Magnetoresistance, specific heat and magnetocaloric effect of equiatomic rare-earth transition-metal magnesium compounds

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Abstract

We present a study of the magnetoresistance, the specific heat and the magnetocaloric effect of equiatomic RETMg intermetallics with RE = La, Eu, Gd, Yb and T = Ag, Au and of GdAuIn. Depending on the composition these compounds are paramagnetic (RE = La, Yb) or they order either ferro- or antiferromagnetically with transition temperatures ranging from about 13 to 81 K. All of them are metallic, but the resistivity varies over three orders of magnitude. The magnetic order causes a strong decrease of the resistivity and around the ordering temperature we find pronounced magnetoresistance effects. The magnetic ordering also leads to well defined anomalies in the specific heat. An analysis of the entropy change leads to the conclusion that generally the magnetic transition can be described by an ordering of localized $S = 7/2$ moments arising from the half-filled $4f^7$ shells of Eu^{2+} or Gd^{3+}. However, for GdAgMg we find clear evidence for two phase transitions, indicating that the magnetic ordering sets in partially below about 125 K and is completed via an almost first-order transition at 39 K. The magnetocaloric effect is weak for the antiferromagnets and rather pronounced for the ferromagnets for low magnetic fields around the zero-field Curie temperature.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The equiatomic rare-earth (RE) transition-metal (T) magnesium compounds RETMg have intensively been investigated in recent years with respect to their crystal chemistry and to a basic

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characterization of their magnetic properties [1–12]. With the trivalent rare-earth elements, the RETMg intermetallics adopt the hexagonal ZrNiAl structure [13–15], while those with a divalent rare-earth metal, i.e. europium and ytterbium, crystallize in the orthorhombic TiNiSi type structure [16]. Interesting magnetic properties have been observed for several of the RETMg compounds. To give some examples, long-range magnetic ordering has been observed for CeTMg (T = Pd, Pt, Au) at 2.1, 3.6, and 2.0 K, respectively [9]. EuAgMg and EuAuMg order ferromagnetically at relatively high Curie temperatures of 22 and 36 K [6]. Similar behaviour was observed for the gadolinium-based compounds GdTMg (T = Pd, Ag, Pt), which show ferromagnetic order at 96, 39, and 98 K for T = Pd, Ag, and Pt, respectively [10]. In contrast, GdAuIn and GdAuMg order antiferromagnetically with Néel temperatures of 13 and 81 K, respectively [12]. Not much is known, however, about the transport and thermodynamic properties of these compounds, in particular about their magnetic field dependences. In this report we present resistivity measurements and specific heat data for some REAgMg and REAuMg compounds and for GdAuIn in the temperature range from about 2 to 300 K and in external magnetic fields up to 14 T. We have also extended the magnetization measurements up to 14 T, which we use to calculate the magnetocaloric effect.

2. Experimental details

Starting materials for the preparation of the intermetallic compounds RETMg and GdAuIn were sublimed ingots of the rare earth elements (Johnson Matthey, Chempur or Kelpin, >99.9%), silver and gold wire (diameter 1 mm, Degussa-Hüls, >99.9%), a magnesium rod (Johnson Matthey, diameter 16 mm, >99.5%), and indium tear drops (Johnson Matthey, 99.9%). GdAuIn was prepared by arc-melting [18] of the elements under an atmosphere of $\simeq$600 mbar argon. The argon was purified over titanium sponge (970 K), silica gel, and molecular sieves prior to use. The arc-melted button was remelted three times to ensure homogeneity. Due to the low boiling point and the high vapour pressure, the magnesium containing samples cannot be obtained via a simple arc-melting procedure, where a significant weight loss would occur through evaporation of magnesium. All these compounds were prepared in sealed high-melting metal tubes. The elements were mixed in the ideal 1:1:1 atomic ratios and sealed in small (tube size $\simeq$1 cm^3) niobium or tantalum tubes under an argon pressure of $\simeq$800 mbar. These tubes were then put in a water-cooled sample chamber [19] of a high-frequency furnace (Hüttinger Elektronik, Freiburg, TIG 1.5/300). The samples were first rapidly heated to $\simeq$1370 K and subsequently annealed at $\simeq$870 K for another two hours. The temperature was controlled through a Sensor Therm Metis MS09 pyrometer with an accuracy of $\pm$30 K. The samples could be separated from the tubes by mechanical fragmentation. No reaction with the metal tubes was observed. The polycrystalline samples are light grey with metallic lustre. For more details concerning the synthesis conditions we refer to the original literature.

