

Superstructures in Room-temperature Ordered Deuterides CeCuSiD_x and CeCuGeD_x

Mathieu Pasturel^a, François Weill^b, and Jean-Louis Bobet^b

^a Unité Sciences Chimiques de Rennes, UMR CNRS 6226, Chimie du Solide et Matériaux, Campus de Beaulieu, bât. 10A, 35042 Rennes Cedex, France

^b Institut de Chimie de la Matière Condensée de Bordeaux, UPR CNRS 9048, 87 av. Dr. Schweitzer, 33608 Pessac Cedex, France

Reprint requests to Dr. Mathieu Pasturel. Fax: +33-(0)2-23-23-67-99.

E-mail: mathieu.pasturel@univ-rennes1.fr

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Dedicated to Dr. Bernard Chevalier on the occasion of his 60th birthday

Crystallographic superstructures in the deuterides CeCuSiD_{1.64(5)} and CeCuGeH_{1.15(5)} have been characterized by neutron diffraction. Deuterium atoms are inserted in [Ce₃Cu] and [Ce₃Si] or [Ce₃Ge] tetrahedral sites available in the hexagonal ZrBeSi-related structure of these deuterides. A partial but ordered occupancy of these tetrahedra by D atoms induces the occurrence of superstructures along the *c* axis, and the CeCuXD_y structures can be described with a *c* parameter multiplied by 3 and 7 for X = Ge and Si, respectively, in comparison with the *c* parameters of the ZrBeSi-type subcells.

Key words: Superstructure, Ordered Hydride, Intermetallics, Cerium, Neutron Diffraction

Introduction

Hydrogenation of cerium-based intermetallics has attracted much interest in recent years, because it was found to be an easy way to modify the physical properties of these compounds. For example, the formation of the hydrides CeNiSnH_{1.0} [1, 2] and CeRhSbH_{0.2} [3] leads to a transition from Kondo semiconductivity to antiferromagnetism.

A strong correlation between the hydrogen insertion sites and the influence on the competition between the RKKY (Ruderman, Kittel, Kasuya, Yosida) interactions and the Kondo effect has been observed in the CeTX (*T* = Mn, Co or Ni, *X* = *p* element) series. Hydrogen atoms located in the [Ce₃Ni] sites available in the structures derived from the AlB₂-type favor the localization of electrons on cerium and the occurrence of magnetic ordering [4, 5]. By contrast, hydrogen insertion into the [Ce₃] planes available in the LaPtSi-type structure of CeNiSi [6] or into the [Ce₄] tetrahedra present in the CeFeSi-type structure of CeCoX or CeMnX [7] favors the Kondo effect. These observations confirm the necessity to determine accurately the position of the hydrogen atoms in the metallic lattice in

order to understand the physical properties of the hydrides.

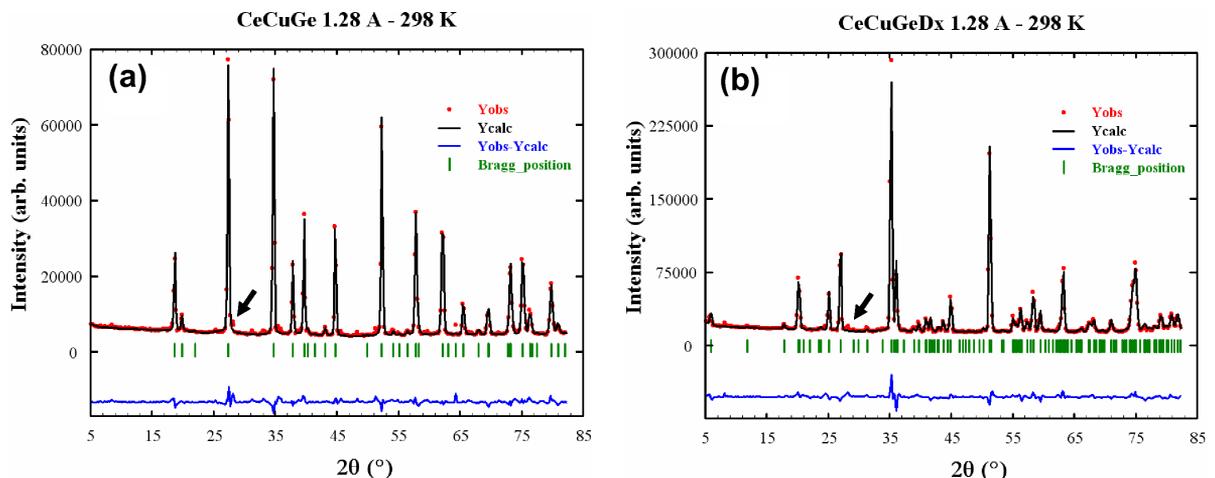
Recently, investigation of CeCuX hydrides (*X* = Ga, Si, Ge, Sn) by TEM diffraction experiments highlighted the occurrence of superstructures along the *c* axis of the hexagonal AlB₂- or ZrBeSi-type parent structures [8]. According to X-ray diffraction, both CeCuSiH_{1.3(1)} and CeCuGeH_{1.0(1)} crystallize in the ZrBeSi-type structure (space group *P6₃/mmc*, No. 194). Nevertheless, electron diffraction showed that the *c* parameters have to be multiplied by 5 and 3, respectively [9, 10], to describe more precisely the structure of these two hydrides. In order to solve these superstructures, CeCuSi and CeCuGe have been deuterated and neutron diffraction experiments were performed. The aim of this paper is to present the results of the structure determination of these two intermetallics and their deuterides.

