

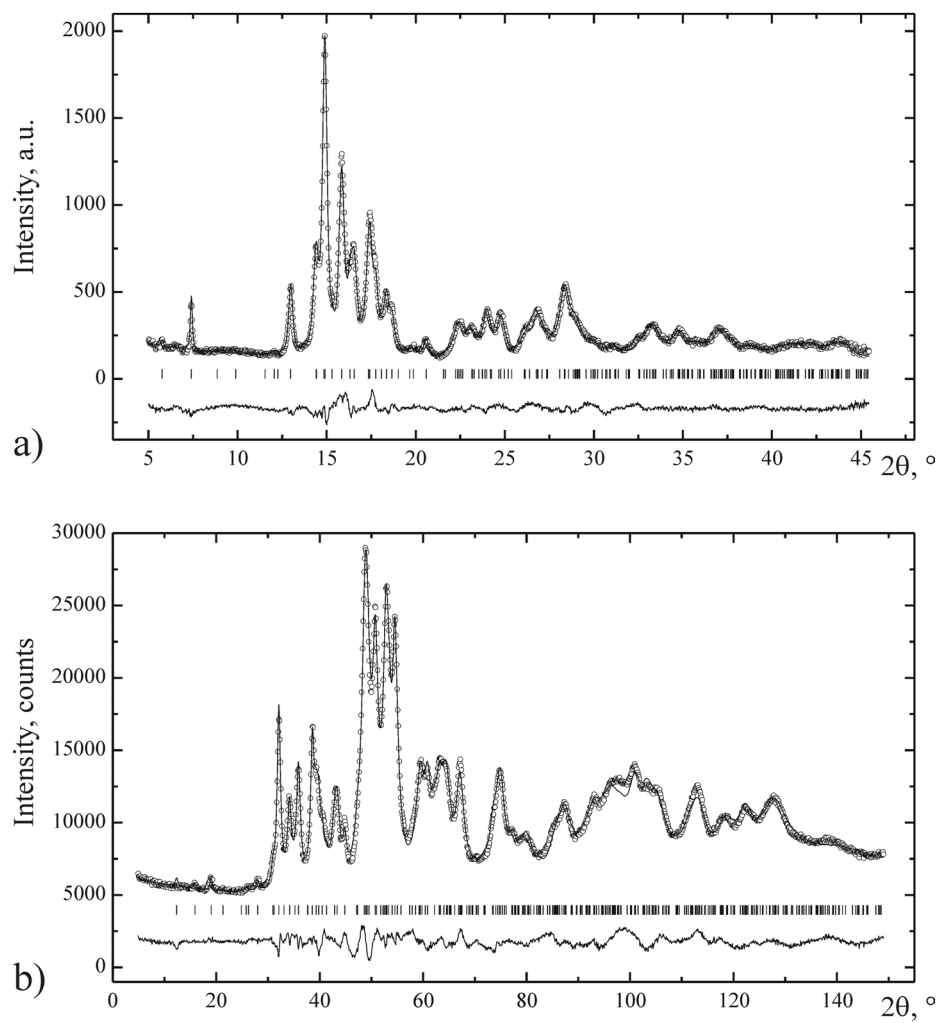
## Deuterium induced copper pairing in Zr<sub>2</sub>CuD<sub>~5</sub> Supporting information

