The Solid Solutions $Gd_2Cu_2In_{1-x}Mg_x$ – Drastic Increase of the Curie Temperature upon In/Mg Substitution

Wilfried Hermes[a], Falko M. Schappacher[b], and Rainer Pöttgen[b]

[a] Department of Chemistry, Polymer & Materials Chemistry, Lund University, P. O. Box 124, SE-22100 Lund, Sweden
[b] Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstraße 30, 48149 Münster, Germany

Reprint requests to R. Pöttgen.
E-mail: pottgen@uni-muenster.de

Z. Naturforsch. **2010**, *65b*, 1516 – 1520; received September 17, 2010

The Mo_2B_2Fe-type intermetallic compounds Gd_2Cu_2In and Gd_2Cu_2Mg form a complete set of solid solutions $Gd_2Cu_2In_{1-x}Mg_x$. The *a* lattice parameter, the Weiss constant and the Curie temperature increase with increasing magnesium content in an almost Vegard-like manner, while the *c* parameter remains almost constant. All members of the solid solutions show ferromagnetism with T_Cs between 114 and 80 K.

Key words: Intermetallics, Gadolinium, Solid Solution, Ferromagnetism

Introduction

Intermetallic rare earth- (*RE*) and uranium-based compounds RE_2T_2X and U_2T_2X (T = late transition metal; X = Mg, Cd, In, Sn, Pb) with the tetragonal Mo_2B_2Fe-type structure have intensively been investigated in the last twenty years with respect to their very interesting magnetic and electrical properties [1, 2], *e. g.* the heavy-fermion system Ce_2Pt_2In [3, 4], the intermediate-valent Ce_2Ni_2Mg [5], the 150 K antiferromagnet Gd_2Ge_2Mg [6], the spin fluctuating system U_2Ir_2Sn [7], or the incommensurately modulated antiferromagnet U_2Pt_2Sn [8].

An interesting task is the modification of the physical properties of these intermetallics. This is possible by chemical substitution on the three crystallographically independent sites. The magnetically active *RE* or U site can be diluted by lanthanum or thorium substitution [9]. Another possibility is the formation of a solid solution by U/*X* substitution as observed in $U_{2.03}Co_2Ga_{0.97}$ [10] or $U_{2.1}Fe_2Sn_{0.9}$ [11]. On the other hand, many of the RE_2Pd_2Sn and U_2Pd_2Sn stannides show solid solutions $RE_2Pd_{2+x}Sn_{1-x}$ and $U_2Pd_{2+x}Sn_{1-x}$ [12 – 14].

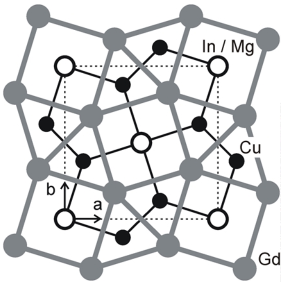

Fig. 1. Projection of the $Gd_2Cu_2In_{1-x}Mg_x$ structure along the short unit cell axis. The distorted AlB_2- and CsCl-related slabs and the two-dimensional $[Cu_2In_{1-x}Mg_x]$ network are emphasized.

Furthermore, one can use solid solutions $RE_2T_{2-x}T'_xX$ [15 – 17]. Substitution of the transition metal modifies the *RE*–*T* hybridization. A recent example are the solid solutions $Gd_2Cu_{2-x}Ni_xMg$ [18], where the magnetic ordering temperature drops from 110.5 K (Gd_2Cu_2Mg, heat capacity data) to 49 K (Gd_2Ni_2Mg) [19], and for the compositions $Gd_2Ni_{0.5}Cu_{1.5}Mg$ and $Gd_2Ni_{1.0}Cu_{1.0}Mg$ one observes a large magnetocaloric effect as a consequence of the Cu/Ni substitution. Such complete solid solutions should be possible for the whole series of RE_2Ni_2Mg [20] and RE_2Cu_2Mg [21] compounds.

