The Ordered Laves Phases $CeNi_4Cd$ and $RECu_4Cd$ (RE = Ho, Er, Tm, Yb)

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The ternary ordered Laves phases $CeNi_4Cd$ and $RECu_4Cd$ (RE = Ho, Er, Tm, Yb) were synthesized by induction-melting of the elements in sealed tantalum tubes. The compounds were characterized by X-ray powder and single crystal diffraction: $MgCu_4Sn$ type, $F\bar{4}3m$, $a = 706.9(2)$ pm for $CeNi_4Cd$, $a = 723.1(2)$ pm for $HoCu_4Cd$, $a = 717.7(3)$ pm for $ErCu_4Cd$, $a = 714.2(1)$ pm for $TmCu_4Cd$, and $a = 713.10(7)$ pm for $YbCu_4Cd$. The nickel and copper atoms build up three-dimensional networks of corner-sharing $Ni_{4/2}$ and $Cu_{4/2}$ tetrahedra. These networks leave voids of coordination number 16 that are filled with the rare earth (RE) and cadmium atoms.

Key words: Laves Phases, Crystal Structure, Solid State Synthesis

Introduction

Every other magnesium positions in the cubic Laves phase $MgCu_2$ [1] can be substituted in an ordered manner leading to the $MgCu_4Sn \equiv (Mg_{0.5}Sn_{0.5})Cu_2$ structure [2, 3]. This ordering results in a symmetry reduction from $Fd\bar{3}m$ to $F\bar{4}3m$. Rare earth (RE) based intermetallics with the $MgCu_4Sn$ structure have intensively been investigated in the last 30 years with respect to their greatly varying magnetic properties. Especially the series of $YbCu_4X$ (X = Mg, Zn, Pd, Ag, Cd, In, Au, Tl) compounds have been studied in great detail, since they exhibit various physical properties associated with valence fluctuations of the ytterbium atoms [4 – 15].

During our systematic studies of the rare earth metal-transition metal-cadmium systems [16 – 25], we recently synthesized the new compounds $CeNi_4Cd$ and $RECu_4Cd$ (RE = Ho, Er, Tm) and confirmed $YbCu_4Cd$ [6]. The structure refinements of these intermetallics are reported herein.

Experimental Section

Synthesis

Starting materials for the preparation of the cadmium intermetallics were ingots of the rare earth elements (Chempur or Johnson Matthey), nickel wire ($\varnothing$ 0.38 mm) or nickel powder (Johnson Matthey), copper wire (Johnson Matthey, $\varnothing$ 1 mm, > 99.9%), and a cadmium rod (Johnson Matthey, $\varnothing$ 8 mm), all with stated purities better than 99.9%. The elements were weighed in the ideal 1:4:1 atomic ratios and sealed in small cylindric tantalum crucibles [26] under an argon pressure of *ca.* 600 mbar. The argon was purified over titanium sponge (900 K), silica gel, and molecular sieves. A synthesis in sealed tubes was necessary due to the low boiling temperature of cadmium (1038 K [27]).

The tantalum containers were put in a water-cooled sample chamber [28] of a high-frequency furnace (Hüttinger Elektronik, Freiburg, Typ TIG 5/300), heated for 1 minute at *ca.* 1170 K and subsequently annealed for another 4 h at *ca.* 970 K. Finally the tube was quenched to room temperature by switching off the power of the generator. The temperature was controlled through a Sensor Therm Metis MS09 pyrometer with an accuracy of ±30 K.

The brittle products could easily be separated from the tantalum tubes. No reaction with the container material was observed. The compact light gray pieces and the dark gray powders of these cadmium compounds are stable in air over months.

Scanning electron microscopy

The single crystals investigated on the diffractometer have been analyzed by EDX measurements using a Leica 420 I scanning electron microscope with CeO_2, HoF_3, ErF_3, TmF_3, YbF_3, elemental copper and cadmium as standards. No impurity elements were detected. The various point analyses on the crystals were in good agreement with the ideal $CeNi_4Cd$ and $RECu_4Cd$ compositions.

Table 1. Crystal data and structure refinement for CeNi$_4$Cd and RECu$_4$Cd (RE = Ho, Er, Tm, Yb), MgCu$_4$Sn type, space group $F\bar{4}3m$, Z = 4.

