Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Electronic Supporting Information

Structural properties of the thermoelectric material $CuCrS_2$ and of deintercalated Cu_xCrS_2 on different length scales: X-ray diffraction, pair distribution function and transmission electron microscopy studies

Anna-Lena Hansen[a], Torben Dankwort[b], Hendrik Groß[b], Martin Etter[c], Jan König[d], Viola Duppel[e] Lorenz Kienle[b], Wolfgang Bensch[a*]

[a]Institute of Inorganic Chemistry, Kiel University, Max-Eyth-Str. 2, D-24118 Kiel, Germany. *Email: WBENSCH@AC.UNI-KIEL.DE

[b]Intitute for Materials Science, Kiel University, Kaiserstrasse 2, 24143 Kiel, Germany.

[c]Deutsches Elektronen-Synchrotron (DESY), Hamburg 22607, Germany.

[d]Fraunhofer Institute for Physical Measurement Techniques IPM, Heidenhofstrasse 8, 79110 Freiburg, Germany.

[e]Nanochemistry, Max Planck Institute for Solid State Research, Heisenbergstrasse 1,D-70569 Stuttgart, Germany.

Figures

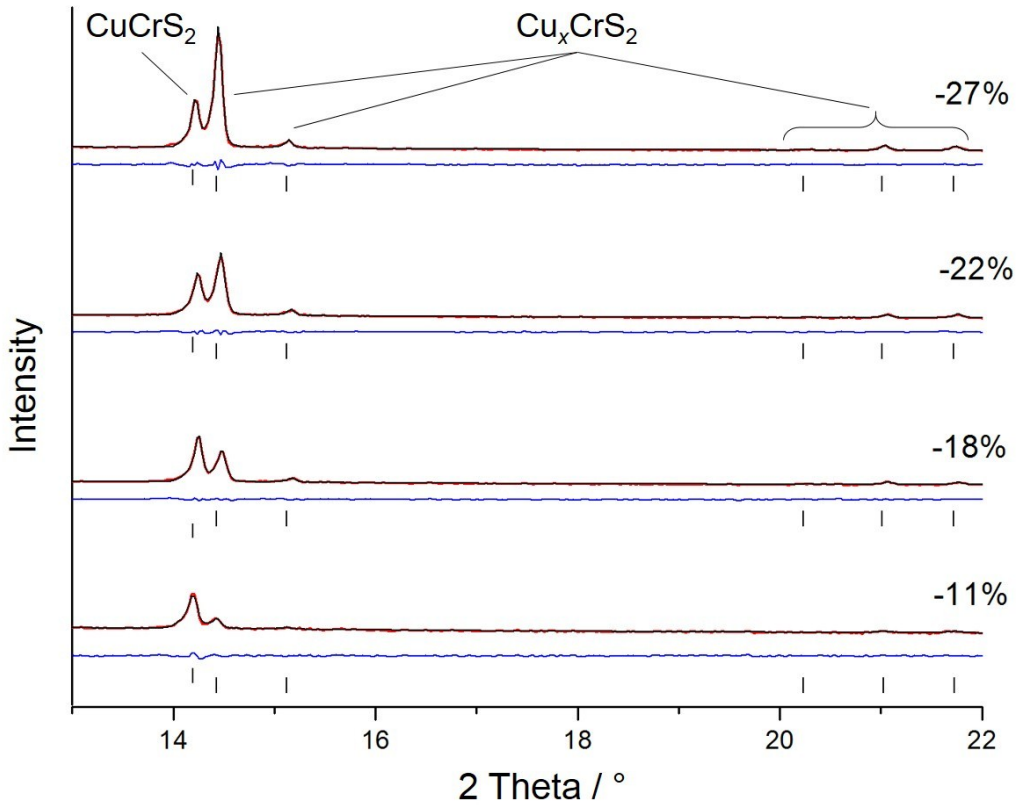


Figure S1: Section of Rietveld refined (red curve) XRD pattern (black) of samples with different deintercalation grade, given on the right (oriented on the copper content after deintercalation). Difference curve is depicted in blue. Measured using an X'Pert Pro MPD diffractometer (PANalytical), λ= 1.5405.

