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Thermal expansion of the magnetically ordering intermetallics RTMg (R = Eu, Gd and T = Ag, Au)

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Abstract

We report measurements of the thermal expansion for two Eu^{2+}- and two Gd^{3+}-based intermetallics which exhibit ferro- or antiferromagnetic phase transitions. These materials show sharp positive (EuAgMg and GdAuMg) and negative (EuAuMg and GdAgMg) peaks in the temperature dependence of the thermal expansion coefficient α which become smeared and/or displaced in an external magnetic field. Together with specific heat data, we determine the initial pressure dependences of the transition temperatures at ambient pressure using the Ehrenfest or Clausius–Clapeyron relation. We find large pressure dependences, indicating strong spin–phonon coupling, in particular for GdAgMg and EuAuMg where a quantum phase transition might be reached at moderate pressures of a few GPa.

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

There has been continuing interest in the equiatomic ternary intermetallic compounds based upon Eu and Gd rare earths, the noble metals Ag and Au, and Mg [1]. In particular, during the past ten years their synthesis, chemical, and physical properties have been studied in some detail [2–9]. The Eu-based compounds crystallize with the orthorhombic TiNiSi structure, while the Gd-based materials adopt the ZrNiAl structure. Recently, the electronic structure has been determined by x-ray photoelectron spectroscopy and compared with LDA + U band structure calculations [8]. Here the valency, Eu^{2+} and Gd^{3+}, was firmly established and a variety of s, p, d-conduction bands were found at the Fermi level. One unusual

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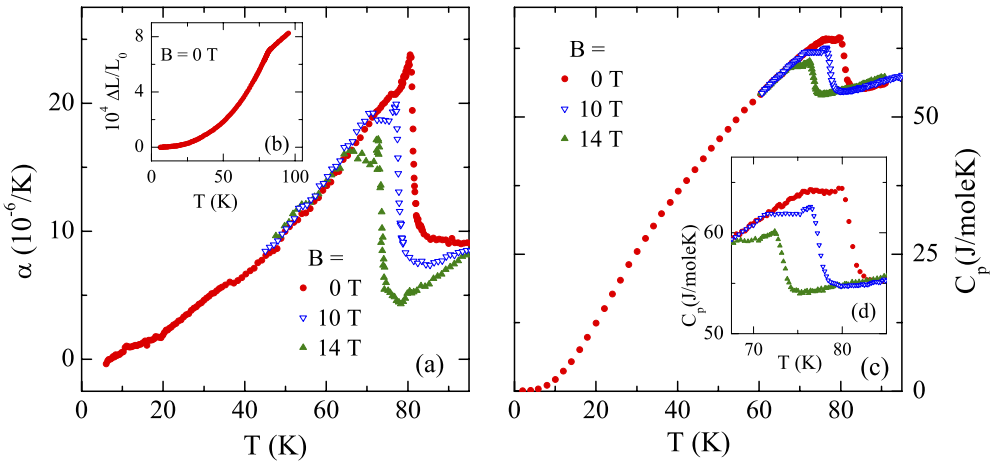

Figure 1. (a) Thermal expansion α, (b) relative length change $\Delta L/L_0$, and (c), (d) specific heat of antiferromagnetic GdAuMg for different magnetic fields.

feature of the photoemission spectra was the localized nature of the Ag and Au d-bands below E_F. Since both Eu^{2+} and Gd^{3+} possess large magnetic moments ($S = 7/2$), their magnetic ordering properties, mediated by the oscillating amplitude RKKY (Ruderman, Kittel, Kasuya, Yoshida) interaction, may strongly depend on spin–orbit and spin–lattice couplings. A recent investigation has characterized many of the bulk thermodynamic and transport properties related to the ferromagnetic transitions of EuAgMg, EuAuMg, and GdAgMg and the antiferromagnetic one of GdAuMg [9]. Information about the above-mentioned magnetoelastic behavior can be obtained from measurements of the thermal expansion.

