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Deuterium-Induced Copper Pairing in $Zr_2CuD_{\sim 5}$

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Deuteration of Zr_2Cu leads to a reconstruction of its $MoSi_2$-type metal atom arrangement. While the tetragonal alloy contains isolated copper atoms (Cu–Cu = 3.22 Å) in a cubic zirconium atom environment, the monoclinic deuteride $Zr_2CuD_{4.71}$ contains Cu_2 dumbbells (Cu–Cu = 2.39 Å), of which each copper atom has a trigonal-prismatic zirconium atom environment. Deuterium occupies five sites, of which four have tetrahedral metal configurations (two Zr_4-type and two Zr_3Cu-type) and are fully occupied while one has a trigonal-bipyramidal metal configuration (Zr_3Cu_2-type) and is partially occupied (71%). Copper is bonded to four deuterium atoms in a saddlelike configuration (Cu–D = 1.73–1.87 Å). Two of the ligands connect copper in a nearly linear Cu–D–Cu arrangement to partially interrupted dimeric $[Cu_2D_6]_n$ ribbons running perpendicular to the Cu_2 dumbbell direction. At the upper phase limit, the ribbons are presumably no longer interrupted and the deuteride can be described by the limiting ionic formula $2Zr^{2+}[Cu^+D_3]^{2-}2D^-$.

Intermetallic compounds are of interest for hydrogen storage applications.[1] Their hydrogenation usually leads to a filling of metal atom interstices followed by a more-or-less anisotropic lattice expansion.[2] The hydrogen atom distributions in such “interstitial” hydrides are mostly disordered, and the hydrogen site occupancies can be modeled to a certain extent by geometric considerations such as interstitial hole size and shortest hydrogen−hydrogen contacts.[3] Hydrogen-induced reconstructions of metal atom arrangements or segregations into binary hydrides and other intermetallic compounds are less common. Examples for reconstructions are found among the so-called body-centered-cubic (bcc) solid solution alloys[4] (e.g., V−Cr−Ti), the structure of which changes from bcc to face-centered-cubic, and for segregations among AB and AB_2 (A = rare earth and B = transition metal) compounds.[5] A compound likely to show both phenomena is Zr_2Cu. It crystallizes with a tetragonal $MoSi_2$-type structure, whose hydrogenation properties have been investigated at various occasions. In an early study,[6] Zr_2Cu was found to absorb hydrogen in the temperature range 550−850 °C and pressure range 0.02−1 bar to compositions of $Zr_2CuH_{0.36}$ (α phase) and $Zr_2CuH_{1.0-1.4}$ (β phase), and evidence was presented for phase segregation into a binary zirconium hydride and a copper-rich compound. Thermodynamic data suggested the α phase to be relatively stable and the β phase to be relatively unstable. A more hydrogen-rich compound was not found under these experimental conditions. Soon after, a hydride of composition $Zr_2CuH_{\sim 4.3}$ was obtained[7] by reaction at room temperature and atmospheric hydrogen pressure but found to decompose above 200 °C. Finally, a hydride of composition $Zr_2CuH_{\sim 4.2}$ was reported[8] to form at room temperature. Differential thermal analysis data confirmed that it decomposed above 200 °C into metallic copper and zirconium dihydride, and NMR data revealed a low activation energy for hydrogen diffusion. X-ray and neutron diffraction patterns could be interpreted in terms of a monoclinic structure but were too complex to be analyzed in terms of deuterium atom positions. Among the various potential hydrogen sites in the structure, those situated in tetrahedral interstices were considered to be most likely to be occupied by hydrogen.

In the present paper, we report on the structure of that phase at the deuterium-rich composition $Zr_2CuD_{\sim 4.7}$ by using high-resolution synchrotron and neutron powder diffraction. It will be shown that the metal atom arrangement is more complex than previously assumed and that deuterium occupies not only tetrahedral but also newly formed trigonal-bipyramidal sites in a nearly ordered manner. As with other “interstitial” metal hydrides undergoing reconstructions of the metal atom arrangement, the deuterium atom distribution needs to be rationalized in terms of electronic rather than geometric factors.

