

In situ hydrogenation of the Zintl phase SrGe

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Supplement

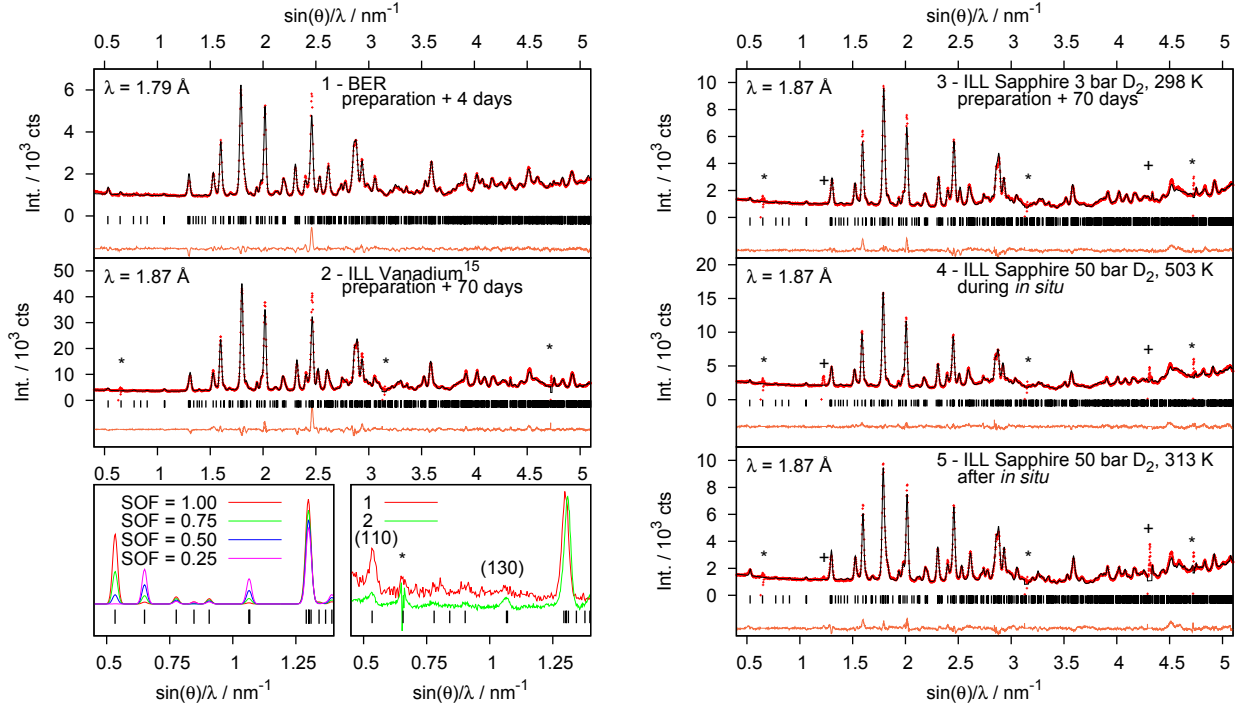


Figure S1: Rietveld refinement of the crystal structure of γ -SrGeD_y based on PND data at different times after the preparation and during the *in situ* experiment. (*) denotes a detector deficiency; (+) denotes reflections of the sapphire cell. The deuterium occupation at site D4 which terminates the Ge-Ge chains is reduced over time (Tab. S1) and can be repopulated during the *in situ* experiment. **Lower left:** Simulation of different occupations for the D4 site and comparison of measurements 1 and 2. Reflections are labeled regarding *Pbnm* setting. The (110) reflection decreases while (130) increases over time. Correlating this behavior with the simulation underlines the deuterium loss on D4 position which was already estimated for isopointal CaSiD_y by Wu *et.al.*¹ An underoccupation of the tetrahedral voids does not correspond to the intensity changes and can be excluded. **R-Values** (corrected for background): **1**: $R_p = 7.94$, $R_{wp} = 9.72$, $S = 1.50$, **2** (published elsewhere²) (numor: 924726-727, 30 min³): $R_p = 8.42$, $R_{wp} = 10.2$, $S = 4.80$, **3** (numor: 926803-817, 30 min³): $R_p = 12.7$, $R_{wp} = 13.4$, $S = 2.24$, **4** (numor: 926882-895, 28 min³): $R_p = 16.5$, $R_{wp} = 14.7$, $S = 2.57$, **5** (numor: 927144-160, 34 min³): $R_p = 12.5$, $R_{wp} = 12.9$, $S = 2.32$.