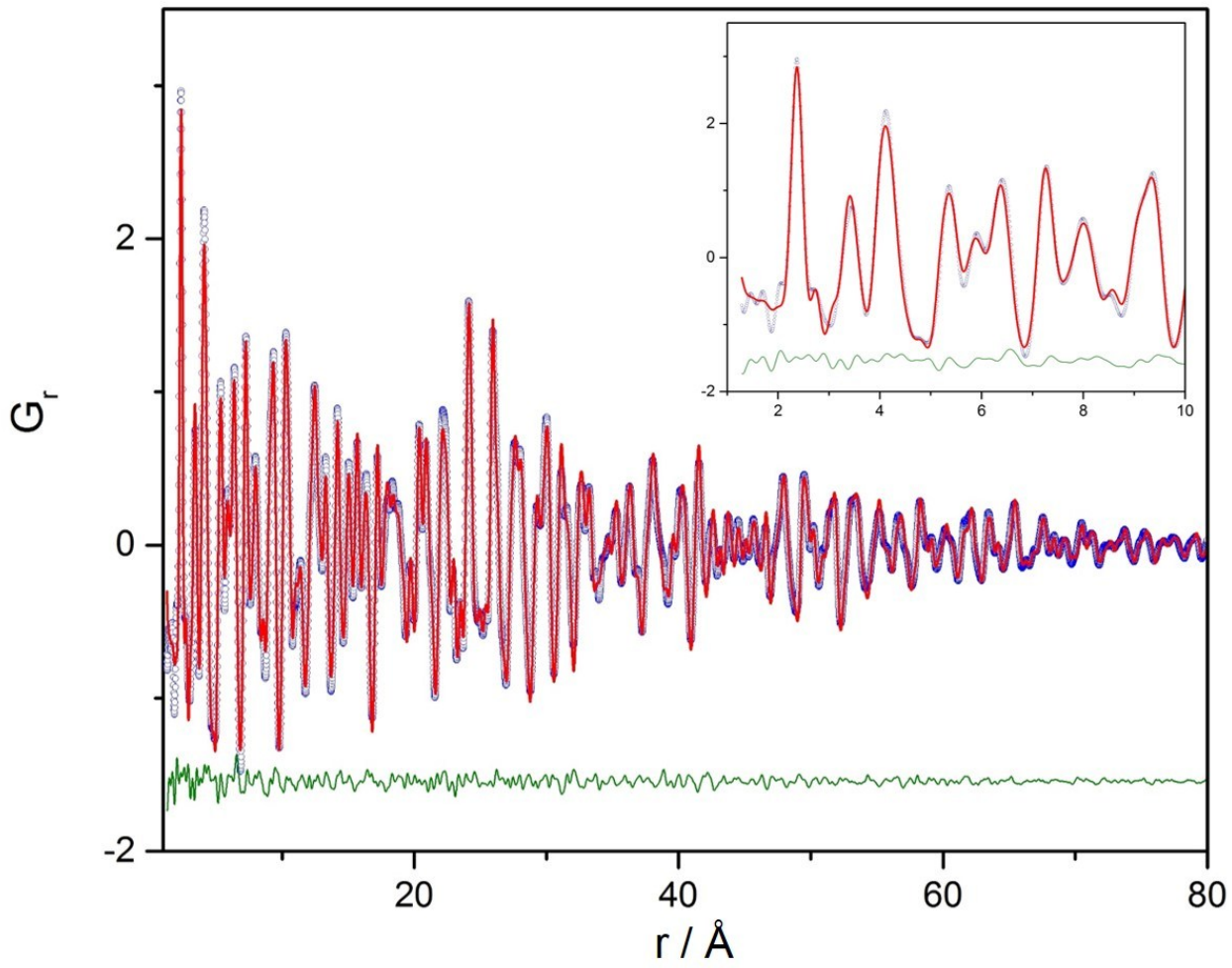


Figure S2: Observed pair distribution function (blure circles), calculated PDF based on the model given in the text (red line) and difference curve (green). Inset shows a good agreement of short range order. R_{WP} = 15.6 %.