The purity of the samples was checked through Guinier powder patterns using Cu Kα_1 radiation and α-quartz as an internal standard. The Guinier camera was equipped with an image plate system (Fujifilm, BAS-1800). The experimental patterns were compared with calculated ones [20], using the atomic positions from the previous single crystal studies [4–12]. All samples were pure phases on the level of x-ray powder diffraction.

For the measurements of resistivity, magnetization and specific heat we have polished larger polycrystalline pieces of irregular shape to a rectangular shape of typical dimensions of about $2 \times 1 \times 1$ mm^3. The specific heat and the magnetization have been studied in a physical property measurement system (PPMS, Quantum Design) using the relaxation time method and a vibrating sample magnetometer, respectively. The resistivity has been measured by a standard DC four-probe technique. All these measurements have been performed in the temperature range from about 2 to 300 K and in magnetic fields up to 14 T.
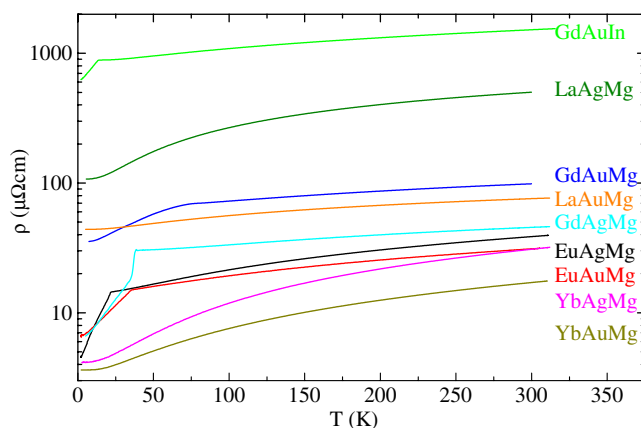
Figure 1. Resistivity of RETMg with RE = Yb, Eu, Gd, or La and T = Au or Ag and of GdAuIn.

3. Results and discussion

3.1. Crystal chemistry

The crystal structures of the RETMg intermetallics depend on the valence of the rare-earth element. With the trivalent rare-earth metals, the RETMg compounds adopt the hexagonal ZrNiAl, type [13–15], while the europium and ytterbium compounds contain Eu^{2+} and Yb^{2+}, and they adopt the orthorhombic TiNiSi type [16]. In both structure types, the transition metal and magnesium atoms build up a three-dimensional [TMg] network in which the rare-earth atoms fill distorted hexagonal channels. GdAuIn also crystallizes with the ZrNiAl structure. For more details on the crystal chemistry and chemical bonding of these RETMg intermetallics we refer to the original literature [4–12, 17].

3.2. Resistivity

Figure 1 gives an overview of the resistivity ρ of the different compounds. For all samples the temperature dependence of ρ is metallic. However, the absolute values are strongly different, ranging from a few $\mu\Omega$ cm in YbAuMg up to mΩ cm in GdAuIn. We find the following trends. The RETMg samples with divalent Yb and Eu have lower ρ values than the compounds with trivalent La and Gd. This indicates that the different ρ is related to the different structure of the divalent (TiNiSi type) and of the trivalent (ZrNiAl type) RE-based compounds. GdAuIn also adopts the ZrNiAl structure, but it has a significantly larger ρ than GdAuMg. Possibly this is related to the different valences of In (trivalent) and Mg (divalent). Combining this observation with the different resistivities of the trivalent and the divalent RE-based compounds, one observes that ρ increases with increasing number of valence electrons for the entire series RETX (X = Mg, In). Moreover, almost all REAuMg samples have lower ρ values than the corresponding REAgMg samples (the only exception is GdTMg). LDA + U band-structure calculations and photoemission studies are currently underway in order to check whether these trends correlate with systematic changes in the band structure for the different compounds.