In view of these interesting results we have extended our studies on solid solutions of RE_2T_2X intermetallics, however, with a different aspect. In several recent studies we could show that complete solid solutions exist for indides and the respective magnesium compounds, *e. g.* Mg_xIrIn_{3-x} [22], $IrIn_{2-x}Mg_x$ and $IrMg_{3-x}In_x$ [23], $Ir_3Mg_{13-x}In_x$ [24], or $CeAuIn_{1-x}Mg_x$ [25]. Based on this finding we investigated the solid solutions $Gd_2Cu_2In_{1-x}Mg_x$ by powder X-ray diffraction and magnetic susceptibility measurements. So far, only the end-members Gd_2Cu_2In [26, 27] and Gd_2Cu_2Mg [19, 21] have been reported.

Experimental Section

Synthesis

Starting materials for the preparation of samples from the solid solutions $Gd_2Cu_2In_{1-x}Mg_x$ were gadolinium in-

0932–0776 / 10 / 1200–1516 $ 06.00 © 2010 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com

Compound	*a* (pm)	*c* (pm)	*V* (nm^3)	Ref.
Gd_2Cu_2In	747.0(2)	376.5(2)	0.2101	[31]
Gd_2Cu_2In	752.8(2)	379.8(2)	0.2160	[26]
Gd_2Cu_2In	752.5(1)	381.3(1)	0.2160	this work
$Gd_2Cu_2In_{0.75}Mg_{0.25}$	754.6(1)	380.9(1)	0.2169	this work
$Gd_2Cu_2In_{0.5}Mg_{0.5}$	758.0(1)	379.8(1)	0.2182	this work
$Gd_2Cu_2In_{0.25}Mg_{0.75}$	762.7(1)	379.1(1)	0.2206	this work
Gd_2Cu_2Mg	765.31(8)	377.22(7)	0.2209	[21]
Gd_2Cu_2Mg	765.7(1)	377.6(1)	0.2214	this work

Table 1. Lattice parameters of samples of the solid solutions $Gd_2Cu_2In_{1-x}Mg_x$ with tetragonal Mo_2B_2Fe-type structure.

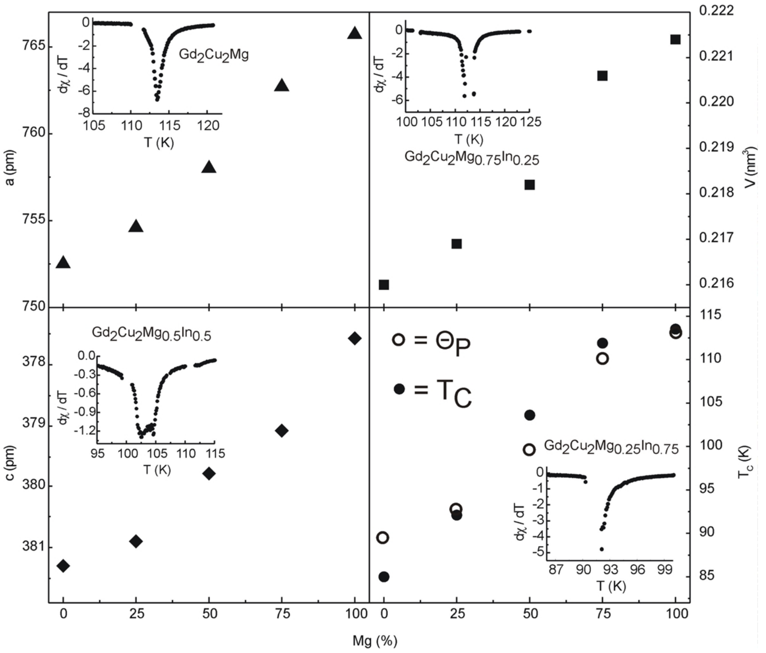

Fig. 2. Course of the lattice parameters *a* and *c* as well as the cell volume within the solid solution $Gd_2Cu_2In_{1-x}Mg_x$. The right bottom rectangle show the values of T_C and θ_P in dependence on the Mg content. The derivatives of the FC measurements at 100 Oe of all measured members of the solid solution are given in the insets.