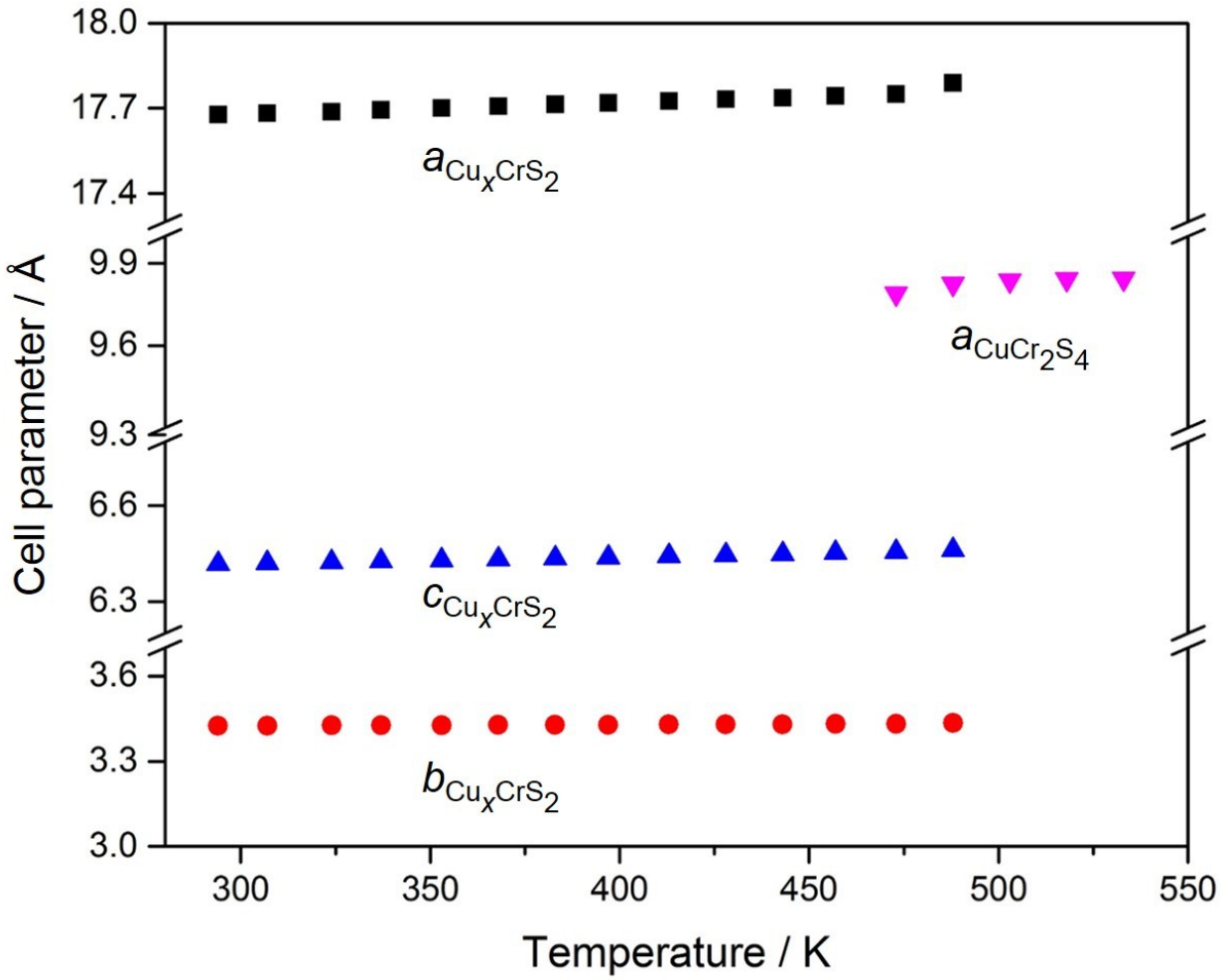


Figure S3: cell parameter against temperature. Estimates standard deviations are smaller than given symbols.