Results and Discussion

CeCuGe and CeCuGeD_x

The neutron diffraction pattern of CeCuGe is shown in Fig. 1(a). In agreement with previous results [10, 11], this pattern can be indexed on the basis of a

	CeCuGe		CeCuGeD _x	
Space group	<i>P6₃/mmc</i> (No. 194)			
Cell parameters, Å	<i>a</i> = 4.2911(2)		<i>a</i> = 4.2290(2)	
	<i>c</i> = 7.8893(4)		<i>c</i> = 24.815(2)	
Atomic positions, (occupancy, if ≠ 1)	Ce1	2 <i>a</i> 0, 0, 0	2 <i>a</i>	0, 0, 0
	Ce2		4 <i>e</i>	0, 0, 1/6
	Cu1	2 <i>d</i> 1/3, 2/3, 3/4	2 <i>d</i>	1/3, 2/3, 3/4
	Cu2		4 <i>f</i>	1/3, 2/3, 0.0910(4)
	Ge1	2 <i>c</i> 1/3, 2/3, 3/4	2 <i>c</i>	1/3, 2/3, 1/4
	Ge2		4 <i>f</i>	1/3, 2/3, 0.5809(5)
	D1		4 <i>f</i>	1/3, 2/3, 0.1618(9) (0.85(2))
	D2		4 <i>f</i>	1/3, 2/3, 0.5114(5) (0.87(2))
Displacement parameters, Å ²	Ce	0.6(1)	Ce	0.6(1)
	Cu	1.2(2)	Cu	1.2(2)
	Ge	0.2(2)	Ge	0.3(2)
	D		D	1.6(2)
<i>V</i> _{cell} , Å ³	125.809(8)		384.35(4)	
ρ_{calc} , g cm ⁻³	7.3		7.2	
Refl. observed	43		139	
Param. refined	11		17	
	<i>R</i> _p	0.115	<i>R</i> _p	0.148
	<i>R</i> _{wp}	0.115	<i>R</i> _{wp}	0.132
Conventional reliability factors	<i>R</i> _e	0.024	<i>R</i> _e	0.015
	χ^2	23.8	χ^2	80.5
	<i>R</i> _{Bragg}	0.041	<i>R</i> _{Bragg}	0.078
	<i>R</i> _f	0.042	<i>R</i> _f	0.12

Table 1. Results of Rietveld refinements of neutron powder diffraction patterns of CeCuGe and CeCuGeD_{1.15(5)}.Fig. 1. Refined powder neutron diffraction patterns of (a) CeCuGe and (b) CeCuGeD_{1.15(5)}. (Arrows indicate an impurity peak).

hexagonal ZrBeSi-type structure with cell parameters $a = 4.2911(2)$ and $c = 7.8893(4)$ Å. The results of the Rietveld refinement are given in Table 1. It is worth pointing out that the limited resolution of the detector (step = 0.2° in 2θ) as well as the presence of an impurity phase (not detected by electron microprobe analysis but highlighted by an arrow in Fig. 1 at $2\theta = 28.2^\circ$) do not allow a fine refinement of the profile and are the reasons for the large values of some reliability factors

(e.g. χ^2). This remark is also valid for the three other refinements.