gots (Johnson Matthey), copper drops (Johnson Matthey), indium drops (Chempur), and a magnesium rod (Johnson Matthey; the surface of the rod was removed on a turning lath in order to remove impurities), all with stated purities better than 99.9 %. In a first step, small pieces of the gadolinium ingots were arc-melted [28] under an argon pressure of *ca*. 600 mbar. The argon was purified with titanium sponge (900 K), silica gel, and molecular sieves. The elements were weighed in the atomic ratios listed in Table 1 and sealed in tantalum tubes under an argon pressure of 700 mbar in the same arc melting apparatus. The tantalum tubes were subsequently positioned in a water-cooled sample chamber of an induction furnace [29] (Hüttinger Elektronik, Freiburg, Germany, Typ TIG 2.5/300), heated to 1420 K, and kept at that temperature for 3 min. Subsequently the tubes were cooled to 1020 K within 5 min and kept at that temperature for another 3 h, followed by quenching. The temperature was controlled by a Sensor Therm Methis MS09 pyrometer with an accuracy of ± 30 K. The brittle samples could readily be separated from the metal tubes by mechanical fragmentation. No reaction with the crucible material was evident. The polycrystalline $Gd_2Cu_2In_{1-x}Mg_x$ samples are stable in air over weeks.

X-Ray powder diffraction

The $Gd_2Cu_2In_{1-x}Mg_x$ samples were characterized by Guinier patterns (imaging plate detector, Fujifilm BAS-1800 readout system) with Cu$K\alpha_1$ radiation and α-quartz (a = 491.30 and c = 540.46 pm) as the internal standard. Also new samples of Gd_2Cu_2In and Gd_2Cu_2Mg have been characterized. The tetragonal lattice parameters (Table 1) were refined by a least-squares routine. Correct indexing was ensured through an intensity calculation [30] taking the atomic positions from Y_2Cu_2Mg [21].

Physical property measurements

The single-phase samples were packed in kapton foil and attached to the sample holder rod of a VSM for measuring the magnetic properties in a Quantum Design Physical-Property-Measurement-System in the temperature range 5 – 305 K with magnetic flux densities up to 80 kOe.

Discussion

Crystal chemistry

Since the crystal chemistry and chemical bonding in the ternary series RE_2Cu_2In [26, 27] and RE_2Cu_2Mg [19, 21] have already been described in detail in recent work, herein we concentrate only on the solid solutions $Gd_2Cu_2In_{1-x}Mg_x$. In order to understand the course of the lattice parameters, we shortly draw back to the $Gd_2Cu_2In_{1-x}Mg_x$ structure (Fig. 1). The latter is built up from slightly distorted AlB_2- and CsCl-related slabs. The *a* parameter of the Mo_2B_2Fe-type compounds is governed by the $[Cu_2In_{1-x}Mg_x]$ network, while the *c* parameter is mainly influenced by the size of the rare earth element, *i. e.* gadolinium in our solid solutions. Comparing the RE_2Cu_2In with the RE_2Cu_2Mg series we showed that the *a* parameters of all indides are substantially smaller (*ca.* 14 pm), while the *c* parameters are almost equal, although indium (150 pm) has a much larger covalent radius [32] than magnesium (136 pm). Electronic structure calculations showed stronger Cu–In bonding as compared to Cu–Mg [21].

This trend is reflected in the solid solutions $Gd_2Cu_2In_{1-x}Mg_x$. With increasing magnesium content we observe an increase of the *a* parameter, accompanied by a weakening of the Cu–In(Mg) interactions. As emphasized in Fig. 2, the course of the *a* parameter shows Vegard-like behavior (small derivations will be explained in the magnetic part). The *c* parameters, expected to be influenced by the larger gadolinium atoms, show little variation. As a consequence, we observe an increase of the cell volume, on going to Gd_2Cu_2Mg. In an earlier report [31], significantly smaller lattice parameters have been reported for Gd_2Cu_2In. The reason for this discrepancy is unclear.