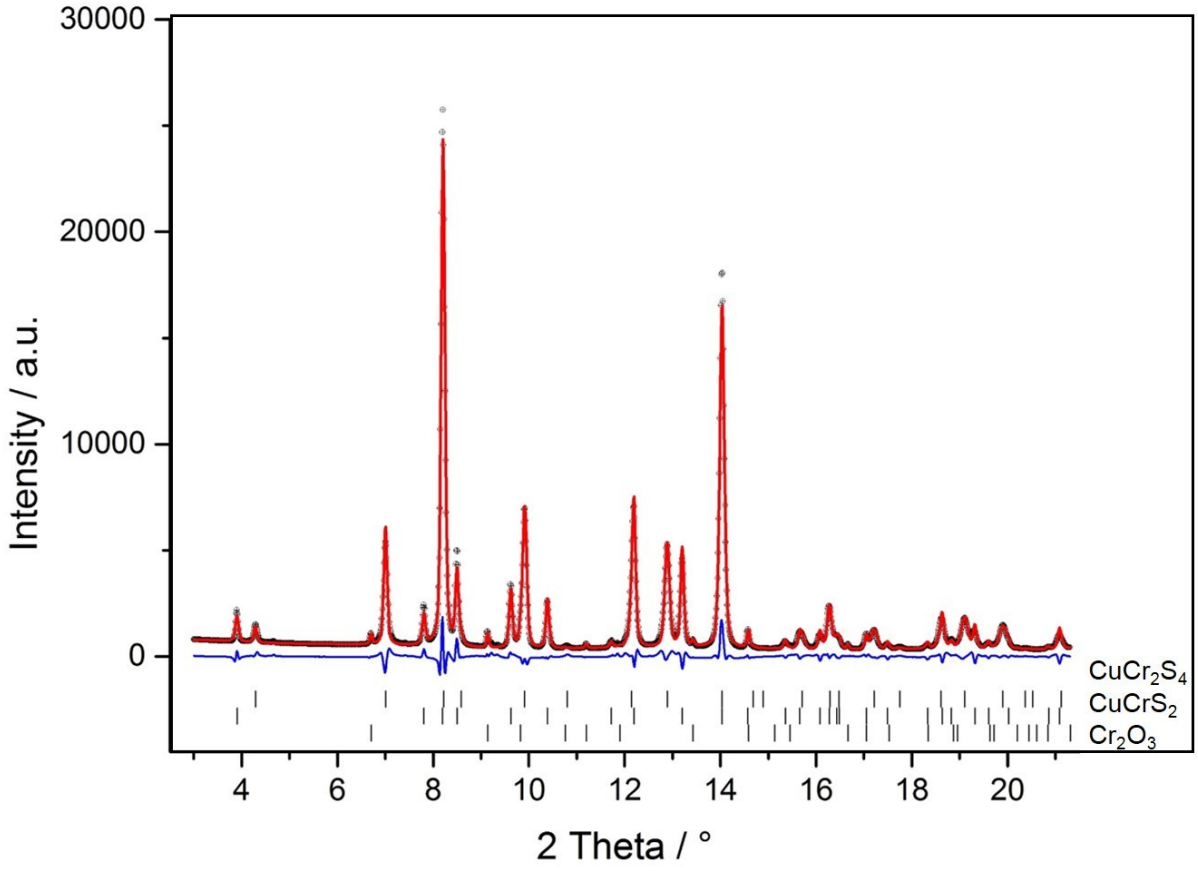


Figure S4: Rietveld refined synchrotron XRPD pattern of deintercalated sample heated above 533 K and cooled to room temperature. Phases are indicated by labelled tic marks. Wavelength λ = 0.4246 Å. Circles represents measured data, red line calculated curve, blue difference curve. R_{wp}= 6.8 %.

