Dependence of the magnetic ordering temperature on hydrostatic pressure for the ternary intermetallic compounds GdAgMg, GdAuMg, EuAgMg, and EuAuMg

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A He-gas compressor system is used to determine the dependence of the Curie temperature T_C of polycrystalline GdAgMg, EuAgMg, and EuAuMg and the Néel temperature T_N of GdAuMg on hydrostatic pressure to 0.8 GPa. The $\partial T_{C,N}/\partial P$ dependences found differ significantly from those estimated from earlier thermal expansion studies on the same samples. Only for GdAgMg does the magnetic ordering temperature decrease with pressure.

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In recent years the magnetic, transport, and thermodynamic properties of the equiatomic ternary intermetallic compounds $(RE)T$Mg, where $RE=$Gd or Eu and $T=$Ag or Au, have been extensively studied.[1–4] Whereas the Gd-based compounds crystallize in the hexagonal ZrNiAl structure, the Eu-based compounds take on the orthorhombic TiNiSi structure.[5,6] Since in these compounds Gd is trivalent[2] and Eu divalent,[1,2,7] the "magnetic" $4f$ shell in both Gd and Eu cations contains seven electrons $(4f^7)$ which provide a total angular momentum $J=L+S=0+7/2=7/2$ and thus a strong local magnetic moment on each rare-earth cation. The indirect Ruderman-Kittel-Kasuya-Yoshida (RKKY) interactions between these magnetic moments lead to magnetic order. Whereas GdAgMg, EuAuMg, and EuAgMg are ferromagnetic with Curie temperatures $T_C=39.5$, 35.0, and 22.0 K, respectively, GdAuMg is antiferromagnetic with Néel temperature $T_N=81$ K.[4,8] Since at ambient pressure the magnetic ordering temperature is observed to increase with decreasing molar volume in all four compounds,[8] one would anticipate that the application of high pressure would enhance T_C or T_N. However, thermal-expansion experiments indicate that $\partial T_{C,N}/\partial P$ is positive for GdAuMg and EuAgMg, but negative for GdAgMg and EuAuMg.[8] In fact, combined thermal-expansion and specific-heat studies on GdAgMg and EuAuMg indicate that their Curie temperatures would be expected to decrease initially at the very rapid rates -35 K/GPa and -14 K/GPa, respectively, implying that for these compounds pressures in the range 1–3 GPa should be sufficient to drive T_C to 0 K, raising the possibility of a pressure-induced quantum phase transition.[8]

In this work we describe the results of hydrostatic (He-gas) high-pressure studies to 0.8 GPa on the above four compounds. We find that $\partial T_{C,N}/\partial P$ differs substantially from the values inferred from previous thermal-expansion experiments both in magnitude and, for EuAuMg, in sign. For GdAgMg this discrepancy is shown at least in part to result from unexpectedly strong texture in the polycrystalline sample. Only for GdAgMg is $\partial T_{C,N}/\partial P$ negative, allowing the estimate that the application of at least 8 GPa pressure would be necessary to drive its Curie temperature to 0 K.

Polycrystalline GdAgMg, GdAuMg, EuAgMg, and Eu-

AgMg samples were prepared from the pure elements ($>99.9\%$) by induction melting in sealed tantalum ampules and subsequent annealing using the temperature conditions described in previous publications.[2,3,7] The purity of the samples was carefully checked through Guinier powder patterns using Cu $K\alpha1$ radiation and α-quartz ($a=491.30$ pm and $c=540.46$ pm) as an internal standard. Bulk pieces were also analyzed in a Leica 420I scanning electron microscope. No impurity phases were detected.

