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Pressure-induced decoupling of the magnetic ordering of the Mn and Gd sublattices in $GdMn_2$

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Abstract. The thermal expansion of $GdMn_2$ was measured under pressures up to 20 kbar. The large positive magnetovolume effect, caused by the onset of the Mn magnetism, is found to be shifted towards lower temperatures with pressure, and vanishes around 15 kbar. Above this pressure only the Gd sublattice shows long-range magnetic order. Between 6 and 15 kbar the Gd and Mn sublattices order separately. The pressure-induced splitting of the ordering temperatures is ascribed to the Mn magnetism instability, which is observed for certain RMn_2 compounds.

1. Introduction

The rare-earth– (R–) manganese Laves phase compounds RMn_2, where R has an incompletely filled 4f shell, are characterized by two magnetic sublattices which are formed by the localized 4f electrons of the rare earth and the itinerant 3d electrons of Mn. The latter are hybridized with the 5d (4d) electrons of R (Y) [1, 2]. As within this series the Mn–Mn exchange interaction is negative and, furthermore, since the Mn ions build up regular tetrahedra in the diamond-type structure, frustration occurs leading to complex magnetic ground states. For example, YMn_2 [3] exhibits a helical angle modulation of the Mn moments with very long periodicity (∼400 Å). In those cases where R carries a local magnetic moment the negative f–d exchange interaction modifies the character of the magnetic configuration in the Mn sublattice; however, the magnetic structure still remains frustrated [4].

The RMn_2 compounds show a number of striking phenomena mainly due to the Mn magnetism instability: with R = Y, Pr, Nd, Sm, Gd, and Tb long-range magnetic order is established in the Mn sublattice, whereas Mn exhibits no intrinsic magnetic moment in $ErMn_2$, $TmMn_2$ and $LuMn_2$ [5, 6, 7, 8]. In $HoMn_2$ and $DyMn_2$ and also in some substituted $(Tb, Sc)Mn_2$ and $(Gd, Lu)Mn_2$ compounds a coexistence of magnetically ordered and paramagnetic Mn sites has been observed by means of NMR and neutron diffraction measurements [8, 9, 10, 11, 12]. Various investigations indicate that the magnetic properties of the RMn_2 compounds are remarkably sensitive to small changes of internal parameters such as the Mn–Mn distance or the f–d exchange field [1, 13, 14, 15]. They are also easily affected by external forces. Prominent is the case of YMn_2 where the antiferromagnetic ordering temperature ($T_N \approx 110$ K) decreases rapidly under applied pressure and disappears

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for pressures above about 3 kbar [16]. In $TbMn_2$ the magnetic state of the Mn sublattice can be changed by both external pressure and magnetic fields [14, 15, 17, 18].

As a consequence of this instability, two magnetic ordering temperatures were observed in $TbMn_2$ [15, 18]. At $T_C = 50$ K the Tb sublattice undergoes a second-order-type ferromagnetic transition, while the Mn subsystem remains paramagnetic, concomitant with there being a negative volume effect on cooling. Note that a similar negative deviation in the temperature-dependent thermal expansion, which was ascribed to possible crystal-field effects, was also detected for $DyMn_2$ and in the system $Tb(Mn, Fe)_2$ [19, 20]. At somewhat lower temperature—which strongly depends on the sample quality—the itinerant d subsystem of $TbMn_2$ exhibits a first-order transition accompanied by an increase in volume of about 1%. The presence of two separate magnetic ordering temperatures, for the two magnetic subsystems, is ascribed to the subsequent magnetic ordering of the Mn sublattice with increasing f–d molecular field as the temperature decreases. In contrast, the increase of both the f–d interaction and of the Mn–Mn distance in $GdMn_2$ favours the stability of the Mn moments. Of certain interest therefore is the question concerning the magnetic state of the Gd subsystem below $T_N \approx 110$ K where the Mn sublattice orders. On the basis on thermal expansion and magnetic measurements [22, 21], a separate ferromagnetic ordering of Gd at $T_C \approx 40$ K was proposed. However, this was not confirmed by NMR, Mössbauer and specific heat measurements [8, 23, 24] and seems to be more consistent with a change in the magnetic structure below T_N. The large pressure response of the Mn ordering temperature in $GdMn_2$ ($\partial T_N/\partial P \approx 5.5$–6 K kbar^{-1}) [25, 26] enables us to drive the magnetic ordering in the itinerant Mn subsystem by pressure. As the localized Gd subsystem is essentially more stable than the itinerant one (compare, e.g., $GdAl_2$: $\partial T_C/\partial P \approx +0.7$ K kbar^{-1} [27]), one can expect for $GdMn_2$ under pressure a splitting of the magnetic ordering temperatures similar to that found for $TbMn_2$. For this reason we have undertaken a study of the pressure response of the magnetic ordering in $GdMn_2$ in order to detect whether there arises a separate ordering of the magnetic sublattices. As the magnetic ordering temperatures show distinctive anomalies in the temperature variation of the volume thermal expansion, this method allows us to trace accurately their respective pressure dependences.