Table S1: Crystal structure data of γ -SrGeD_y at different times after the preparation and from the *in situ* PND experiment. For the BER II data set Debye-Waller factors were kept at reasonable values. Measurements 2 and 3 were done on the same sample and instrument. It can be noticed, that in this case Debye-Waller factors are strongly overestimated using the sapphire cell. In contrast the site occupancy factors (SOF) match well between these two experiments, thus, a strong correlation with the SOF can be excluded. This effect can be seen for the whole *in situ* experiment. Thus, we assume a systematical error from the sapphire cell set up that is compensated by the Debye-Waller factors. Therefore B-values lose their physical meaning and need to be considered cautiously. The SOF values for D1-D3 were equal to full occupation within 1 e.s.u. and therefore they were fixed to 1.0. Data are given in non-standard setting *Pbnm* (No. 62, *Pnma* with a' = b, b' = c, c' = a).

No: institute: container:		1 BER II vanadium	2 ILL ² vanadium	3 ILL sapphire cell 0.3(1)MPa D ₂ 298(2) K	4 ILL sapphire cell 5.0(1) MPa D ₂ 503(2) K	5 ILL sapphire cell 5.0(1) MPa D ₂ 313(4) K
time after preparation:		+ 3 days	+ 70 days	+ 70 days	during <i>in situ</i>	after <i>in situ</i>
Space group: (standard setting)		<i>Pbnm</i> (No. 62, <i>Pnma</i>)	<i>Pbnm</i> (No. 62, <i>Pnma</i>)	<i>Pbnm</i> (No. 62, <i>Pnma</i>)	<i>Pbnm</i> (No. 62, <i>Pnma</i>)	<i>Pbnm</i> (No. 62, <i>Pnma</i>)
Sr1	x	0.3413(8)	0.3415(7)	0.3467(11)	0.3434(11)	0.3376(8)
	y	0.3119(4)	0.3153(4)	0.3173(6)	0.3169(7)	0.3100(6)
	z	1 / 4	1 / 4	1 / 4	1 / 4	1 / 4
	B _{iso} / Å ²	0.2	0.35(9)	1.35(11)	2.65(11)	1.62(10)
Sr2	x	0.6463(7)	0.6480(7)	0.6541(9)	0.6501(9)	0.6520(8)
	y	0.3408(4)	0.3398(4)	0.3349(6)	0.3380(7)	0.3422(6)
	z	1 / 4	1 / 4	1 / 4	1 / 4	1 / 4
	B _{iso} / Å ²	0.2	0.35	1.35	2.65	1.62
Sr3	x	0.0134(7)	0.0122(4)	0.0134(7)	0.0096(8)	0.0118(7)
	y	0.3682(6)	0.3655(4)	0.3657(6)	0.3658(7)	0.3648(7)
	z	1 / 4	1 / 4	1 / 4	1 / 4	1 / 4
	B _{iso} / Å ²	0.2	0.35	1.35	2.6	1.62
Ge1	x	0.7384(4)	0.7410(4)	0.7429(4)	0.7391(6)	0.7367(4)
	y	0.0409(7)	0.0403(4)	0.0418(7)	0.0426(8)	0.0440(7)
	z	1 / 4	1 / 4	1 / 4	1 / 4	1 / 4
	B _{iso} / Å ²	0.4	0.66(7)	1.50(10)	3.33(11)	1.36(7)
Ge2	x	0.3109(4)	0.3125(4)	0.3103(6)	0.3055(7)	0.3017(6)
	y	0.0483(6)	0.0470(4)	0.0447(7)	0.0466(8)	0.0452(7)
	z	1 / 4	1 / 4	1 / 4	1 / 4	1 / 4
	B _{iso} / Å ²	0.4	0.66	1.50	3.33	1.36
Ge3	x	0.5318(6)	0.5288(4)	0.5299(6)	0.5304(7)	0.5353(6)
	y	0.5492(4)	0.5451(4)	0.5461(6)	0.5468(7)	0.5475(6)
	z	1 / 4	1 / 4	1 / 4	1 / 4	1 / 4
	B _{iso} / Å ²	0.4	0.66	1.50	3.33	1.36
D1	x	0.5064(8)	0.5040(6)	0.5045(8)	0.5040(11)	0.5043(9)
	y	0.2227(6)	0.2240(4)	0.2272(6)	0.2245(7)	0.2245(7)
	z	1 / 4	1 / 4	1 / 4	1 / 4	1 / 4
	B _{iso} / Å ²	1	1.21(10)	3.08(14)	4.74(17)	3.11(12)
D2	x	0.1580(8)	0.1570(7)	0.1592(11)	0.1551(14)	0.1569(11)
	y	0.2559(6)	0.2546(4)	0.2507(7)	0.2531(8)	0.2520(7)
	z	1 / 4	1 / 4	1 / 4	1 / 4	1 / 4
	B _{iso} / Å ²	1	1.21	3.08	4.74	3.11
D3	x	0.8421(8)	0.8383(7)	0.8464(11)	0.8412(13)	0.8463(9)
	y	0.2767(6)	0.2765(4)	0.2719(7)	0.2722(8)	0.2699(7)
	z	1 / 4	1 / 4	1 / 4	1 / 4	1 / 4
	B _{iso} / Å ²	1	1.21	3.08	4.74	3.11
D4	x	0.4406(9)	0.4397(7)	0.4371(11)	0.43014(14)	0.4440(11)
	y	0.0396(9)	0.0380(8)	0.0363(11)	0.03687(14)	0.0322(11)
	z	1 / 4	1 / 4	1 / 4	1 / 4	1 / 4
	B _{iso} / Å ²	1	1.21	3.08	4.74	3.11
	SOF	0.684(10)	0.598(8)	0.616(12)	0.642(12)	0.672(10)