Details of the thermal-expansion apparatus used in both the previous studies and the new thermal-expansion results presented here are given in Ref. 9. To generate hydrostatic pressures as high as 0.8 GPa, a He-gas compressor system (Harwood Engineering) at ambient temperature was connected by a long, flexible capillary tube to a CuBe pressure cell (Unipress) located in a two-stage closed-cycle refrigerator (Balzers) capable of reaching temperatures down to 5 K. Except for the GdAgMg compound, pressures were changed at near-ambient temperatures and held for 30–45 min before cooling down to measure T_C. ac susceptibility measurements at 0.1 Oe rms and 1023 Hz were carried out under pressure to the same high accuracy as measurements at ambient pressure by surrounding the sample with a calibrated primary/secondary compensated coil system connected to a Stanford Research SR830 digital lock-in amplifier via a SR554 transformer preamplifier. Measurements were carried out by slowly warming up through the magnetic transition at the rate ~100 mK/min. All susceptibility measurements were repeated at least once to verify that the reproducibility of the ferromagnetic or antiferromagnetic transition temperature $T_{C,N}$ was within 20 mK. Unfortunately, due to the temperature-dependent background signal, it was not possible to reliably extract the Curie constant or Curie-Weiss temperature from the paramagnetic ac susceptibility in the temperature range above $T_{C,N}$. All pressures were determined at a temperature near $T_{C,N}$ using a calibrated digital manganin gauge located near the compressor system at ambient temperature. Further details of the He-gas techniques used are given elsewhere.[10]

In Fig. 1(a) the ferromagnetic transition in the ac susceptibility for GdAgMg is shown at four different pressures. The
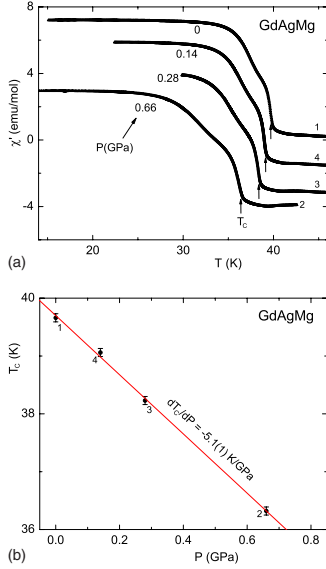
FIG. 1. (Color online) (a) Temperature dependence of the real part of the ac susceptibility for ferromagnetic GdAgMg at four different pressures. Integers give order of measurement. Ordinate scale applies to curve 1 at 0 GPa; other data are shifted vertically for clarity. Vertical arrows mark Curie temperature T_C defined by temperature at steepest slope. (b) Dependence of Curie temperature on pressure. Straight line is least-squares fit to data.

point of steepest slope is used to define the Curie temperature $T_C \simeq 39.7$ K which is very close to the published value of 39.5 K.[8] Following the measurement at ambient pressure (0 GPa), approximately 0.75 GPa He-gas pressure was applied at a temperature near ambient which reduced to 0.66 GPa upon cooling down to a temperature near T_C. Two further decreases in pressure to 0.28 GPa and 0.14 GPa were carried out at 150 K and 50 K, respectively. The ferromagnetic transition is seen to clearly shift to lower temperatures with increasing pressure, as inferred from the earlier thermal-expansion measurements;[8] however, as seen in Fig. 1(b), the rate of decrease in T_C is seen to be far weaker (-5.1 K/GPa versus -35 K/GPa).

Substituting Au for Ag in GdAgMg changes the character of the magnetic ordering from ferromagnetic to antiferromagnetic. As seen in Fig. 2(a), the changes in the ac susceptibility when GdAuMg orders magnetically are relatively weak. The vertical arrows in this figure mark the temperatures T_N, T_{a1}, and T_{a2} at which anomalies in $\chi'(T)$ are seen, specifically, abrupt changes in slope for 0 GPa near 81.8 and 60.7 K with a maximum at 68.3 K. The anomalies in $\chi'(T)$ for this compound differ substantially from one publication to another;[2,4] this may arise from the sensitivity of the ac susceptibility signal in a magnetically weak, antiferromagnetically ordered spin system to a multitude of spurious effects such as texture or crystalline defects. However, all publications agree that there is a slope change near 81 K which marks the Néel temperature T_N.

