Magnetostructural irreversibilities in $R_5\text{Ge}_3$ ($R = \text{Gd, Nd}$) intermetallics

M Doerr$^1$, M Rotter$^2$, A Devishvili$^{2,3}$, A Stunault$^3$, J J Perenboom$^4$, T Tsutaoka$^5$, A Tanaka$^5$, Y Narumi$^6$, M Zschintzsch$^7$ and M Loewenhaupt$^1$

$^1$ Technische Universität Dresden, Institut für Festkörperphysik, D-01062 Dresden, Germany
$^2$ University of Oxford, Dept. of Physics, Clarendon Lab., Parks Road, OX1 3PU Oxford, UK.
$^3$ Institute Laue-Langevin Grenoble, 6 rue Jules Horowitz, F-38042 Grenoble, France
$^4$ St. Radboud University, HFML, P.O. box 9010, NL-6500-GL Nijmegen, The Netherlands
$^5$ Hiroshima University, Graduate School of Education, Higashi-Hiroshima 739-8524, Japan
$^6$ University of Tokyo, Institute for Solid State Physics, Kashiwa, Chiba 277-8581, Japan
$^7$ Technische Universität Dresden, Institut für Strukturphysik, D-01062 Dresden, Germany
E-mail: doerr@physik.tu-dresden.de

Abstract. Magnetoelastic phenomena of irreversible character were investigated on the rare-earth germanides Nd$_5$Ge$_3$ and Gd$_5$Ge$_3$, which are prominent members of the hexagonal $R_5\text{Ge}_3$ series. Both compounds order antiferromagnetically at 52 K and 76 K, respectively. A strong magnetostructural irreversibility (i.e. a relative length change of about $10^{-3}$ which can be induced by a magnetic field and stays stable after ramping down the field) was detected for both samples by measurements of magnetostriction and thermal expansion using capacitive dilatometry. This transition can be reversed by heating the sample near the ordering temperature. Additional experiments by X-ray and neutron scattering at Gd$_5$Ge$_3$ in order to analyze the effect itself and the structural reversal on an atomistic scale indicate the polymorphic (or metastable) magnetic character (e.g. several propagation vectors $((0 \ 0 \ 0.4)$ and $(0.3 \ 0.3 \ 0)$ were found) which allow to induce strong lattice distortions by an external magnetic field via the magnetoelastic coupling.

In recent years, a significant number of rare-earth compounds with a magnetostructural irreversibility was investigated. A prominent example is the $R\text{Cu}_2$ series at which a multivariant structure can be induced by an external magnetic field [1]. This effect is mainly driven by the strong rare-earth anisotropy and is accompanied by a magnetostrictive distortion of the order of $10^{-2}$. Another class of materials which came into the spotlight are the compounds containing rare-earth and germanium. The special interest is motivated by unusual effects as for example the magnetocaloric effect of Gd$_5$Ge$_4$ [2] and the strong magnetostriction of Gd$_5$(Ge$_{1-x}$Si$_x$)$_4$ [3].

Additional to these compounds the $R_5\text{Ge}_3$ series became scientifically promising. In Gd$_5$Ge$_3$ a magnetic irreversibility has been observed by magnetization, i.e. a transition to a metastable magnetic structure in an external field of about 3 T (at 4.2 K) [4]. The $R_5\text{Ge}_3$ compounds crystallize in the hexagonal Mn$_5$Si$_3$ structure (space group $P6_3/mcm$) where the $R^{3+}$ ions occupy two different crystallographic sites (4d and 6g) [5]. The layers formed by the rare-earth ions are stacked along the hexagonal c axis. Magnetic ordering temperatures of 52 K (Nd$_5$Ge$_3$) [6] and 76 K (Gd$_5$Ge$_3$, with a further reorientation at 52 K) were obtained by susceptibility [5]. The magnetic structure is still an open question. A first phenomenological model of the spin
arrangement of Gd$_3$Ge$_5$ with simple antiferromagnetism on the 4d sites and a 120° structure on the 6g sites has been proposed [4]. Magnetization on Nd$_3$Ge$_3$ show antiferromagnetism, but also a ferrimagnetic component at some of the samples was detected. Moreover, the magnetizing process of this substance was also found to be of irreversible character.