Empirial formula	CeNi$_4$Cd	HoCu$_4$Cd	ErCu$_4$Cd	TmCu$_4$Cd	YbCu$_4$Cd
Molar mass	487.36 g/mol	531.49 g/mol	533.82 g/mol	535.49 g/mol	539.6 g/mol
Lattice parameter	$a = 706.9(2)$ pm	$a = 723.1(2)$ pm	$a = 717.7(3)$ pm	$a = 714.2(1)$ pm	$a = 713.10(7)$ pm
(Guinier data)	$V = 0.3532$ nm^3	$V = 0.3781$ nm^3	$V = 0.3697$ nm^3	$V = 0.3643$ nm^3	$V = 0.3626$ nm^3
Calculated density	9.16 g/cm^3	9.34 g/cm^3	9.59 g/cm^3	9.76 g/cm^3	9.88 g/cm^3
Crystal size	$20 \times 20 \times 40$ μm^3	$20 \times 20 \times 60$ μm^3	$30 \times 40 \times 80$ μm^3	$20 \times 20 \times 40$ μm^3	$20 \times 20 \times 20$ μm^3
Transmission (max : min)	3.20	1.58	2.58	2.54	2.82
Absorption coefficient	39.1 mm^{-1}	48.0 mm^{-1}	50.4 mm^{-1}	52.5 mm^{-1}	54.1 mm^{-1}
$F(000)$	872	924	928	932	936
θ Range	5 to 35$°$	4 to 35$°$	4 to 40$°$	4 to 30$°$	4 to 35$°$
Range in hkl	$\pm11, \pm11, \pm11$	$\pm11, \pm11, \pm11$	$\pm12, \pm12, \pm12$	$\pm10, \pm10, +10$	$\pm11, \pm11, +11$
Total no. reflections	1470	1638	1987	573	861
Independent reflections	101($R_{\mathrm{int}} = 0.138$)	111($R_{\mathrm{int}} = 0.198$)	146($R_{\mathrm{int}} = 0.108$)	78($R_{\mathrm{int}} = 0.041$)	111($R_{\mathrm{int}} = 0.191$)
Reflections with $I > 2\sigma(I)$	93($R_{\mathrm{sigma}} = 0.046$)	106($R_{\mathrm{sigma}} = 0.062$)	146($R_{\mathrm{sigma}} = 0.036$)	77($R_{\mathrm{sigma}} = 0.019$)	108($R_{\mathrm{sigma}} = 0.090$)
Data/restraints/parameters	101 / 0 / 7	111 / 0 / 7	146 / 0 / 7	78 / 0 / 8	111 / 0 / 7
Goodness-of-fit on F^2	0.941	1.109	0.552	1.238	1.147
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.020$	$R1 = 0.034$	$R1 = 0.014$	$R1 = 0.013$	$R1 = 0.046$
	$wR2 = 0.036$	$wR2 = 0.079$	$wR2 = 0.037$	$wR2 = 0.034$	$wR2 = 0.091$
R Indices (all data)	$R1 = 0.023$	$R1 = 0.036$	$R1 = 0.014$	$R1 = 0.013$	$R1 = 0.047$
	$wR2 = 0.037$	$wR2 = 0.080$	$wR2 = 0.037$	$wR2 = 0.034$	$wR2 = 0.093$
Extinction coefficient	0.0054(6)	0.0002(5)	0.0037(3)	0.0086(6)	0.0021(9)
Flack parameter	0.07(8)	$-0.02(7)$	$-0.01(2)$	0.02(3)	0.07(7)
Largest diff. peak and hole	0.97 and -1.34 e/Å^3	3.98 and -1.24 e/Å^3	0.63 and -0.81 e/Å^3	0.36 and -0.39 e/Å^3	3.01 and -4.68 e/Å^3

X-ray film data and structure refinements

All samples were analysyed through Guinier powder patterns using Cu Kα_1 radiation and α-quartz ($a = 491.30$, $c = 540.46$ pm) as an internal standard. The Guinier camera was operated with an image plate system (Fujifilm-BAS1800). The cubic lattice parameters (Table 1) were obtained from least-squares fits of the Guinier data. To assure proper indexing, the experimental patterns were compared to calculated ones [29], using the positional parameters obtained from the structure refinements.

Irregularly shaped crystals were selected from the crushed samples. They were glued to thin glass fibers and examined on a Buerger precession camera (equipped with an image plate and white Mo radiation) in order to establish the suitability for intensity data collection. Single crystal intensity data were collected at room temperature by use of a four-circle diffractometer (CAD4) with graphite monochromatized Mo-K$_\alpha$ radiation and a scintillation counter with pulse-height discrimination. The scans were taken in the $\omega/2\theta$ mode and empirical absorption corrections were applied on the basis of psi-scan data, followed by spherical absorption corrections. All crystallographic data and details for the data collections are listed in Table 1.