For GdAuMg the pressure was changed at temperatures near ambient. Following measurement 1 at ambient pressure, the pressure was increased to 0.78 GPa before being decreased to 0.35 GPa and then 0 GPa (measurement 4). The
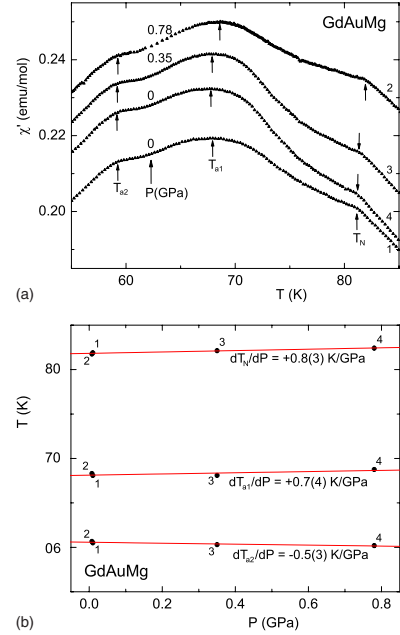

FIG. 2. (Color online) (a) Temperature dependence of the real part of the ac susceptibility for antiferromagnetic GdAuMg at three different pressures. Integers give order of measurement. Ordinate scale applies to curve 1 at 0 GPa; other data are shifted vertically for clarity. Vertical arrows mark three features in data at T_{a1} and T_{a2} and at the Néel temperature T_N. (b) Dependence of (top to bottom) T_N, T_{a1}, and T_{a2} on pressure. Straight lines give least-squares fits to data.

difference in shape of the two measurements 1 and 4 at 0 GPa may arise from a small rotation of the sample in the ac susceptibility pick-up coils. The dependences of T_N, T_{a1}, and T_{a2} on pressure are shown in Fig. 2(b); the temperature of all three features changes reversibly with pressure. The Néel temperature $T_N \simeq 81.8$ K is seen to increase slowly with pressure with $\partial T_N / \partial P \simeq +0.8(3)$ K/GPa, a rate much less than that inferred from the thermal-expansion measurements.[8] The magnitudes of $\partial T_{a1} / \partial P$ and $\partial T_{a2} / \partial P$ are even smaller.

In Fig. 3(a) the temperature dependence of the ac susceptibility is shown for the ferromagnet EuAgMg at four different pressures which were all applied near ambient temperature. The value of the Curie temperature at ambient pressure, $T_C \simeq 22.1$ K, agrees well with previous studies.[4,8] In Fig. 3(b) the Curie temperature is seen to increase reversibly with pressure with the slope $\partial T_C / \partial P \simeq +3.5(1)$ K/GPa, a smaller rate than that estimated from previous thermal-expansion measurements.[8]

The substitution of Au for Ag in EuAgMg results in the ferromagnetic compound EuAuMg which exhibits the temperature-dependent magnetic susceptibility shown in Fig. 4(a). Two features are seen labeled by vertical arrows at the temperature of maximum slope. The lower temperature $T_C \simeq 36.3$ K at ambient pressure is identified as the primary ferromagnetic transition. This value agrees reasonably well with previous studies where 35.0 K was reported.[4,8] However, the feature near $T_a \simeq 50$ K has no counterpart in published electrical resistivity, specific heat, or thermal-
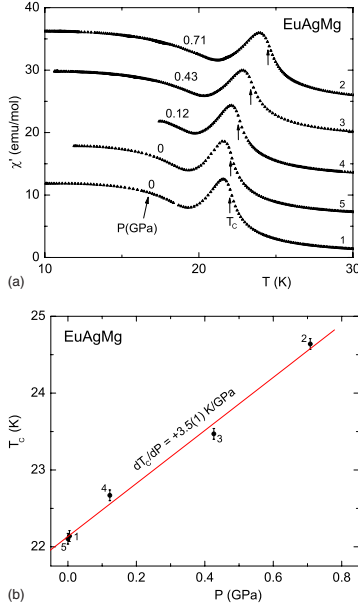
FIG. 3. (Color online) (a) Temperature dependence of the real part of the ac susceptibility for ferromagnetic EuAgMg at four different pressures. Integers give order of measurement. Ordinate scale applies to curve 1 at 0 GPa; other data are shifted vertically for clarity. Vertical arrows mark Curie temperature T_C defined by temperature at steepest slope. (b) Dependence of Curie temperature on pressure. Straight line is least-squares fit to data.