While we were able to prepare the intermetallic compound Zr_2Cu in a relatively straightforward manner, its hydrogenation/deuteration needed certain precautions.[9] Our experiments showed that it can be charged with deuterium near ambient

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conditions to the almost stoichiometric composition $Zr_2CuD_{\sim5}$, provided the temperature and pressure do not exceed certain thresholds. In agreement with previous work,[7] deuteration at/above 200 °C and 1−2 bar of pressure or heating the deuteride to 250° in a quartz capillary led to segregation into zirconium deuteride and metallic copper. Structure analysis[10] revealed a monoclinic cell twice as large as that reported previously[8] and a refined deuterium content of $Zr_2CuD_{4.71}$. The relationship between the tetragonal cell of the alloy and the monoclinic cell of the deuteride can be seen in Figure 1 and described by the transformation matrix

$$\begin{matrix}\mathbf{a}_m\\ \mathbf{b}_m\\ \mathbf{c}_m\end{matrix} \cong \begin{pmatrix}2.5 & 0 & 0.5\\ 0 & 1 & 0\\ -1.5 & 0 & 0.5\end{pmatrix}\begin{matrix}\mathbf{a}_t\\ \mathbf{b}_t\\ \mathbf{c}_t\end{matrix}$$

which implies a doubling of the cell volume. Compared to the alloy structure, the hydride expands along $\mathbf{b}_m$ (by 11.3%) and $\mathbf{c}_m$ (by 13.3%), while it contracts along $\mathbf{a}_m$ (by 4.5%) and distorts in the $\mathbf{a}_m-\mathbf{c}_m$ plane (by 7.3°). The overall volume expansion during deuteration is 17.5%.

As shown in Figure 1, the metal atom arrangement during deuteration undergoes drastic changes, in particular with respect to the atom coordinations. While the alloy contains isolated copper atoms (Cu−Cu = 3.22 Å) in a cubic zirconium atom environment, the deuteride contains Cu_2 dumbbells [Cu−Cu = 2.393(9) Å as determined from neutron and 2.430(7) Å from synchrotron powder diffraction], in which each copper atom has a trigonal-prismatic zirconium atom environment. This arrangement corresponds closely to the $OsGe_2$-type structure. The orientation of the Cu_2 dumbbells correlates with the cell contraction along $\mathbf{a}_m$. In contrast to the alloy that shows one zirconium site having cubic Zr_4Cu_4 metal coordination with five face-centering Zr atoms (CN = 8 + 5), the deuteride shows two zirconium sites with an irregular metal environment (Zr1, CN = 12; Zr2, CN = 11). A similar local metal atom environment and Cu−Cu pairing were reported in an amorphous Zr_2Cu alloy.[11]

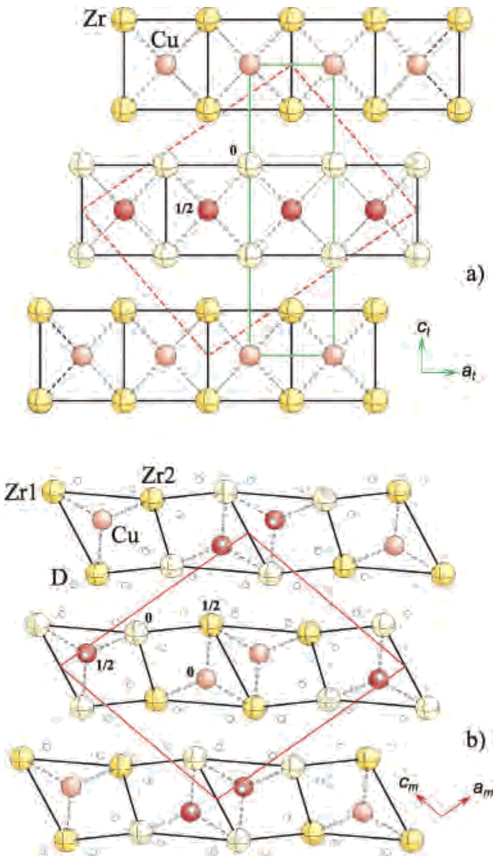

Figure 1. Metal atom structure of body-centered tetragonal Zr_2Cu (a) and monoclinic $Zr_2CuD_{4.7}$ (b). The unit cell of the alloy structure is shown in green, and those of the deuteride are in red. The small open circles in part b represent D atoms.

The deuteride displays five deuterium atom sites. As shown in Figure 2, four (D1−D4) have tetrahedral metal configurations and show full occupancy, while one (D5) has a trigonal-bipyramidal metal configuration and shows partial occupancy (71%). Full occupancy of the later site corresponds to the composition Zr_2CuD_5, which is presumably the deuterium-rich phase limit of the solid solution. Among the four tetrahedral sites two (D1 and D2) are coordinated by Zr only and two (D3 and D4) by three Zr atoms and one Cu atom, while the trigonal-bipyramidal site (D5) is coordinated by three Zr (triangle) and two Cu (apexes) atoms. The Zr_4 tetrahedra and the trigonal-bipyramidal site are new

