Magnetic Properties of Compounds RE_2Cu_2Mg (RE = Y, La, Pr, Nd)

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The Mo_2FeB_2 type magnesium intermetallics RE_2Cu_2Mg (RE = Y, La, Pr, Nd) were synthesized from the elements by reactions in sealed tantalum tubes in a high-frequency furnace. Temperature-dependent magnetic susceptibility measurements of Y_2Cu_2Mg and La_2Cu_2Mg indicate Pauli paramagnetism. Pr_2Cu_2Mg and Nd_2Cu_2Mg show Curie-Weiss behaviour with experimental magnetic moments of 3.67(2) μ_B/Pr and 3.47(2) μ_B/Nd, respectively. Both compounds are ordered ferromagnetically at Curie temperatures of 12.0(5) (Pr_2Cu_2Mg) and 43.0(5) K (Nd_2Cu_2Mg). Pr_2Cu_2Mg shows a very complex magnetization behavior with an additional magnetic transition around 2.5 T. The neodymium compound shows a pronounced square loop behavior in the magnetization at 4.5 K with a high remanent magnetization of 1.55(1) μ_B/Nd atom and a coercive field of 0.31(1) T.

Key words: Magnesium, Rare Earth Compounds, Magnetism

Introduction

Ternary indides and stannides R_2T_2In and R_2T_2Sn (R = rare earth or actinoid metal; T = transition metal) with Mo_2FeB_2 type structure (ordered U_3Si_2 variant) have intensively been investigated in the past with respect to their intriguing magnetic and electrical properties such as ferromagnetism, antiferromagnetism, mixed- or intermediate-valence, spin fluctuations or heavy fermion behavior. All these data have been summarized in a current review article [1].

Recently it has been demonstrated that the indium and tin atoms in these compounds can completely be substituted by magnesium or cadmium [2 – 10]. Although the electron count is reduced, the magnesium and cadmium compounds are still isotypic with the indides and stannides. The change of the electron count has drastic effects on the magnetic properties of these intermetallics. To give an example, the Néel temperature increases from 5 K for Pr_2Pd_2In [11] to 15 K for Pr_2Pd_2Mg [10]. $Ce_2Rh_{1.86}Cd$ [9] is an intermediate-valent system while cerium is tetravalent in Ce_2Rh_2In [12].

We have now extended our studies on the RE_2T_2Mg compounds to include the magnetic properties. The data on Y_2Cu_2Mg, La_2Cu_2Mg, Pr_2Cu_2Mg, and Nd_2Cu_2Mg are reported herein. Crystal chemical data of these copper compounds have been reported in a previous paper [8].

Experimental Section

Starting materials for the preparation of the RE_2Cu_2Mg compounds were ingots of the rare earth metals (Johnson Matthey, $>$ 99.9%), copper wire (Johnson Matthey, ∅ 1 mm, $>$ 99.9%), and a magnesium rod (Johnson Matthey, ∅ 16 mm, $>$ 99.95%). Small arc-melted buttons [8,13] of the rare earth metals were mixed with the copper wire and magnesium pieces in the ideal 2 : 2 : 1 atomic ratio and sealed in small tantalum tubes under an argon atmosphere of about 800 mbar. The argon was purified over titanium sponge (900 K), silica gel, and molecular sieves.

The elements were subsequently reacted by high-frequency annealing of the sealed metal tubes in a water-cooled quartz glass sample chamber in a high-frequency furnace (Hüttinger TIG 1.5 / 300, 1.5 kW) under flowing argon [14]. For details of the temperature programme we refer to the preceding paper [8]. The samples could easily be separated from the tantalum tubes. No reactions of the samples with the tubes could be detected. The compounds were obtained in amounts of about 1 g. Compact pieces are light grey with metallic lustre. The samples are stable in moist air. No decomposition was observed after several months.

The purity of the samples was checked by Guinier powder patterns using Cu-$K_{\alpha1}$ radiation and α-quartz (a = 491.30,

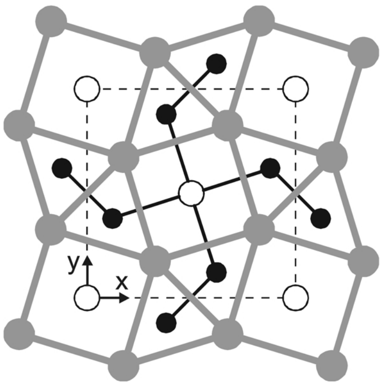

Fig. 1. The crystal structure of Y_2Cu_2Mg. All atoms lie on mirror planes at $z = 0$ (thin lines) and $z = 1/2$ (thick lines). Yttrium, copper and magnesium atoms are drawn as grey, filled and open circles, respectively. The two-dimensional $[Cu_2Mg]$ network is emphasized.