These facts motivate a detailed investigation of the coupling between magnetic and lattice properties of R$_3$Ge$_5$ (R=Gd,Nd) by dilatometric measurements dependent on field and temperature. A combination of these magnetostrictive results with results of scattering experiments, with X-rays as well as with neutrons, should i) clarify the origin of the magnetostructural irreversibility and ii) give some hints to possible sources of the anisotropy of Gd$_3$Ge$_5$ (dipolar interaction, higher order exchange etc).

Single crystals of Nd$_3$Ge$_3$ and Gd$_3$Ge$_5$ were prepared by a Czochralski crystal growing procedure in a tri-arc furnace. The crystals were cut into rectangular pieces with a characteristic length of 2 mm, approximately. All pieces were annealed at 300 °C for 24 h in an evacuated quartz tube [4] and stored under protective Ar atmosphere till mounting into the dilatometer.

The measurements of magnetostriction and thermal expansion were carried out using a miniaturized capacitive dilatometer (outer diameter 20 mm) [7] mounted in the variable temperature insert of a 14 T cryomagnet. A similar dilatometer (outer diameter 18 mm) [8] could be inserted into the high field magnet of the HMFL Nijmegen with a maximum steady field of 33 T in order to determine the saturation field of Gd$_3$Ge$_5$. Neutron experiments on single crystals to analyze the magnetic structure of Gd$_3$Ge$_5$ have been done at the D3 neutron diffractometer at the hot source of the ILL, Grenoble.

The results of macroscopic magnetoelastic measurements at Gd$_3$Ge$_5$ are shown in figs. 1-4. Figs. 1 and 2 represent the temperature dependence of the relative sample length in the hexagonal plane (a direction) or perpendicular to this plane (c direction), respectively. The significant kink in the zero field cooling curves is connected to the onset of antiferromagnetic order at 76 K. The other graphs illustrate the annealing behaviour after application of a strong magnetic field at low temperatures: The sample shrinks in a direction by about $-3 \times 10^{-4}$ and expands in c direction by $+9 \times 10^{-4}$. From 20 K the thermal expansion follows the virgin state curve. These facts are directly connected to the isothermal striction of the samples in magnetic fields (figs. 3 and 4). An increase of the relative sample length of the same value, approximately, was measured at 3 T (5 K) and about 2 T (20 K) in a direction. Another anomaly is visible at 4 T, probably connected to a change of the magnetic structure in field (see below). In contrast to $\Delta a/a$ the sample length $\Delta c/c$ decreases (field applied parallel to c). For comparison the magnetostriction at 100 K (above the ordering temperature = parastriction) is given and does not show any transition. Additionally, unusual features should be noted: the magnetostriction at 5 K is of irreversible character, i.e. the distortion in field is stored and the sample length does not come back to the original value after ramping the field to zero. The second (to negative fields) and third (again to positive ones) field sweep graphs are more or less flat. Only a temperature increase (figs. 1 and 2) can reverse the effect. At 20 K this irreversibility does not occur anymore. However, the magnetostriction curves at 20 K are of hysteretic character.