In this work we present the results of the thermal expansion coefficient measured over a large temperature range (4–200 K) in applied magnetic fields reaching 14 T. We observe sharp peaks at the magnetic phase transitions in the uniaxial thermal expansion $\alpha(T) = \frac{1}{L_0}\frac{\partial \Delta L}{\partial T}$, where L_0 is the sample length and ΔL its temperature-induced change. In all four compounds we observe pronounced anomalies $\Delta\alpha$ at the magnetic ordering transitions. For EuAgMg and GdAuMg the sign of $\Delta\alpha$ is positive, while it is negative for EuAuMg and GdAgMg. These anomalies are smeared and/or displaced upon applying the magnetic field. By comparing $\Delta\alpha$ with the corresponding anomalies ΔC_p of the specific heat [9] at $T_{C,N}$ we obtain the pressure dependences of the critical temperatures for a first- or second-order phase transition via the Clausius–Clapeyron or the Ehrenfest relation, respectively. The results are most interesting for the ferromagnets GdAgMg and EuAuMg, where we find a first- and a second-order phase transition, respectively, with very large negative pressure dependences of T_C. In both materials, a finite pressure of the order of a few GPa should drive T_C to zero, suggesting pressure-induced quantum phase transitions.

Polycrystalline samples of the above compounds were synthesized, annealed and characterized as described previously [7–9]. The thermal expansion was measured in a capacitance dilatometer inserted in a ^{4}He gas-flow cryostat covering a temperature range from about 2–300 K [10]. By using a superconducting magnet, fields up to 14 T could be applied over the entire temperature range. Accordingly, the length changes $\Delta L/L_0$ could be accurately detected through the magnetic transitions with and without the external field.

Figure 1(a) displays $\alpha(T)$ in various magnetic fields for GdAuMg. The antiferromagnetic ordering at $T_N = 81$ K causes a step-like anomaly $\Delta\alpha(T)$ of positive sign with a small upturn

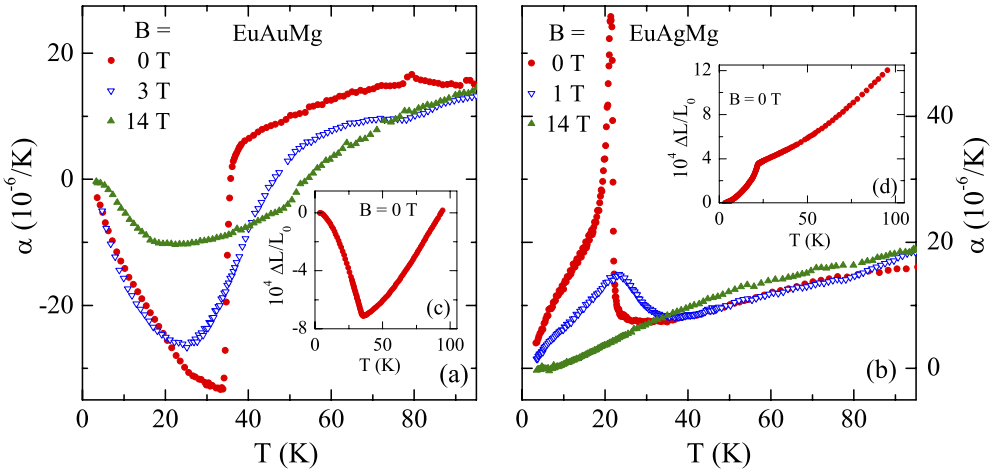

Figure 2. Thermal expansion α of the ferromagnetic compounds (a) EuAuMg and (b) EuAgMg for various magnetic fields. The respective insets (c) and (d) show the relative length changes $\Delta L/L_0$ for zero field.

around T_N. The step in α is typical for the mean-field anomaly of a second-order phase transition while the upturn signals the presence of fluctuations. A very similar anomaly is present in the specific heat, as shown in figures 1(c) and 1(d). The enhanced thermal expansion below T_N signals a spontaneous contraction in the magnetically ordered phase, which is also directly seen in $\Delta L(T)/L_0$ displayed in figure 1(b). The application of a magnetic field causes a systematic shift of the anomalies $\Delta\alpha$ and ΔC_p towards lower temperature, signaling a decreasing T_N. As expected, the antiferromagnetic order is destabilized by a magnetic field, although the rate $\partial T_N/\partial B \simeq -0.4\ \mathrm{K\ T^{-1}}$ in 14 T appears relatively large in view of the high T_N.