There are pronounced kinks in $\rho(T)$ of the Gd- and Eu-based compounds. These kinks arise from the ferro- or antiferromagnetic ordering of the 4f moments of Gd and Eu. In contrast, the La- and Yb-based materials show continuous $\rho(T)$ curves without any anomalies
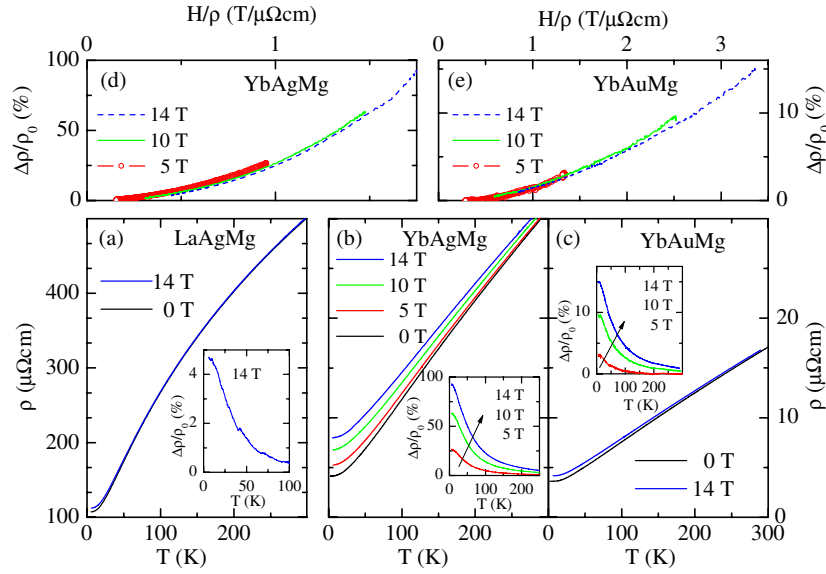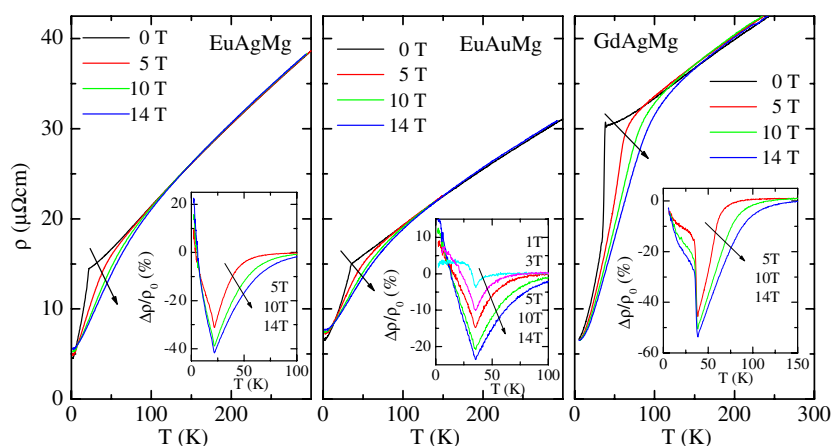
Figure 2. Resistivity of paramagnetic RETMg for different magnetic fields (panels (a)–(c)). The respective insets show the magnetoresistance $\Delta\rho/\rho_0 = [\rho(H) - \rho(H = 0)]/\rho(H = 0)$ (increasing field strength is indicated by the arrows). Panels (c) and (d) show that the magnetoresistance curves for different field strengths follow a single line if $\Delta\rho/\rho_0$ is plotted as a function of H/ρ_0 as is expected from Kohler's rule.

reflecting that the latter materials are paramagnetic down to the lowest temperature. In figure 2 we show the resistance of the paramagnets for different magnetic fields. For all samples we find a systematic increase of ρ with increasing field. This increase becomes the more pronounced the lower the temperature is. In the insets of figure 2 we present the normalized magnetoresistance $\Delta\rho/\rho_0 = [\rho(H) - \rho(H = 0)]/\rho(H = 0)$. For YbAgMg $\Delta\rho/\rho_0$ reaches more than 90% at about 5 K and a field of 14 T, whereas only about 15% is obtained for YbAuMg. In LaAgMg the absolute change $\Delta\rho$ is comparable to that of YbAgMg, but the relative change $\Delta\rho/\rho_0$ is reduced by about a factor of 20 due to the larger ρ_0 of LaAgMg. The field-induced increase of ρ is a consequence of the additional scattering of the charge carriers due to the Lorentz force as is observed in many metals [21]. Within semiclassical transport theory one expects the so-called Kohler's rule to hold, which predicts that $\Delta\rho/\rho_0$ follows a universal function $f(H/\rho_0)$ over the entire field and temperature range. As shown in the upper panels of figure 2, this is rather well fulfilled. For both Yb-based samples $f(x)$ is roughly proportional to x^2.[4]

In figure 3 the resistivity of EuTMg with T = Ag and Au and of GdAgMg is shown, which undergo a transition to a ferromagnetic order at $T_c \simeq 22$ K, $\simeq 36$ K, and $\simeq 39$ K, respectively. With increasing magnetic field we find a suppression of ρ, which is most pronounced in the temperature range around T_c. Again we show $\Delta\rho/\rho_0$ in the insets of figure 3. In a field of 14 T the maximum values of $\Delta\rho/\rho_0$ range from about -55% for GdAgMg to about -25% for EuAuMg at the respective T_c. Whereas for higher temperature $\Delta\rho/\rho_0$ continuously approaches zero, we observe a sign change for EuTMg below T_c. Around 5 K $\Delta\rho/\rho_0$ reaches up to $+20\%$ and $+15\%$ for T = Ag and Au, respectively. For GdAgMg such a sign change is not observed,

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[4] For the La-based compounds we cannot show the Kohler plot, because we have performed only one field dependent ρ measurement (ρ (14 T) of LaAgMg).