The extinction conditions *P-c* on the TEM diffraction patterns of CeCuGeH_{1.0(1)} are compatible with space groups *P6₃/mmc*, *P6₃mc*, or *P6̄2c*, with a *c* parameter multiplied by 3 in comparison with the ZrBeSi-type structure [8]. Considering the space group *P6₃/mmc* and the cell parameters $a = 4.2290(2)$ and $c = 24.815(2)$ Å, it was possible to index all the

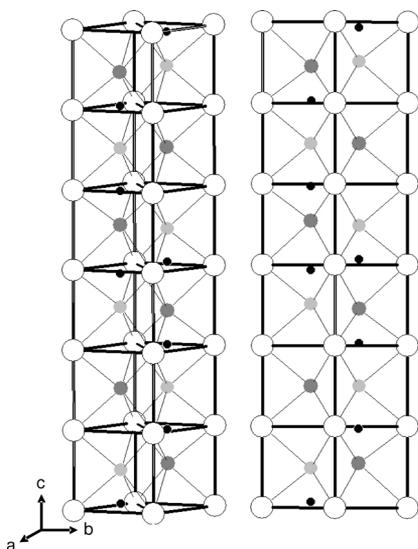


Fig. 2. Structure of the CeCuGeD_{1.15(5)} deuteride (left side) and its projection onto the (110) plane (right side). (Ce: large white circles, Cu: dark grey medium circles, Ge: light grey medium circle, and D: small black circles).

peaks of the neutron diffraction pattern (Fig. 1(b)) of CeCuGeD_x. Then, the metal atoms could be placed in the structure according to X-ray results [10] and the deuterium atoms localized using difference Fourier maps analysis. Two different $4f$ ($1/3, 2/3, z$) sites have been found to be occupied by deuterium atoms: one corresponding to a [Ce₃Cu] tetrahedral site and another one, more surprisingly, corresponding to a [Ce₃Ge] tetrahedron. In both cases, and as expected according to the higher affinity of Ce as compared to Cu for D, the D atoms are located close to the [Ce₃] base of the tetrahedra.

The results of the Rietveld refinement are given in Table 1. A presentation of the structure and its projection onto the (110) plane are shown in Fig. 2. The structure can be described as a stacking of [Ce₆] trigonal prisms with Cu and Ge atoms distributed in an ordered way at their centres. Notably, the refinement of the z coordinates of Cu and Ge in the $4f$ sites indicates a very small shift of these atoms away from the center of the [Ce₆] prisms ($z = 0.0910(4)$ instead of 0.0833 for Cu, *i. e.* a 0.20 Å shift, and $z = 0.5809(5)$ instead of 0.5833 for Ge, *i. e.* a 0.06 Å shift). The deuterium atoms are located in the smaller tetrahedra formed by these displaced Cu or Ge atoms and three Ce atoms. The slightly larger [Ce₃Cu] or [Ce₃Ge] sites formed by these displaced atoms, or those formed by non-displaced Cu ($2d$) and Ge ($2c$) atoms do not contain

Table 2. Interatomic distances (Å) in CeCuSi and its deuteride as calculated from the parameters of Table 1.

CeCuGe		CeCuGeD _{1.15(5)}	
Ce–6 Ce	4.29	Ce–6 Ce	4.23
Ce–2 Ce	3.94	Ce–2 Ce	4.14
Ce–6 Cu	3.17	Ce1–6 Cu2	3.33
		Ce2–3 Cu2	3.08
		Ce2–3 Cu1	3.20
Ce–6 Ge	3.17	Ce1–6 Ge2	3.16
		Ce2–3 Ge1	3.20
		Ce2–3 Ge2	3.24
		Ce1–6 D2	2.46
		Ce2–3 D1	2.44
		Cu2–1 D1	1.76
		Ge2–1 D2	1.72
		D2–3 D2	2.51

any D atoms. Interatomic distances in this deuteride are presented in Table 2.

