

Structural differences in Cu substrates as a function of Li deposition parameters

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I. INTRODUCTION

Here we investigate structural differences in the primary Cu component of Li-deposited thin films as a function of the independent variables: electrolyte type, sample ageing, and thickness. Our general strategy is to refine each experimental thin film pair distribution function (TF-PDF) over a wide R-range to a starting bulk Cu model in order to assess trends in the cubic lattice constant. We also try and validate these trends by showing high similarity in the fit residuals for individual sample sets (originating from the Cu thin film texture) and increasing dissimilarity compared to two Cu reference measurements. In addition, we show that there is no cross-correlation in these trends to refined sample geometry parameters, since we have employed a self-calibration routine. In this report we provide the results for all *ex-situ* measurements, a report on two *in-situ* time dependent measurements is to follow.

II. SAMPLES

A sample catalog is provided in Tables I-IV.

TABLE I: Lithium films deposited on $18\mu m$ thick Cu, enclosed in $225\mu m$ polyester

Sample	Electrolyte	Ageing (hrs)	Expected Thickness (μm)
CL-PF-1	LiPF6	0	5
CL-PF-2	LiPF6	0	15
CL-PF-3	LiPF6	0	25
CL-TF-1	LiTFSI	0	5
CL-TF-2	LiTFSI	0	15
CL-TF-3	LiTFSI	0	25
CL-PF-1-age	LiPF6	120	5
CL-PF-2-age	LiPF6	120	15
CL-PF-3-age	LiPF6	120	25
CL-TF-1-age	LiTFSI	120	5
CL-TF-2-age	LiTFSI	120	15
CL-TF-3-age	LiTFSI	120	25

TABLE II: Lithium films deposited on $20nm$ sputtered Au on $18\mu m$ thick Cu, enclosed in $225\mu m$ polyester

Sample	Electrolyte	Ageing (hrs)	Expected Thickness (μm)
CAL-PF-1	LiPF6	0	5
CAL-PF-2	LiPF6	0	15
CAL-PF-3	LiPF6	0	25
CAL-TF-1	LiTFSI	0	5
CAL-TF-2	LiTFSI	0	15
CAL-TF-3	LiTFSI	0	25
CAL-PF-1-age	LiPF6	120	5
CAL-PF-2-age	LiPF6	120	15
CAL-PF-3-age	LiPF6	120	25
CAL-TF-1-age	LiTFSI	120	5
CAL-TF-2-age	LiTFSI	120	15
CAL-TF-3-age	LiTFSI	120	25

TABLE III: Lithiated graphite films deposited on $18\mu m$ thick Cu, enclosed in $225\mu m$ polyester

Sample	Electrolyte	Ageing (hrs)	Expected Thickness (μm)
GLPF-1-1	LiPF6	0	10
GLPF-1-2	LiPF6	12	10
GLPF-1-3	LiPF6	24	10
GLTF-1-1	LiTFSI	0	10
GLTF-1-2	LiTFSI	12	10
GLTF-1-3	LiTFSI	24	10
GLPF-2-1	LiPF6	0	20
GLPF-2-2	LiPF6	12	20
GLPF-2-3	LiPF6	24	20
GLTF-2-1	LiTFSI	0	20
GLTF-2-2	LiTFSI	12	20
GLTF-2-3	LiTFSI	24	20

TABLE IV: Reference and background measurements. BT2 refers to a reproducibility test two weeks following the original beamtime.

Sample	Notes
Pure Cu	18um; BT1
Pure Li	BT1
LiCu	BT1
AuCu-bkg	BT1
polyester	225um; BT1
Pure Cu	18um; BT2
LiCu	Pressed; room temp; 25hrs; BT2
LiCu	Pressed; 100C; 2hrs; BT2
polyester	225um; BT2

III. EXPERIMENTS

The experiments were carried out at the XPD beamline (NSLS-II; Brookhaven National Lab) using the rapid acquisition PDF method (RAPDF)⁷. A 2D Perkin Elmer amorphous silicon detector was placed approximately 206.5 mm behind the thin film samples (see section VII for details). The incident wavelength of the X-rays was $\lambda = 0.1834 \text{ \AA}$. Calibration of the experimental

setup was done using both Ni and *CeO₂* calibrants.

Datasets were collected at room temperature. The detector exposure time was fixed at 0.1 seconds, but total acquisition times were varied for each thin film.

Raw data were summed and corrected for polarization effects before being integrated along arcs of constant angle to produce 1D powder diffraction patterns using the program FIT2D. Corrections were then made to the data and normalizations carried out to obtain the total scattering structure function, $F(Q)$, which was Fourier transformed to obtain the PDF using PDFgetX3⁷ within xPDF-suite. The maximum range of data used in the Fourier transform (Q_{max} , where $Q = 4\pi \sin \theta / \lambda$ is the magnitude of the momentum transfer on scattering) was chosen to be 23\AA^{-1} based on the signal quality. Fig. ?? shows the data in various stages of the analysis, from raw intensity at the top, through $F(Q)$ in the middle, to $G(r)$ at the bottom. Here we provide the reduced data for both 3nm and 5nm samples, although the structural modeling and analysis discussed in this report is restricted to the 5nm sample.

IV. THE PDF METHOD

The PDF method is a total scattering technique for determining local order in nanostructured materials.[?] The technique does not require periodicity, so it is well suited for studying nanoscale features in a variety of materials.[?] The experimental PDF, denoted $G(r)$, is the truncated Fourier transform of the total scattering structure function, $F(Q) = Q[S(Q) - 1]$:[?]

$$G(r) = \frac{2}{\pi} \int_{Q_{min}}^{Q_{max}} F(Q) \sin(Qr) dQ, \quad (1)$$

where Q is the magnitude of the scattering momentum. The structure function, $S(Q)$, is extracted from the Bragg and diffuse components of x-ray, neutron or electron powder diffraction intensity. For elastic scattering, $Q = 4\pi \sin(\theta) / \lambda$, where λ is the scattering wavelength and 2θ is the scattering angle. In practice, values of Q_{min} and Q_{max} are determined by the experimental setup and Q_{max} is often reduced below the experimental maximum to eliminate noisy data from the PDF since the signal to noise ratio becomes unfavorable in the high- Q region.

Once the experimental PDFs are determined they can be analyzed directly or through modeling. A powerful approach is simply to compare experimentally determined PDFs from samples under study and from known control samples.[?] A great deal can be learned simply from visual inspections and by taking differences to look for residual signals. Numerical tools that compare the likeness, or degree of correlation, between two curves also give insight.[?] The Pearson correlation coefficient

is one such tool.⁷

The PDF gives the scaled probability of finding two atoms in a material a distance r apart and is related to the density of atom pairs in the material.⁷ For a macroscopic scatterer, $G(r)$ can be calculated from a known structure model according to

$$G(r) = 4\pi r [\rho(r) - \rho_0], \quad (2)$$

$$\rho(r) = \frac{1}{4\pi r^2 N} \sum_i \sum_{j \neq i} \frac{b_i b_j}{\langle b \rangle^2} \delta(r - r_{ij}).$$

Here, ρ_0 is the atomic number density of the material and $\rho(r)$ is the atomic pair density, which is the mean weighted density of neighbor atoms at distance r from an atom at the origin. The sums in $\rho(r)$ run over all atoms in the sample, b_i is the scattering factor of atom i , $\langle b \rangle$ is the average scattering factor and r_{ij} is the distance between atoms i and j .

We use Eqs. 2 to fit the PDF generated from a structure model to a PDF determined from experiment. For this purpose, the delta functions in Eqs. 2 are Gaussian-broadened and the equation is modified to account for experimental effects. PDF modeling, where it is carried out, is performed by adjusting the parameters of the structure model, such as the lattice constants, atom positions and anisotropic atomic displacement parameters, to maximize the agreement between the theoretical and an experimental PDF. This procedure is implemented, for example, in PDFGUI⁷ and Diffpy-CMI.⁷