Figure 2 shows $\alpha(T)$ in various fields for EuAuMg and EuAgMg, which order ferromagnetically at $T_C = 35$ K and 22 K, respectively. In zero field we again find a step-like anomaly $\Delta\alpha$ for EuAuMg. However, in contrast to GdAuMg the sign of $\Delta\alpha$ is negative, meaning that the ferromagnetic ordering in EuAuMg is accompanied by a spontaneous expansion, as shown in figure 2(c). For EuAgMg the sign of the zero-field anomaly $\Delta\alpha$ is again positive, i.e. a spontaneous contraction occurs, but in this case $\Delta\alpha$ has a lambda-like shape, as is typical for a second-order phase transition where the fluctuations are more pronounced. Such a difference in the anomaly shapes is also present in the specific heat anomalies [9]. For both Eu-based compounds the application of a magnetic field causes a drastic broadening of the anomalies. This is expected for a ferromagnet because in a finite magnetic field a sizeable magnetization is already present well above the zero-field T_C. As a consequence the magnetization does not develop spontaneously below a critical temperature anymore and, strictly speaking, a ferromagnetic transition temperature can only be defined for zero magnetic field.

In the ferromagnet GdAgMg we observe a huge anomaly $\Delta\alpha$ of negative sign at $T_C = 39.5$ K as is illustrated in figure 3(a). The shape of the α anomaly corresponds to an almost jump-like change of $\Delta L/L_0$, as shown in figure 3(b). This is a clear indication for a first-order transition in GdAgMg, in agreement with our conclusions from the specific heat measurements, where a very similar anomaly shape is present at T_C [9]. Moreover, we observe an additional smaller anomaly of α at $T^\star \simeq 125$ K which hardly changes in an applied magnetic field, see figure 3(c). In contrast, the sharp low-temperature anomaly drastically

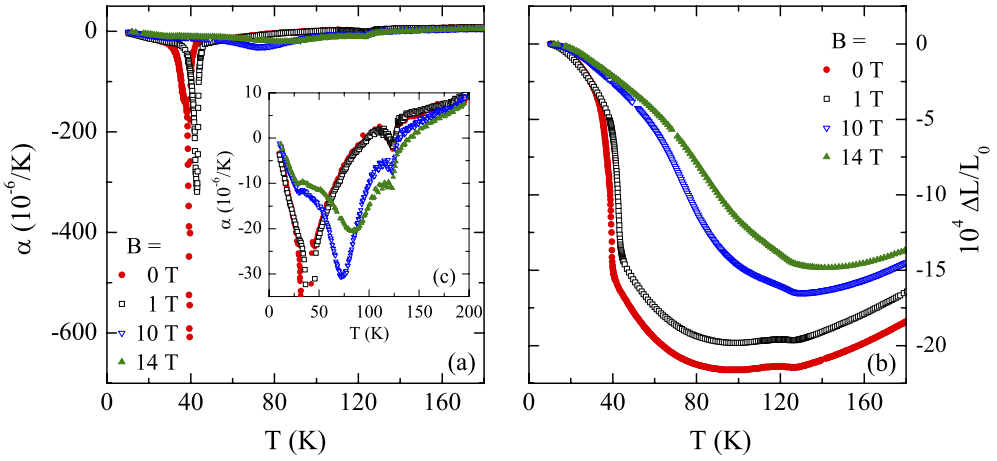

Figure 3. (a) Thermal expansion α and (b) relative length changes $\Delta L/L_0$ (b) of the ferromagnet GdAgMg for various magnetic fields. The inset (c) shows an expanded view of α in order to visualize the additional anomaly at 125 K.