Details of synthesis: Two 6 gram pellets of the Zr<sub>2</sub>Cu alloy were synthesized by arc-melting Zr (m3N5, Ventron) and Cu ingots (99.999%, Alfa). To ensure homogeneity the pellets were turned up side down and remelted four times. No weight losses were observed. According to binary phase diagrams Zr<sub>2</sub>Cu forms congruently from the melt at 1000°C. Preliminary X-ray powder diffraction showed a single Zr<sub>2</sub>Cu phase with MoSi<sub>2</sub> type structure and tetragonal cell parameters of  $a = 3.2163(3) \text{ \AA}$ ,  $c = 11.1721(12) \text{ \AA}$ ,  $V = 115.57(2) \text{ \AA}^3$ . Therefore, the as-cast alloys were used in the deuteration experiments. Two samples were synthesized. For the first sample the alloy was crushed and activated in vacuum at 300°C for a few hours and then at 100°C for one day. Deuterium was introduced at 1.3 bar pressure, while the system was kept at 100°C. The reaction started only after 8 hours, and the temperature was then decreased to 60°C. During the reaction the absorbed deuterium gas was compensated in small portions by keeping the maximum pressure around 1 bar. After four days at 60°C the deuteration appeared to be complete. The sample was allowed to cool to room temperature before the autoclave was opened. For the second sample 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 same experimental procedure was used as that for the first sample. The deuteride samples were black and had nearly the same shape as the alloys. **They were single-phase, i.e.** no segregation had occurred. They were stable on air as judged from their powder patterns that did not change over a period of six months. The patterns of the samples 1 and 2 were nearly indistinguishable. The second sample was used for all diffraction experiments. No hydride sample was synthesized and no desorption experiment was performed.

Details of structure analysis: The deuteride sample was filled into a vanadium container that was sealed with indium wire and placed on the powder diffractometer HRPT at SINQ (PSI; Villigen;  $\lambda = 1.49381(2) \text{ \AA}$ ,  $2\theta$  range 4-164°, step size 0.1°, data collection time 6.6 hours). A silicon standard was used to calibrate the wavelength, zero-shift and instrumental resolution. Although the diffraction peaks were intrinsically broad, high resolution were essential for successful indexing. The sample was filled into a thin-walled glass capillary, a synchrotron diffraction pattern was collected at the Swiss-Norwegian beamline at ESRF ( $\lambda = 0.69911(1) \text{ \AA}$ , just above the Zr K-absorption edge at 0.68877 Å, Debye-Scherrer

geometry,  $2\theta$  range  $3.2\text{--}45.4^\circ$ , step size  $0.025^\circ$ ). The wavelength and zero-shift was refined from a  $\text{LaB}_6$  standard. Positions of 16 peaks were extracted from these data and indexed on a monoclinic cell by using Dicvol91.<sup>a</sup> The correct solution had the highest figure of merit ( $M(16) = 7.7$ ,  $M'(16) = 23$ ). The systematic extinctions suggested a body centered cell with space group  $I2/m$ . Profile matching carried out with the Fullprof Suite<sup>b</sup> described all observed intensities in a satisfactory manner and produced profile parameters for structure solution. In a first step the metallic sub-structure was determined on synchrotron data only by using FOX.<sup>c</sup> Two fully occupied Zr positions and one Cu position were located in space group  $I2/m$ . In a second step, the metal atom positions were fixed and five deuterium sites were located by using the neutron data and FOX. Structure refinements were carried in space group  $I2/m$  by using the cell providing the monoclinic angle closest to  $90^\circ$ .<sup>d</sup> For the synchrotron data 6 coordinates and 3 temperature factors were refined. Background was described by a polynomial with five refined parameters. A pseudo-Voigt profile was used, instrumental UVW were fixed during refinement. The broadening of the diffraction peaks is obviously intrinsic for the  $\text{Zr}_2\text{CuD}_{4.7}$ . The peak widths were approximated by a monoclinic strain model implemented in Fullprof, refinement led to the following strain parameters:  $\sigma(a) = 1.69(4)$ ,  $\sigma(b) = 26.1(4)$ ,  $\sigma(c) = 3.58(7)$ ,  $\sigma(\beta) = 3.66(15)$ , and their correlations  $\text{corr}(b,c) = -0.36(3)$ ,  $\text{corr}(b,\beta) = 0.33(3)$ . In total 26 parameters were refined:  $a = 9.3514(12)$ ,  $b = 3.5784(6)$ ,  $c = 8.3628(18) \text{ \AA}$ ,  $\beta = 104.301(13)^\circ$ ,  $V = 271.17(8) \text{ \AA}^3$ ,  $R_B = 0.040$ ,  $R_F = 0.025$ ,  $\chi^2 = 4.39$ ,  $R_p = 0.088$ ,  $R_{wp} = 0.096$ , 223 “independent” reflections, 55 “effective” reflections. For the neutron data 16 coordinates and 4 temperature factors (one common for all D-atoms) were refined. Background was described by a polynomial with five refined parameters. A pseudo-Voigt profile was used, instrumental UVW were fixed during refinement. The peak widths approximated by a monoclinic strain model were close to those derived from synchrotron diffraction data:  $\sigma(a) = 1.79(5)$ ,  $\sigma(b) = 23.1(4)$ ,  $\sigma(c) = 3.31(5)$ ,  $\sigma(\beta) = 4.04(14)$ ,  $\text{corr}(b,c) = 0.04(6)$ ,  $\text{corr}(b,\beta) = 0.69(4)$ . In total 38 parameters were refined:  $a = 9.3357(12)$ ,  $b = 3.6030(6)$ ,  $c = 8.3429(15) \text{ \AA}$ ,  $\beta = 104.291(12)^\circ$ ,  $V = 271.94(8) \text{ \AA}^3$ ,  $R_B = 0.019$ ,  $R_F = 0.011$ ,  $\chi^2 = 10.3$ ,  $R_p = 0.047$ ,  $R_{wp} = 0.057$ , 357 “independent” reflections, 60 “effective” reflections. Four D-atom positions turned out to be fully (D1-D4) and one (D5) partially occupied at 71(1)%. **Negative B-values occurred only for Zr1 in the synchrotron, and Zr2 in the neutron data. They are within zero by less a few estimated standard deviations, and thus do not affect the main conclusions of the paper.**