V. TEXTURE

VI. REPRODUCIBILITY

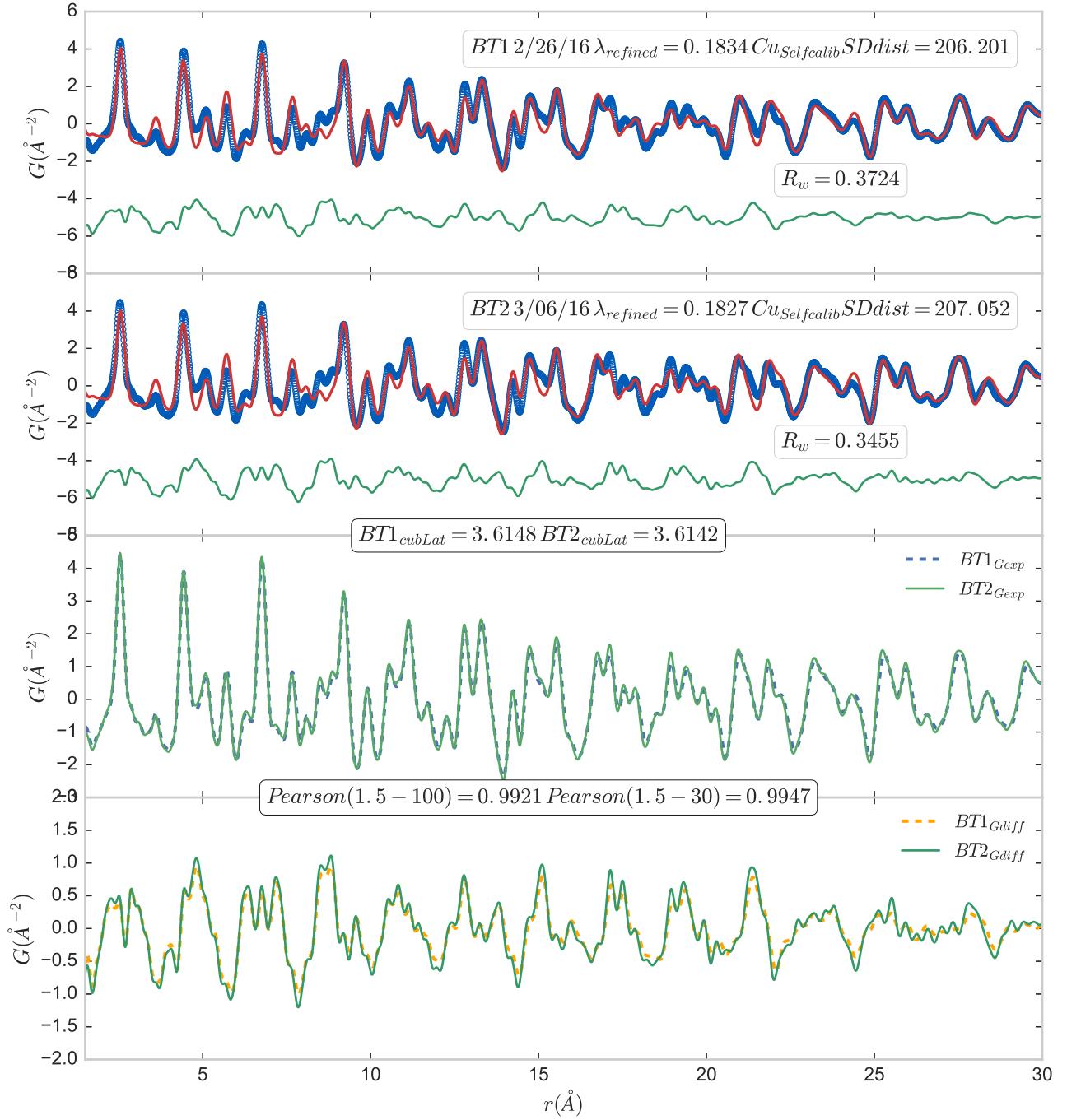


FIG. 1: Cu-reference measurements

VII. CALIBRATION

VIII. RESULTS

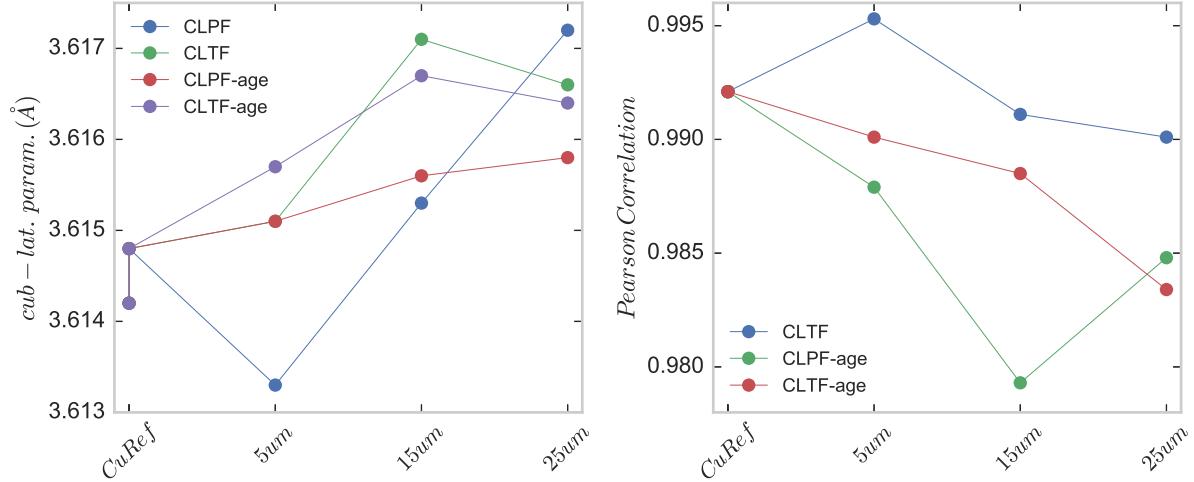


FIG. 2: Seeking to show positive correlation of lattice parameter, and negative correlation of similarity with Cu reference as a function of Li deposition thickness. Pearson correlation is calculated for Gexp (Li-dep thin film) vs Gexp CuRef from 1.5-100 angstroms.

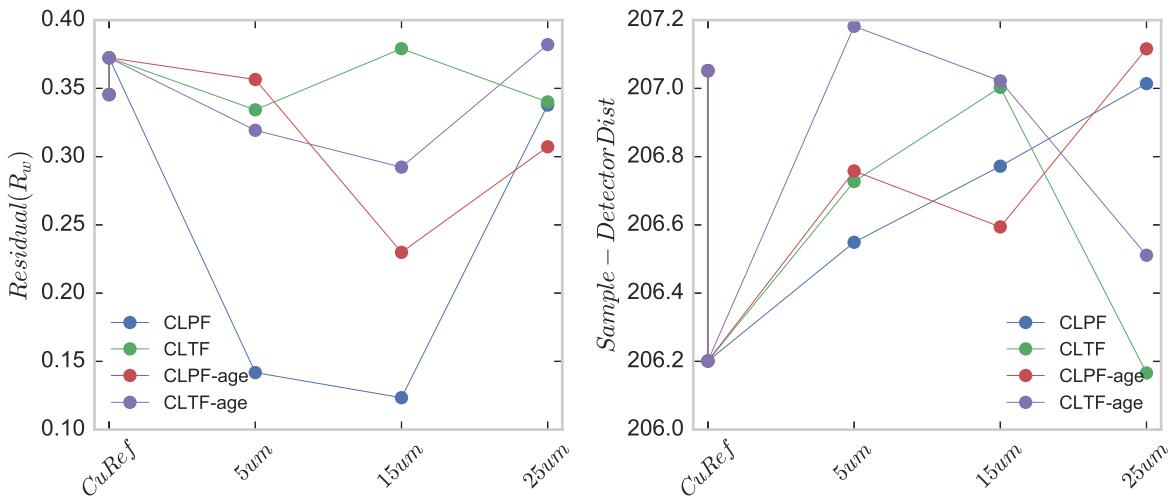


FIG. 3: Seeking to show lack of correlation, especially with SD-dist...

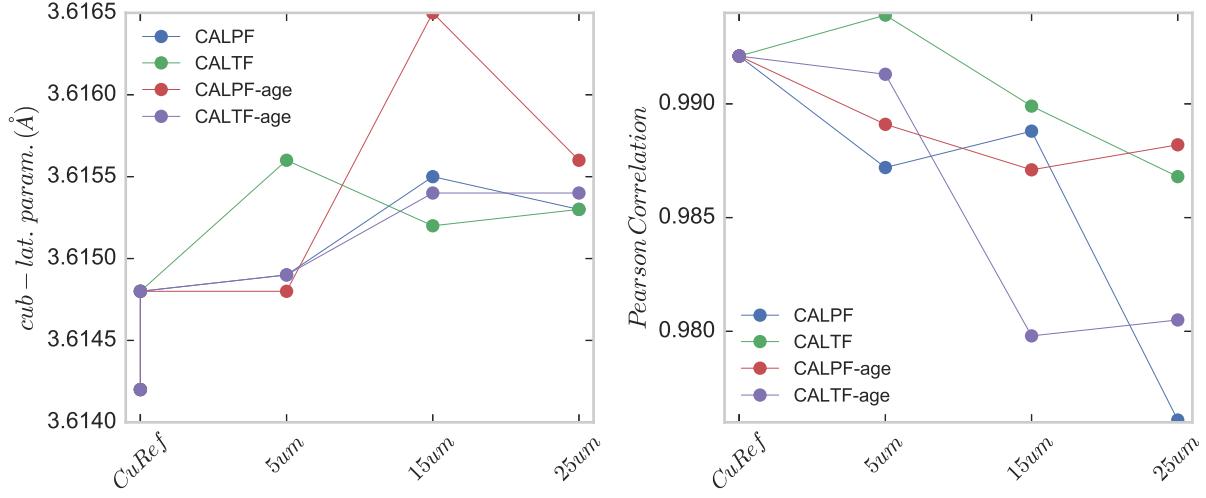


FIG. 4: Seeking to show positive correlation of lattice parameter, and negative correlation of similarity with Cu reference as a function of Li deposition thickness (with Au sputtering). Pearson correlation is calculated for Gexp (Li-dep thin film) vs Gexp CuRef from 1.5-100 angstroms.

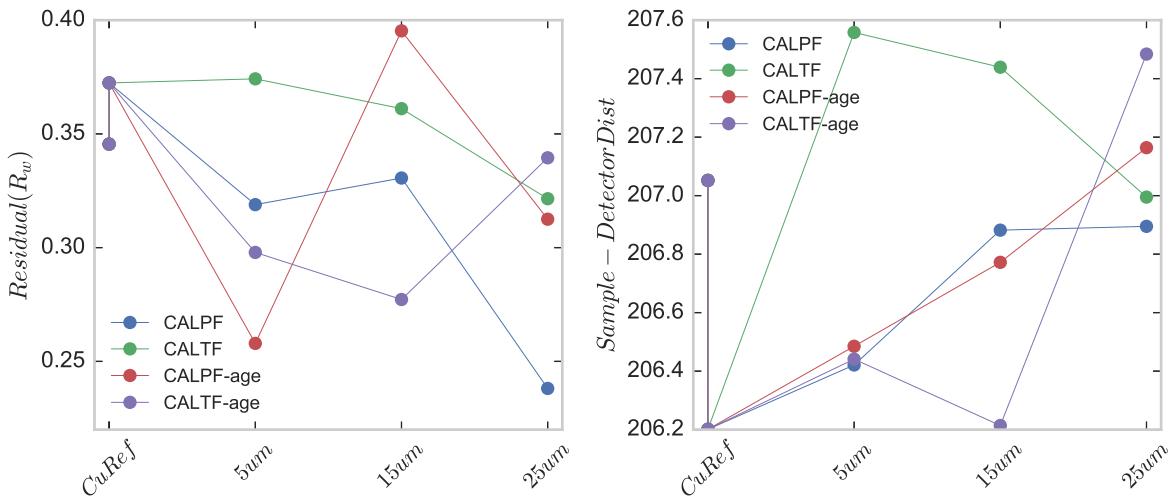


FIG. 5: Seeking to show lack of correlation, especially with SD-dist...