The data sets showed the systematic extinctions for a face-centered cubic lattice. In agreement with a previous investigation on TmNi$_4$In [30], space group $F\bar{4}3m$ was found to be correct. The atomic parameters of the indium compound were taken as starting values and the five structures were refined with anisotropic displacement parameters for all atoms

Table 2. Atomic coordinates and isotropic displacement parameters for CeNi$_4$Cd and RECu$_4$Cd (RE = Ho, Er, Tm, Yb), MgCu$_4$Sn type, space group $F\bar{4}3m$.

Atom	Wyckoff position	x	y	z	U_{eq}[a]
CeNi$_4$Cd					
Ce	4c	1/4	1/4	1/4	53(3)
Ni	16e	0.6257(2)	x	x	55(3)
Cd	4a	0	0	0	74(4)
HoCu$_4$Cd					
Ho	4d	3/4	3/4	3/4	80(4)
Cu	16e	0.3742(2)	x	x	78(4)
Cd	4a	0	0	0	92(5)
ErCu$_4$Cd					
Er	4d	3/4	3/4	3/4	74(1)
Cu	16e	0.37426(6)	x	x	85(1)
Cd	4a	0	0	0	89(2)
TmCu$_4$Cd					
Tm	4c	1/4	1/4	1/4	78(3)
Cu	16e	0.62586(7)	x	x	79(3)
Cd[b]	4a	0	0	0	90(5)
YbCu$_4$Cd					
Yb	4d	3/4	3/4	3/4	87(5)
Cu	16e	0.3741(2)	x	x	89(5)
Cd	4a	0	0	0	112(5)

[a] U_{eq} (pm^2) is defined as one third of the trace of the orthogonalized U_{ij} tensor; [b] the cadmium site of the thulium compound is occupied only by 96.2(7)%.

using SHELXL-97 (full-matrix least-squares on F^2) [31]. The occupancy parameters were refined in a separate series of least-squares cycles. With the exception of the cadmium

Table 3. Interatomic distances (pm), calculated with the powder lattice parameters in the structures of CeNi$_4$Cd and YbCu$_4$Cd. All distances of the first coordination spheres are listed (standard deviations in parentheses).

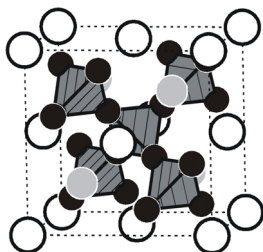| CeNi$_4$Cd				YbCu$_4$Cd			
Ce:	12	Ni	293.2(1)	Yb:	12	Cu	295.8(1)
	4	Cd	306.1(1)		4	Cd	308.8(1)
Ni:	3	Ni	248.6(4)	Cu:	3	Cu	250.4(3)
	3	Ni	251.3(4)		3	Cu	253.9(3)
	3	Cd	292.9(1)		3	Cd	295.5(1)
	3	Ce	293.2(1)		3	Yb	295.8(1)
Cd:	12	Ni	292.9(1)	Cd:	12	Cu	295.5(1)
	4	Ce	306.1(1)		4	Yb	308.8(1)

Fig. 1. The crystal structure of CeNi$_4$Cd (MgCu$_4$Sn type, space group $F\bar{4}3m$). The cerium, nickel, and cadmium atoms are drawn as medium gray, filled, and open circles, respectively. The three-dimensional network of corner-sharing Ni$_{4/2}$ tetrahedra is emphasized.

site in TmCu$_4$Cd, all sites were fully occupied within three standard deviations. In the final cycles the ideal occupancy parameters were assumed again for those sites. The 4a cadmium site of the thulium crystal showed an occupancy parameter of only 96.2(7)%, and this parameter was refined as a least-squares variable in the final cycles. The crystals showed full ordering of the rare earth metal and cadmium atoms. Refinement of the correct absolute structure was ensured through refinement of the Flack parameter [32, 33] (Table 1). Final difference Fourier synthesis revealed no significant residuals peaks for all five data sets. The atomic parameters and the interatomic distances are listed in Tables 2 and 3. Further details on the structure refinements are available.*

Results and Discussion

The crystal structures of five ordered Laves phases, *i. e.* CeNi$_4$Cd and RECu$_4$Cd (RE = Ho, Er, Tm, Yb) have been refined on the basis of single crystal X-ray

data. So far, only X-ray powder data of YbCu$_4$Cd have been published. The reported lattice parameters of 713.5 pm [9] and 713.3 pm [10] are in good agreement with the value of 713.10(7) pm determined in the present investigation. The lattice parameter of the RECu$_4$Cd intermetallics decreases from the holmium to the ytterbium compound as expected from the lanthanoid contraction.