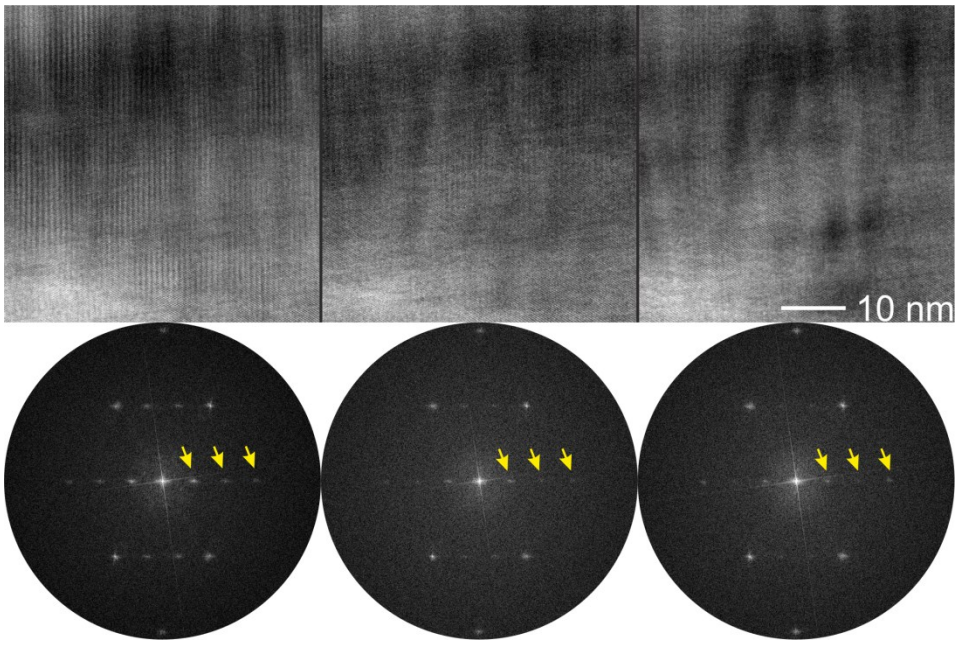


Figure S5: Gradual decay of the superlattice reflections along *a** due to short electron beam irradiation.

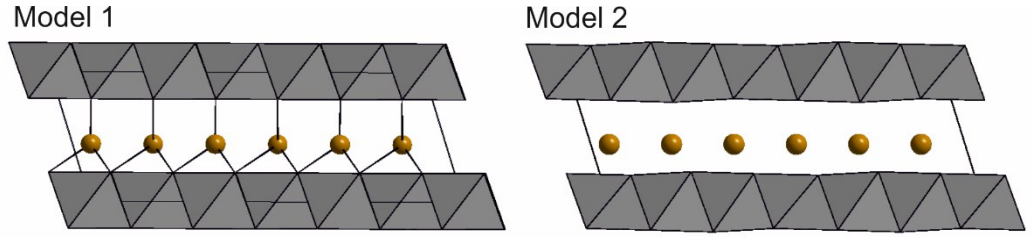


Figure S6: Both models used for HRTEM contrast simulations.