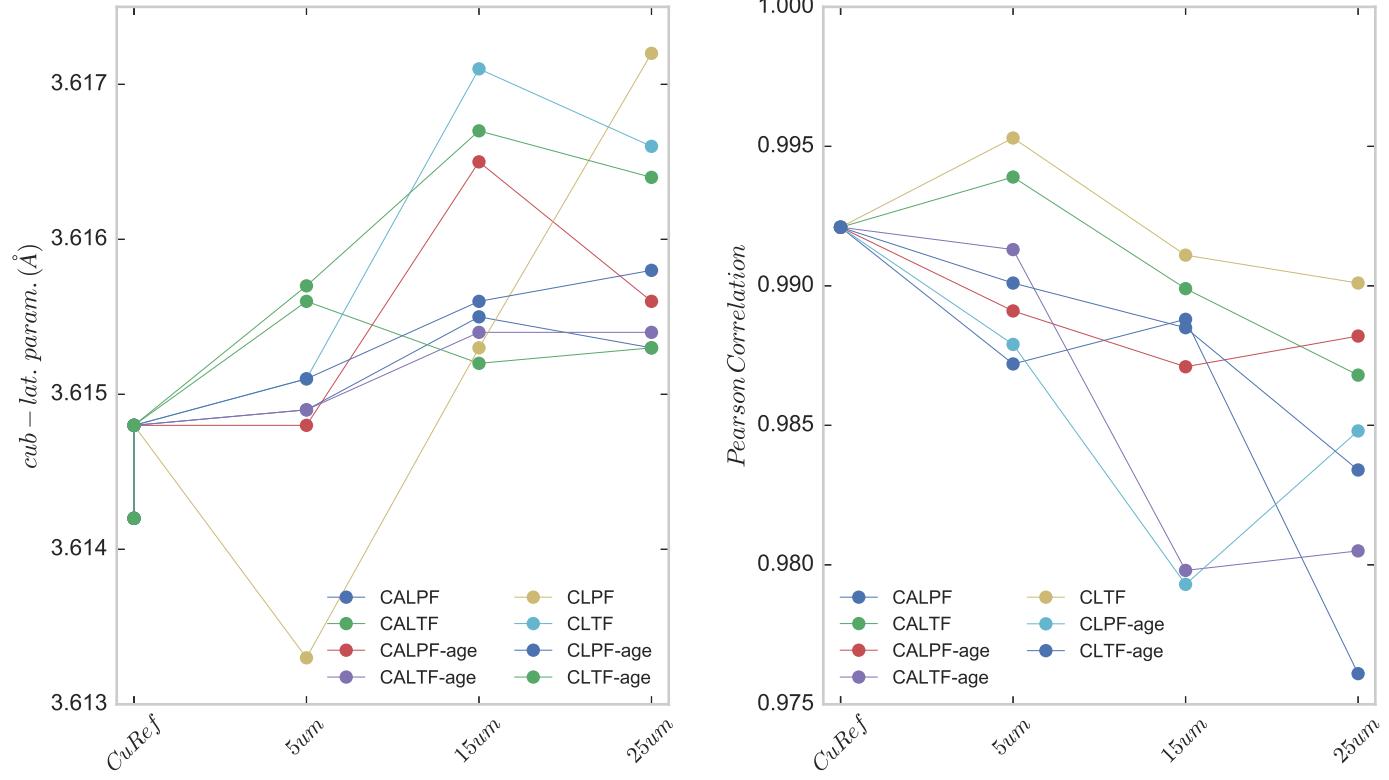


FIG. 6: Seeking to show positive correlation of lattice parameter, and negative correlation of similarity with Cu reference as a function of Li deposition thickness. However, no significant trends are seen when comparing films with/without Au sputtering.

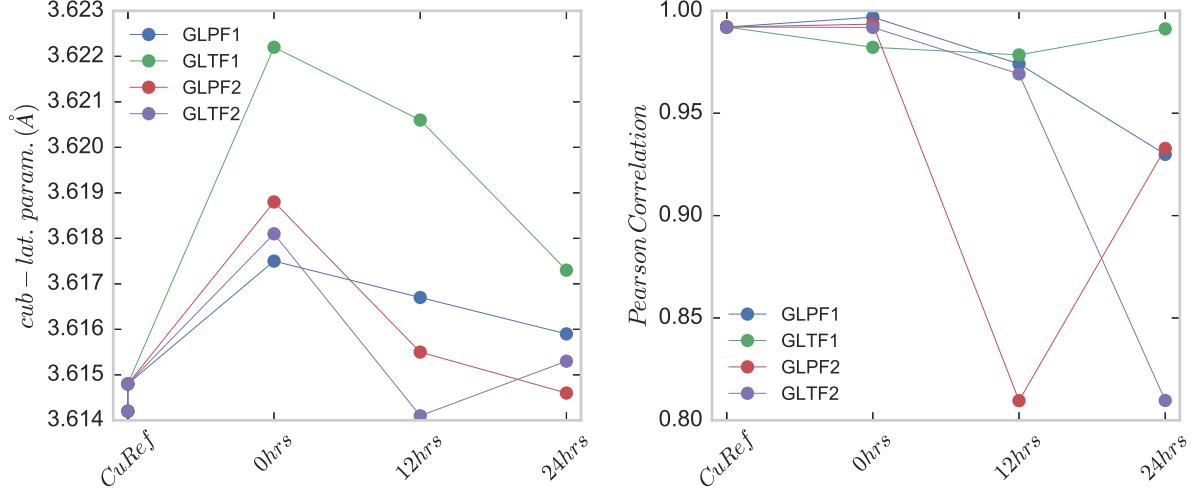


FIG. 7: Seeking to show negative correlation of lattice parameter, and no significant correlation in similarity with Cu reference as a function of ageing for Lithiated graphite samples. Also, GLPF/TF1 corresponds to an expected Li-Cx thickness of 10um while GLPF/TF2 corresponds to an expected Li-Cx thickness of 20um. It is not clear from this plot, but there is a negative correlation in lattice parameter for thicker films here, which is opposite from our films without Graphite. Unsure if this is physical or not.

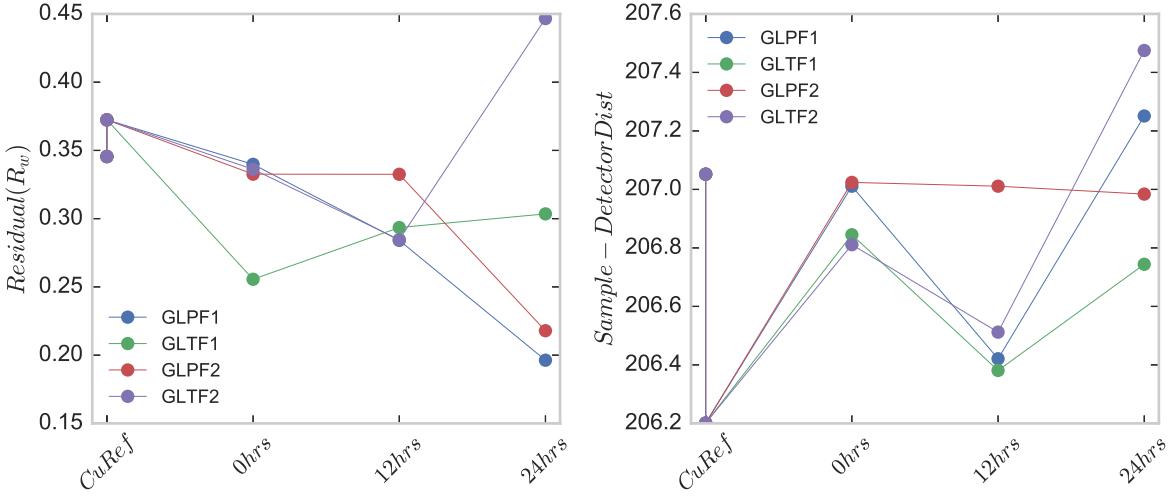


FIG. 8: Seeking to show lack of correlation, especially with SD-dist...