The CeNi$_4$Cd structure is presented as an example in Figure 1. The nickel atoms build up a three-dimensional network of slightly distorted corner-sharing Ni$_{4/2}$ tetrahedra. The cerium and cadmium atoms fill larger cages of coordination number 16 (Frank-Kasper polyhedra [34, 35]) within this network. The small distortion of the nickel tetrahedra is due to the difference in size between cerium and cadmium [36]. The interatomic distances in CeNi$_4$Cd can be compared to the intermediate-valence compound Ce$_2$Ni$_2$Cd [16]. The Ni–Ni distances (259 pm) in the Ni$_2$ dumb-bells of Ce$_2$Ni$_2$Cd are slightly longer that in the tetrahedral network of CeNi$_4$Cd (249–251 pm). Also the Ni–Cd distances are shorter in CeNi$_4$Cd (293 *vs* 301 pm). They are both significantly longer than the sum of the covalent radii of 256 pm [27]. On the other hand, the Ce–Ni distances in Ce$_2$Ni$_2$Cd (288–294 pm) and CeNi$_4$Cd (293 pm) are comparable. They are shorter than the Ce–Ni distance of 299 pm in the binary Laves phase CeNi$_2$ [37] and we can assume a significant degree of Ce–Ni bonding in both Ce$_2$Ni$_2$Cd and CeNi$_4$Cd.

The isotypic copper compounds have slightly larger interatomic distances, due to the larger size of the copper atoms (128 pm atomic radius) as compared to nickel (125 pm) [27, 36]. Otherwise, the bonding pattern in the copper compounds is similar. For a more detailed discussion on the crystal chemistry and chemical bonding in such Laves phases we refer to [1] and to recent review articles [38–41, and ref. therein].

*Details may be obtained from: Fachinformationszentrum Karlsruhe, D–76344 Eggenstein-Leopoldshafen (Germany), by quoting the Registry No's. CSD 415194 (CeNi$_4$Cd), CSD 415195 (HoCu$_4$Cd), CSD 415196 (ErCu$_4$Cd), CSD 415197 (TmCu$_4$Cd), and CSD 415198 (YbCu$_4$Cd).

[1] F. Laves, Theory of Alloy Phases, Am. Soc. Met., Cleveland (1956).

[2] E. I. Gladyshevskii, P. I. Kripiakevich, M. J. Tesliuk, Dokl. AN SSSR **85,** 81 (1952).

[3] K. Osamura, Y. Murakami, J. Less-Common Met. **60,** 311 (1978).

[4] C. Rossel, K. N. Young, M. B. Maple, Z. Fisk, E. Zirngibel, J. D. Thompson, Phys. Rev. B **35**, 1914 (1987).

[5] I. Felner, I. Nowik, D. Vaknin, U. Potzel, J. Moser, G. M. Kalvius, G. Wortmann, G. Schmiester, G. Hilscher, E. Gratz, C. Schmitzer, N. Pillmayr, K. G. Prasad, H. de Waard, H. Pinto, Phys. Rev. B **35**, 6956 (1987).

[6] K. Hiraoka, K. Kojima, T. Hihara, T. Shinohara, J. Magn. Magn. Mater. **140-144**, 1243 (1995).

[7] J. L. Sarrao, C. D. Immer, C. L. Benton, Z. Fisk, J. M. Lawrence, D. Mandrus, J. D. Thompson, Phys. Rev. B **54**, 12207 (1996).

[8] E. Figueroa, J. M. Lawrence, J. L. Sarrao, Z. Fisk, M. F. Hundley, J. D. Thompson, Solid State Commun. **106**, 347 (1998).

[9] J. L. Sarrao, C. D. Immer, Z. Fisk, C. H. Booth, E. Figueroa, J. M. Lawrence, R. Modler, A. L. Cornelius, M. F. Hundley, G. H. Kwei, J. D. Thompson, F. Bridges, Phys. Rev. B **59**, 6855 (1999).

[10] K. Hiraoka, K. Murakami, S. Tomiyoshi, T. Hihara, T. Shinohara, K. Kojima, Physica B **281&282**, 173 (2000).

[11] J. M. Lawrence, P. S. Riseborough, C. H. Booth, J. L. Sarrao, J. D. Thompson, R. Osborn, Phys. Rev. B **63**, 054427 (2001).