2. Experimental details

Polycrystalline samples of $GdMn_2$ were prepared from starting materials with the purity of 99.9% using high-frequency melting under a protective argon atmosphere. In order to avoid the formation of R_6Mn_{23} a stoichiometry of 1:1.93 was chosen. Subsequently, the ingots were homogenized at 750 °C for one day in an argon atmosphere. The phase purity of the samples was proved via x-ray analysis. The thermal expansion was measured by means of a standard strain gauge method in the temperature range 4.2 to 300 K. The strain gauges (Kyowa engyo, KFL02-C1-11, gauge factor 2.06) were glued onto a clean surface on each specimen. The reference material was 5N copper, with thermal expansion values taken from [28]. The thermal expansion coefficient α (K^{-1}) $= (1/l)(\mathrm{d}l/\mathrm{d}T)$ was obtained by differentiating $\Delta l/l$ with respect to temperature. The accuracy in determining α was $\pm 3 \times 10^{-7}$ K^{-1} above 10 K and $\pm 5 \times 10^{-7}$ K^{-1} below 10 K. The temperature was measured by means of a calibrated Cu(Fe)–chromel thermocouple. Pressures up to 20 kbar were generated by means of a piston–cylinder device with Flurenite (F70 and F77) as the pressure-transmitting medium. Pressure was kept constant during the measurement within the limits of $\pm 1\%$ by monitoring the oil pressure on the piston.

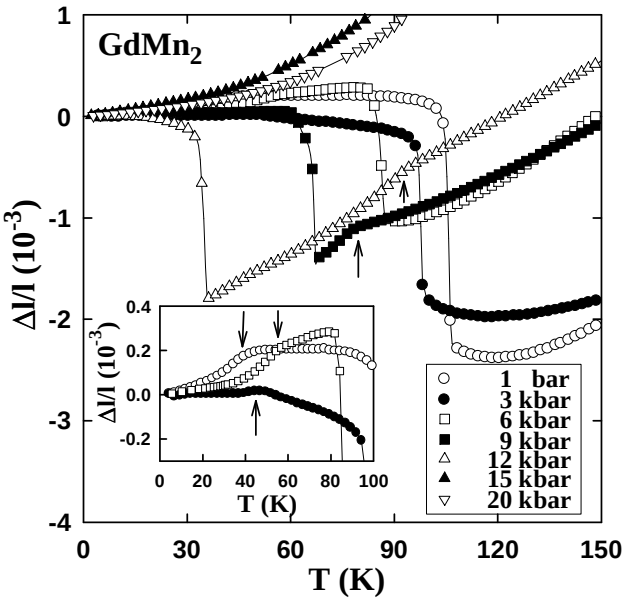

Figure 1. The temperature-dependent thermal expansion $\Delta l/l$ of $GdMn_2$ for pressures up to 20 kbar. Arrows indicate the respective magnetic ordering temperatures. Lines are drawn as a guide to the eyes.

3. Results and discussion

In figure 1, the temperature dependence of the linear thermal expansion of $GdMn_2$ at different external pressures is shown. Data obtained at ambient pressure are in good agreement with that reported in the literature [5, 6, 22]: during cooling from the paramagnetic temperature range and far above T_N $\Delta l/l$ exhibits an enhanced thermal expansion coefficient ($\alpha \approx 35 \times 10^{-6}$ K^{-1}), followed by a large positive volume effect at 107 K. This temperature coincides with the antiferromagnetic ordering temperature T_N of $GdMn_2$ and indicates the occurrence of long-range magnetic order of the itinerant Mn subsystem. Furthermore, a kink-like anomaly is observed below about 40 K (see the inset of figure 1).

The observed pressure-dependent results can be divided into two groups. Up to about 6 kbar all the $\Delta l/l\,(T)$ curves show a pronounced positive slope above the first-order-type transition; however, the absolute value of α in the paramagnetic temperature range decreases with increasing pressure. In accordance with the itinerant character of Mn magnetism and the results obtained for $GdMn_2$ as well as for other RMn_2 compounds we can consider the increase in volume at T_N on cooling as evidence for the onset of long-range magnetic order in the itinerant Mn subsystem. The pressure-dependent results shown in figure 1 are in good agreement with those reported in the temperature range from 80 K up to room temperature and pressures up to 5 kbar [29].

