Abstract

Layered double hydroxides (LDHs) occur naturally and are synthesised for catalysis, drug delivery and contaminant remediation. They consist of Me(II)-Me(III) hydroxide sheets separated by hydrated interlayers and weakly held anions. Often, LDHs are nanocrystalline and sheet stacking and Me(II)-Me(III) arrangement can be disordered, which influence reactivity and complicate structural characterisation. We have used pair distribution function (PDF) analysis, to provide detailed information about local and medium range order (< 9 nm), to determine the structure of synthetic Fe(II)-Fe(III)/Al(III) LDH. The data are consistent with ordered Me(II) and Me(III) in hydroxide sheets, where structural coherence along the c axis decreases with
increasing Al content. The PDF for Fe(II)-Al(III) LDH (nikischerite) is best matched by a pattern for a single metal hydroxide sheet. Parallel to decreased structural coherence between layers, coherence within layers decreased to ~6 nm for synthetic nikischerite. Thus, disorder developed within and between the sheets, resulting in mosaic crystals with coherent scattering domains decreasing in all directions. The high density of grain boundary terminations would affect reactivity. Based on classical nucleation theory and the Kossel crystal growth model, we propose that loss of structural coherence stems from increased supersaturation and the presence of Al-hydroxides during formation of the Al-rich LDH.

1. Introduction

Layered double hydroxides (LDH) consist of metal hydroxide layers that contain both divalent and trivalent metals (Me(II) and Me(III)), that are separated by interlayers with loosely held water, anions and sometimes, cations. The metals of the hydroxide layers are octahedrally coordinated, connected by edges, yielding a structure where the metals can be easily substituted. A wide range of Me(II) and Me(III) can be accommodated, at variable ratios.¹ The incorporation of Me(III) in the hydroxide layers results in excess positive charge, that is compensated by intercalation of anions in the hydrated interlayers. Cl⁻, SO₄²⁻, and CO₃²⁻ are the most common anions in synthetic and natural LDHs but more exotic anions can also be intercalated, including larger organic anions. Once intercalated, anions can be replaced by ion exchange, analogous to the cation exchange of silicate clay minerals. The diversity in LDH composition and their anion exchange capacity has attracted considerable attention in materials science, where LDH compounds are investigated for a range of purposes, such as catalysts and catalyst support, vehicles for drug delivery and anion exchangers for environmental remediation. e.g., 2, 3, 4, 5
Although much progress has been made in understanding the nature of LDH and how to manipulate it, several fundamental aspects about its structure are poorly defined and remain controversial. Better understanding of structure and the degree of ordering would improve prediction of LDH properties. Theoretically, the Me(II) and Me(III) in the hydroxide layers can be perfectly ordered at certain Me(II):Me(III) ratios, e.g., 2 and 3, but the actual arrangement has been reported to range from fully ordered\(^6\) to disordered or outright random.\(^7,8\) For example, a seminal study interpreted that order developed when Me(II) and Me(III) had comparable ion size\(^9\) but later work showed that order can also develop in unequally matched Me(II/III) such as Mg(II) and Al(III) in hydrotalcite.\(^10\) Because LDH crystal size is often small and the stacking sequence of the hydroxide layers can be disordered, unambiguous determination of cation ordering is difficult using traditional techniques, such as laboratory based X-ray diffraction.\(^11\)