IX. APPENDIX1

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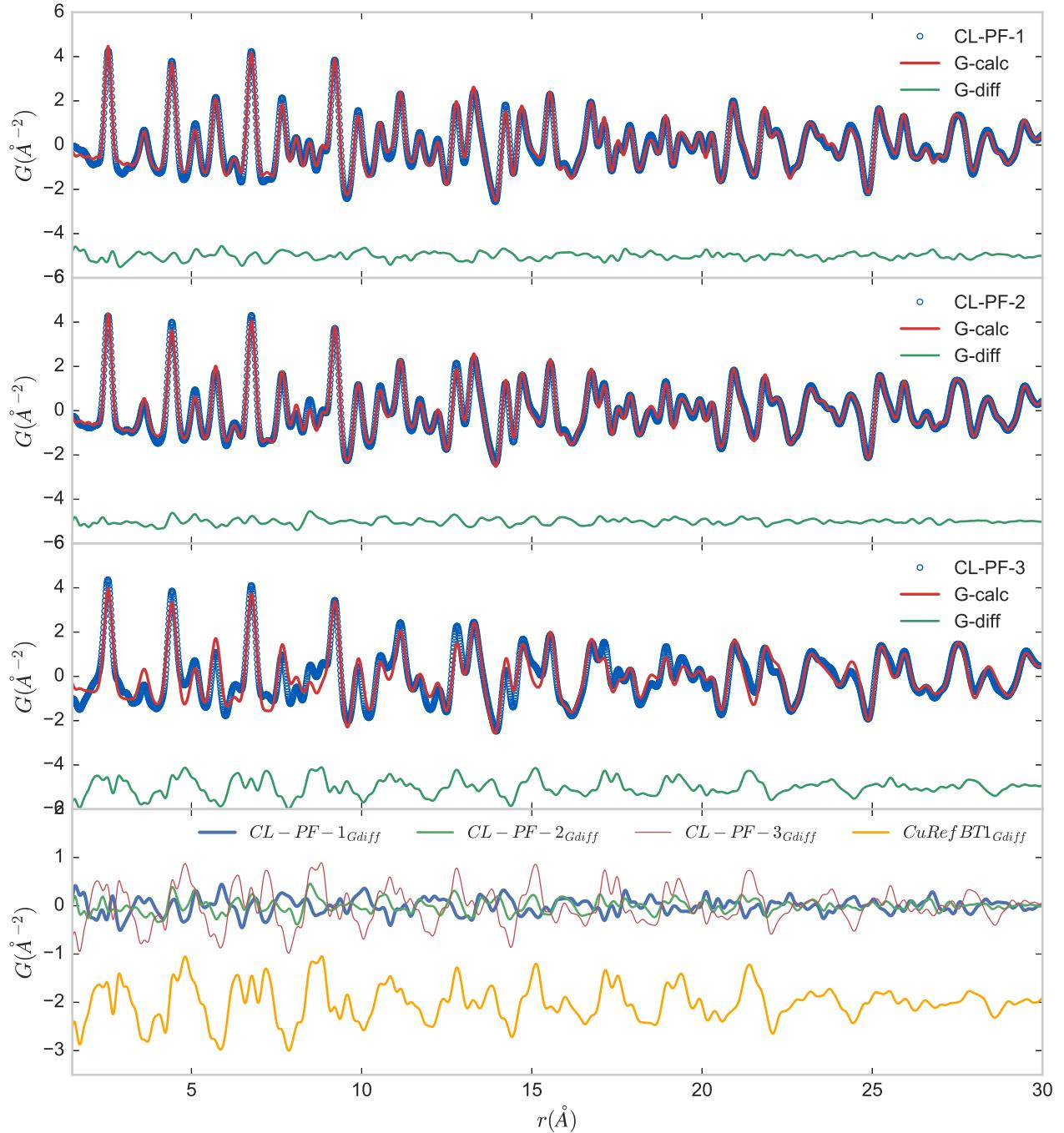


FIG. 9: CL-PF-(1-3)

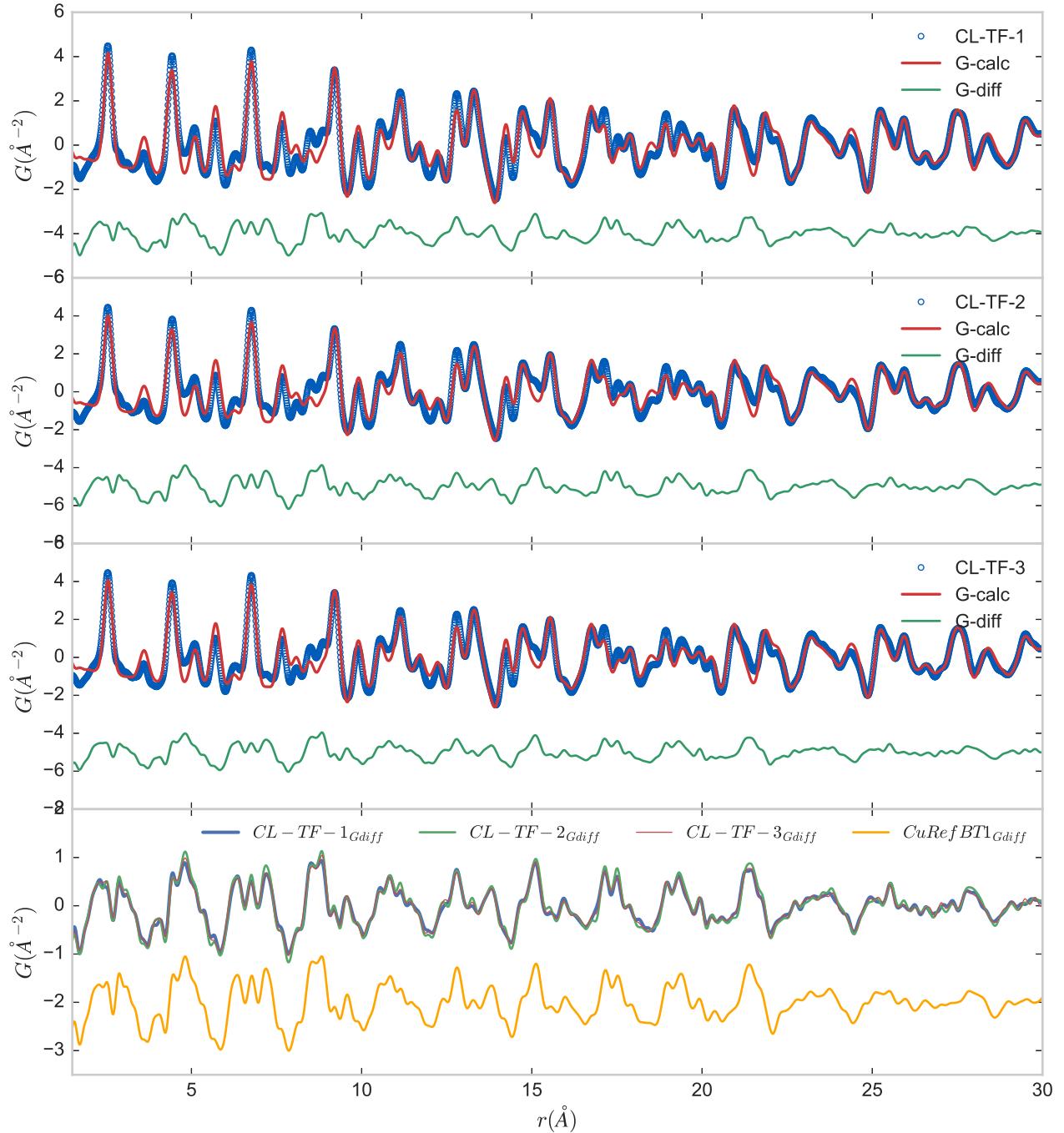


FIG. 10: CL-TF-(1-3)

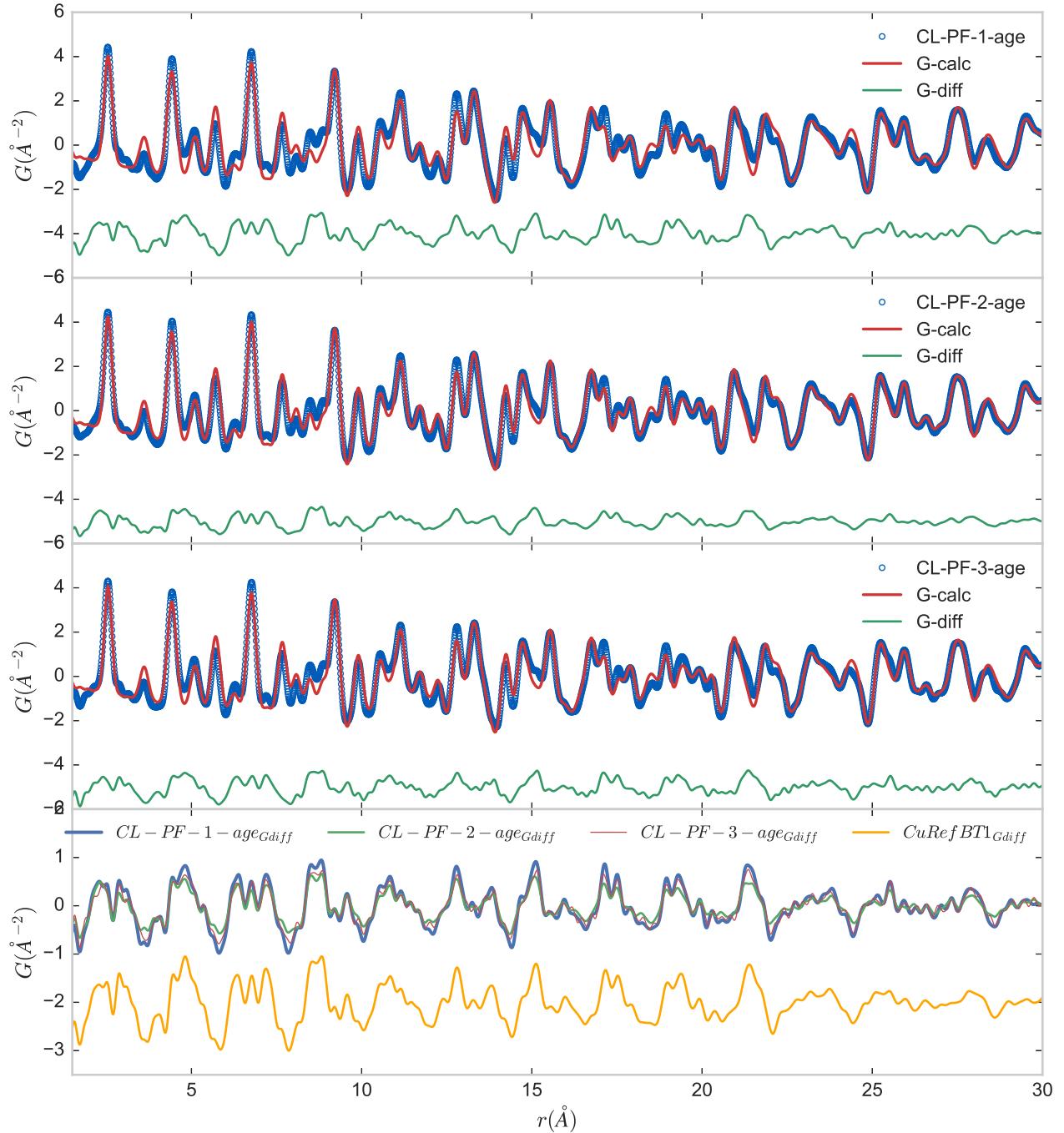


FIG. 11: CL-PF-age(1-3)