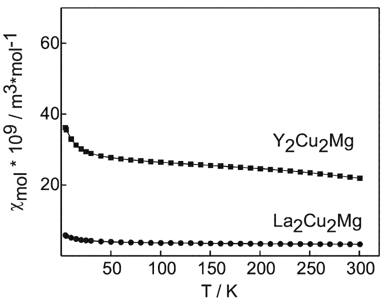

Fig. 2. Temperature dependence of the magnetic susceptibility of Y_2Cu_2Mg and La_2Cu_2Mg measured at an external flux density of 3 T.

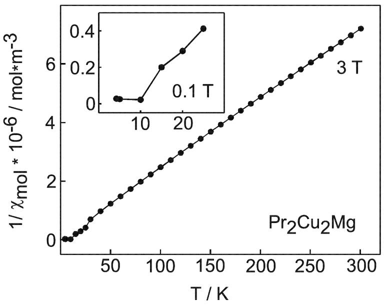

Fig. 3. Temperature dependence of the inverse magnetic susceptibility of Pr_2Cu_2Mg measured at an external flux density of 3 T. The low-temperature data at 0.1 T are shown in the insert.

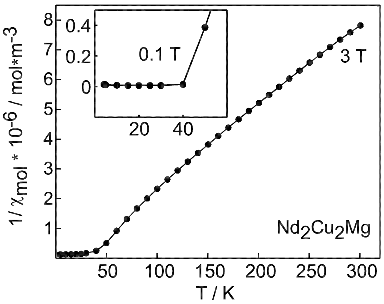

Fig. 4. Temperature dependence of the inverse magnetic susceptibility of Nd_2Cu_2Mg measured at an external flux density of 3 T. The low-temperature data at 0.1 T are shown in the insert.

$c = 540.46$ pm) as an internal standard. The powder patterns of the four compounds showed only the reflections of the tetragonal Mo_2FeB_2 type phases and the refined lattice parameters were in good agreement with published results [8].

The magnetic susceptibilities of polycrystalline, powdered samples of Y_2Cu_2Mg, La_2Cu_2Mg, Pr_2Cu_2Mg, and Nd_2Cu_2Mg were determined with a MPMS *XL* SQUID magnetometer (Quantum Design, Inc.) in the temperature range of 2 to 300 K with magnetic flux densities up to 5 T. The samples were cooled to 2 K in zero magnetic field and slowly heated to room temperature in the applied external fields.

Results and Discussion

Crystal chemistry

As an example we present a projection of the Y_2Cu_2Mg structure onto the *xy* plane in Fig. 1. Since the crystal chemistry and chemical bonding of the RE_2Cu_2Mg intermetallics has been described in detail in reference [8], we give only a very brief account here. The Y_2Cu_2Mg structure is built up from distorted AlB_2- and CsCl-related slabs of compositions YCu_2 and *YMg*. The copper atoms within the AlB_2 slab have a Cu–Cu bond length of 262 pm, close to the Cu–Cu distance of 256 pm in *fcc* copper [15]. An important parameter for the magnetic interactions is the *RE*–*RE* distance. Each rare earth metal atom has seven nearest rare earth metal neighbors, five within the *xy* plane at $z = 0$ and two neighbors along the *c*-axis. For Y_2Cu_2Mg the Y–Y distances range from 370 to 400 pm.

Magnetic properties

The temperature-dependence of the magnetic susceptibility of Y_2Cu_2Mg and La_2Cu_2Mg is displayed in Fig. 2. The susceptibility of the lanthanum compound is almost independent of temperature with a room temperature value of $3.2(1) \times 10^{-9}$ m^3/mol. This small value arises from the Pauli susceptibility. The yt-

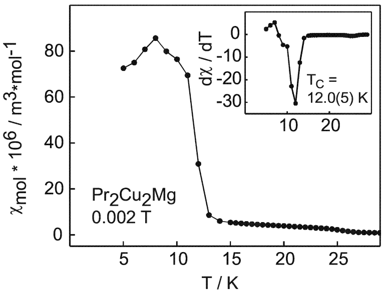

Fig. 5. Susceptibility of Pr_2Cu_2Mg measured in field-cooling mode at an external flux density of 0.002 T. The Curie temperature was determined from the derivative dχ/dT (insert).

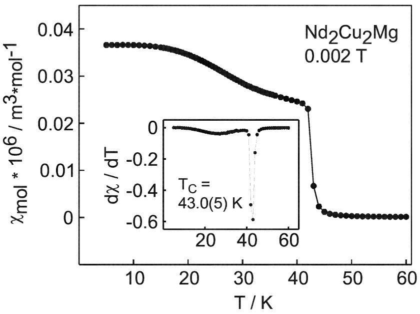

Fig. 6. Susceptibility of Nd_2Cu_2Mg measured in field-cooling mode at an external flux density of 0.002 T. The Curie temperature was determined from the derivative dχ/dT (insert).

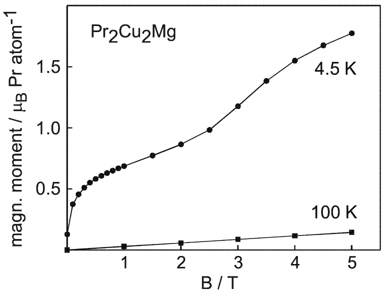

Fig. 7. Magnetization *vs* external magnetic flux density of Pr_2Cu_2Mg measured at 4.5 and 100 K.