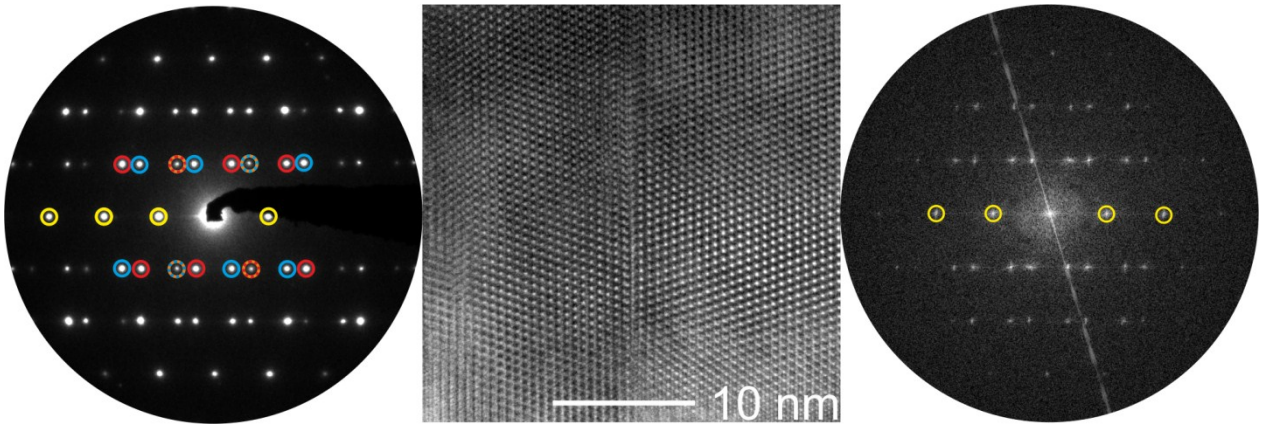


Figure S7: ED pattern, HRTEM micrograph and corresponding FFT of a Σ3 twin boundary of $CuCr_2S_4$ on edge (zone axis [110]). Yellow circles in the diffraction pattern and the FFT highlight the (111) twin boundary. Red and blue circles mark the two different domains while the orange striped circles mark intensities due to double diffraction for the respective domain.

Powder diffraction data

$CuCrS_2$, PETRA III, DESY; λ = 0.20722 Å Rietveld Refinement, R_{WP} = 6.15 %, R_{BRAGG} = 2.43 %

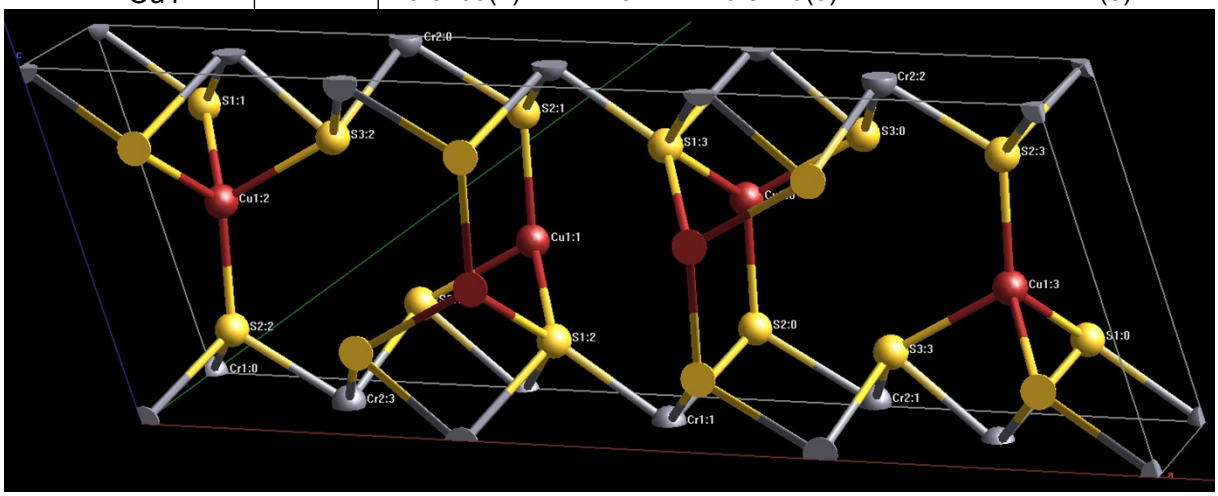
Table S1: Unit cell parameters, atomic coordinates and B_{iso} values obtained by Rietveld Refinement. Estimated standard deviations are given in parentheses.