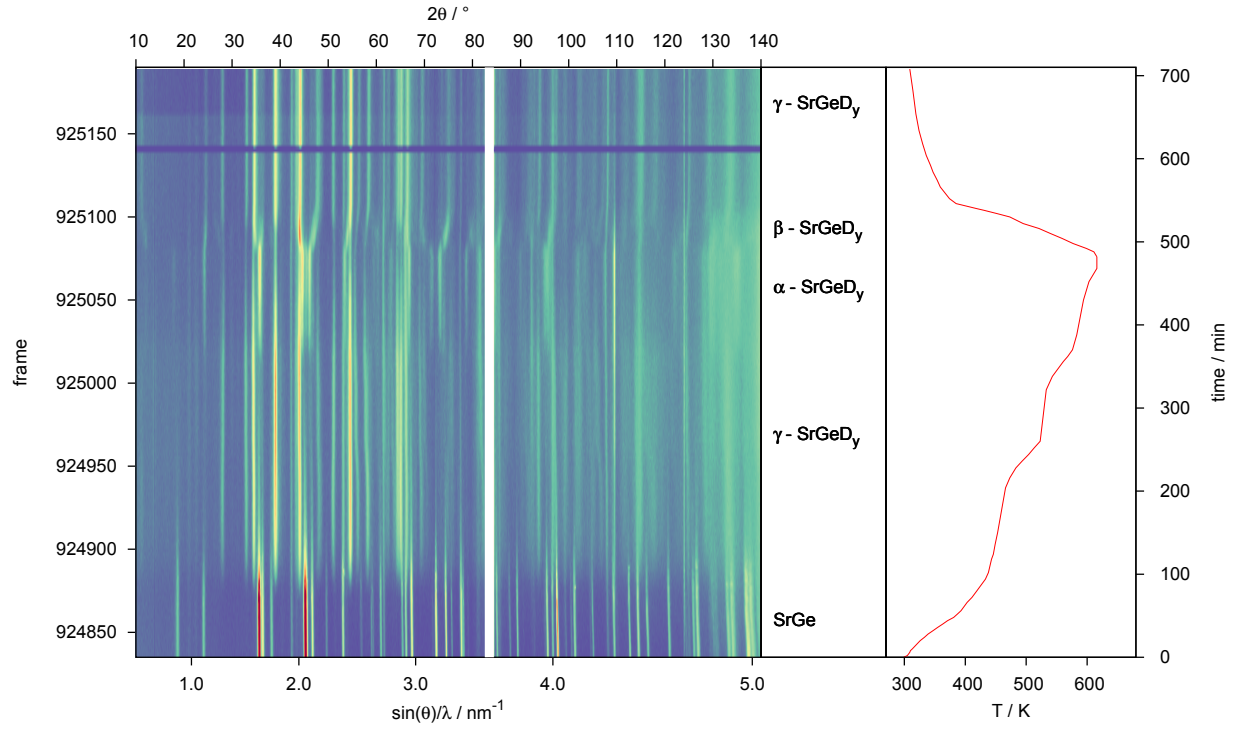


Figure S2: *In situ* neutron diffraction (ILL, D20, $\lambda = 1.87$ Å) of SrGe under 5.0(1) MPa deuterium pressure; overview of the whole angular range. The white bar excludes a single crystal reflection of the sapphire cell. Frame numbers correspond to the ILL numbering.³

