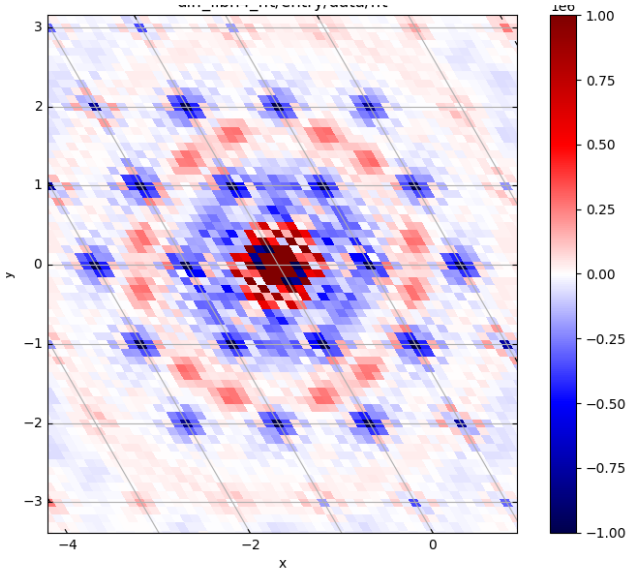
Analysis of the disordered crystal structure of $LiBH_4$ by 3D-Δ-PDF

Reinhard B. Neder[1], James Weng[2], Matt Krogstad[2], James Martin[3]

[1]Kristallographie und Strukturphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg, reinhard.neder@fau.de, Germany, [2]Advanced Photon Source, Argonne, USA, [3]Dep. of Chemistry Department, North Carolin State University, Raleigh, USA

The high temperature phase of $LiBH_4$, described in space group $P6_3mc$ [1] is reported to be unstable according to DFT calculations [2]. The structure refinement in [1] gives a plausible analysis, yet with extremely high APD's. Our own data collected at the APS just above the transition temperature to the low temperature phase shows strong circular diffuse scattering in layers normal to c, predominantly at odd l. As the diffuse scattering is stronger close to the origin of reciprocal space a substitutional disorder model with columnar order qualitatively fits the observations.



The 3D-Δ-PDF reveals intricate details with moderately long range along c, while the maxima abruptly weaken in the a-b-plane beyond roughly two unit cells. Within the a-b-plane the short range order is characterized by negative correlations for the first two nearest neighboring columns at uww=[1,0,0] and [2,0,0], while the PDF maxima at uvw=[1/3, 2/3, w] indicate a positive correlation between immediate neighboring columns. The innermost maxima show that the simple structure model [1] is incomplete as we observe the BH_4 tetrahedron not only with its C3-axis parallel to c but with the C2-axis as well, similar to the low temperature phase.

[1] Filinchuk Y, Chernyshow D, Cerny R. Lightest Borohydride Probed by Synchrotron X-ray Diffraction. J. Phys. Chem. C **112**, 10579 (2008)

[2] Lodziana Z, Vegge T. Structural Stability of Complex Hydrides: $LiBH_4$ Revisited. Phys. Rev. Lett. 93, 145501 (2004).