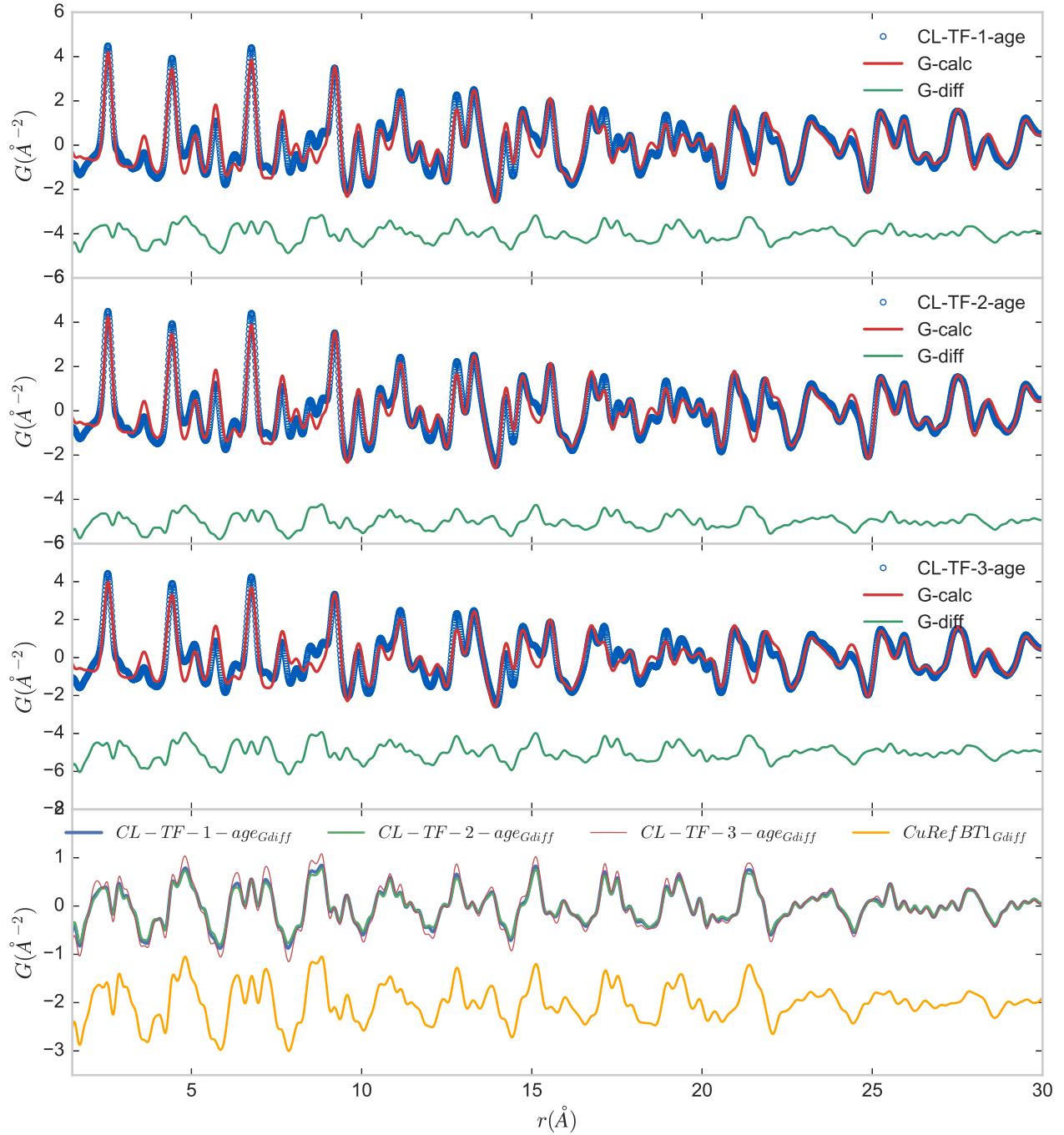


FIG. 12: CL-TF-age(1-3)

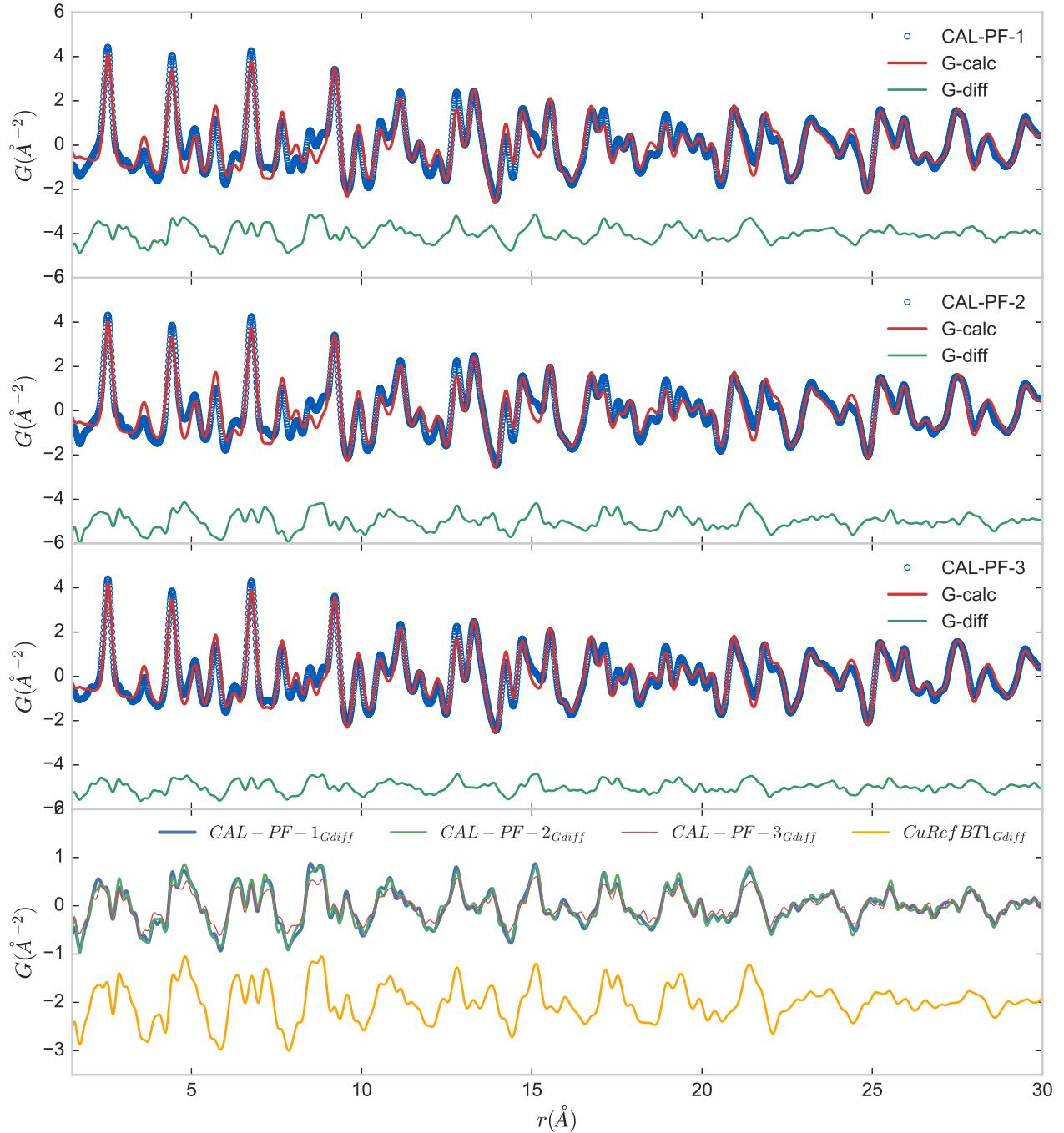


FIG. 13: CAL-PF(1-3)