Here, we focus on the order and disorder in LDH with Fe(II) and the common trivalent cations, Fe(III) and Al(III). The presence of Fe(II) confers redox reactivity to LDH, making them attractive reactants for reduction of contaminants in environmental engineering and important for understanding natural redox reactions in the Earth sciences. The Fe(II)/Fe(III) variant, green rust (GR), is a product of corrosion\(^12\) and can reduce a range of contaminants thereby immobilising them. Examples include U(VI), Cr(VI) and Np(V).\(^13,14,15,16\) In addition, chlorinated ethenes, such as trichloroethylene, which pose a significant environmental threat, can be degraded rapidly by green rust in combination with bonechar.\(^17\) GR can form during bacterial iron reduction\(^18\) and its presence in nature has been reported.\(^19,20,21\) Laboratory work shows that green rust can reduce nitrate at appreciable rates,\(^22\) meaning abiotic nitrogen reduction by GR could be significant in soils and sediments. Finally, experiments indicate that GR is likely to have formed in Archean oceans, with potentially important implications for ancient marine environments.\(^23\)
The Fe(II)-Al(III) LDH, also known as nikischerite and classified within the wermlandite group, is also redox active and can readily form at circumneutral to slightly acidic pH from adsorption of Fe(II) to aluminium oxides and to aluminium containing phyllosilicate clay minerals. This suggests that Al(III) and Fe(II) bearing LDH, either as a pure phase or as Al(III) substituted green rust, could be quite common at redox boundaries where bacterial iron reduction occurs.

Aspects of the redox activity of GR and nikischerite can, however, vary fundamentally. Based on circumstantial experimental evidence, several studies have suggested that electrons are mobile in GR, similar to what has been observed for Fe(III)-(oxyhydr)oxides. Modelling supports this hypothesis, predicting appreciable electron mobility, in particular within the hydroxide sheet, through hopping as small polarons. From the perspective of cation ordering in the hydroxide layers, this could mean that the electrons can redistribute themselves during and after synthesis to produce an Fe(II) and Fe(III) distribution, that minimises crystal energy. Aluminium, on the other hand, has no divalent state so its valence would be unaffected by electron mobility and the element would have to resort to diffusion to redistribute in the lattice.

The aim of this work was to characterise the order and disorder of LDH with a range of Al(III) in the sodium and sulphate bearing GR - nikischerite series (NaFe(II)<sub>x</sub>Fe(III)<sub>x</sub>Al(III)<sub>3</sub>·x(OH)<sub>18</sub>(SO<sub>4</sub>)<sub>2</sub>·12 H<sub>2</sub>O, where 0 < x < 3) and determine the controls on ordering. Materials were synthesised in the laboratory and characterised using synchrotron X-ray pair distribution function analysis, a technique able to resolve material structure even when only local or medium range order exists. The new structural insights were complemented with Mössbauer spectroscopy and transmission electron microscopy (TEM).
2. Materials and Methods

2.1 Synthesis

We used an anaerobic chamber (Coy Laboratory Products) for synthesis and sample preparation. Temperature was ~26 °C and the N₂/H₂ atmosphere (H₂ ≈ 2%) was maintained anoxic using palladium pellets to remove O₂ (< 20 ppm detection limit). Prior to use, all labware was cleaned with 1 M HCl and rinsed three times with deionized water (DI, resistivity = 18.2 MΩcm).

Reagent grade 0.25 M FeSO₄·7H₂O, 0.1 M NaOH and 0.25 M Al₂(SO₄)₃·7H₂O were used to prepare three stock solutions with DI water, which had previously been deoxygenated by N₂ purging for 4 h.

All LDH was synthesised following the constant pH oxidation method. 34 150 mL of 0.05 M Fe²⁺ solution was prepared by filtering (0.22 µm) an aliquot of the FeSO₄·7H₂O stock solution and diluting it with deoxygenated DI water inside a Teflon beaker. For Al-LDH syntheses, the total cation concentration was kept constant (nFe²⁺ + nAl³⁺ = 0.05 M) but the Al molar fraction of was increased to xₐl = 0.03, 0.1, 0.2 and 0.33, with xₐl = nAl³⁺/(nFe²⁺+nAl³⁺). Oxidation at constant pH 7 was performed by sparging the solution continuously with CO₂ free air (cleaned using a 1 M NaOH trap) and automatic base addition by a titrator system (785 DMP Titrino, Metrohm with Ag/AgCl pH-electrode). For these materials, the onset of Fe(II) bearing LDH formation was visible by the blue-green colour of the suspension. LDH synthesis was complete when the NaOH addition rate suddenly decreased. Based on trial experiments, the synthesis was stopped shortly before this inflection point, to minimise formation of other Fe oxides, such as goethite and magnetite. For xₐl = 0.33, the synthesis was performed without O₂ oxidation to prevent the formation of Fe(III) and its incorporation in the product. The experiment was terminated when about 16 mL of 1M NaOH had been titrated to the solution. The resulting suspension was white with a slightly bluish tint. Wet solid samples for characterisation were obtained by centrifugation and removal of the supernatant.
2.2 Analytical methods