$CuCrS_2$ R3m		*a* Å	*b* Å	*c* Å	°	
		3.4802(1)	3.4802(1)	18.697(1)		
Atom	*Wyckoff position*	*x*	*y*	*z*	occ	Biso Å²
Cr1	*3a*	0	0	0	1	0.85(3)
S1	*3a*	0	0	0.2651(2)	1	0.54(5)
S2	*3a*	0	0	0.7423(2)	1	0.54(5)
Cu1	*3a*	0	0	0.1478(1)	1	2.27(5)

Cu_xCrS_2, PETRA III, DESY; λ = 0.20722 Å Rietveld Refinement, R_{WP} = 6.4 %, R_{BRAGG} = 4.53 %

Table S2: Unit cell parameters, atomic coordinates and B_{iso} values obtained by Rietveld Refinement. Estimated standard deviations are given in parentheses.

Cu_xCrS_2 C2/m		*a* Å	*b* Å	*c* Å	*ß* °	
		17.6782(9)	3.4266(1)	6.4177(3)	107.203(4)	
Atom	*Wyckoff position*	*x*	*y*	*z*	occ	Biso Å²
Cr1	2 *a*	0	0	0	1	1.03(7)
Cr2	4 *i*	0.3218(2)	0	0.9875(7)	1	1.03(7)
S1	4 *i*	0.9109(3)	0	0.2176(9)	1	0.47(5)
S2	4 *i*	0.5817(3)	0	0.2051(9)	1	0.47(5)
S3	4 *i*	0.7543(3)	0	0.7682(9)	1	0.47(5)
Cu1	4 *i*	0.6163(2)	0	0.5729(5)	1	1.74(5)



List of bond lengths:

Cr1:0 S2:5 2.373(4)
S2:4 2.373(4)
S2:5 2.373(4)
S2:4 2.373(4)
S1:0 2.393(7)
S1:1 2.393(7)
Cr2:0 S3:4 2.313(4)
S3:4 2.313(4)
S3:1 2.349(9)
S2:1 2.384(9)
S1:4 2.494(5)
S1:4 2.494(5)
Cu1:1 2.707(6)
Cr2:5 3.107(8)
Cr2:5 3.107(8)

S1:0 Cu1:5 2.315(5)
Cu1:5 2.315(5)
Cr1:0 2.393(7)
Cr2:4 2.494(5)
Cr2:4 2.494(5)
S2:0 Cu1:0 2.256(7)
Cr1:4 2.373(4)
Cr1:4 2.373(4)
Cr2:1 2.384(9)
S3:0 Cr2:4 2.313(4)
Cr2:4 2.313(4)
Cr2:1 2.349(9)
Cu1:0 2.390(7)
Cu1:0 S2:0 2.256(7)
S1:5 2.315(5)
S1:5 2.315(5)
S3:0 2.390(7)
Cr2:1 2.707(6)

Total Scattering data – Pair distribution Function Analysis

Cu_xCrS_2 PETRA III, DESY; λ = 0.20722 Å,

Table S3: Refined unit cell parameters and atomic positions used for modelling the pair distribution function. Starting with the structure model obtained by XRD, first the lattice parameters, the delta parameter (accounting the correlated atomic motion) and the scale factor were refined. We then refined the DW factors of all atoms and all atomic positions. The DW factors of Cr and S did not change, therefore the values were fixed (u11 = u22 = u33 = 0.0126) in all following refinements. In the last refinement cycle the anisotropic DW factors of Cu, the atomic position of Cu and the lattice parameters were refined.

Cu_xCrS_2 C2/m	*a* Å	*b* Å	*c* Å	*ß* °			
	17.686	3.429	6.423	107.21			
Atom	*x*	*y*	*z*	u11	u22	u33	u13
Cr1	0	0	0	0.0126	0.0126	0.0126	
Cr2	0.3221	0	0.9891	0.0126	0.0126	0.0126	
S1	0.9102	0	0.213	0.0126	0.0126	0.0126	
S3	0.5812	0	0.2122	0.0126	0.0126	0.0126	
S4	0.755	0	0.763	0.0126	0.0126	0.0126	
Cu1	0.6172	0	0.5701	0.023	0.027	0.0049	0.0052

PDF REFINEMENT

Using PDFFIT version : 1.1a

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PHASE 1 : AH3014E3_CuxCrS2_C2/m