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(9) A 6-g pellet of the Zr_2Cu alloy was synthesized by arc-melting of the elements. X-ray powder diffraction showed a single Zr_2Cu phase with a $MoSi_2$-type structure and tetragonal cell parameters of $a = 3.2163(3)$ Å, $c = 11.1721(12)$ Å, and $V = 115.57(2)$ Å^3. The alloy was finely crushed and put under 1 bar of deuterium gas at room temperature without preliminary activation. The deuterium pressure did not change over 5 days; therefore, the temperature was slowly increased to 60 °C. When the reaction started, the absorbed deuterium gas was compensated for in small portions by keeping the maximum pressure around 1 bar. After 4 days at 60 °C, the deuteration appeared to be complete. The sample was cooled to 20 °C before the autoclave was opened. The deuteride was black and had nearly the same shape as the alloy. It was single-phase; i.e., no segregation had occurred. It was stable in air as judged from its powder patterns that did not change over a period of 6 months.

(10) A synchrotron powder diffraction pattern was collected on the deuteride at the Swiss−Norwegian Beamline at ESRF ($\lambda = 0.699\,11(1)$ Å, just above the Zr K-absorption edge at 0.68877 Å, Debye−Scherrer geometry, 2θ range 3.2−45.4°, step size 0.025°). A neutron powder diffraction pattern was collected on the diffractometer HRPT at SINQ (PSI, Villigen; $\lambda = 1.493\,81(2)$ Å, 2θ range 4−164°, step size 0.1°). The wavelengths, zero shifts, and instrumental resolution were calibrated with LaB_6 and Si standards. The positions of 16 peaks were extracted from synchrotron data and indexed on a monoclinic cell by using Dicvol91.[11a] After a profile matching, two fully occupied Zr positions and one Cu position were located in space group $I2/m$ on synchrotron data only by using FOX.[11c] The metal atom positions were fixed, and five deuterium sites were located by using the neutron data and FOX. Structure refinements were carried out in $I2/m$ by using the cell providing the monoclinic angle closest to 90°.[11d] Strong broadening of the diffraction peaks is obviously intrinsic for $Zr_2CuD_{4.7}$. The peak widths were approximated by a monoclinic strain model implemented in Fullprof.[11b] In total, 26 parameters were refined on synchrotron data: $a = 9.3514(12)$ Å, $b = 3.5784(6)$ Å, $c = 8.3628(18)$ Å, $\beta = 104.301(13)°$, $V = 271.17(8)$ Å^3, $R_B = 0.040$, $R_F = 0.025$, $\chi^2 = 4.39$, $R_p = 0.088$, $R_{wp} = 0.096$, 223 "independent" reflections, 55 "effective" reflections. For the neutron data, in total, 38 parameters were refined: $a = 9.3357(12)$ Å, $b = 3.6030(6)$ Å, $c = 8.3429(15)$ Å, $\beta = 104.291(12)°$, $V = 271.94(8)$ Å^3, $R_B = 0.019$, $R_F = 0.011$, $\chi^2 = 10.3$, $R_p = 0.047$, $R_{wp} = 0.057$, 357 "independent" reflections, 60 "effective" reflections. Four D atom positions (D1−D4) turned out to be fully occupied and one (D5) partially occupied at 71(1)%. (a) Boultif, A.; Louër, D. *J. Appl. Crystallogr.* **1991**, *24*, 987. (b) Rodriguez-Carvajal, J. *FULLPROF SUITE*; LLB Saclay & LCSIM: Rennes, France, 2003. (c) Favre-Nicolin, V.; Cerný, R. *J. Appl. Crystallogr.* **2002**, *35*, 734. (d) Mighell, A. D. *Acta Crystallogr.* **2003**, *B59*, 300.

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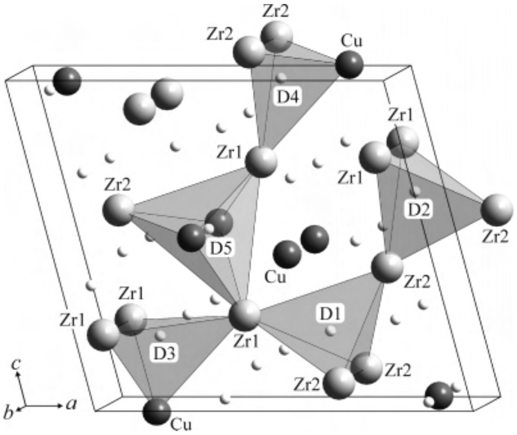

Figure 2. D atom environments in monclinic $Zr_2CuD_{4.7}$. The D1−D4 sites are fully occupied, and D5 is partially occupied (~71%).