Figure 3. Resistivity of ferromagnetic RETMg for different magnetic fields (increasing field strength is indicated by the arrows). The insets show the magnetoresistance $\Delta\rho/\rho_0 = [\rho(H) - \rho(H=0)]/\rho(H=0)$.

but from the steep slope of $\Delta\rho/\rho_0$ at 2 K we suspect that it will also occur at somewhat lower temperature. Qualitatively, the behaviour of $\Delta\rho/\rho_0$ can be explained as follows: at the lowest temperature the magnetic moments are almost completely ordered and the (magneto-)resistance of the ferromagnetic RETMg is comparable to that of the paramagnetic YbTMg with respect to both the absolute value $\rho(0\,\text{T})$ and the increase in magnetic field. With increasing temperature ferromagnetic spin waves are excited and the spontaneous magnetization decreases. Therefore, the charge carriers may be scattered by magnetic excitations and as a consequence $\rho(T)$ (in zero field) increases much faster for the ferromagnets than for the paramagnets. The strongest increase of $\rho(T)$ occurs close to T_c. Although this scattering is present in the ferromagnets above T_c, the difference between $\rho(T)$ of the ferromagnets and the paramagnets decreases with further increasing temperature, since for higher temperature scattering by phonons becomes more and more dominant and one may expect that the scattering by phonons is not too different for the various compounds. In the temperature range around T_c the magnetization strongly increases with increasing magnetic field. Thus, the magnetic scattering of charge carriers can be effectively suppressed in that temperature range because the localized moments become aligned by increasing the magnetic field. With further increasing temperature thermal fluctuations increase. Thus the large negative magnetoresistance decreases again, because the influence of the magnetic field on the magnetization decreases. Note that LaAgMg does not fit into this explanation, since its ρ is much larger than ρ of the isostructural GdTMg. It remains to be clarified why ρ of LaAgMg is so large although there is no magnetic scattering present.

Figure 4 displays the resistivity of GdAuIn and GdAuMg, which order antiferromagnetically at $T_N \simeq 13$ K and $\simeq 81$ K, respectively. Again we observe a negative magnetoresistance in the temperature range around the ordering temperature which can be traced back to the suppression of magnetic fluctuations in a magnetic field. Compared to the ferromagnetic compound, this effect is, however, much less pronounced because the magnetic field tends to align the magnetic moments parallel whereas the exchange favours an antiparallel alignment. Despite the large absolute values of ρ of GdAuIn its magnetoresistance is rather strong. From the low T_N of this compound we conclude that the antiferromagnetic coupling is rather weak and the field has a strong influence. For example, T_N strongly shifts towards lower temperature with increasing field and it seems that the enhanced resistivity due to magnetic fluctuations
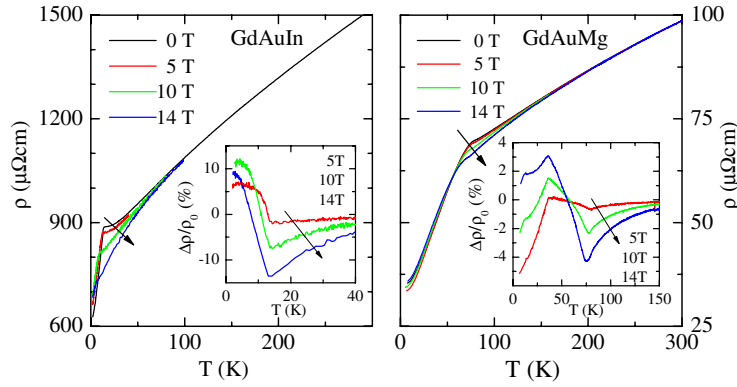
Figure 4. Resistivity of antiferromagnetic GdAuIn and GdAuMg for different magnetic fields (increasing field strength is indicated by the arrows). The insets show the magnetoresistance $\Delta\rho/\rho_0 = [\rho(H) - \rho(H = 0)]/\rho(H = 0)$.