Deuterium atom D1 located in [Ce₃Cu] has a Ce–D distance of 2.445 Å, which is smaller than the distance reported in CeCuSnD_{0.33} (2.618(1) Å) [12] but bigger than the Ce–D distances reported in the CeNiX compounds (*e. g.* 2.35–2.38 Å in CeNiSiD_{1.2} [6]). The Cu–D distance (1.76 Å) agrees with a metallic radius of Cu of 1.278 Å [13] and a D radius of about 0.4 Å.

Deuterium atom D2 located in [Ce₃Ge] has a slightly longer Ce–D distance (2.458 Å). The Ge–D distance of 1.725 Å is smaller than the Si–D distance observed in CeNiSiD_{1.2} [6] or the Sn–D distance observed in CeCuSnD_{0.33} [12], but is compatible with an atomic radius of Ge of 1.25 Å. Relatively short D–D distances (2.506 Å) are calculated between these D2 atoms, but are still larger than the Shoemaker criterion [14].

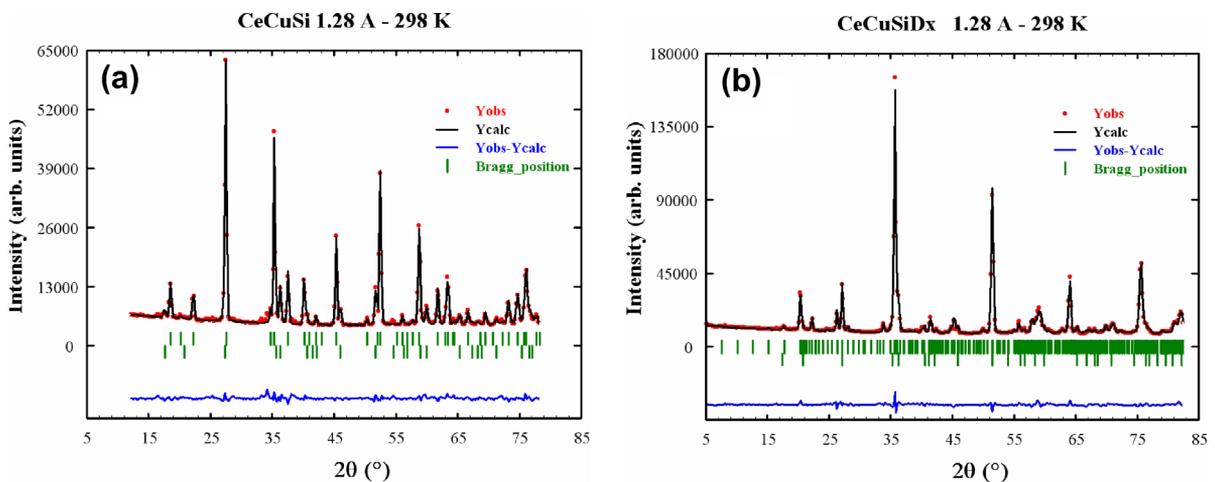
The refined occupation rates of the $4f$ sites by D1 and D2 which are equal to 0.85(2) and 0.87(2), respectively, lead to the composition CeCuGeD_{1.15(5)} which is in good agreement, taking into account the accuracy of both methods, with the experimental formula CeCuGeH_{1.0(1)} determined by Sievert's method.

CeCuSi and CeCuSiD_x

Fig. 3 presents the neutron diffraction patterns and the results of the Rietveld refinement for CeCuSi and its deuteride.

In agreement with previously reported results [9, 15, 16], the CeCuSi phase can be indexed in the hexagonal ZrBeSi-type structure with $a = 4.2194(2)$ and $c = 7.9548(4)$ Å. A second minor phase has been identified as a disordered version of CeCuSi crystallizing in the hexagonal AlB₂-type structure (space group