Transmission electron microscopy (TEM): A small amount of the wet solid was resuspended in deoxygenated DI water. A 3 µL drop of the suspension was placed on a formvar/carbon coated copper grid and dried for 30 minutes. The specimen was placed in an air-tight container and transported to the TEM (Phillips CM 20) for imaging at an accelerating voltage of 200 kV.

Mössbauer Spectroscopy (MS): LDH slurries with approximately 24 g/L Fe were prepared by centrifugation and resuspension in a smaller volume of supernatant. The slurries were put into Plexiglas sample holders and then capped with silicon grease. When ready, the samples were taken out of the anaerobic chamber, quickly shaken and then dropped immediately into liquid nitrogen, to protect the material from oxidation during transport (about 1 hour) to the spectrometer. $^{57}$Fe Mössbauer spectroscopy was carried out at 80 K, using constant acceleration spectrometers with $^{57}$Co in Rh as the source. The zero point velocity for the spectra was calibrated to that of $\alpha$-Fe metal. Absorption lines in the spectra were fitted with Lorentzian peak form with line widths and intensities of the absorption pairs constrained to be identical.

Synchrotron pair distribution function (PDF) analyses: Wet solids were dried inside the anaerobic chamber, crushed with a mortar and pestle and loaded into glass capillaries (0.9 mm inner diameter; Mark Röhrchen). The tubes were sealed with paraffin and placed in airtight containers for transportation to the Advanced Photon Source, Argonne National Laboratory, USA. We demonstrated that highly oxygen sensitive samples remained anoxic for at least 1 week when prepared this way. $^{35}$High energy X-ray scattering measurements were made at the 11-1D-B beamline (58.6 keV, $\lambda = 0.2114$ Å), using a 40 × 40 cm amorphous Si 2D detector (Perkin-Elmer) and a sample-to-detector distance of ~16 cm. A CeO$_2$ standard was used to calibrate the sample-to-detector distance and the tilt angle with respect to the beam path. In addition to the samples, we measured an empty glass capillary for background correction and a
goethite standard for determining the instrument parameters. The 2D data were polarization corrected and azimuthally integrated to 1D scattering patterns using the software Fit-2D. 36,37 PDFs were obtained from the scattering patterns using PDFgetX2. 38 Standard data processing in PDFgetX2 included background subtraction, normalization, and corrections for angular dependent, nonlinear detector efficiency and incoherent scattering. Because the reduced scattering structure function, $F(Q)$, i.e. $Q[S(Q) - 1]$, for some samples contained spikes at $Q > 22 \text{ Å}^{-1}$, the Fourier transform included data only to $Q_{\text{max}} = 22 \text{ Å}^{-1}$. In the data treatment, the composition of the samples was assumed to be $\text{NaFe(II)}_x\text{Fe(III)}_{3-x}\text{Al(III)}_{3-x}(\text{OH})_{18}(\text{SO}_4)_2\cdot 12\text{H}_2\text{O}$ for the layered double hydroxides, with $x$ derived from the Fe(III)/Fe(II) ratio in Mössbauer spectra or assumed to be 0 for the unoxidised, synthetic nikischerite.

**Atomic absorption spectroscopy:** To determine the time dependent decrease in dissolved Fe(II) during LDH synthesis, 0.5 mL samples were removed at regular time steps, centrifuged and the supernatant filtered ($0.2 \mu\text{m}$) and acidified (2% nitric acid) for subsequent analysis using atomic absorption spectroscopy (AAS, Perkin Elmer AAnalyst 800). The measured absorbance was compared to a series of Fe standards prepared and measured the same way.