around T_N can be almost completely suppressed in 14 T. We also observe a sign change of $\Delta\rho/\rho_0$ with decreasing temperature, but at the lowest temperature ρ does not monotonically increase with field, in contrast to the other RETMg compounds (see figures 2 and 3). We think that this more complex behaviour arises from the interplay of the antiferromagnetic coupling and the strong magnetic field, which both suppress magnetic fluctuations but also act against each other. A more detailed study down to lower temperature and to higher magnetic fields is currently underway and will be presented elsewhere. Since GdAuMg has the highest ordering temperature of all the compounds studied, it will also have the strongest (antiferromagnetic) coupling. Consequently, its magnetoresistance is rather weak even in a field of 14 T. Again, there is a sign change of $\Delta\rho/\rho_0$ below T_N. However, around 36 K $\Delta\rho/\rho_0$ shows a sharp kink and a sign change of its slope. This kink of $\Delta\rho/\rho_0$ is present for all fields since it arises from a tiny kink of the zero-field $\rho(T)$ curve at $\simeq$36 K, whereas the $\rho(T)$ curves for larger fields do not show such an anomaly. Additional anomalies also occur in our DC magnetization data below about 50 K and have been observed in AC susceptibility measurements [12]. The additional anomalies in AC susceptibility are most pronounced at 19 K and have been interpreted as evidence for a transition to a canted antiferromagnetic phase at 19 K. Thus, one may speculate whether the kink in the zero-field $\rho(T)$ curve is related to a precursor of such a spin-reorientation.

3.3. Specific heat

In figure 5 we summarize the results of our specific heat measurements for all compounds. As one may expect, the paramagnets (YbAgMg, YbAuMg, and LaAgMg) show rather similar $C_p(T)$ curves without any anomalies, since there are no phase transitions (neither structural nor magnetic ones)[5]. The ferromagnets EuTMg (T = Ag, Au) and the antiferromagnets GdAuX (X = Mg, In) show well defined anomalies at the respective Curie and Néel temperatures, respectively. In all four cases the anomaly shape is typical for a (mean-field) second-order phase transition without strong fluctuations. Above the respective ordering temperature the $C_p(T)$ curves are again very similar to each other and to those of the paramagnets. A clearly

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[5] For YbAuMg there is a very tiny anomaly in $C_p(T)$ around 2.3 K, which cannot be resolved in figure 5. This anomaly is suppressed in a magnetic field of 3 T and most probably arises from a small amount of an impurity phase of Yb_2O_3.
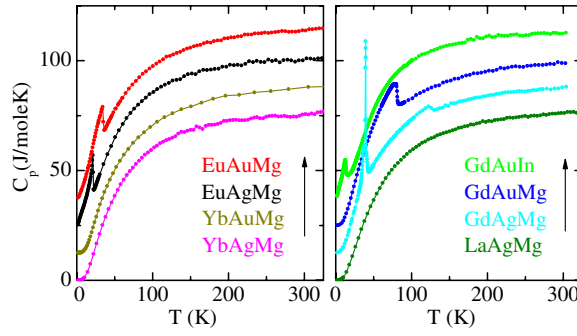
Figure 5. Specific heat of RETMg and GdAuIn as a function of temperature. In both panels the curves are shifted by 12.5 J mol^{-1} K^{-1} with respect to each other for the different compounds as is indicated by the arrows.

different behaviour is observed for GdAgMg. Here, the anomaly of C_p at $T_c \simeq 39.5$ K is very narrow and much higher than in the other compounds. This anomaly resembles more the λ-shape of a second-order phase transition with strong fluctuations or a broadened δ-anomaly of a weakly first-order phase transition. In addition, there is another clear anomaly of $C_p(T)$ around 125 K, whose shape is again typical for a mean-field second-order phase transition.

In order to further investigate the origin of these anomalies we analyse the change of (magnetic) entropy at the respective phase transitions. For both the Eu and the Gd compounds we expect that the magnetic entropy will be dominated by the half-filled 4f shells with $S = 7/2$ of Eu^{2+} or Gd^{3+}. In addition, there may be an additional contribution from a partial polarization of the 5d, 6s and 6p valence bands, but this will be much smaller than the 4f contribution of $S_{mag} = N_A k_B \ln(2S+1) \simeq 17.3$ J mol^{-1} K^{-1} (N_A and k_B denote Avogadro's and Boltzmann's constant, respectively). We assume that the total entropy consists of the sum of magnetic, phononic and electronic contributions, i.e.