[12] H. Sato, K. Hiraoka, M. Taniguchi, Y. Takeda, M. Arita, K. Shimada, H. Namatame, A. Kimura, K. Kojima, T. Muro, Y. Saitoh, A. Sekiyama, S. Suga, J. Synchrotron Rad. **9**, 229 (2002).

[13] H. Sato, Y. Nishikawa, F. Nagasaki, H. Fujino, Y. Takeda, M. Arita, K. Shimada, H. Namatame, A. Kimura, M. Taniguchi, K. Hiraoka, K. Kojima, Surf. Rev. Lett. **9**, 1079 (2002).

[14] H. Sato, K. Hiraoka, M. Taniguchi, Y. Nishikawa, F. Nagasaki, H. Fujino, Y. Takeda, M. Arita, K. Shimada, H. Namatame, A. Kimura, K. Kojima, J. Phys.: Condens. Matter **14**, 4445 (2002).

[15] T. Koyama, M. Matsumoto, T. Tanaka, H. Ishida, T. Mito, S. Wada, J. L. Sarrao, Phys. Rev. B **66**, 014420 (2002).

[16] D. Niepmann, R. Pöttgen, B. Künnen, G. Kotzyba, J. Solid State Chem. **150,** 139 (2000).

[17] R. Pöttgen, A. Fugmann, R.-D. Hoffmann, U. Ch. Rodewald, D. Niepmann, Z. Naturforsch. **55b,** 155 (2000).

[18] R. Mishra, R. Pöttgen, R.-D. Hoffmann, D. Kaczorowski, H. Piotrowski, P. Mayer, C. Rosenhahn, B. D. Mosel, Z. Anorg. Allg. Chem. **627,** 1283 (2001).

[19] Th. Fickenscher, G. Kotzyba, R.-D. Hoffmann, R. Pöttgen, Z. Naturforsch. **56b,** 598 (2001).

[20] F. Stadler, Th. Fickenscher, R. Pöttgen, Z. Naturforsch. **56b,** 1241 (2001).

[21] R.-D. Hoffmann, R. Pöttgen, Th. Fickenscher, C. Felser, K. Łątka, R. Kmieć, Solid State Sci. **4,** 609 (2002).

[22] Th. Fickenscher, R.-D. Hoffmann, R. Mishra, R. Pöttgen, Z. Naturforsch. **57b,** 275 (2002).

[23] K. Łątka, R. Kmieć, A. W. Pacyna, Th. Fickenscher, R.-D. Hoffmann, R. Pöttgen, J. Magn. Magn. Mater. **280,** 90 (2004).

[24] A. Doğan, D. Johrendt, R. Pöttgen, Z. Anorg. Allg. Chem. **631,** 451 (2005).

[25] Th. Fickenscher, U. Ch. Rodewald, D. Niepmann, R. Mishra, M. Eschen, R. Pöttgen, Z. Naturforsch. **60b,** 271 (2005).

[26] R. Pöttgen, Th. Gulden, A. Simon, GIT-Laborfachzeitschrift **43,** 133 (1999).

[27] J. Emsley, The Elements, Oxford University Press, Oxford (1999).

[28] D. Kußmann, R.-D. Hoffmann, R. Pöttgen, Z. Anorg. Allg. Chem. **624,** 1727 (1998).

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

[30] M. Lukachuk, Ya. M. Kalychak, T. Nilges, R. Pöttgen, Z. Naturforsch. **60b,** 393 (2005).

[31] G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, University of Göttingen, Germany (1997).

[32] H. D. Flack, G. Bernadinelli, Acta Crystallogr. **55A,** 908 (1999).

[33] H. D. Flack, G. Bernadinelli, J. Appl. Crystallogr. **33**, 1143 (2000).

[34] F. C. Frank, J. S. Kasper, Acta Crystallogr. **11**, 184 (1958).

[35] F. C. Frank, J. S. Kasper, Acta Crystallogr. **12**, 483 (1959).

[36] J. Donohue, The Structures of the Elements, Wiley, New York (1974).

[37] T. C. Shields, J. Mayers, I. R. Harris, J. Magn. Magn. Mater. **63/64**, 587 (1987).

[38] A. Simon, Angew. Chem. **95**, 94 (1983).

[39] R. Nesper, Angew. Chem. **103**, 805 (1991).

[40] R. L. Johnston, R. Hoffmann, Z. Anorg. Allg. Chem. **616**, 105 (1992).

[41] R. Nesper, G. J. Miller, J. Alloys Compd. **197**, 109 (1993).