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PDF analysis of ferrihydrite: Critical assessment of the under-constrained akdalaite model

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Abstract

In an effort to shed light on the intricate structure of ferrihydrite, its pair distribution function (PDF) derived from high-energy X-ray scattering (HEXS) data was refined with the single-phase akdalaite model, possessing 20% of the Fe atoms in tetrahedral coordination, and a modified akdalaite model in which Fe has only octahedral coordination. The second model is analogous to the predominant f-phase (ABAC stacking sequence) of classical multi-phase ferrihydrite. The contribution from the disordered d-phase component (randomly stacked ABA and ACA double-layer fragments) of the classical model was recovered in the modified akdalaite description by increasing the atomic motion of the ABAC motif above the double-layer distance 4.2 Å to simulate aperiodic stacking faults. Results show that the original and modified akdalaite representations provide near-identical fits to the ferrihydrite PDF. In the original single-phase and periodic model, the plurality of the Fe-O and Fe-Fe distances resulting from phase mixtures and defects are reconciled artificially by taking a large unit cell with three independent Fe sites, two Fe coordinations, and under-constrained atomic positions. Correlation matrices reveal that many fitted parameters are linearly correlated, thus explaining the crystallographic and chemical inconsistencies of the as-refined akdalaite model which have been identified in the literature. Structurally more constrained, the modified akdalaite model does not suffer from bias and provides a more robust description of the PDF data. However, because structural defects and inhomogeneities are not physically present but introduced artificially in PDF modeling, the crystallographic description of ferrihydrite by real-space modeling of HEXS data has an idealized character. To facilitate further understanding of the ferrihydrite structure, the PDF data are provided as supplementary material[1] for interlaboratory testing, and as a resource as more sophisticated tools may be brought to bear on this complex problem.

Keywords: Structure, ferrihydrite, pair distribution function, PDF, HEXS