In contrast to the low-pressure data, $\Delta l/l$ versus T for $P \geqslant 9$ kbar shows a qualitatively different behaviour. At temperatures well above the first-order-type volume expansion, the kink in $\Delta l/l$ (shown by arrows in figure 1) indicates a further phase transition. While the former can again be related to the itinerant Mn subsystem, the latter seems to be due to the ferromagnetic ordering of the Gd sublattice, which obviously orders in $GdMn_2$

under high pressure. Indeed, both the character of the temperature dependence and the value of the negative deviation of $\Delta l/l$ are similar to those observed below T_C in $DyMn_2$ and in $Tb(Mn, Fe)_2$. For $P \geqslant 15$ kbar the first-order positive volume effect is no longer observable. Note that at pressures above about 9 kbar the electrical resistivity of $GdMn_2$ also reveals two anomalies at the same temperatures as $\Delta l/l$ does [26]. Furthermore, the peculiar shape of the resistivity curves in that pressure range accords with a change from a ferromagnetic type of structure to an antiferromagnetic one at T_N. The strengthening of a ferromagnetic component of the Gd sublattice with pressure was also shown by recent Mössbauer measurements up to 30 kbar [30].

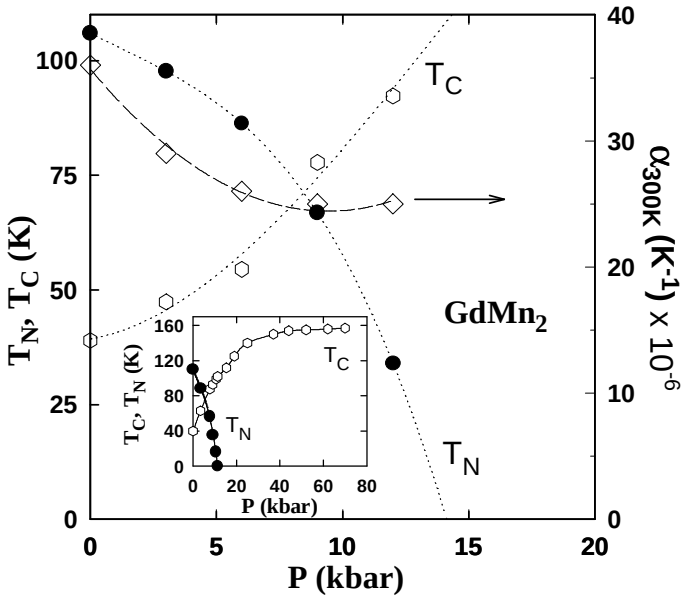

Figure 2. The pressure dependence of T_N and T_C and the coefficient of the thermal expansion α obtained at 300 K. The inset shows the pressure dependence of the magnetic ordering temperatures as obtained from electrical resistivity measurements [32]. Lines are drawn as a guide to the eyes.

An additional small anomaly can also be seen in $\Delta l/l$ versus T for $GdMn_2$ at lower values of pressure (see the inset of figure 1). The respective temperatures coincide with those temperatures where the antiferromagnetic order changes to a ferrimagnetic state with a markedly detectable spontaneous magnetization [21]. Magnetization measurements under pressure have also revealed that this anomaly shifts to higher temperatures with increasing pressure [31]. In figure 2 the pressure dependence of the characteristic temperatures determined from the distinct anomalies in the thermal expansion measurements is shown. For the reasons given above we assume that due to the suppression of Mn magnetism by external pressure, the two magnetic sublattices of $GdMn_2$ order separately between 9 and 15 kbar. In this pressure range the situation is very similar to that of $TbMn_2$ and has to be considered as a natural consequence of the different pressure responses of the Mn and Gd sublattices.

As indicated in figure 2, magnetic order in the Mn sublattice vanishes above some critical value of pressure P_C ($P_C \approx 15$ kbar). High-pressure resistivity measurements up to 80 kbar show that above 20 kbar, $\partial T_C/\partial P$ becomes comparable with that of simple Gd

compounds such as $GdAl_2$ [32] (see the inset of figure 2). In our opinion, the strongly non-linear variation of $T_C(P)$ above this critical pressure still arises from the influence of the Mn subsystem. For $P > 15$ kbar, where the contribution from the f–d exchange to the total free energy is strongly reduced in comparison with the f–f exchange, $\partial T_C/\partial P$ decreases considerably with further increasing pressure and becomes nearly constant above about 20 kbar.