### 3. Results and Discussion

#### 3.1 Pair distribution function analysis

Figure 1 depicts the intensity of scattered X-rays as a function of the magnitude of the scattering vector, $I(Q)$, for various $\text{Al(III)}/(\text{Al(III)}+\text{Fe(III)})$ molar ratio in the solid (denoted $x_{\text{Al}}$). $Q$ is inversely related to the spacing between lattice planes, $d$, with $Q = 2\pi/d$. All samples show pronounced peaks at $Q \approx 0.57, 1.14$ and $1.71 \text{ Å}^{-1}$, the positions expected for the basal plane reflections for GR ($x_{\text{Al}} = 0$)39 and nikischerite ($x_{\text{Al}} = 0.33$)40. With increasing $x_{\text{Al}}$, the peaks
broaden somewhat. In contrast, peaks located at \( Q \approx 2.35 \text{ to } 3.67 \text{ Å}^{-1} \), which often represent \((0kl)\) reflections (Figure 1B), substantially decrease in intensity as the proportion of Al increases.

They broaden considerably and shift position. Such preferential decrease in the intensity of many \((0kl)\) peaks is expected from disordered stacking along the \( c \) axis.\(^1\),\(^9\)

The first part of the PDF pattern at \( r < 11 \text{ Å} \) largely reflects the structure of the electron dense metal (Me) hydroxide sheet (Figure 2A) and does not include correlations across the interlayer from atomic pairs located in different hydroxide layers, which are separated by \( \sim 11 \) Å. The first intense peak at \( \sim 2.1 \text{ Å} \) has contributions from first neighbour Me-O pairs. The second intense peak at \( \sim 3.15 \text{ Å} \) results from first neighbour Me-Me pairs in edge sharing octahedra. Based on inspection of the structure of the metal hydroxide sheet, the next two peaks at \( \sim 4 \text{ Å} \) and \( \sim 5 \text{ Å} \) stem from Me-O pairs, followed by three intense peaks from Me-Me pairs. These peaks are present for all samples, a signature of the local bonding environment expected for the LDH structure. With increase in \( x_{\text{Al}} \), many peaks shift position towards lower \( r \), reflecting substitution of Fe(III) for the smaller cation, Al(III). In addition, a small amount of Al could be present as an Al hydroxide with coherent scattering domains of a size that make them difficult to detect. An example of a PDF from a precipitate formed in a solution with only \( \text{Al}_2(\text{SO}_4)_3 \) is presented in Figure SI1. This compares with the small peak at \( r \approx 2.8 \text{ Å} \) in the PDF for the sample with \( x_{\text{Al}} = 0.33 \) (Fig. 2A and B), which corresponds in position to that of the second peak in the precipitate from \( \text{Al}_2(\text{SO}_4)_3 \) solutions (Fig. SI1) and to the peak expected for O-O and edge sharing Al-Al atomic pairs in basaluminite (\( \text{Al}_4(\text{OH})_{10}(\text{SO}_4)_4\cdot4\text{H}_2\text{O}) \)).\(^4\) Thus, we cannot fully exclude that a small amount of basaluminite is present alongside the LDH.

The first intense peak at \( \sim 2.1 \text{ Å} \) (Me-O pairs) broadens with increasing \( x_{\text{Al}} \), its maxima shifts to higher \( r \) and a shoulder develops towards lower \( r \) (Figure 2B). This shows that several atom pairs, with differences in \( r \), contribute to the peak, i.e., Fe(II)-O, Fe(III)-O, and Al-O in Al-LDH samples. Similar distinct Me-O distances in LDH have been observed previously with X-ray
absorption spectroscopy e.g., and PDF. To deconvolute the first Me-O peak into 2 (for GR) and 3 components (for Al-LDH), Gaussian fitting was applied, minimising the sum of squared residuals between measured and calculated patterns (Figure 2B; method in Supplementary Information). In the fitting, the effects on the PDF from the sloping base line, instrument dampening and size of coherent scattering domains were ignored. To constrain the fit, the peak for LDH with \( x_{Al} = 0 \) was first fit with two Gaussian shaped contributions, where relative areas were constrained to 2.3, based on the Fe(II)/Fe(III) ratio determined with MS (ignoring slight differences in electron density of Fe(II) and Fe(III)). Next, the pattern for nikischerite with \( x_{Al} = 0.33 \) was fit with three Gaussian contributions where position and FWHM of the contributions were set to the values determined for pure GR but their intensity was optimised. In addition, the position of the Al-O contribution was set to 1.895 Å based on the ionic radii presented by Shannon for octahedrally coordinated Al and O in threefold coordination and the peak intensity and FWHM was fit. Finally, the PDFs for GR with \( x_{Al} = 0.03, 0.1, \) and 0.2 were fit by setting positions and FWHM's to those already derived and allowing only intensity to vary.