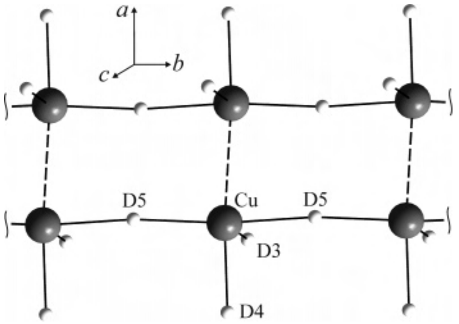

Figure 3. Polymeric $[Cu_2D_6]_n$ fragments in the structure of $Zr_2CuD_{4.7}$. D3 and D4 sites are fully occupied, and D5 is partially occupied (~71%). Cu−Cu = 2.39 Å (dashed lines); Cu−D = 1.87 (D3), 1.73 (D4), 1.80 (D5) Å.

interstices that appeared as a result of the reconstruction of the metallic matrix of the alloy.

As shown in Figure 3, copper is bonded to four deuterium atoms in a saddlelike configuration, of which two (those of the partially occupied site) connect copper in a nearly linear arrangement [Cu−D5−Cu and D5−Cu−D5 angles 174.0(6)°] to partially interrupted dimeric $[Cu_2D_6]_n$ ribbons running perpendicular to the Cu_2 dumbbell direction. None of the D atoms bridges the Cu_2 dumbbells. At the upper phase limit Zr_2CuD_5, the D5 site of the linear Cu−D5−Cu unit is presumably fully occupied, and these ribbons are no longer interrupted. The Cu−D bonds are significantly longer (1.73−1.87 Å), on average, than those in the tetrahedral $[CuD_4]^{3-}$ complexes of $Ba_7Cu_3D_{17}$ (Cu−D = 1.64−1.75 Å),[12] which is the only known copper-based complex transition-metal deuteride.[13] They are comparable to the Cu−H distances in copper borohydride complexes (1.70−1.97 Å)[14] and in the binary wurtzite-type copper deuteride CuD (1.73 Å).[15] The zirconium atoms have distorted-cubic (Zr2, CN = 8) or monocapped-cubic (Zr1, CN = 8 + 1) deuterium atom environments with bond lengths in the ranges Zr1−D = 2.10−2.28 Å and Zr2−D = 1.98−2.26 Å. They are consistent with those in zirconium deuteride (cubic ZrD_8, Zr−D = 2.02 Å)[16] and other zirconium-containing metal hydrides.[17] The shortest D−D contacts are longer than 2.1 Å and thus consistent with repulsive D−D interactions. Altogether, these structural features suggest at the upper phase limit the limiting ionic formula $2Zr^{2+}[CuD_3]^{2-}2D^-$. The formula implies monovalent copper (Cu^I) and two sorts of D atoms, one bonded to copper as in $Ba_7Cu_3H_{17}$ and the other (D^-) to zirconium only as in ZrH_2. While short Cu−Cu contacts are typical for Cu^I compounds showing cuprophilic interactions,[18] values of ~2.40 Å as found in the present deuteride are rare. A very short Cu^I−Cu^I contact of 2.35 Å has recently been reported and described as nonbonded in $Cu_2(C_7N_3H_{12})_2$.[19] Whether or not the Cu−Cu interactions in $Zr_2CuD_{4.71}$ are bonding is an open question.

In conclusion, we have found a further example for a hydrogen-induced metal atom reconstruction in a metal−hydrogen system. Compared to other systems, the reconstruction in $Zr_2CuD_{4.7}$ is unique because it occurs near ambient conditions, thus underlining the crucial role of hydrogen for the dynamics of such systems. Clearly, the hydrogen atom distributions in this and similar systems cannot be predicted from geometric factors alone because the reconstructions lead to the formation of new hydrogen interstices. Other factors play a dominant role, such as the electronic configuration of the transition element. In the Mg_2Ni−H[20] and $LaMg_2Ni$−H systems,[21] for example, nickel tends to become zerovalent (Ni^0) and to form tetrahedral $[NiH_4]^{4-}$ complexes. These complexes have closed-shell 18-electron configurations and are responsible for the onset of hydrogen-induced metal−nonmetal transitions.[22] While the present deuteride is presumably metallic, at least at the composition $Zr_2CuD_{4.7}$, it could become nonmetallic at the upper phase limit Zr_2CuD_5. In situ neutron diffraction and electric resistance measurements in a hydrogen atmosphere are needed to confirm this hypothesis.

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Supporting Information Available: Details of synthesis, structure refinement, positional and displacement parameters, interatomic distances, X-ray and neutron structural data as CIF files, and diffraction patterns. This material is available free of charge via Internet at http://pubs.acs.org.

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