	CeCuSi		CeCuSiD _x	
Space group	<i>P</i> 6 ₃ / <i>mmc</i> (No. 194)			
Cell parameters, Å	<i>a</i> = 4.2194(2)		<i>a</i> = 4.1803(2)	
	<i>c</i> = 7.9548(4)		<i>c</i> = 58.150(3)	
Ce1	2 <i>a</i>	0 0 0	2 <i>a</i>	0 0 0
Ce2			4 <i>e</i>	0, 0, 0.0714
Ce3			4 <i>e</i>	0, 0, 0.1428
Ce4			4 <i>e</i>	0, 0, 0.2143
Cu1	2 <i>d</i>	1/3, 2/3, 3/4	2 <i>d</i>	1/3, 2/3, 3/4
Cu2			4 <i>f</i>	1/3, 2/3, 0.0368(5)
Cu3			4 <i>f</i>	1/3, 2/3, 0.1778(6)
Cu4			4 <i>f</i>	1/3, 2/3, 0.6042(6)
Atomic positions (occupancy, if ≠ 1)	Si1	2 <i>c</i>	1/3, 2/3, 1/4	2 <i>c</i>
	Si2			4 <i>f</i>
	Si3			4 <i>f</i>
	Si4			4 <i>f</i>
	D1			4 <i>f</i>
	D2			4 <i>f</i>
	D3			4 <i>f</i>
	D4			4 <i>f</i>
	D5			4 <i>f</i>
	D6			4 <i>f</i>
	D7			4 <i>f</i>
Displacement parameters, Å ²	Ce	0.6(1)		0.3(2)
	Cu	0.62(8)		0.7(2)
	Ge	0.7(2)		0.0(2)
	D			1.6(2)
<i>V</i> _{cell} , Å ³		122.65(1)		880.05(7)
ρ_{calc} , g cm ⁻³		6.3		6.2
Refl. observed		62		323
Param. refined		18		36
	<i>R</i> _p	0.106		0.115
	<i>R</i> _{wp}	0.107		0.102
Conventional reliability factors	<i>R</i> _e	0.028		0.020
	χ^2	14.6		25.1
	<i>R</i> _{Bragg}	0.036		0.062
	<i>R</i> _f	0.037		0.085

Table 3. Results of Rietveld refinements of neutron powder diffraction patterns of CeCuSi and CeCuSiD_{1.64(5)}.Fig. 3. Refined powder neutron diffraction patterns of (a) CeCuSi and (b) CeCuSiD_{1.64(5)}. The second minor phase corresponds to a disordered hexagonal AlB₂-type CeCuSi phase. (See text for details).

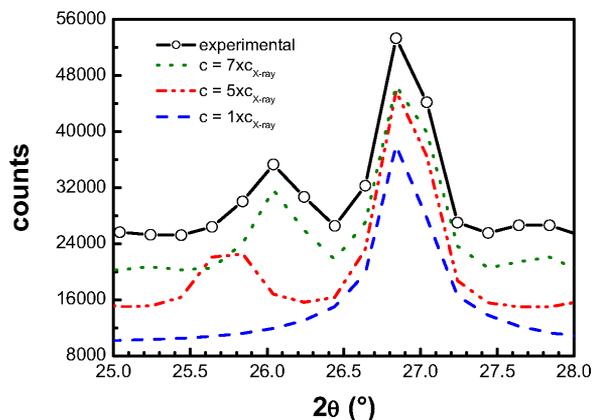


Fig. 4. Enlarged area of the experimental CeCuSiD_x neutron diffraction pattern (black line + symbols) and calculated profiles for $c = k \times c_{X\text{-ray}}$ with $k = 1$ (dashed line), 5 (dashed-dotted line) and 7 (dotted line). Curves have been shifted vertically for clarity.

$P6/mmm$, no. 191, random distribution of Cu and Si on the $2d$ site with cell parameters $a = 4.1080(4)$ and $c = 4.1887(7)$ Å. The refined parameters for this phase are included in the total number of refined parameters of Table 3.

As this last AlB_2 -type phase absorbs deuterium, the cell parameters are finally changed to $a = 4.1123(5)$ and $c = 4.2295(9)$ Å (Fig. 3(b)). It is almost impossible to get more reliable information about this deuteride because most reflections show superposition with those of the major ZrBeSi -derived phase.