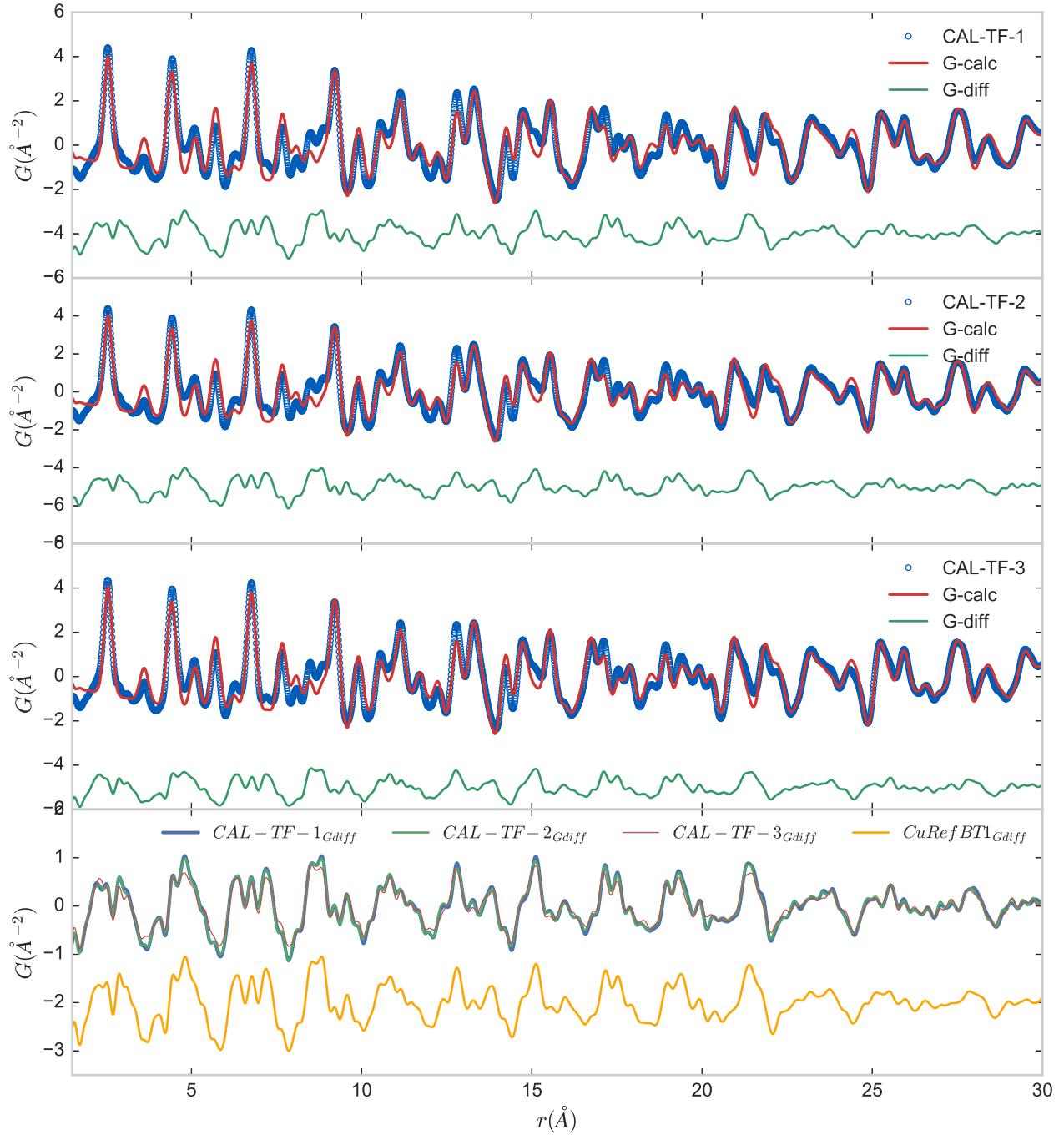


FIG. 14: CAL-TF(1-3)

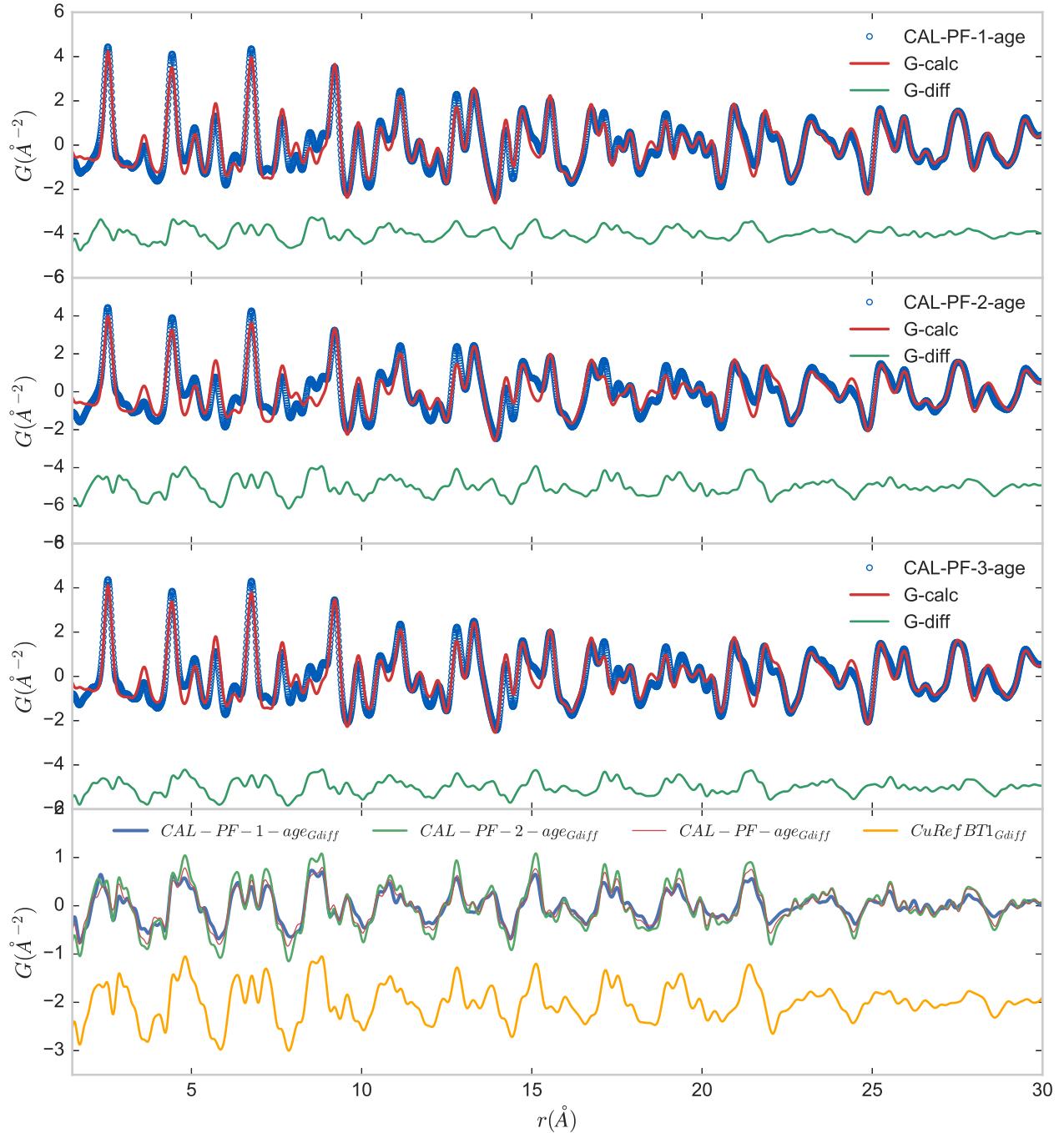


FIG. 15: CAL-PF-age(1-3)

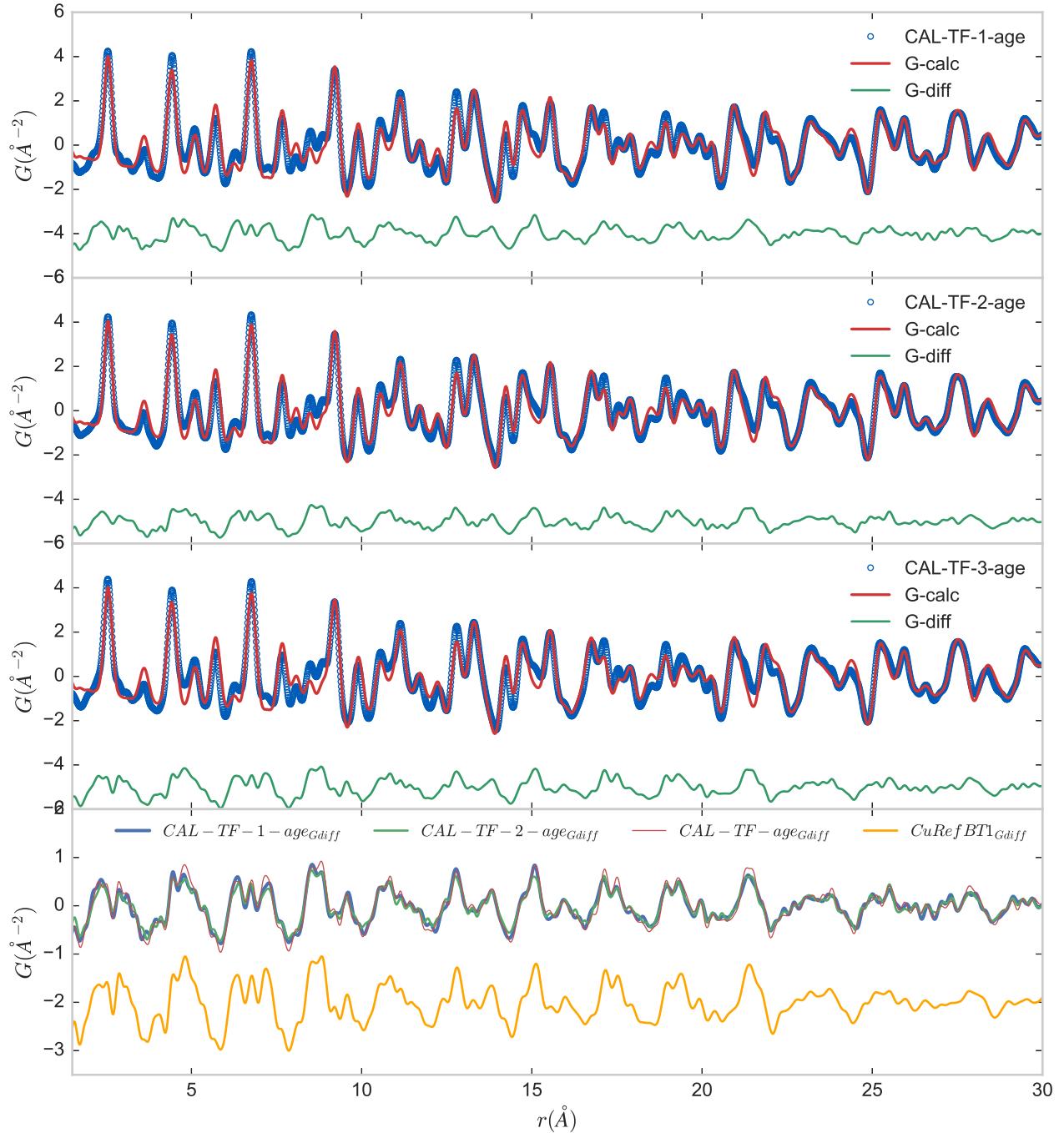


FIG. 16: CAL-TF-age(1-3)