broadens and shifts upwards in temperature. In the highest field this broadening even extends to temperatures above about 175 K, i.e. to $T \gg T^\star$. Based on an analysis of the entropy change, we suspected that the complete magnetic ordering in GdAgMg might be achieved via both transitions at T_C and $T^\star$ [9]. However, the transition at $T^\star$ is not seen in our measurements of the magnetic susceptibility χ. Above about 50 K, χ shows clear Curie–Weiss behavior, i.e. $\chi(T) = \mu_{\text{eff}}^2/3k_B(T - \Theta)$ with $\Theta = 39.7$ K and $\mu_{\text{eff}} = 7.96\mu_B$ close to the expected values of a ferromagnet with an $S = 7/2$ and $T_C = 39.5$ K. This and the very different field dependences, in particular the fact that the field-induced broadening of the T_C anomaly even exceeds $T \gg T^\star$, makes a common origin of both anomalies very unlikely.

Since $T^\star$ does not change with field, one may suspect a structural origin of this anomaly; however, no low-temperature diffraction data have been recorded yet. Alternatively, the $T^\star$ anomaly could arise from small amounts of impurity phases, e.g. GdAg and GdMg. Although our sample shows phase purity in x-ray powder diffraction, we cannot exclude the presence of a few per cent of such impurity phases. Both of these binary intermetallic compounds exhibit magnetic phase transitions between 96 and 130 K [11, 12]. In GdMg a ferromagnetic order occurs at 120 K followed by a canting transition at 96 K, while a single antiferromagnetic phase develops in GdAg below 133 K. The presence of GdMg appears also to be unlikely, since even for a few per cent of such an impurity phase the spontaneous magnetization due to the ferromagnetic order should be visible in $\chi(T)$ and the anomaly should broaden in a magnetic field. In contrast, the presence of a few per cent of GdAg cannot be excluded from our data: (i) due to the large background of the paramagnetic majority phase the expected weak magnetization change at T_N cannot be resolved in $\chi(T)$, and (ii) magnetic fields up to 14 T will not affect the antiferromagnetic order since the ordering temperature is so high. Because the $T^\star$ anomaly most probably arises from an impurity phase, it will not be considered in the following discussion of the pressure dependences.

The measurements of thermal expansion and specific heat at ambient pressure allow us to derive the initial slope of the change of $T_{N,C}$ under finite pressure using either the Clausius–Clapeyron relation for a first-order transition

$$\left.\frac{\partial T_{N,C}}{\partial p}\right|_{p_0} = \frac{\Delta V}{\Delta S}, \tag{1}$$

Table 1. Some characteristic properties of RTMg.

Material	V_{mol} (cm^3 mole^{-1})	Magnetic order	$T_{\mathrm{N,C}}$ (K)	$\partial T_{\mathrm{N,C}}/\partial p$ (K GPa^{-1})
GdAuMg	41.03	Antiferro	81.0	12(2)
GdAgMg	43.04	Ferro	39.5	−35(5)
EuAuMg	45.01	Ferro	35.0	−14(2)
EuAgMg	48.70	Ferro	22.0	9(2)

or the Ehrenfest relation for a second-order phase transition

$$\left.\frac{\partial T_{\mathrm{N,C}}}{\partial p}\right|_{p_0} = 3\,T_{\mathrm{N,C}}\,V_{\mathrm{mol}}\frac{\Delta\alpha}{\Delta C_p}. \tag{2}$$

