Comment on "Examination of Spinel and Nonspinel Structural Models for γ-Al$_2$O$_3$ by DFT and Rietveld Refinement Simulations"

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Using DFT and models fitted by Rietveld analysis to X-ray diffraction (XRD) data, Sun et al.[1] investigated 12 hydrogenated and nonhydrogenated spinel structural models of γ-Al$_2$O$_3$ relative to a solitary nonspinel model presented by Digne et al.[2,3] From a comparison of Rietveld refinement fits to XRD data and the achieved coordination ratio, it was concluded that "the spinel-related structure model is better than the nonspinel model in description of the bulk structure of γ-Al$_2$O$_3$".

We have found this result interesting because it reports the suitability of spinel (over nonspinel) models on the basis of Rietveld analysis of data, which is not characteristic of γ-Al$_2$O$_3$. The major physical argument presented by Sun et al.[1] is that the nonspinel model is "out of phase with the experimentally observed SXPD pattern at 2θ between 13° and 19°, while the spinel-related models match the major peak positions reasonably well". The distinction between the X-ray diffraction patterns of γ-Al$_2$O$_3$ and δ-Al$_2$O$_3$ can be seen in Figure 4 of Repelin and Husson[4] and Figure 1 of ref 3, both of whom show a characteristic diffraction pattern of the two phases. The diffraction pattern of Sun et al.[1] is clearly of similar appearance to that of δ-Al$_2$O$_3$, not γ-Al$_2$O$_3$. In γ-Al$_2$O$_3$, the (220) peak is a broad, diffuse hump in the X-ray diffraction pattern and a broad streak in the corresponding electron diffraction pattern.[5−8] In δ-Al$_2$O$_3$, the (220) reflection is split and becomes sharper, the (400) peak develops a shoulder, the (111) and (333) reflections sharpen, and a new peak forms at (033). These δ-Al$_2$O$_3$ features are clearly observed in the SXPD pattern of Sun et al.,[1] including the (033) reflection, which is not indexed in Figure 8 of their manuscript. It is therefore not surprising that Sun et al.[1] find the nonspinel model out of phase with their data and find in favor of the spinel model, as δ-Al$_2$O$_3$ has a triple-cell spinel structure.

In their model refinements, Sun et al.[1] did not account for a more extensive series of work of similar nature,[9−11] of particular relevance to their study, that provided comparatively better fits to the data and produced opposite findings. Three of these papers were cited, but this was only nominal and, more importantly, was misrepresentative of the findings in those studies. Hence, we make note of it here. In ref 9 and, in particular, ref 7, all of the possible structural models for γ-Al$_2$O$_3$ known to us at the time were examined. This included spinel, nonspinel (that introduced in the groundbreaking Zhou and Snyder[12] study and
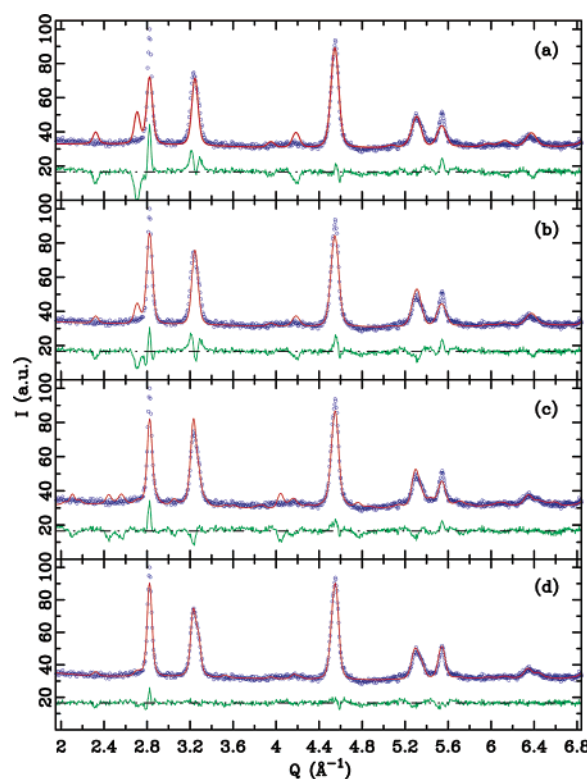
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Figure 1. Examples of Rietveld refinement fits to neutron diffraction data for a deuterated γ-Al$_2$O$_3$ sample:[7] (a) fully hydrogenated H$_3^T$ H^O Al$_5^T$ Al$_{15}^O$ O$_{32}$ model (poorest fitting of all models), (b) defect spinel $\square_2^O$ Al$_6^T$ Al$_{10}^O$ O$_{24}$ model, (c) nonspinel model presented by Digne et al.,[2] and (d) tetragonal nonspinel c symmetry-based (nonhydrogenated) model.