Physical properties

Recently we have shown the influence of Ru on the solid solutions $GdRu_{1-x}Cd_x$. Substitution of 20 % Cd in GdCd by ruthenium leads to a decrease of T_C from about 200 to 62 K [33]. Regarding Gd_2Cu_2Mg, the substitution of Mg by In has also a strong influence on the T_Cs. Gd_2Cu_2Mg has a T_C of 110.5 K [18] and Gd_2Cu_2In a T_C of 85.5 K [27]. Since all members of the solid solutions $Gd_2Cu_2In_{1-x}Mg_x$ show similar behavior of χ(T) and *M*(H), only that of $Gd_2Cu_2Mg_{0.75}In_{0.25}$ is shown herein as an example.

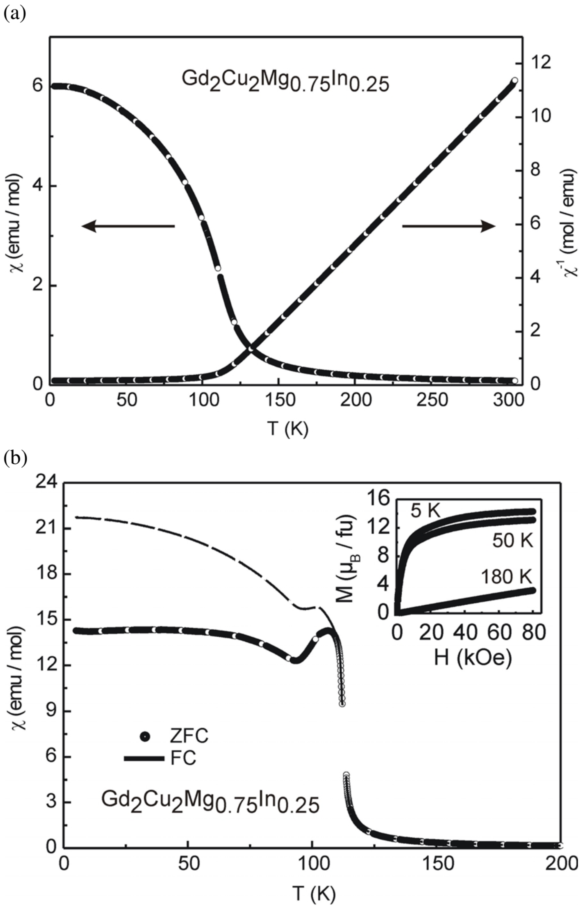

Fig. 3. (a) $\chi(T)$ and $\chi^{-1}(T)$ of $Gd_2Cu_2Mg_{0.75}In_{0.25}$ measured at 10 kOe. (b) ZFC-FC of $Gd_2Cu_2Mg_{0.75}In_{0.25}$ measured with an external applied field strength of 100 Oe. The inset shows $M(H)$ for the latter compound at 5, 50 and 180 K.

Fig. 3a shows $\chi(T)$ and $\chi^{-1}(T)$ of $Gd_2Cu_2Mg_{0.75}In_{0.25}$. Above T_C, Curie-Weiss behavior with the values given in Table 2 is observed. All members show slightly enhanced magnetic moments, which can be ascribed to $4f$-$5d$ exchange interactions, with a contribution from d-electrons. This was also observed in the Gd-Cu-based intermetallic compounds crystallizing in the same structure type [18]. All members show ferromagnetic ordering between 85 and 120 K. This is in agreement with the positive paramagnetic Curie temperatures given in Table 2, which are indicative of ferromagnetic interactions in the paramagnetic range. θ_P increases almost linearly in Vegard-like manner with increasing Mg content (Fig. 2).

The precise ordering temperatures of all members (except Gd_2Cu_2Mg, which was taken from [27]) were

Table 2. Magnetic data of samples from the solid solutions $Gd_2Cu_2In_{1-x}Mg_x$. T_C: Curie temperature, Θ_P: Weiss constant, μ_{eff}: experimental magnetic moment, M_S: saturation magnetization.