$$S = S_{mag} + S_{ph} + S_{el}. \tag{1}$$

In order to separate the magnetic (C_{mag}) from the sum of the phononic (C_{ph}) and the electronic contribution (C_{el}) we estimate $C_{ph} + C_{el}$ of the (anti-)ferromagnetic compounds by using the measured $C_p(T)$ of the isostructural paramagnets, for which $C_{mag} = 0$. As a typical example, we show the analysis for EuAuMg in the right panel of figure 6, where $C_p(T)$ of YbAuMg has been used to estimate $C_{ph}(T)$ of EuAuMg. For this estimate we rescale the temperature axis of C_p^{YbAuMg} until it agrees with the measured C_p^{EuAuMg} in the temperature range above T_c. In this particular case a 6% rescaling $T' = 0.94 \cdot T$ causes a very good agreement up to the highest temperature (even at 300 K the curves deviate by less than 1%). The entropy change due the phase transition is then calculated from the difference $\Delta C_p(T) = C_p^{EuAuMg}(T) - C_p^{YbAuMg}(T')$ via integration $\Delta S(T) = \int \Delta C_p(T')/T' \, dT'$. In all cases the integration constant has been chosen such that above the phase transition $S_{mag} \simeq 17.3$ J mol^{-1} K^{-1} is reached as is expected for an $S = 7/2$ system.

The right panel of figure 6 shows the calculated entropy changes. We find that $S_{mag}(T)$ strongly decreases below the ordering temperature and roughly approaches zero for vanishing temperature for all compounds except for GdAgMg. This is clear evidence that the magnetic phase transitions can be viewed as an ordering of a system with localized $S = 7/2$ moments. In other words, the hybridization of the 4f states with the valence bands and/or a polarization of the valence bands hardly influence S_{mag}. For GdAgMg the situation is more complex. Here, the entropy change connected with the proposed magnetic ordering at $T_c \simeq 39.5$ K amounts
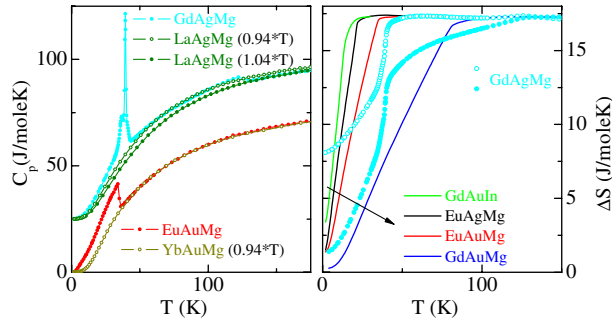
Figure 6. Left: specific heat of REAgMg for magnetically ordering RE = Eu, Gd and for paramagnetic RE = Yb, La. For the paramagnets the temperature has been rescaled (the factors a are given in the brackets) in such a way that the $C_p(a*T)$ curves allow us to estimate the phononic contributions $C_{ph}(T)$ for RE = Eu and Gd. Right: entropy changes due to the phase transitions obtained via an integration of the differences $[C_p(T) - C_{ph}(T)]/T$ for the different compounds. As expected for the half-filled 4f shell the magnetic entropy $S_{mag} = N_A k_B \ln(2S+1)$ with $S = 7/2$ is approached in most cases (lines). For GdAgMg (symbols) this is, however, only the case when the entropy changes due to both transitions are considered (see text).

only to about 50% of the expected $17.3 \, \text{J} \, \text{mol}^{-1} \, \text{K}^{-1}$. In the right panel of figure 6 this is shown by the open symbols, which are obtained when we estimate the phononic background C_{ph}^{GdAgMg} by scaling C_p^{LaAgMg} such that it coincides with the measured C_p^{GdAgMg} above about 40 K (see upper curves in the left panel of figure 6). However, it is also possible to scale C_p^{LaAgMg} such that it fits the measured C_p^{GdAgMg} only above the upper transition, i.e. above about 130 K. In this case the difference between both curves yields the sum of the entropy changes due to both transitions. As is shown by the full symbols in the right panel of figure 6 the total entropy change is again close to the expected $S_{mag} \simeq 17.3 \, \text{J} \, \text{mol}^{-1} \, \text{K}^{-1}$. This indicates that for GdAgMg a partial ordering of the magnetic moments sets in already below $T_c^1 \simeq 125$ K and the complete ordering is obtained only below $T_c^2 \simeq 39$ K. We have also performed DC magnetization measurements as a function of temperature on that sample, but we could not resolve any anomaly around 125 K. However, some small additional features, which start below about 120 K, have been observed in AC susceptibility measurements [10].