Considering the major ordered phase and according to TEM diffraction experiments, space groups $P6_3/mmc$, $P6_3mc$ or $P\bar{6}2c$, with a c parameter multiplied by 5 in comparison with the ZrBeSi -type structure, can be expected [8]. Fig. 4 presents a zoomed area of the experimental neutron diffraction pattern (black line and symbols) from 25° to 28° , as well as 3 fits – using the Debye method – with different values of the c parameter. A peak occurring at 26.84° is expected from a single ZrBeSi -type phase and is well fitted by all three profiles using $c = k \times c_{X\text{-ray}}$ with $k = 1, 5$ or 7 . A superstructure peak occurs at 26.04° , which is not calculated for $c = c_{X\text{-ray}}$ (dashed line). According to TEM measurements, $c = 5 \times c_{X\text{-ray}}$ is expected, but the fitting of the neutron data (dashed-dotted line) shows a smaller 2θ position for the superstructure peak compared with the experimental one. Finally, a structure with space group $P6_3/mmc$ and a c parameter multiplied by 7 must be considered (dotted line). The reason for this anomaly is given later.

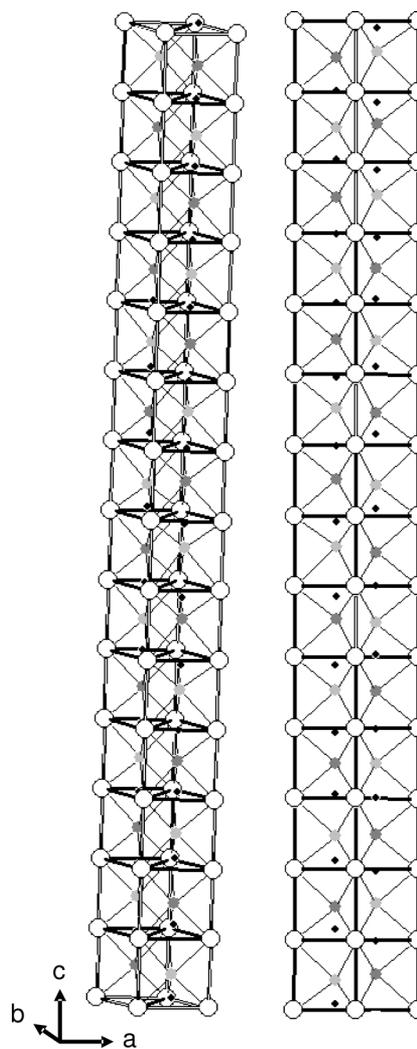


Fig. 5. Structure of the $\text{CeCuSiD}_{1.64(5)}$ deuteride (left side) and its projection onto the (110) plane (right side). (Ce: large white circles, Cu: medium dark grey circles, Si: medium light grey circle, and D: small black circles).

D atoms have been localized in the cell by the difference Fourier method. As for $\text{CeCuGeD}_{1.15(5)}$, two types of tetrahedral sites, namely $[\text{Ce}_3\text{Cu}]$ and $[\text{Ce}_3\text{Si}]$, are occupied (Fig. 5).

The atomic positions obtained by Rietveld refinement are given in Table 3 and the resulting pattern is shown in Fig. 3(b). Small displacements along the c axis of Cu or Si atoms from the center of the $[\text{Ce}_6]$ trigonal prisms are observed: $0.05\text{--}0.06$ Å for Cu₂, Cu₃ and Si₂, 0.13 Å for Si₃, 0.17 Å for Cu₄, and 0.28 Å for Si₄. These displacements create two tetrahedral sites in each prism with slightly different sizes. Deuterium

Table 4. Distances (Å) between D atoms and Ce atoms, Cu or Si-atoms and [Ce₃] planes.

Distance from	Ce	Cu or Si		[Ce ₃]
		Atom	Distance	
D1	2.49	Cu4	1.28	0.63
D2	2.43	Cu1	1.81	0.27
D3	2.41	Cu2	1.97	0.05
D4	2.42	Si2	1.85	0.16
D5	2.41	Si1	2.03	0.05
D6	2.46	Si3	1.48	0.47
D7	2.45	Si4	1.40	0.40

atoms are found to be systematically located in the smaller ones. In the case of Cu1 and Si1, located in the center of the [Ce₆] trigonal prisms, two equivalent tetrahedral sites are available and are both occupied by D atoms. As seen in Fig. 5, the maximum of available 4*f* sites are occupied by D atoms with such a distribution. All other empty tetrahedral sites are sharing a common face with one occupied site and cannot be filled with a D atom according to the Shoemaker-Westlake rules [14, 17].