Compound	T_C (K)	Θ_P (K)	μ_{eff} (μ_B Gd^{-1})	M_S (μ_B fu^{-1})	Ref.
Gd_2Cu_2In	85.0(5)	90.5(5)	–	slightly above 7[a]	[27]
$Gd_2Cu_2In_{0.75}Mg_{0.25}$	92.1(3)	94(1)	8.35(1)	7.40(2)	this work
$Gd_2Cu_2In_{0.5}Mg_{0.5}$	103.6(3)	99(1)	8.72(1)	7.30(2)	this work
$Gd_2Cu_2In_{0.25}Mg_{0.75}$	111.9(3)	109.6(1)	8.31(1)	7.15(2)	this work
Gd_2Cu_2Mg	113.5(3)	114(1)	8.41(1)	7.33(2)	this work

[a] Only graphical data are reported in ref. [27].

determined from ZFC-FC measurements at 100 Oe (Fig. 3b) and therefore the derivatives of FC ($d\chi / dT$) were used (insets in Fig. 2). The course of T_C depending on the magnesium content is plotted in Fig. 2. The small deviations from Vegard-like behavior are mainly due to domains with slightly different composition. Therefore, it is also clear that the transitions in the solid solutions are somewhat broadened (insets in Fig. 2). This effect is more visible in the course of the T_C data as compared to the cell parameters, reflecting the higher sensitivity of magnetic measurements. It should be mentioned that SEM- together with EDX-measurements show homogeneity for all members in the range of the instruments accurancy. The effect of domains with different stoichiometry (in other words, the small discrepancy between magnetic measurements and X-ray powder data) on the magnetism was recently shown for the solid solution $EuRh_{2-x}Zn_x$ [34].

M(H) data (inset of Fig. 3) clearly show ferromagtism, which is slightly canted. No hysteresis was observed, and the saturation magnetizations for all members of $Gd_2Cu_2In_{1-x}Mg_x$ are slightly enhanced when compared to the theoretical value $g \times S$ ($7\mu_B$ / Gd atom), for which the same explanation as mentioned for the enhanced effective magnetic moments is valid.

Acknowledgements

This work was financially supported by the Deutsche Forschungsgemeinschaft. W. H. is indebted to the DAAD (Deutscher Akademischer Austauschdienst, *German Academic Exchange Service*) for a postdoctoral fellowship.

---

[1] M. Lukachuk, R. Pöttgen, *Z. Kristallogr.* **2003**, *218*, 767.

[2] U. Ch. Rodewald, B. Chevalier, R. Pöttgen, *J. Solid State Chem.* **2007**, *180*, 1720.

[3] R. Hauser, H. Michor, E. Bauer, G. Hilscher, D. Kaczorowski, *Physica B* **1997**, *230 – 232*, 211.

[4] Y. V. Galadzhun, R. Pöttgen, *Z. Anorg. Allg. Chem.* **1999**, *625*, 481.

[5] G. Geibel, U. Klinger, M. Weiden, B. Buschinger, F. Steglich, *Physica B* **1997**, *237 – 238*, 202.

[6] W. Choe, G. J. Miller, E. M. Levin, *J. Alloys Compd.* **2001**, *329*, 121.

[7] L. Havela, V. Sechovský, P. Svoboda, H. Nakotte, K. Prokeš, F. R. de Boer, A. Seret, J. M. Winand, J. Rebizant, J. C. Spirlet, A. Purwanto, R. A. Robinson, *J. Magn. Magn. Mater.* **1995**, *140 – 144*, 1367.

[8] K. Prokeš, P. Svoboda, A. Kolomiets, V. Sechovský, H. Nakotte, F. R. de Boer, J. M. Winand, J. Rebizant, J. C. Spirlet, *J. Magn. Magn. Mater.* **1999**, *202*, 451.

[9] L. C. J. Pereira, J. C. Waerenborgh, I. Catarino, G. Bonfait, M. Godinho, M. Almeida, *J. Alloys Compd.* **2001**, *317 – 318*, 419.

[10] A. V. Zelinskii, A. A. Fedorchuk, *Inorg. Mater.* **1995**, *31*, 1355; *Neorg. Mater.* **1995**, *31*, 1491.