The specific heat of the paramagnetic La- and Yb-based compounds does not show any measurable magnetic-field dependence. For the antiferromagnetic materials GdAuIn and GdAuMg the specific-heat anomaly is systematically shifted towards lower temperature with increasing field. As shown in the left panel of figure 7, T_N decreases from $\simeq 13.5$ to $\simeq 10$ K for GdAuIn in a field of 10 T, and from $\simeq 81$ to $\simeq 78$ K for GdAuMg. In figure 7 we also present the magnetic-field influence on C_p for the ferromagnet EuAgMg. Here, the transition is almost completely smeared out already in a field of 5 T. This is typical for ferromagnets because larger fields cause a strong magnetization already well above the zero-field T_c and the magnetization does not develop spontaneously below a critical temperature anymore. Strictly speaking, a ferromagnetic transition temperature can only be defined for zero magnetic field.

The strong magnetic-field influence on C_p around the transition temperature means that the (magnetic) entropy is strongly field dependent. Thus, these materials are of potential interest with respect to cooling or heating by adiabatic (de-)magnetization. Usually only the magnetic entropy is magnetic-field dependent and for an effective cooling S_{mag} should therefore be large, which is the case in our samples due to the large spin of 7/2 of the half-filled 4f shell. The magnetocaloric effect, i.e. the magnetic-field induced variation of the sample temperature under adiabatic conditions, can be either directly measured or it can be calculated from measurements
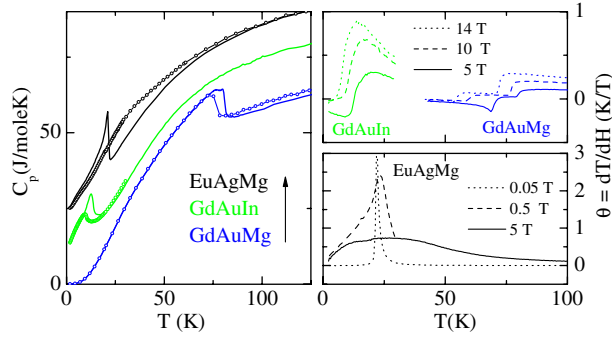
Figure 7. Left: specific heat in zero (——) and a finite magnetic field (○) of 5 T (EuAgMg) or 10 T (GdAuIn and GdAuMg). For clarity the curves of the different compounds are shifted with respect to each other. Right: differential magnetocaloric effect $\Theta = \frac{\partial T}{\partial H}$ of the different compounds for various magnetic-field strengths (see text).

of specific heat and magnetization via the thermodynamic relation

$$\Theta = \frac{\partial T}{\partial H} = -\frac{T}{C} \left. \frac{\partial M}{\partial T} \right|_H. \tag{2}$$

Equation (2) yields an expression for the differential magnetocaloric effect Θ as a function of temperature for a fixed magnetic field and the field-induced temperature change $\Delta T = T(H_1) - T(H_2)$ can be obtained by numerical calculation from measurements in constant magnetic fields with $H_1 \leqslant H \leqslant H_2$.

The upper right panel of figure 7 shows the differential magnetocaloric effect of the antiferromagnetic compounds. In a field of 5 T we find for GdAuIn a small positive $\Theta \simeq 0.3$ K T^{-1} above and $\simeq -0.2$ K T^{-1} below T_N, and Θ vanishes towards both higher and lower temperatures. This behaviour is expected via equation (2) from the typical behaviour of an antiferromagnet. With decreasing temperature $-\partial M/\partial T$ increases according to a Curie–Weiss law and C_p decreases. Both effects cause an increase of Θ until T_N is reached. For low fields the magnetization usually changes its slope at T_N, and Θ its sign. For $T \rightarrow 0$ K the magnetization usually approaches a constant value, i.e. Θ is expected to vanish. For fields lower than 5 T the temperature dependences of the $\Theta(T)$ curves are very similar to that of $\Theta(T)$ in $H = 5$ T. However, the absolute values of $\Theta(T)$ are reduced, because in low fields the magnetization of an antiferromagnet is roughly proportional to the applied field, whereas C_p/T does not change too much. Therefore, the proportionality $\Theta \propto H$ is roughly fulfilled for $H < 5$ T. For higher fields the maximum of Θ further increases, but Θ remains positive, because the sign change of $\partial M/\partial T$ is suppressed in large enough fields. For example, a field of 14 T causes a low-temperature magnetization of more than 80% of the saturation moment of 7 μ_B/fu of the half-filled 4f shell. For GdAuMg one would expect a qualitatively similar behaviour as observed in GdAuIn, but with smaller absolute values of Θ due to the larger T_N. This is, however, not the case. The main difference is that Θ only shows a step-like decrease close to T_N, whereas the sign change occurs about 10–15 K below T_N. This more complex behaviour points towards a magnetic-field dependent reorientation of the magnetic moments. As already mentioned above, evidence for such a behaviour has also been found from measurements of low-field AC susceptibility and Mössbauer spectroscopy [12].