(a) Boultif, A.; Louër, D. *J. Appl. Cryst.* **1991**, 24, 987. (b) Rodriguez-Carvajal, J. *FULLPROF SUITE*, LLB Sacley & LCSIM: Rennes, France, 2003. (c) Favre-Nicolin, V.; Cerný R. *J. Appl. Cryst.* **2002**, 35, 734 (d) Mighell, A.D. *Acta Cryst.* **2003**, B59, 300.



**Figure 1s.** Observed (points), calculated (line) and difference (bottom line) synchrotron (a) and neutron (b) diffraction patterns for  $Zr_2CuD_{4.7}$ .

**Table 1s.** Atomic coordinates and thermal parameters for  $\text{Zr}_2\text{CuD}_{4.7}$  from synchrotron X-ray (upper lines in **bold**)<sup>1</sup> and neutron (bottom lines in *italic*)<sup>2</sup> powder diffraction data; space group  $I2/m$ ; all sites are fully occupied, except D5.

Atom	Wyckoff site	$x$	$y$	$z$	$B_{\text{iso}}, \text{\AA}^2$
Zr1	4i	<b>0.0823(4)</b> <i>0.0768(7)</i>	0	<b>0.2423(4)</b> <i>0.2320(8)</i>	<b>-0.12(11)</b> <i>1.52(19)</i>
Zr2	4i	<b>0.6726(4)</b> <i>0.6653(6)</i>	0	<b>0.0991(5)</b> <i>0.0860(6)</i>	<b>0.72(12)</b> <i>-0.34(8)</i>
Cu	4i	<b>0.3810(5)</b> <i>0.3792(7)</i>	0	<b>0.5340(5)</b> <i>0.5250(9)</i>	<b>0.73(11)</b> <i>1.68(9)</i>
D1	4i	<i>0.1385(7)</i>	0	<i>0.7211(9)</i>	<i>1.04(5)</i>
D2	4i	<i>0.4617(6)</i>	0	<i>0.1419(8)</i>	<i>B(D1)</i>
D3	4i	<i>0.3155(7)</i>	0	<i>0.2938(7)</i>	<i>B(D1)</i>
D4	4i	<i>0.1883(6)</i>	0	<i>0.4839(11)</i>	<i>B(D1)</i>
D5 <sup>3</sup>	4i	<i>0.8895(8)</i>	0	<i>0.0291(15)</i>	<i>B(D1)</i>