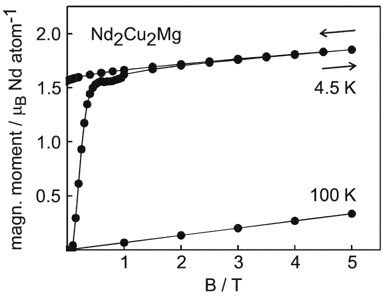

Fig. 8. Magnetization *vs* external magnetic flux density of Nd_2Cu_2Mg measured at 4.5 and 100 K.

trium compound shows a slightly higher susceptibility with an increase at lower temperatures indicating a small paramagnetic contribution. A fit of the susceptibility data according to a modified Curie-Weiss expression $\chi = \chi_0 + C/(T - \Theta)$ resulted in an experimental magnetic moment of 0.5 μ_B per formula unit and a temperature independent contribution $\chi_0 = 21(1) \times 10^{-9}$ m^3/mol. The small magnetic moment may be attributed to magnetic impurities rather than to an intrinsic property. The temperature-independent contribution is in the order of magnitude of a Pauli paramagnet and most likely results from the conduction electrons of this metallic compound.

Pr_2Cu_2Mg and Nd_2Cu_2Mg show Curie-Weiss behavior above 100 K with experimental magnetic moments of 3.67(2) μ_B/Pr atom and 3.47(2) μ_B/Nd atom, respectively (Figures 3 and 4). The μ_{exp} values are close to the μ_{eff} values of 3.58 μ_B and 3.62 μ_B expected for the free Pr^{3+} and Nd^{3+} ions in the $J = 4$ and 9/2 Hund's rule ground state indicating that the $4f$ electrons are almost localized within the praseodymium and neodymium atoms [16]. The paramagnetic Curie temperatures (Weiss constants) of $\Theta = -5(1)$ (Pr_2Cu_2Mg) and 6(1) K (Nd_2Cu_2Mg) have been determined by linear extrapolation of the high temperature parts ($>$ 100 K) of the $1/\chi$ *vs.* T plots to $1/\chi = 0$. The $1/\chi$ plots show deviations from Curie-Weiss behavior below 100 K, most likely due to an influence of the crystal electric field.

Ferromagnetic ordering of the praseodymium and neodymium magnetic moments was detected at low temperatures. The precise Curie temperatures of $T_C = 12.0(5)$ K for Pr_2Cu_2Mg and of $T_C = 43.0(5)$ K for Nd_2Cu_2Mg were determined from the derivatives dχ/dT of kink-point measurements (Figures 5 and 6) at a magnetic flux density of 0.002 T.

The magnetization *vs* external magnetic field dependence for Pr_2Cu_2Mg and Nd_2Cu_2Mg is linear at 100 K (Figures 7 and 8) as expected for a paramagnetic material. At 4.5 K, well below the magnetic ordering temperatures, the magnetization behavior is different for both compounds. Nd_2Cu_2Mg behaves like a classical ferromagnet. Already at an external flux density of 1 T the magnetization tends towards saturation with a magnetic moment of 1.85(2) μ_B/Nd-atom at the highest obtainable field of 5 T. The magnetization has reached only 57% of the possible maximum value of 3.27 μ_B/Nd-atom according to $g \times J$ [16]. Also for isotypic Nd_2Pd_2In [11], a reduced moment of 1.87 μ_B has been observed, however, this indide is a metamagnet with a critical field of about 1 T. Nd_2Cu_2Mg shows a pronounced square loop behavior in the magnetization at 4.5 K with a high remanent magnetization of 1.55(1) μ_B/Nd atom and a coercive field of 0.31(1) T. For ferromagnetic Nd_2PtSi_3 [17] much smaller values of 0.6 μ_B/Nd and 0.1 T have been detected.

In contrast to Nd_2Cu_2Mg, a more complex magnetization behavior is observed for the praseodymium compound. The magnetization shows a strong increase up to 0.5 T, however, with a magnetic moment of only 0.6 μ_B/Pr-atom. The slope becomes smaller with increasing external field strength and we observe a not very pronounced inflection point around 2.5 T indicating a further magnetic transition (spin reorientation). We expect a further increase of the magnetization with increasing field strength. At the highest obtainable magnetic field of 5 T the magnetization amounts to 1.78(2) μ_B/Pr, significantly reduced when compared with the maximal value of 3.20 μ_B/Pr according to $g \times J$ [16]. The reduced moment can most likely be attributed to crystal field splitting. Similar reduced moments have also been observed for the ferromagnets PrCuAl (1.30 μ_B/Pr) [18], PrRhIn (1.60 μ_B/Pr) [19] and PrCuSi (2.02 μ_B/Pr) [20], and for the metamagnet Pr_2Pd_2Mg (2.65 μ_B/Pr) [10].

Acknowledgements

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