrometer are given elsewhere [5]. The spectrum obtained is shown in Fig. 3.

We analysed the spectrum by means of a least-squares fitting procedure based on the diagonalization of the full nuclear Hamiltonian and used a transmission integral. The independently refined variables consisted of the isomer shift (IS), the effective hyperfine field ($H_{eff}$) and the quadrupole splitting (QS) (or the electric field gradient tensor element $V_{zz}$, obtained via the relation $QS = (1/4)eQV_{zz}(3\cos^2\theta - 1)$, where the value $Q = 1.30 \times 10^{-28}$ m$^2$ was taken from Tanaka *et al.* [6]. The fitting procedure has furthermore been performed with the constraint that the angle $\theta$ between $H_{eff}$ and the c-axis be 90° as was derived from results obtained previously for the isotypic compound $GdMn_6Sn_6$. The absorber and source line widths were constrained to 0.25 and 0.36 mm s$^{-1}$ for the transmission integral. The hyperfine parameters corresponding to the best fit are listed in Table 1, where they can be compared with the hyperfine parameters obtained previously [2] for the isotypic compound $GdMn_6Sn_6$. It can be seen from Table 1 that the electric field gradient $V_{zz}$ at the nuclear Gd site has increased by more than 60% compared with $GdMn_6Sn_6$.

TABLE 1. Hyperfine parameters derived from fitting the $^{155}$Gd Mössbauer spectra at 4.2 K of $GdMn_6Ge_6$ and $GdMn_6Sn_6$

| Compound | $V_{zz}$ ($10^{21}$ V m$^{-2}$) | $\lvert B_{eff}\rvert$ (T) | IS (mm s$^{-1}$) | $\theta$ (deg) | $\eta$ |
|---|---|---|---|---|---|
| $GdMn_6Ge_6$ | $-3.4 \pm 0.3$ | $7.4 \pm 0.5$ | $0.49 \pm 0.01$ | 90 | 0 |
| $GdMn_6Sn_6$ | $-2.0 \pm 0.3$ | $11.6 \pm 0.9$ | $0.55 \pm 0.001$ | 90 | 0 |

The electric field gradient in $GdMn_6Sn_6$ was discussed extensively in a previous report [2] where a comparison was made between the crystal structures and the expected $V_{zz}$ values in $CeCo_3B_2$ type structures and $HfFe_6Ge_6$ type structures. Both structure types have in common that the central minority atom is surrounded in the equatorial plane by a hexagon of six s,p atoms while in the plane below and above the equatorial plane there are hexagons consisting of transition metal atoms. For Gd-based compounds this coordination is able to produce large asphericities of the 6p and 5d on-site valence electrons of Gd which in turn produces a large value of $V_{zz}$ [7, 8]. However, in the $HfFe_6Ge_6$-type structure there are two additional near neighbour s,p atoms along the *c* direction which have a strongly detrimental influence on the on-site valence electron asphericities of Gd, explaining the comparatively low value of $V_{zz}$ in $GdMn_6Sn_6$. This detrimental influence on $V_{zz}$ is expected to be larger the lower the electron density at the atomic cell boundaries of the s, p element [9]. Given the fact that the latter quantity is lower for Sn than for Ge [10] one may conclude that the detrimental influence of the two s, p-neighbour atoms in the Gd coordination shell is less severe in $GdMn_6Ge_6$ than in $GdMn_6Sn_6$, explaining the higher value of $V_{zz}$ in the former compound compared with the latter. Further investigations are planned to study the correlations between the $V_{zz}$ values found in $GdMn_6Ge_6$ and $GdMn_6Sn_6$ and the corresponding rare earth sublattice anisotropies in the series $RMn_6Ge_6$ and $RMn_6Sn_6$.

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