<sup>1</sup>  $a = 9.3514(12)$ ,  $b = 3.5784(6)$ ,  $c = 8.3628(18)$   $\text{\AA}$ ,  $\beta = 104.301(13)^\circ$ ,  $V = 271.17(8)$   $\text{\AA}^3$ ,  $R_B = 0.040$ ,  $R_F = 0.025$ ,  $\chi^2 = 4.39$ ,  $R_p = 0.088$ ,  $R_{wp} = 0.096$ , 223 “independent” reflections, 55 “effective” (accounting resolution [Fullprof ref.]) reflections.

<sup>2</sup>  $a = 9.3357(12)$ ,  $b = 3.6030(6)$ ,  $c = 8.3429(15)$   $\text{\AA}$ ,  $\beta = 104.291(12)^\circ$ ,  $V = 271.94(8)$   $\text{\AA}^3$ ,  $R_B = 0.019$ ,  $R_F = 0.011$ ,  $\chi^2 = 10.3$ ,  $R_p = 0.047$ ,  $R_{wp} = 0.057$ , 357 “independent” reflections, 60 “effective” reflections.

<sup>3</sup> Occupancy  $0.71(1)$

**Table 2s.** Deuterium-metal distances (Å) in Zr<sub>2</sub>CuD<sub>4.7</sub>.

D1		D2		D3		D4		D5	
Zr1	2.141(9)	2×Zr1	2.161(5)	Zr1	2.160(9)	Zr1	2.103(11)	2×Zr1	2.112(13)
Zr2	2.119(9)	Zr2	2.066(9)	2×Zr1	2.100(5)	2×Zr2	2.027(5)	Zr2	2.258(10)
2×Zr2	2.172(5)	Zr2	1.977(9)	Cu	1.873(9)	Cu	1.730(9)	2×Cu	1.8039(7)

**Table 3s.** Interatomic distances in Zr<sub>2</sub>CuD<sub>4.7</sub> from synchrotron data. Coordination spheres are limited to 3.6 Å for Zr-Zr distances, and to 3.1 Å for Zr-Cu.

Zr1-2×Zr1	3.5784(6)	Zr2-2×Zr1	3.402(5)	Cu-2×Zr1	2.857(4)
Zr1-2×Zr1	3.586(5)	Zr2-2×Zr1	3.493(5)	Cu-2×Zr1	3.009(4)
Zr1-2×Zr2	3.402(5)	Zr2-2×Zr2	3.5784(6)	Cu-2×Zr2	2.796(5)
Zr1-2×Zr2	3.493(5)	Zr2-2×Zr2	3.140(5)	<b>Cu-Cu</b>	<b>2.430(7)</b>
Zr1-2×Cu	2.857(4)	Zr2-Zr2	3.244(6)		
Zr1-2×Cu	3.009(4)	Zr2-2×Cu	2.796(5)		

**Table 4s.** Selected interatomic distances in Zr<sub>2</sub>CuD<sub>4.7</sub> from neutron data, all D-D distances > 2 Å.

Zr1-D1	2.141(9)	Zr2-D1	2.119(9)	Cu-2×Zr1	2.839(7)
Zr1-2×D2	2.161(5)	Zr2-2×D1	2.172(5)	Cu-2×Zr1	2.906(8)
Zr1-D3	2.160(9)	Zr2-D2	2.066(9)	Cu-2×Zr2	2.827(7)
Zr1-2×D3	2.100(5)	Zr2-D2	1.977(9)	<b>Cu-Cu</b>	<b>2.393(9)</b>
Zr1-D4	2.103(11)	Zr2-2×D4	2.027(5)	Cu-D3	1.873(9)
Zr1-D5	2.112(13)	Zr2-D5	2.258(10)	Cu-D4	1.730(9)
Zr1-D5	2.276(14)			Cu-2×D5	1.8039(7)