According to the occupation rate of the 4*f* sites by deuterium, a composition CeCuSiD_{1.64(5)} is obtained for this deuteride. The amount of deuterium per formula unit is higher than the amount of hydrogen determined experimentally (*i. e.* CeCuSiH_{1.35(10)}). This can be explained by isotopic effects or by slightly different experimental procedures (longer deuteration time). This difference in stoichiometry is probably responsible for the difference of the superstructure translation along the *c* axis observed between TEM and neutron diffraction.

Table 4 summarizes the distances between each deuterium and the Ce, Cu or Si atoms surrounding it, as well as its distance from the [Ce₃] planes. The distances found for D2, D3, D4, D5 are in good agreement with those in CeCuGeD_{1.15(5)} and in previous work [6, 12]. In the case of D6 and D7, the distances of 1.48 and 1.40 Å to Si3 and Si4, respectively, are much shorter than those reported in CeNiSiD_{1.2(1)} [6], but are in the order of magnitude of bond lengths in transition metal silanes (1.48 Å) [18]. Si–D distances of these two sites are close to a covalent bond length. More surprising is the very short distance between D1 and Cu4 (1.28(1) Å). To the best of our knowledge, such a short Cu–D distance has not been reported so far. The smallest distance found in the literature is 1.55 Å in (H–CuPH₃)₂ complexes [19]. Three hypotheses can be raised to explain this short distance: (i) this Cu atom is in an ionic state (+I or +II) and a strong interaction ex-

ists with the D atom; (ii) the 4*f* site of D1 is only half-filled and the refined positions of D1 and Cu4 are mean values of the positions over the cell, this small distance thus being an average value of a long (filled 4*f*_D)–Cu and a short (empty 4*f*_D)–Cu distance; (iii) the distance of D1 from the [Ce₃] plane is much longer than the other ones, making a mistake in the refinement of its *z* coordinate possible.

Conclusion

The crystal structures of CeCuGeD_{1.15(5)} and CeCuSiD_{1.64(5)} have been determined by neutron diffraction. In both cases, an ordered occupation of the available tetrahedral sites [Ce₃Cu] and [Ce₃X] (*X* = Si or Ge) by deuterium atoms in the hexagonal ZrBeSi-type structure induces the occurrence of a superstructure along the *c* axis and $c_{\text{deuteride}} = k \times c_{\text{ZrBeSi}}$ with $k = 3$ for CeCuGeD_{1.15(5)}, $k = 5$ for CeCuSiH_{1.35(10)}, and $k = 7$ for CeCuSiD_{1.64(5)}. Due to the odd values of *k*, the two deuterides crystallize in space groups *P*6₃/*mmc* which are isomorphic subgroups of index 3 and 7 of *P*6₃/*mmc*. Such superstructures induced by a partial but ordered occupancy of available sites have already been reported, for example in the TiMn_{1.5} hydride [20] and in the *hcp* cobalt deuterides at low temperature [21].

With TEM diffraction on CeCuSnH_{0.2(1)} showing a similar behavior, it will be interesting to reinvestigate the corresponding deuteride structure by neutron diffraction.

Energy levels will have to be calculated in order to understand why the hydrogen atoms in CeCuX (*X* = Si, Ge, Sn) are ordered at r. t. while they are randomly distributed in the corresponding CeNiX phases.

Experimental Section

The ternary intermetallics CeCuSi and CeCuGe were synthesized by arc-melting of stoichiometric mixtures of the pure elements (purity above 99.8%) in a high-purity argon atmosphere. The samples were turned and remelted several times to ensure homogeneity. Then, annealing was performed at 1073 K for 2 weeks by sealing the samples in evacuated quartz tubes.

Samples were deuterated at 473 K and $p(\text{D}_2) = 2$ MPa for 48 h, after an activation of the samples at the same temperature under vacuum.

Neutron powder diffraction was performed on the D1-B diffractometer at the Institut Laue Langevin (Grenoble, France). The patterns were measured on powder samples at r. t. (298 K) with a neutron wavelength of 1.28 Å. The data were analyzed with the Rietveld profile method using the

FULLPROF program [22]. Difference Fourier calculations were carried out with the GFOURIER program available as part of the FULLPROF suite.