expansion measurements;[3,4,8] we cannot exclude the possibility that it originates from an impurity phase although no evidence for this is present in the x-ray powder diffraction pattern.
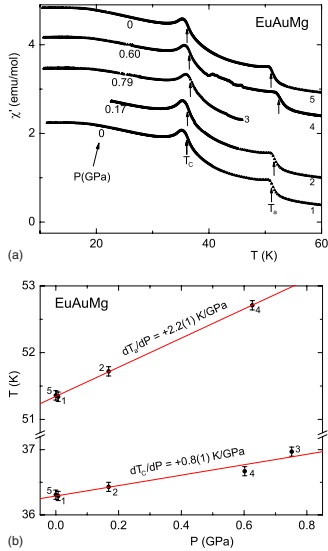

FIG. 4. (Color online) (a) Temperature dependence of the real part of the ac susceptibility for ferromagnetic EuAuMg at four different pressures. Integers give order of measurement. Ordinate scale applies to curve 1 at 0 GPa; other data are shifted vertically for clarity. Vertical arrows mark temperature at steepest slope for two features in data at T_a and at the Curie temperature T_C. (b) Dependence of T_C and T_a on pressure. Straight lines give least-squares fits to data.

As seen in Fig. 4(b), both features at T_C and T_a shift to higher temperatures with pressure, where $\partial T_C / \partial P \simeq$ +0.8(1) K/GPa. This value of $\partial T_C / \partial P$ has the opposite sign to that estimated from the thermal-expansion studies[8] and a much smaller magnitude.

The results of the present high-pressure experiments are summarized in Table I where the pressure derivatives of the magnetic ordering temperatures from the present hydrostatic (He-gas) high-pressure experiments $\partial T_{C,N}^{hp} / \partial P$ are compared to those derived from thermal-expansion measurements $\partial T_{C,N}^{te} / \partial P$. For all four compounds the magnitude of the former derivative is seen to be significantly smaller than the latter. This puzzling result prompted us to repeat the thermal-expansion measurements on GdAgMg to check whether or not the polycrystalline sample is truly isotropic, the basis for the previous analysis and estimate of $\partial T_C^{te} / \partial P$.[8]

If the crystallites of a polycrystalline sample are randomly orientated, the linear thermal expansion does not depend on the sample orientation so that the volume-expansion coefficient $\beta \equiv V^{-1}(\partial V / \partial T)$ is related to the linear thermal-expansion coefficient $\alpha \equiv L^{-1}(\partial L / \partial T)$ by the relation $\beta = 3\alpha$. The pressure dependencies $\partial T_{C,N}^{te} / \partial P$ derived in Ref. 8 were based on this assumption.

However, our more recent data reveal that the uniaxial thermal expansion of GdAgMg is highly anisotropic. In Fig. 5 we show the linear thermal expansion measured along three mutually orthogonal directions L_i. In this case, the volume-expansion coefficient is given by $\beta = \Sigma_i \alpha_i$, which is obviously very different from $\beta = 3\alpha_i$ for all $i = 1, 2, 3$. The very large $\partial T_C^{te} / \partial P \simeq -35$ K/GPa derived in Ref. 8 was obtained from the measurement of $\Delta L_1 / L_1$ in Fig. 5 which shows the largest anomaly at T_C. The anomalies in $\Delta L_i / L_i$ for $i = 2, 3$ are smaller and have opposite signs. As a consequence, the actual volume change in GdAgMg at T_C is roughly a factor of three smaller than assumed in Ref. 8 and the Clausius-Clapeyron equation $\partial T_C / \partial P = \Delta V / \Delta S$ yields the smaller value $\partial T_C^{te} / \partial P \approx -12$ K/GPa. Still, this value is more than twice as large as the result from the present direct measurements under hydrostatic pressure. This remaining difference may, at least partly, arise from an underestimation of the entropy change ΔS in the above equation. The entropy change has been calculated from the specific-heat data measured by the relaxation-time technique in a physical properties measurement system (PPMS, Quantum Design Inc.).[3] As has been outlined in detail in Ref. 11, this technique system-
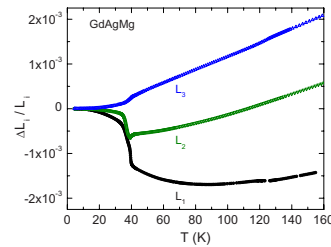

FIG. 5. (Color online) Temperature dependence of change in length of GdAgMg sample with respect to its value at 4.2 K measured along three mutually orthogonal directions L_i. The pronounced anisotropy reveals that the polycrystalline sample is highly textured.