Note that the high-pressure resistivity data also reflect the presence of pronounced spin fluctuations, becoming gradually suppressed with increasing pressure. A similar behaviour was observed from resistivity measurements of YMn_2 under pressure [32]. Here, we want to stress that the thermal expansion coefficient α of $GdMn_2$, obtained at room temperature, decreases on applying external pressure (figure 2). Assuming that the enhanced value of α is due to the presence of spin fluctuations [1], the decrease of α can be explained by the pressure-induced suppression of such spin fluctuations in the Mn subsystem.

We note that in YMn_2, which has nearly the same lattice constant and magnetic ordering temperature as $GdMn_2$, long-range antiferromagnetic order disappears for pressures less than 4 kbar, i.e. at considerably lower pressures. This fact can be related to the absence of the f–d exchange interaction in YMn_2, which makes the Mn magnetism more stable in $GdMn_2$.

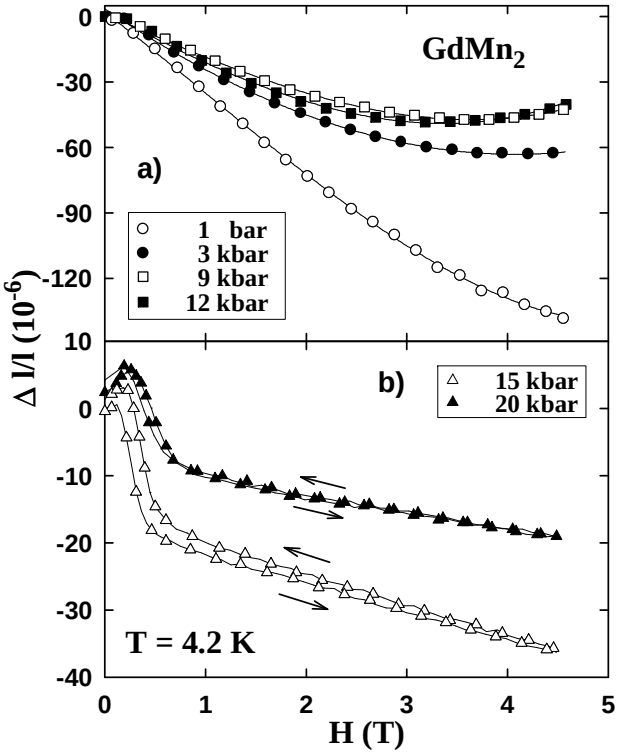

Figure 3. The transversal magnetostriction of $GdMn_2$ at 4.2 K measured under various external pressures. Lines are drawn as a guide to the eyes.

In the vicinity of the Mn magnetism instability in the $T-P$ phase diagram one can induce a drastic change of the magnetic structure by applying external magnetic fields, as has been shown, e.g., for $TbMn_2$ [18]. The change in the character of $\Delta l/l$ versus H when crossing the $T_N(P)$ phase line is clearly seen in figure 3 where the transversal

magnetostriction data at 4.2 K are presented. Below 15 kbar, when the Mn sublattice is ordered, the magnetostriction is negative, whereas for $P \geqslant 15$ kbar the initial slope of $\Delta l/l$ versus H becomes positive. The sharp transitions observed at 0.3 T ($P = 15$ kbar) and 0.45 T ($P = 20$ kbar) can be interpreted as the onset of long-range magnetic order in the Mn sublattice induced by an external magnetic field. With further increase in H, $\Delta l/l$ decreases again. However, additional measurements, in particular concerning the longitudinal magnetostriction, are needed to clarify the origin of this transition.

4. Conclusion

The analysis of the thermal expansion measurements of $GdMn_2$ indicates that a separate magnetic ordering of the Gd and Mn sublattices can be induced in $GdMn_2$ by external pressure. A similar effect is observed at ambient pressure in some other intermetallic compounds containing R and 3d transition metals, e.g., RMn_{12} ($T_N \approx 110$ K for the Mn sublattice and $T_C \approx 5$–7 K for the R sublattice [33]) and RMn_2Ge_2 (T_N for the Mn sublattice exceeds 400 K while the R sublattice orders below about 80 K [34]). However, in contrast to the case for these intermetallics where T_N for the Mn sublattice is considerably higher than T_C for the R sublattice and where the separate ordering is usually considered as a consequence of the weak intersublattice f–d exchange interaction, in $GdMn_2$ this effect is of different origin. As in the case of $TbMn_2$, the splitting of the magnetic ordering temperature arises from the Mn magnetism instability, which is strongly affected by the Mn–Mn distance and can therefore be easily suppressed by external pressure.

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