[11] A. P. Gonçalves, H. Noël, J. C. Waerenborgh, *J. Magn. Magn. Mater.* **2002**, *251*, 1.

[12] F. Fourgeot, P. Gravereau, B. Chevalier, L. Fournès, J. Etourneau, *J. Alloys Compd.* **1996**, *238*, 102.

[13] D. Laffargue, F. Bourée, B. Chevalier, T. Roisnel, P. Gravereau, J. Etourneau, *J. Magn. Magn. Mater.* **1997**, *170*, 155.

[14] B. Chevalier, F. Fourgeot, D. Laffargue, R. Pöttgen, J. Etourneau, *J. Alloys Compd.* **1998**, *275 – 277*, 537.

[15] Y. Ijiri, F. J. DiSalvo, *J. Alloys Compd.* **1996**, *233*, 69.

[16] S. Bordère, S. Buzdin, B. Chevalier, D. Laffargue, J. Etourneau, *J. Magn. Magn. Mater.* **1997**, *175*, 263.

[17] V. H. Tran, A. Hoser, M. Hofmann, *J. Phys.: Condens. Matter* **2000**, *12*, 1029.

[18] S. Linsinger, W. Hermes, M. Eul, R. Pöttgen, *J. Appl. Phys.* **2010**, *108*, 043909.

[19] K. Łątka, R. Kmieć, A. W. Pacyna, R. Mishra, R. Pöttgen, *Solid State Sci.* **2001**, *3*, 545.

[20] R.-D. Hoffmann, A. Fugmann, U. Ch. Rodewald, R. Pöttgen, *Z. Anorg. Allg. Chem.* **2000**, *626*, 1733.

[21] R. Mishra, R.-D. Hoffmann, R. Pöttgen, *Z. Naturforsch.* **2001**, *56b*, 239.

[22] V. Hlukhyy, R.-D. Hoffmann, R. Pöttgen, *Z. Anorg. Allg. Chem.* **2004**, *630*, 68.

[23] V. Hlukhyy, R.-D. Hoffmann, R. Pöttgen, *Intermetallics* **2004**, *12*, 383.

[24] V. Hlukhyy, R. Pöttgen, *J. Solid State Chem.* **2004**, *177*, 1646.

[25] S. Rayaprol, B. Heying, R. Pöttgen, *Z. Naturforsch.* **2006**, *61b*, 495.

[26] Y. M. Kalychak, V. I. Zaremba, V. M. Baranyak, P. Yu. Zavalii, V. A. Bruskov, L. V. Sysa, O. V. Dmytrakh, *Izv. Akad. Nauk SSSR, Neorg. Mater.* **1990**, *26*, 94.

[27] I. R. Fischer, Z. Islam, P. C. Canfield, *J. Magn. Magn. Mater.* **1999**, *202*, 1.

[28] R. Pöttgen, T. Gulden, A. Simon, *GIT Labor-Fachzeitschrift* **1999**, *43*, 133.

[29] R. Pöttgen, A. Lang, R.-D. Hoffmann, B. Künnen, G. Kotzyba, R. Müllmann, B. D. Mosel, C. Rosenhahn, *Z. Kristallogr.* **1999**, *214*, 143.

[30] K. Yvon, W. Jeitschko, E. Parthé, *J. Appl. Crystallogr.* **1977**, *10*, 73.

[31] A. M. Bakar, Y. M. Kalychak, *Izv. Vyssh. Uchebn. Zaved. (Tsvetn. Metall.)* **1990**, 99.

[32] J. Emsley, *The Elements*, Oxford University Press, Oxford **1999**.

[33] F. Tappe, F. M. Schappacher, W. Hermes, M. Eul, R. Pöttgen, *Z. Naturforsch.* **2009**, *64b*, 356.

[34] W. Hermes, T. Harmening, R. Pöttgen, *Chem. Mater.* **2009**, *21*, 3325.

Nachdruck – auch auszugsweise – nur mit schriftlicher Genehmigung des Verlags gestattet
Druck: AZ Druck und Datentechnik GmbH, Kempten