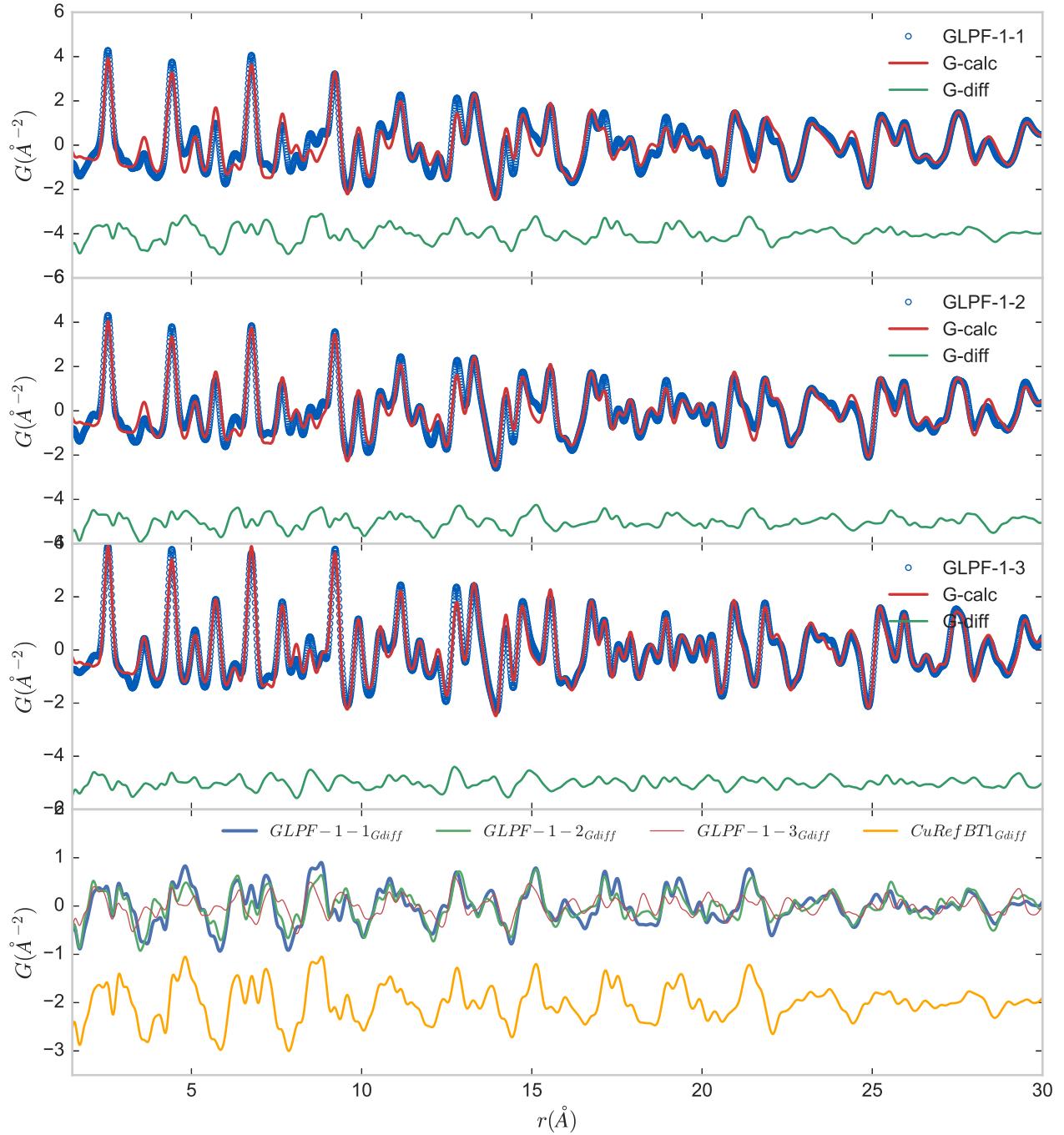


FIG. 17: GLPF-1-(1-3)

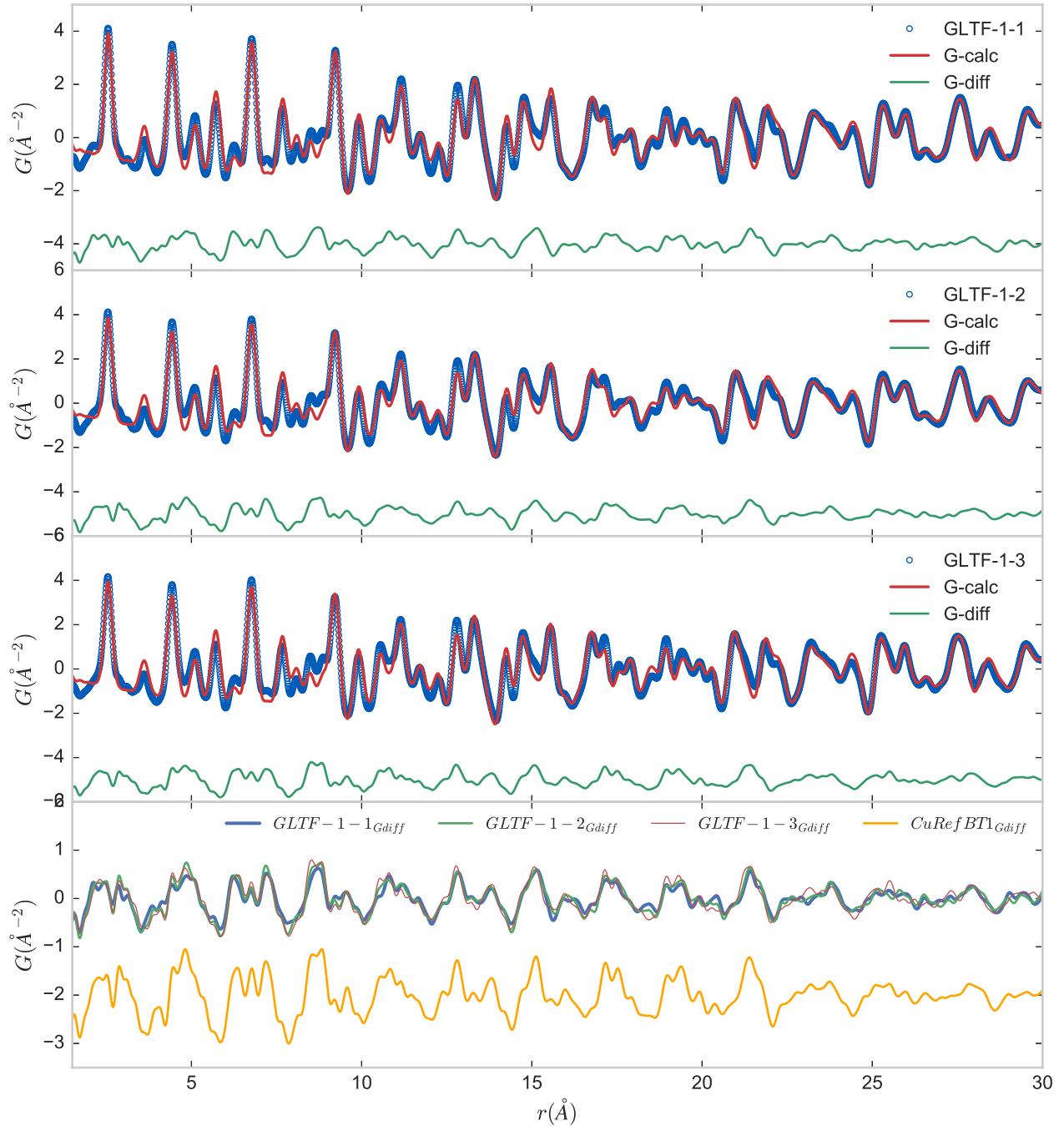


FIG. 18: GLTF-1-(1-3)