Here, ΔV (ΔS) denotes the discontinuous volume (entropy) change at $T_{\mathrm{N,C}}$. Since phase transitions in real solids are typically not infinitely sharp, the changes of V and S may become very steep but finally remain continuous. In order to get a measure of the jump-like changes of the volume and entropy we use the integration $\Delta V = V_{\mathrm{mol}} \int 3\,\alpha(T)\,\mathrm{d}T$ and $\Delta S = V_{\mathrm{mol}} \int C_p(T)/T\,\mathrm{d}T$, respectively. The temperature range ($\simeq 4$ K) of integration around $T_{\mathrm{N,C}}$ reflects the broadening of the first-order phase transition. We note that one has to use $3\,\alpha$ here and in equation (2), since the hydrostatic pressure dependence is related to the volume expansion β, which is given by $\beta = 3\,\alpha$ for a homogeneous polycrystal. Since the Ehrenfest relation is derived for a mean-field transition, it does not consider fluctuations and thus $\Delta\alpha$ (ΔC_p) refers to a discontinuous jump of α (C_p) at $T_{\mathrm{N,C}}$. Thus, in a real solid one has again to consider the broadening of the transition on the one hand and the influence of fluctuations on the other. The latter aspect has been discussed in detail recently [13]. Since for GdAuMg and EuAuMg the influence of fluctuations is weak, we use the peak height of the α and C_p anomaly as a measure of $\Delta\alpha$ and ΔC_p, respectively. In the case of EuAgMg, the idealized mean-field jumps of α and C_p are about half as large as the total peak heights. This makes an unambiguous separation of the mean-field contribution from that of fluctuations difficult. However, as long as the same procedures are used to idealize the α and C_p anomaly, the resulting $\partial T_{\mathrm{N,C}}/\partial p$ does not change too much. For example, using idealized mean-field jumps for $\Delta\alpha$ and ΔC_p in equation (2) yields $\partial T_{\mathrm{N,C}}/\partial p \simeq 7$ K GPa^{-1} while taking the peak heights gives $\simeq$10 K GPa^{-1}.

The obtained pressure dependences $\partial T_{\mathrm{N,C}}/\partial p$ together with some other characteristic properties are given in table 1 for all four compounds. Obviously, we obtain rather large absolute values of $\partial T_{\mathrm{N,C}}/\partial p$ of different signs depending on the sign of the respective α anomaly. These large values confirm the presence of a large spin–lattice coupling in these RTMg compounds, which we attribute to the oscillatory nature of the RKKY interaction. This may also be the main reason for the variation from ferro- to antiferromagnetic order and the wide range of different transition temperatures in the different RTMg compounds, although their structures are not too different. We find the largest pressure dependence in GdAgMg and associate this with the first-order nature of the magnetic transition. In order to drive a magnetic phase transition to first order a strong spin–lattice coupling is required and this would also provide the mechanism for a large pressure dependence $\partial T_{\mathrm{N,C}}/\partial p$.

We emphasize that our estimates of $\partial T_{\mathrm{N,C}}/\partial p$ based on the Ehrenfest or the Clausius–Clapeyron relation only yield the initial slopes at ambient pressure and extrapolations of our data to finite pressure have to be treated with caution. Nevertheless, the obtained negative values of $\partial T_{\mathrm{C}}/\partial p = -14$ and -35 K GPa^{-1} for EuAuMg and GdAgMg, respectively, are so large, that a complete suppression of the ferromagnetic order may be reached for both compounds when a rather moderate hydrostatic pressure of a few GPa is applied. Therefore

both compounds are interesting candidates where pressure-induced quantum phase transitions can be studied.

In summary, due to the significant spin–lattice coupling we were able to probe the magnetic ordering transitions of EuAgMg, GdAuMg, EuAuMg, and GdAgMg via thermal expansion measurements. Using also specific heat data we were able to derive the initial pressure shifts of $T_{C,N}$, which are quite large for all four compounds. The largest effects are observed in EuAuMg and GdAgMg, and in both materials the ferromagnetic order is expected to be completely suppressed by hydrostatic pressure of a few GPa. Direct high-pressure experiments of $T_{N,C}$ on these compounds are highly desirable.

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