Acknowledgements

These investigations are part of the study of the influence of hydrogenation on the crystallographic and physical properties of CeTX intermetallics (T = transition metal, $X = p$ el-

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- [1] V. A. Yartys, B. Ouladdiaf, O. Isnard, O. Yu. Khyzhun, K. H. J. Buschow, *J. Alloys Compd.* **2003**, 359, 62.
- [2] B. Chevalier, M. Pasturel, J.-L. Bobet, J. Etourneau, O. Isnard, J. Sanchez Marcos, J. Rodriguez Fernandez, *J. Magn. Magn. Mater.* **2004**, 272–276, 576.
- [3] B. Chevalier, R. Decourt, B. Heying, F. M. Schappacher, U. Ch. Rodewald, R.-D. Hoffmann, R. Pöttgen, R. Eger, A. Simon, *Chem. Mater.* **2007**, 19, 28.
- [4] B. Chevalier, M. Pasturel, J.-L. Bobet, R. Decourt, J. Etourneau, O. Isnard, J. Sanchez Marcos, J. Rodriguez Fernandez, *J. Alloys Compd.* **2004**, 383, 4.
- [5] M. Stange, V. Paul-Boncour, M. Latroche, A. Percheron-Guégan, O. Isnard, V. A. Yartys, *J. Alloys Compd.* **2005**, 404–406, 144.
- [6] M. Pasturel, F. Weill, F. Bourée, J.-L. Bobet, B. Chevalier, *J. Alloys Compd.* **2005**, 397, 17.
- [7] B. Chevalier, M. Pasturel, J.-L. Bobet, O. Isnard, *Solid State Commun.* **2005**, 134, 529.
- [8] F. Weill, M. Pasturel, J.-L. Bobet, B. Chevalier, *J. Phys. Chem. Solids* **2006**, 67, 1111.
- [9] M. Pasturel, J.-L. Bobet, F. Weill, B. Chevalier, *J. Alloys Compd.* **2004**, 383, 118.
- [10] B. Chevalier, M. Pasturel, J.-L. Bobet, F. Weill, R. Decourt, J. Etourneau, *J. Solid State Chem.* **2004**, 177, 752.
- [11] F. Yang, J. P. Kuang, J. Li, E. Brück, H. Nakotte, F. R. de Boer, X. Wu, Z. Li, Y. Wang, *J. Appl. Phys.* **1991**, 69, 4705.
- [12] J. P. Maehlen, M. Stange, V. A. Yartys, R. G. Delaplane, *J. Alloys Compd.* **2005**, 404–406, 112.
- [13] E. Teatum, K. Gschneidner, J. Waber, *Compilation of calculated data useful in predicting metallurgical behaviour of the elements in binary alloy systems*, LA-2345, Los Alamos Scientific Laboratory, Los Alamos, **1960**.
- [14] D. P. Shoemaker, C. B. Shoemaker, *J. Less-Common Met.* **1979**, 68, 43.
- [15] A. Iandelli, *J. Less-Common Met.* **1983**, 90, 121.
- [16] D. Gignoux, D. Schmitt, M. Zerguine, *Solid State Commun.* **1986**, 58, 559.
- [17] D. G. Westlake, *J. Less-Common Met.* **1983**, 90, 251.
- [18] J. Y. Corey, J. Braddock-Wilking, *Chem. Rev.* **1999**, 99, 175.
- [19] L. Magnko, M. Schweizer, G. Rauhut, M. Schütz, H. Stoll, H.-J. Werner, *Phys. Chem. Chem. Phys.* **2002**, 4, 1006.
- [20] B. K. Singh, A. K. Singh, A. M. Imam, O. N. Srivastava, *Int. J. Hyd. Ener.* **2001**, 26, 817.
- [21] V. K. Fedotov, V. E. Antonov, T. E. Antonova, E. L. Bokhenkov, B. Dorner, G. Grosse, F. E. Wagner, *J. Alloys Compd.* **1999**, 291, 1.
- [22] J. Rodríguez-Carvajal, FULLPROF, A Program for Rietveld Refinement and Pattern Matching Analysis, Satellite Meeting on Powder Diffraction of the 15th International Congress of the IUCr, Toulouse (France) **1990**, p. 127. See also: J. Rodríguez-Carvajal, *Physica B* **1993**, 192, 55–69.