those we introduced in the studies), cubic (spinel and nonspinel), tetragonal (spinel and nonspinel), dual phase, and hydrogenated models. In the case of the hydrogenated models, the amount of hydrogen included was based on the physically measured hydrogen content, and trial models were constructed according to the traditional γ-Al$_2$O$_3 \cdot n$H$_2$O stoichiometry and the newly introduced Sohlberg et al.[13] stoichiometry, H$_{3m}$Al$_{2-m}$O$_3$. Under these two types of hydrogenated stoichiometries, all possible combinations of configurations were tested: spinel, nonspinel, cubic, and tetragonal. From the fitting of these combinations it was determined that the nonhydrogenated nonspinel models, in particular, the tetragonal c symmetry-based nonspinel model, performed the best, with an R_{wp} of 2.47%. Overall, the fits to the data in ref 7 exhibited far better agreement with the data than those presented by Sun et al.[1] Furthermore, the refinement results that suggest a nonhydrogenated bulk crystalline structure were then supported by the neutron vibrational spectroscopy (NVS) and IR/FTIR results in ref 10, not the SAXS and PGAA experiments that were performed, as stated by Sun et al.[1]

Following the results of refs 7, 8, and 10, ref 11 details the examination of $\sim$1.47 billion spinel configurations using geometric analysis followed by interatomic potential and DFT derivative method calculations. None of the spinel configurations produced a simulated diffraction pattern that is characteristic of γ-Al$_2$O$_3$. This procedure was then repeated using configuration based on the nonspinel models presented in ref 7, and it was demonstrated that these particular models produce diffraction patterns that closely match the characteristic diffraction

TABLE 1: Rietveld and PDF Refinement Statistical Fitting Parameters for Models Presented by Sun et al. and Models from Ref 7

model	Rietveld analysis R_{wp}, χ^2, R_{Bragg}, R_p (%)	PDF analysis[a,b] R_{wp} (%)
models from Sun et al.[1]		
nonspinel from Digne et al.[2] [c,g]	3.77, 5.06, 3.73, 5.04	30.0
defect spinel		
$\square_2^O\ Al_6^T\ Al_{10}^O\ O_{24}$[d]	3.82, 5.90, 3.62, 5.45	31.6
$\square^O\square^T\ Al_5^T\ Al_{11}^O\ O_{24}$[d]	3.68, 5.38, 3.08, 5.20	31.1
$\square_2^T\ Al_4^T\ Al_{12}^O\ O_{24}$[d]	3.63, 5.32, 3.62, 5.17	31.9
partially hydrogenated		
$H^T\ \square^O\square^T\ Al_6^T\ Al_{15}^O\ O_{32}$[e]	3.82, 6.13, 3.83, 5.56	32.7
$H^T\ \square^T\ 2\ Al_5^T\ Al_{16}^O\ O_{32}$[e]	3.69,5.51, 3.89, 5.26	32.7
$H^O\ \square^O\square^T\ Al_7^T\ Al_{14}^O\ O_{32}$[e]	3.80, 6.03, 4.43, 5.50	32.8
$H^O\ \square^O\ 2\ Al_6^T\ Al_{15}^O\ O_{32}$[e]	3.86, 7.239, 4.10, 6.04	32.7
fully hydrogenated		
$H_4^T\ Al_4^T\ Al_{16}^O\ O_{32}$[e]	4.72, 10.29, 6.64, 7.12	37.5
$H_4^O\ Al_8^T\ Al_{12}^O\ O_{32}$[e]	4.33, 9.91, 4.66, 7.06	33.0
$H_3^T\ H^O\ Al_5^T\ Al_{15}^O\ O_{32}$[e]	4.50, 10.54, 5.66, 7.29	32.4
$H_2^T\ H_2^O\ Al_6^T\ Al_{14}^O\ O_{32}$[e]	4.42, 10.17, 5.49,7.16	32.1
$H^T\ H_3^O\ Al_7^T\ Al_{13}^O\ O_{32}$[e]	4.36, 9.94, 5.14, 7.08	32.2
models from Paglia et al.[7]		
cubic spinel (nonhydrogenated)	3.45, 3.42, 2.48, 4.26	32.3
tetragonal spinel (nonhydrogenated)	3.04, 3.32, 2.41, 4.08	31.0
Zhou & Snyder	3.18, 3.42, 1.65, 4.34	25.2
best fitting hydrogenated model (hydrogenated tetragonal c symmetry-based)[e,f]	3.04, 3.17, 2.77, 3.99	19.1
cubic nonspinel c symmetry-based (non-hydrogenated)	3.07, 3.16, 1.35, 4.22	20.2
tetragonal nonspinel c symmetry-based	2.47, 1.96, 0.99, 3.23	17.7

[a] For the PDF refinement code used, PDFFIT, R_{wp} is the only statistical measure for the fit quality used. Note that PDF analysis yields higher relative R_{wp} values than Rietveld analysis. Excellent fits exhibit R_{wp} values under 20%. [b] Refinements performed over 8.0 Å < r < 25.0 Å. [c] Internal coordinates became unstable when relaxed during refinement. [d] When internals relaxed during refinement, these values converged to the same structure. [e] Exhibited high or negative thermal values that required fixing to physically reasonable values during refinement. [f] The majority of refinements resulted in various unstable structural possibilities and hence required fixing to physically reasonable values. Refer to ref 7. [g] Fits comparably, and has a similar configuration, with the cubic c symmetry-based nonspinel model of ref 7 when coordinates are reoriented to $Fd\overline{3}m$ symmetry; the relative occupancies after reorientation are 0.17 × 8a, 0.33 × 16c, 0.67 × 16d, and 0.08 × 48f.