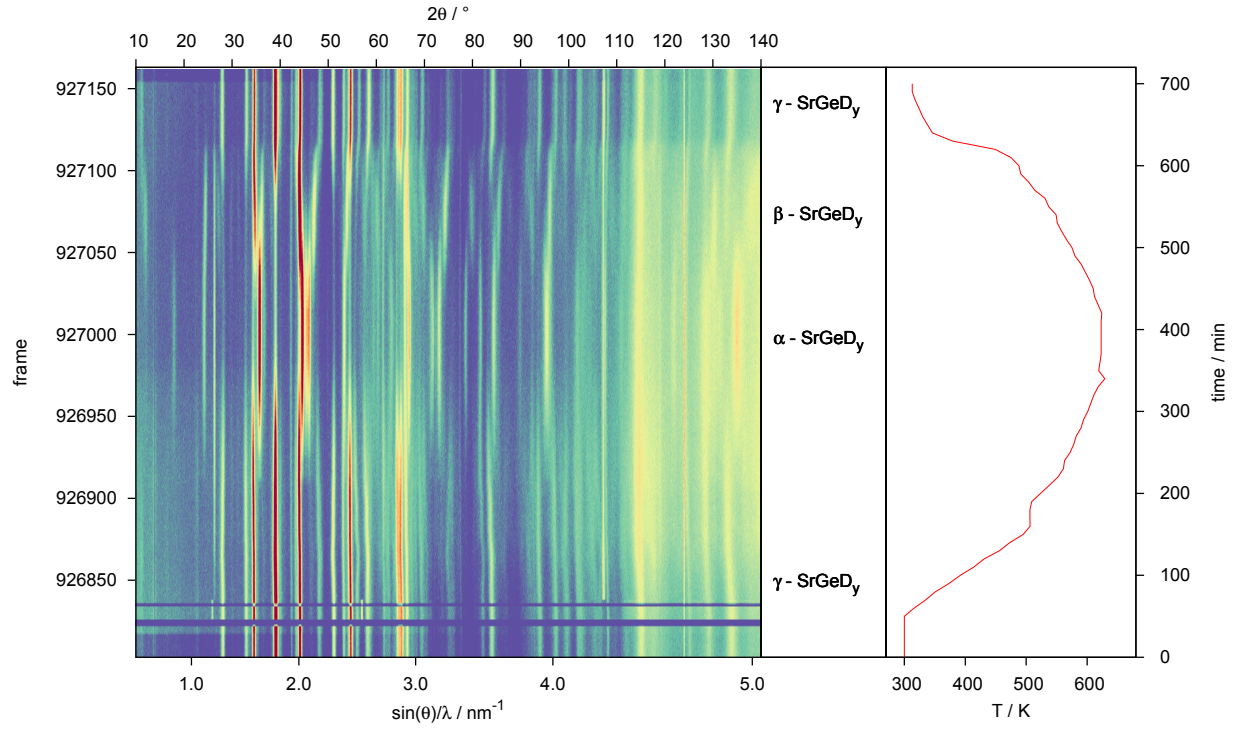


Figure S3: *In situ* neutron diffraction (ILL, D20, $\lambda = 1.87 \text{ \AA}$) of γ -SrGeD_x under 5.0(1) MPa deuterium pressure; overview of the whole angular range. Frame numbers correspond to the ILL numbering.³

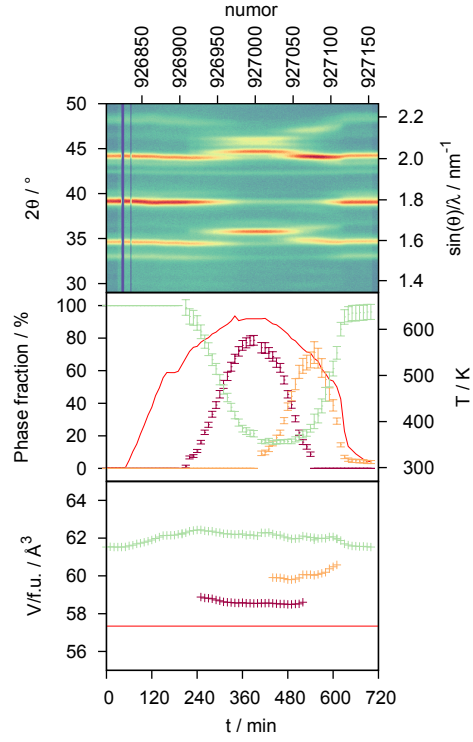


Figure S4: *In situ* PND data (ILL D20, $\lambda = 1.87 \text{ \AA}$, $p = 5.0(1) \text{ MPa D}_2$) starting from γ -SrGeD_y. Phase fractions and volumes correspond to α -, β - and γ -SrGeD_y, respectively. Error bars are shown as 3 e.s.u. as obtained from Rietveld refinement. Numor-labeling corresponds to the ILL numbering.³