Scale factor : 0.529382

Particle diameter : not applied

Step cutoff : not applied

Quad. corr. factor : 0

Lin. corr. factor : 1.83707

Low r sigma ratio : 1

R cutoff [A] : 0

Lattice parameters : 17.6869 (0.014) 3.42985 (0.0024) 6.42319 (0.0038)

& angles : 90 107.219 (0.054) 90

Atom positions & occupancies :

CR	0	0	0	1
CR	0.5	0.5	0	1
CR	0.322202	0	0.989096	1
CR	0.677798	0	0.0109035	1
CR	0.822202	0.5	0.989096	1
CR	0.177798	0.5	0.0109035	1
S	0.910178	0	0.212891	1
S	0.0898221	0	0.787109	1
S	0.410178	0.5	0.212891	1
S	0.589822	0.5	0.787109	1
S	0.58104	0	0.212267	1
S	0.41896	0	0.787733	1
S	0.08104	0.5	0.212267	1
S	0.91896	0.5	0.787733	1
S	0.754908	0	0.762894	1
S	0.245092	0	0.237106	1
S	0.254908	0.5	0.762894	1
S	0.745092	0.5	0.237106	1
CU	0.617184	0	0.570205	1
CU	0.382816	0	0.429795	1
CU	0.117184	0.5	0.570205	1
CU	0.882816	0.5	0.429795	1

Anisotropic temperature factors :

CR	0.0126652	0.0126652	0.0126652
CR	0.0126652	0.0126652	0.0126652
CR	0.0126652	0.0126652	0.0126652
CR	0.0126652	0.0126652	0.0126652
CR	0.0126652	0.0126652	0.0126652
CR	0.0126652	0.0126652	0.0126652
S	0.0126652	0.0126652	0.0126652
S	0.0126652	0.0126652	0.0126652
S	0.0126652	0.0126652	0.0126652
S	0.0126652	0.0126652	0.0126652

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S 0.0126652 0.0126652 0.0126652

CU 0.0230243 (0.0084) 0.0267392 (0.008) 0.0049829 (0.0038)

0 0.00524545 (0.0049) 0

CU 0.0230243 (0.0084) 0.0267392 (0.008) 0.0049829 (0.0038)

0 0.00524545 (0.0049) 0

CU 0.0230243 (0.0084) 0.0267392 (0.008) 0.0049829 (0.0038)

0 0.00524545 (0.0049) 0

CU 0.0230243 (0.0084) 0.0267392 (0.008) 0.0049829 (0.0038)

0 0.00524545 (0.0049) 0

DATA SET : 1 (string)

Data range in r [A] : 1.29 -> 80 Step dr : 0.01

Calculated range : 1.29 -> 81.7691

Refinement r range : 1.29 -> 80 Data pts : 0 -> 7871

Reduced chi squared : 0.00486105

Rw - value : 0.156994

Experimental settings :

Radiation : X-Rays

Termination at Qmax : 21.31 A**-1

DQ dampening Qdamp : 0.02729 A**-1

DQ broadening Qbroad : not applied

Scale factor : 1

PARAMETER INFORMATION :

Number of constraints : 62

Number of refined parameters : 8

Number of fixed parameters : 12

Refinement parameters :

1: 17.6869 (0.014) 2: 3.42985 (0.0024) 3: 6.42319 (0.0038)

4: 107.219 (0.054) 5: 0.529382 6: 1.83707

271: 0.322202 273: 0.989096 311: 0.910178

313: 0.212891 351: 0.58104 353: 0.212267

391: 0.754908 393: 0.762894 431: 0.617184

433: 0.570205 1014: 0.0230243 (0.0084) 1015: 0.0267392 (0.008)

1016: 0.0049829 (0.0038) 1018: 0.00524545 (0.0049)

REFINEMENT INFORMATION:

Number of iterations : 7

Reduced chi squared : 0.00486105

Rw - value : 0.156994

Correlations greater than 0.8 :

*** none ***