In order to see, if this magnetoelastic behaviour and the irreversibility are common properties of the R$_3$Ge$_5$ compounds or are only connected to the pure spin system Gd$_3$Ge$_5$ without any crystal field striction the measurements were repeated at Nd$_3$Ge$_3$ (figs. 5-8). In contrast to the second order phase transition at $T_N$ observed in Gd$_3$Ge$_5$ the thermal expansion in Nd$_3$Ge$_3$ indicates a third order transition. From magnetization measurements it is inferred that the crystal electric field in Nd$_3$Ge$_3$ leads to a strong easy hexagonal axis anisotropy, which possible induces a frustrated state with strong correlations extending to temperatures above $T_N \approx 52$ K. Note that this ordering temperature is significant higher than expected from a de Gennes scaling. The features observed in the magnetostriction of Gd$_3$Ge$_5$ are also present in Nd$_3$Ge$_3$, but of a smaller magnitude and with an exchanged tendency: the a-axis is nearly not affected by the
field. The changes are in the order of $10^{-5}$ (fig. 7). At the first field sweep the sample contracts in $a$-direction (clearly visible at the 20 K) curve, but this process is more smoothed compared to Gd$_5$Ge$_3$. The contraction vanishes by an annealing up to 30 K, approximately (fig. 5). Also the behaviour along $c$ is in contrast to the Gd case: An expansion of about $+6 \times 10^{-5}$ (5 K) and $+4 \times 10^{-5}$ (20 K) takes place at the first sweep which cannot be repeated at all following sweeps. Only a temperature treatment above 25 K (fig. 6), brings the sample back to its original state.

In conclusion, both investigated rare-earth germanides Gd$_5$Ge$_3$ and Nd$_5$Ge$_3$ are characterized by a complex magnetoelasticity. A magnetostructural irreversibility is induced by fields of about 1..2 T. It can be reversed by annealing the sample to 20..30 K. The magnetostriction of Gd$_5$Ge$_3$ additionally has a reversible anomaly at about 4 T. In order to get more insight into this behaviour we performed neutron diffraction in magnetic field. The zero field propagation (0 0 0.4) is not affected by the transition at 1.2 T. However, its intensity decreases significantly above 4 T. Other experimentally determined interesting facts are the remarkably high saturation field of about 30 T for Gd$_5$Ge$_3$. Interestingly, a second sample of Gd$_5$Ge$_3$ showed the same $T_N$, but a propagation of (0.3 0.3 0) and field induced phase transitions were found at much higher fields. All these facts need further experimental and theoretical investigation in order to come to a complete understanding of the magneto-structural behaviour of the $R_5$Ge$_3$ series.
Figure 5. Thermal expansion of Nd$_5$Ge$_3$ in the hexagonal plane.

Figure 6. Thermal expansion of Nd$_5$Ge$_3$ along the hexagonal axis.

Figure 7. Longitudinal magnetostriction of Nd$_5$Ge$_3$ in the hexagonal plane (curves shifted).

Figure 8. Longitudinal magnetostriction of Nd$_5$Ge$_3$ along the hexagonal axis.

Acknowledgments
This study was partly supported by the Deutsche Forschungsgemeinschaft within the SFB463. Another part was supported by EuroMagNet under EU contract RII-CT-2004-506239.

References
[1] Raasch S, Doerr M, Kreyssig A, Loewenhaupt M, Rotter M and Hoffmann J U 2006 Phys. Rev. B 73 064402.
[2] Pecharsky V K and Gschneidner K A 1997 Phys. Rev. Lett. 78(23) 4494.
[3] Morellon L, Blasco J, Algarabel P A and Ibarra M R 2000 Phys. Rev. B 62 1022.
[4] Narumi Y et al. 2008 J. Phys. Soc. Jpn. 77 053711.
[5] Tsutaoka T, Nishiume Y and Tokunaga T 2004 J. Magn. Magn. Mat. 272-276, e421.
[6] Schobinger-Papamantellos P and Buschow K H J 1985 J. Magn. Magn. Mat. 49, 349.
[7] Rotter M, Müller H, Gratz E, Doerr M and Loewenhaupt M 1998 Rev. Sci. Instrum. 69 2742.
[8] Doerr M, Rotter M, Brooks J, Jobiliong E, Lindbaum A, Vasic R and Loewenhaupt M 2006 AIP Conf. Proc. 850 1239.