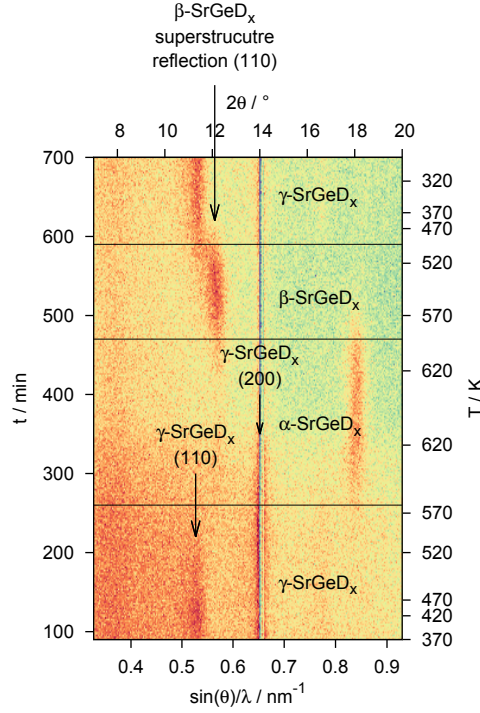


Figure S5: Low angle reflections from *in situ* PND measurement (ILL D20, $\lambda = 1.87 \text{ \AA}$, 5.0(1) MPa D_2). During the formation of β -SrGeD_y the occurrence of the superstructure reflection (110) can be seen. The supercell corresponds to a doubling of a and b lattice parameter. The depopulation of the D4-site of γ -SrGeD_y is accounted for by the vanishing of the (110) reflection while the (200) reflection keeps constant intensity (compare to inset Fig. S1). Unfortunately there are some deficient detector cells at the (200) reflection position.

References

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