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Subtle details revealed via powder diffraction and validated by charge flipping

Peter W. Stephens*

Department of Physics and Astronomy, Stony Brook University, Stony Brook, New York 11794-3800, USA. *Correspondence e-mail: pstephens@stonybrook.edu

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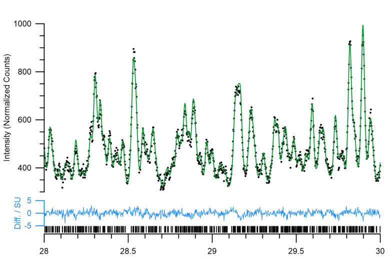
The paper by Lake & Von Dreele (2025) published in this issue of *Acta Crystallographica Section B* provides an informative look at the current state of the art in powder diffraction, and subtleties that can be revealed through its careful application. It concerns an examination of the remarkable structure of the related minerals mcgovernite and carlfrancisite, which have a rhombohedral unit cell with a 204 Å *c* axis, the longest unit-cell dimension of any mineral species known to date. The closely related structures of both minerals were originally solved from single crystals using direct methods in 2018 in the centrosymmetric space group $R\bar{3}c$ by the distinguished mineralogist, F. C. Hawthorne.

Starting from high-resolution powder X-ray diffraction data on mcgovernite, Lake and Von Dreele obtained a preliminary structure using the charge flipping algorithm of Oszlányi and Sütő (2004) as implemented in *GSAS-II* (Toby & Von Dreele, 2013). Charge flipping requires knowledge of the unit-cell dimensions but is agnostic with respect to space group, unlike the more widely used direct methods in which the space group must be hypothesized in advance. In this case, the issue of interest was whether the structure was centrosymmetric (space group $R\bar{3}c$) or non-centrosymmetric ($R3c$). The charge density map so produced was very similar to the structure published by Hawthorne (2018) but showed some deviations from inversion symmetry. This may not be entirely surprising since the mcgovernite structure is similar to hematolite which occurs in the non-centrosymmetric space group $R3$, with a *c* axis one sixth that of mcgovernite. On the other hand, the observed absence of piezoelectricity would support the hypothesis of a centrosymmetric structure.

The powder data (43676 data points encompassing 8707 reflections) were refined according to both the $R3c$ structure from charge flipping and the $R\bar{3}c$ published by Hawthorne (2018). The Rietveld fit of the former model is shown in Fig. 3 in the paper by Lake and Von Dreele, but it is not possible to appreciate the quality of the fit, or the quantity of information it contains, from that figure. A small fraction of the fit is shown here in Fig. 1.

The non-centrosymmetric structure from charge flipping gave a better fit than that in space group $R\bar{3}c$ ($R_{\rm wp}$ = 0.05952 for 237 refined parameters, *versus* $R_{\rm wp}$ = 0.06072 for 148 parameters), but some care is required to determine if the improvement in *R* factor is sufficient to distinguish the two models. The relevant statistical framework is described by Prince & Spiegelman (2006). There is a complication related to specifying the number of independent measurements contained in a powder diffraction pattern as each measured datum may include contributions from multiple Bragg reflections and the diffracted intensity of a particular reflection is distributed among multiple measured data in the pattern. It is evident from Fig. 1 that there are more overlapping reflections within each peak of the observed data, so that the number of observations is less than either the number of data points in the pattern or the number of allowed reflections. In this case, the difference between space groups $R3c$ and $R\bar{3}c$ is probably not statistically significant at the 95% level of confidence in the powder diffraction data.



However, motivated by this observation, Hawthorne's single crystal data were also reanalyzed by the charge flipping method and Lake and Von Dreele show that the mcgovernite structures from powder and single-crystal data are in very good agreement. As shown in their Table 1, the 26181 independent observations in Hawthorne's single crystal data decisively support the non-centrosymmetric space group $R3c$ for mcgovernite ($R_{\rm w}$ = 0.0562 for 342 parameters *versus* 0.0682 for 261 parameters) as well as carlfrancisite ($R_{\rm w}$ = 0.04329 for 342 parameters *versus* 0.04448 for 259 parameters with 27966 observations).

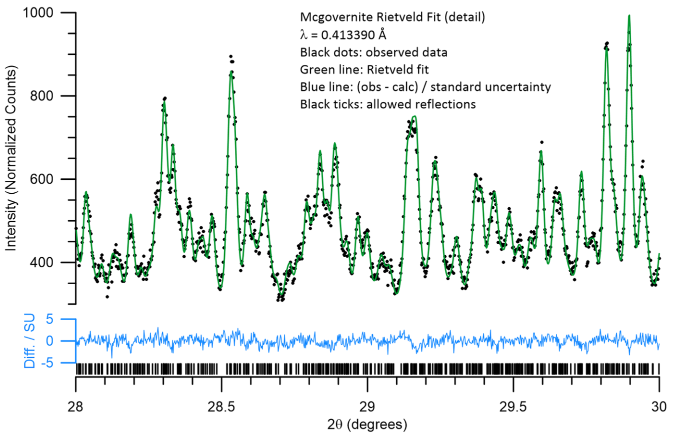


Figure 1
A portion of the Rietveld fit to the powder diffraction data of mcgovernite presented in Lake & Von Dreele (2025). Black dots are the experimental data; the green line is the calculated fit. The blue trace is the difference, observed minus calculated, divided by the standard uncertainty of the measurement. The black tick marks along the bottom show the positions of allowed diffraction peaks.

A noteworthy feature of Hawthorne's original single-crystal structure is the presence of certain partially occupied sites that are impossibly close to one another. This is readily interpreted as static disorder with one conflicting site or the other randomly occupied throughout the lattice. It turns out that this disorder is also present in the newly published *R*3*c* result. Lake and Von Dreele interpret these defect sites as pseudo-inversion centers which induce merohedral twinning in the crystal, so that, even accounting for resonant scattering, mirror-related reflections have equal intensity. The work of all three scientists on this remarkable mineral is a *tour de force* of modern crystallographic technique.

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