The lower right panel displays the differential magnetocaloric effect for ferromagnetic EuAgMg. In the lowest field of 50 mT we find a very sharp peak with $\Theta \simeq 3$ K T^{-1}, which is located close to the zero-field T_c. With increasing field the peak rapidly decreases in height and strongly broadens. For example, Θ lies between 0.6 and 0.7 K T^{-1} over a temperature range

from about 10 to 40 K in a field of 5 T. Such a behaviour is typical for a ferromagnet because the transition strongly smears out with increasing field. Due to the large spin the magnetocaloric effect of EuAgMg is relatively large. However, larger effects are found e.g. in some REM_2 compounds with RE = Dy, Ho, Er and M = Co, Ni, Al. Here, larger magnetic entropy changes occur due to the larger $J = L + S$ values of RE, additional crystalline electric field effects, and contributions from magnetic Co [22–24]. Moreover, a so-called giant magnetocaloric effect observed in $Gd_5(Si_2Ge_2)$ has attracted a lot of attention [25]. This giant magnetocaloric effect is related to a second-order transition from a para- to a ferromagnetic(I) state, which then transforms via a first-order transition to a ferromagnetic(II) state.

4. Summary

We have performed a systematic study of the resistance and the specific heat as a function of temperature (2 K < T < 300 K) and magnetic field (up to 14 T) on a series of rare-earth (RE) transition-metal (T) Mg compounds RETMg and on GdAuIn. For RE = La (Yb) the 4f shell is empty (filled) and the respective compounds are paramagnetic metals, whereas the Eu- and Gd-based materials show ferro- or antiferromagnetic ordering arising from the half-filled 4f shell of Eu^{2+} or Gd^{3+}. All compounds show a metallic resistivity, but the absolute values of ρ vary over three orders of magnitude from a few $\mu\Omega$ cm in YbAuMg to mΩ cm in GdAuIn. The absolute value of ρ increases with increasing number of valence electrons, which may arise from the different crystal structures of the di- (Yb, Eu) and trivalent (La, Gd) RE-based compounds. Both the ferromagnetic and the antiferromagnetic ordering causes an abrupt decrease of ρ below the respective Curie and Néel temperatures, because the scattering of charge carriers on magnetic excitations freezes out in the ordered phase. For the ferromagnets we find a large negative magnetoresistance, which is most pronounced close to T_c, where a decrease of ρ of order $-5\%\ T^{-1}$ is observed for fields below 5 T. As expected, a significantly smaller decrease of ρ (of order $-0.2\%\ T^{-1}$) is found for the antiferromagnets close to T_N. With decreasing temperature the magnetoresistance becomes weaker and for most of the magnetically ordered compounds it is positive at the lowest temperature and comparable to the positive magnetoresistance of the paramagnets. For all ferro- and antiferromagnetic compounds the magnetic ordering causes well defined anomalies in the specific heat. Our analysis of the related entropy change clearly shows that the magnetic transitions are well described by an ordering of localized $S = 7/2$ moments of the half-filled 4f shell of Eu^{2+} or Gd^{3+}. Additional effects, e.g. from a polarization of the valence bands or a hybridization between 4f states and the valence bands, play a minor role. However, for GdAgMg we find clear evidence for two transitions at 125 and 39 K. In susceptibility measurements a sizeable spontaneous magnetization is only found below 39 K, but the entropy change due to this transition is only about half as large as expected for an $S = 7/2$ system. The expected magnetic entropy change is achieved when the sum of the entropy changes due to both transitions is considered. Thus, the specific heat data suggest that the complete magnetic order is reached via two transitions. This more complex behaviour of GdAgMg is not yet understood and deserves further investigations. For both the ferro- and the antiferromagnetic compounds we observe a sizeable magnetocaloric effect Θ, which is most pronounced for the ferromagnets in low fields and close to T_c. For EuAgMg a relatively large $\Theta \geqslant 0.6\ K\ T^{-1}$ is present over a large field and temperature range, but this value still remains well below those observed in various other rare-earth based materials.

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