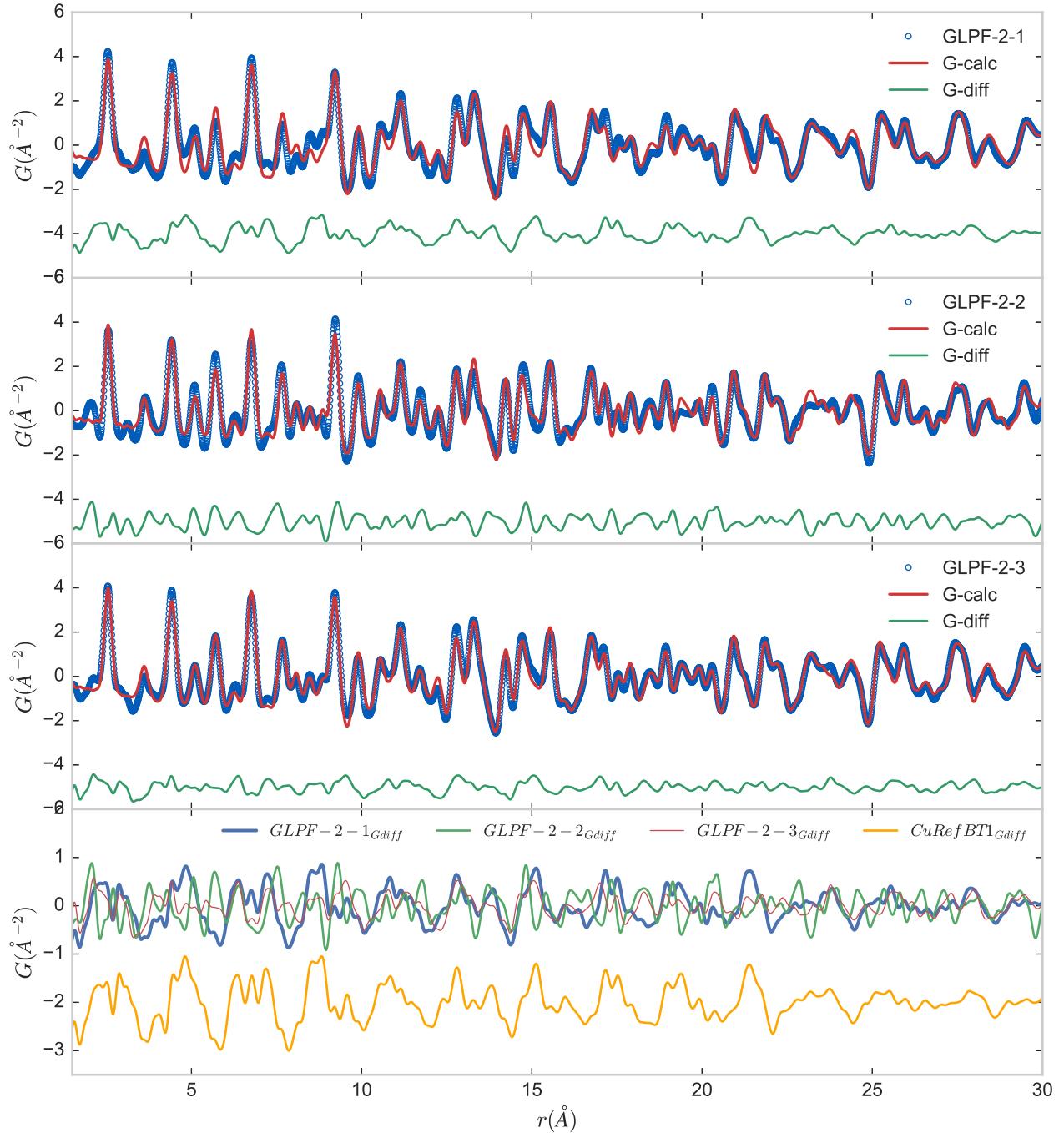


FIG. 19: GLPF-2-(1-3)

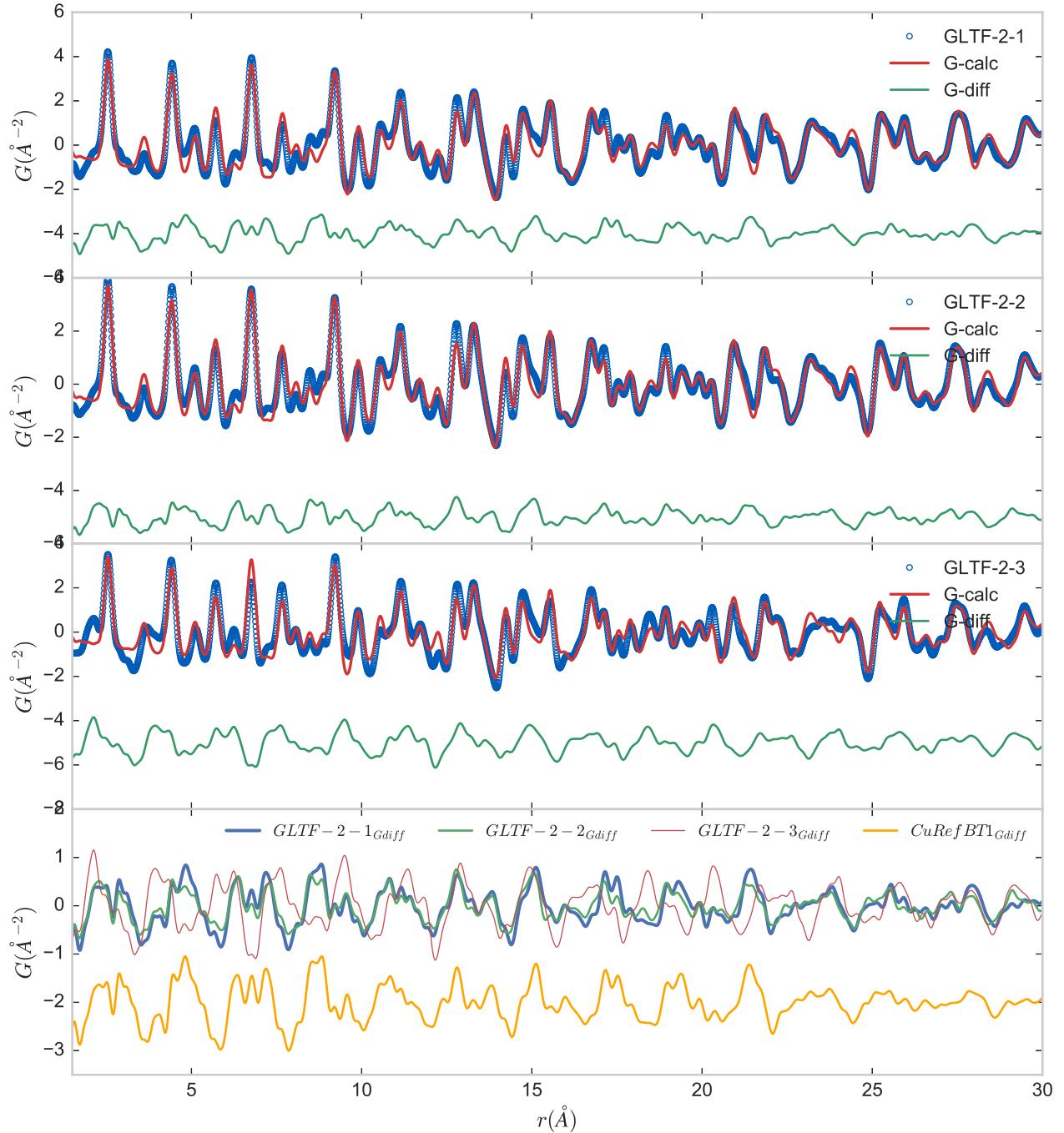


FIG. 20: GLTF-2-(1-3)

X. APPENDIX2

Sample	Electrolyte	Ageing (hrs)	Exp.	Thickness (um)	Lat-a	Rw	SD	Dist.	Pearson (vs Cu Ref G-exp)
CL-PF-1	LiPF6	0		5	3.6133	0.1418	206.549		0.8562
CL-PF-2	LiPF6	0		15	3.6153	0.1234	206.772		0.9316
CL-PF-3	LiPF6	0		25	3.6172	0.3378	207.014		0.9951
CL-TF-1	LiTFSI	0		5	3.6151	0.3343	206.727		0.9953
CL-TF-2	LiTFSI	0		15	3.6171	0.3791	207.003		0.9911
CL-TF-3	LiTFSI	0		25	3.6166	0.3401	206.166		0.9901
CL-PF-1-age	LiPF6	120		5	3.6151	0.3565	206.758		0.9879
CL-PF-2-age	LiPF6	120		15	3.6156	0.2299	206.594		0.9793
CL-PF-3-age	LiPF6	120		25	3.6158	0.3072	207.116		0.9848
CL-TF-1-age	LiTFSI	120		5	3.6157	0.3193	207.182		0.9901
CL-TF-2-age	LiTFSI	120		15	3.6167	0.2923	207.022		0.9885
CL-TF-3-age	LiTFSI	120		25	3.6164	0.3821	206.511		0.9834
CAL-PF-1	LiPF6	0		5	3.6149	0.3189	206.421		0.9872
CAL-PF-2	LiPF6	0		15	3.6155	0.3306	206.882		0.9888
CAL-PF-3	LiPF6	0		25	3.6153	0.2381	206.895		0.9761
CAL-TF-1	LiTFSI	0		5	3.6156	0.3742	207.558		0.9939
CAL-TF-2	LiTFSI	0		15	3.6152	0.3611	207.439		0.9899
CAL-TF-3	LiTFSI	0		25	3.6153	0.3215	206.995		0.9868
CAL-PF-1-age	LiPF6	120		5	3.6148	0.2579	206.485		0.9891
CAL-PF-2-age	LiPF6	120		15	3.6165	0.3953	206.772		0.9871
CAL-PF-3-age	LiPF6	120		25	3.6156	0.3125	207.164		0.9882
CAL-TF-1-age	LiTFSI	120		5	3.6149	0.2979	206.441		0.9913
CAL-TF-2-age	LiTFSI	120		15	3.6154	0.2772	206.214		0.9798
CAL-TF-3-age	LiTFSI	120		25	3.6154	0.3395	207.484		0.9805
GLPF-1-1	LiPF6	0		10	3.6175	0.3398	207.011		0.9969
GLPF-1-2	LiPF6	12		10	3.6167	0.2841	206.421		0.9741
GLPF-1-3	LiPF6	24		10	3.6159	0.1963	207.251		0.9299
GLTF-1-1	LiTFSI	0		10	3.6222	0.2556	206.845		0.9822
GLTF-1-2	LiTFSI	12		10	3.6206	0.2935	206.381		0.9785
GLTF-1-3	LiTFSI	24		10	3.6173	0.3035	206.744		0.9912
GLPF-2-1	LiPF6	0		20	3.6188	0.3326	207.024		0.9935
GLPF-2-2	LiPF6	12		20	3.6155	0.3325	207.011		0.8096
GLPF-2-3	LiPF6	24		20	3.6146	0.2179	206.984		0.9328
GLTF-2-1	LiTFSI	0		20	3.6181	0.3362	206.811		0.9919
GLTF-2-2	LiTFSI	12		20	3.6141	0.2846	206.512		0.9692
GLTF-2-3	LiTFSI	24		20	3.6153	0.4466	207.475		0.8097
CuRef-BT1					3.6148	0.3724	206.201		0.9921
CuRef-BT2					3.6142	0.3455	207.052		0.9921

TABLE V: Analysis Summary

XI. ACKNOWLEDGEMENTS

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