TABLE I. Properties of ternary compounds studied: molar volume V_{mol}, type of magnetic order, magnetic ordering temperature $T_{C,N}$ at ambient pressure, as well as its initial pressure derivative derived from thermal-expansion experiments $\partial T_{C,N}^{te}/\partial P$ (Ref. 8) or measured directly in the present high-pressure experiments $\partial T_{C,N}^{hp}/\partial P$.

Material	V_{mol} (cm^3/mole)	Magnetic order	$T_{C,N}^{te}$ (K)	$T_{C,N}^{hp}$ (K)	$\partial T_{C,N}^{te}/\partial P$ (K/GPa)	$\partial T_{C,N}^{hp}/\partial P$ (K/GPa)
EuAgMg	48.70	Ferro	22.0	22.1	+9(2)	+3.5(1)
EuAuMg	45.01	Ferro	35.0	36.3	−14(2)	+0.8(1)
GdAgMg	43.04	Ferro	39.5	39.7	−35(5)	−5.1(1)
GdAuMg	41.03	Antiferro	81.0	81.8	+12(2)	+0.8(3)

atically underestimates the magnitude of the specific-heat anomalies at first-order phase transitions. Because the phase transition of GdAgMg is of first order, it appears very likely that correcting for this effect will further reduce the remaining discrepancy between the result obtained indirectly via the Clausius-Clapeyron equation, on the one hand, and the directly measured $\partial T_C/\partial P$, on the other.

In Table I we see that the other three compounds GdAuMg, EuAgMg, and EuAuMg show similar behavior to that of GdAgMg, i.e., the magnitude of $\partial T_{C,N}^{hp}/\partial P$ in the high-pressure experiments is notably less than that derived from the thermal-expansion studies. It is thus reasonable to infer that strong texture effects are likely responsible for the deviations in the estimates of $\partial T_{C,N}^{te}/\partial P$ in all four compounds.

As pointed out above and readily seen in Table I, at ambient pressure the values of the magnetic ordering temperatures for the four compounds studied are anticorrelated with the molar volume, the Néel temperature of 81 K being highest for GdAuMg, the compound with the lowest molar volume. On the other hand, there appears to be no obvious correlation between the molar volume and the sign or magnitude of the pressure derivative $\partial T_{C,N}^{hp}/\partial P$. Were the interatomic separations of all magnetic cations to scale down identically under hydrostatic pressure (only possible in a cubic system), the magnetic ordering temperature would increase as the inverse cube of the interatomic separation or, equivalently, the inverse molar volume ($T_{C,N} \propto r^{-3} \propto V_{mol}^{-1}$). However, the present ternary compounds are not cubic. This means that under pressure all properties are expected to be anisotropic within each crystallite, including the compressibility and the oscillatory long-range RKKY interactions between all rare-earth (Gd or Eu) cations which ultimately lead to the magnetic ordering. It is, therefore, not surprising that the sign and magnitude of the pressure dependence of the magnetic ordering temperature do not exhibit a simple correlation. The first step in a more quantitative analysis would be to determine the anisotropic compressibility of these four compounds in single-crystalline form.

In summary, the dependences of the magnetic ordering temperatures on hydrostatic pressure to 0.8 GPa have been accurately determined for the four ternary compounds Eu-AgMg, EuAuMg, GdAgMg, and GdAuMg and are found to differ significantly from those inferred in previous thermal-expansion studies. These deviations arise at least in part from unexpectedly strong texture effects in polycrystalline GdAgMg and likely in the three remaining compounds. The strong negative pressure dependence of the Curie temperature in GdAgMg points to a possible quantum-critical point for pressures exceeding 8 GPa.

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