pattern of γ-Al_2O_3. These findings were also supported in another theoretical study that was published soon after,[14] and a published manuscript which employs the atomic pair distribution function (PDF) method.[15]

There is also the issue of using XRD patterns to perform Rietveld refinements of hydrogenated models. X-rays simply cannot "see" hydrogen because the scattering originates predominantly from an electron−phonon interaction. The use of X-rays is also nonideal for determining the cation arrangement in γ-Al_2O_3 because the diffuse contribution predominantly arises from the highly disordered cation sublattice; this has clearly been shown in several diffraction studies with the aid of electron diffraction.[5−8] For this reason, in ref 7, neutron diffraction data of deuterated γ-Al_2O_3 samples were examined so that the presence of hydrogen could be accounted for directly in the

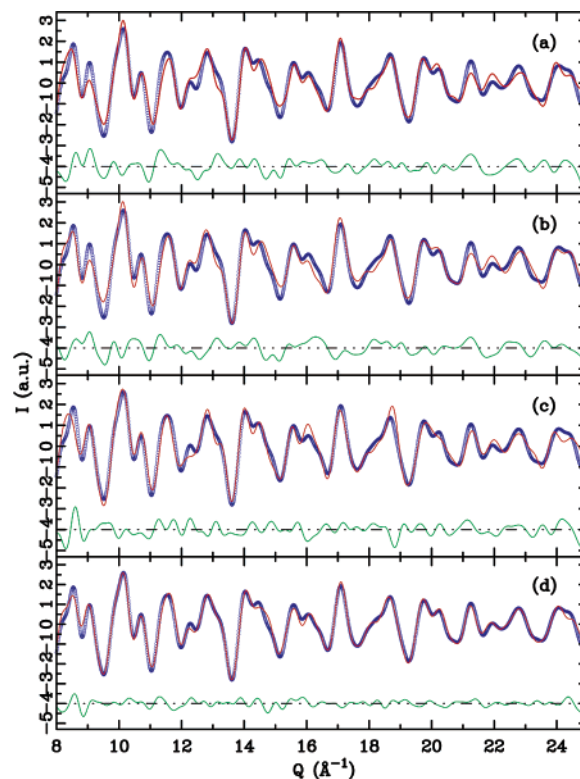**Figure 2.** Examples of PDF refinement fits over 8.0 Å < r < 25.0 Å to data obtained from γ-Al_2O_3 derived from well crystalline boehmite:[7,15] (a) fully hydrogenated $H_3^T\ H^O\ Al_5^T\ Al_{15}^O\ O_{32}$ model (poorest fitting of all models), (b) defect spinel $\square_2^O\ Al_6^T\ Al_{10}^O\ O_{24}$ model, (c) nonspinel model presented by Digne et al.,[2] and (d) tetragonal nonspinel c symmetry-based (nonhydrogenated) model.

Rietveld refinements (deuterium was refined for hydrogen). The quality of the fits by Sun et al.[1] is also an issue. The R_p values obtained were greater than 10%, which is particularly high by Rietveld analysis standards. This is reflected by the observed disparity between the calculated and experimental diffraction patterns in Figures 7 and 8 of the Sun et al.[1] manuscript.

Because γ-Al_2O_3 produces highly diffuse XRD patterns, using Rietveld analysis can be difficult. This is in part because Rietveld analysis only considers Bragg scattering and ignores the diffuse component, and profile functions are not always sufficient to fit extremely broad features such as those observed for γ-Al_2O_3. (Neutron diffraction patterns do not suffer as significantly from this effect.) Therefore, when using X-rays, it may be more beneficial to use a technique such as the atomic PDF method.[16] The PDF is effectively a Fourier transform of powder diffraction data but has the advantage of quantitatively measuring both the diffuse and Bragg components.

We thought it useful to examine the models presented in the Sun et al.[1] manuscript by both using Rietveld analysis of neutron diffraction data obtained from deuterated γ-Al_2O_3[7] and fitting to the PDF obtained using synchrotron X-ray data.[15] These were collated along with the best fitting spinel and hydrogenated models from ref 7 for comparison. Also included is the best fitting of all the models, the nonhydrogenated tetragonal c symmetry-based model (also termed tetragonal 8c). The purpose of this is to provide a summary of the relative fits of the types of structural models available for γ-Al_2O_3. The method for generating the structural models is well-known; however, specific details can be found in the related references. The resulting fit parameters are tabulated in Table 1. Figures 1 and 2 illustrate examples of the fits. We have found that the Digne

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et al.[2] nonspinel model does not perform as poorly as indicated by Sun et al.[1] and actually fits comparably to the best fitting spinel model they examined. We also found that nonhydrogenated models all result in better fits to both the neutron diffraction and PDF data than the hydrogenated models, consistent with ref 7.

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