The 2-component fit for GR gave distances of 2.13 Å for Fe(II)-O and 2.00 Å for Fe(III)-O, which agree well with data from Shannon as well as the peak positions for Fe(II)(OH)\(_2\) and a range of Fe(III) oxides. For Al-LDH samples, where the Al-O distance was constrained to 1.895 Å, the FWHM for the three Me-O pairs decreased with a decrease in cation radius, with values for the Gaussian peaks of 0.26 Å for Fe(II)-O, 0.24 Å for Fe(III)-O and 0.17 Å for Al-O. This suggests that thermal or static atomic displacement of oxygen atoms affects the longer and weaker Fe(II)-O bond more, which is reasonable. Finally, the calculated Fe(III)/Fe(II) ratios from the area of the Gaussian peaks are consistent with those determined from Mössbauer spectroscopy (Figure 2D; Figure SI2; Table SI1).

For the second intense peak in the PDF, representing first neighbour Me-Me distance, a single Gaussian contribution fits the peaks well (Fig. 2B) and yields peak positions decreasing from...
3.17 Å for $x_{Al} = 0$ to 3.12 Å for $x_{Al} = 0.33$, correlating with the Al/Fe(II) ratio derived from the PDF data (Figure SI3). This shows that the structural changes induced by Al incorporation during synthesis are systematic. The FWHM derived from the fitting changes slightly with increasing $x_{Al}$, from ~0.24 Å for GR to ~0.25 Å for intermediate Al-Fe(III) LDH and ~0.23 Å for nikischerite (Fig. 2C). Although the width represents both thermal and static atomic displacement, the trend is consistent with intermediate $x_{Al}$ resulting in some disorder in the hexagonal pattern of the metals. This would be expected for substitution involving two differently sized ions.

The changes in Me-Me distance and peak width suggests that the Me part of the lattice contracts fairly uniformly in response to Al incorporation, with some disorder for intermediate $x_{Al}$, whereas the marked changes of the Me-O distance indicate that oxygen in the hydroxyl becomes substantially displaced. Given the Me-O and Me-Me distances, we can determine the distance between O atoms that link two edge sharing metals, based on Heron's formula\(^4\) (details in Figure SI4). Calculations for Fe(III)-Fe(II) and Al(III)-Fe(II) configurations yield O-O distances of 2.64 Å and 2.53 Å, i.e. a decrease in the O-O distance for O atoms that coordinate Al(III) to a value approaching the expected 2.44 Å for closest packing, from ionic radius from Shannon.\(^4\)

For an ideal LDH structure, where all O atoms are identically coordinated within the hydroxide sheet (i.e. to one Me(III) and two Me(II), ignoring weaker bonding to interlayer atoms), shortening of O-O distance would most likely occur by contraction of the sheet along the $c$ axis as well as by rotation of the top and bottom O-triads of the Me(II) octahedra to bring the O atoms closer to each other. Such a model is consistent with that proposed by Bellotto et al.\(^9\)

However, if the metals are randomly positioned but at Me-Me distances from the PDF fitting, O-O distances for Al(III)-Al(III) configurations would have to be very short, 2.14 Å.

In the full PDF, the pattern for the GR with $x_{Al} = 0$ has peaks from atoms with correlated positions up to ~90 Å (Figure 3). Compared with the pattern measured for a well crystalline
goethite standard, this decay in peak intensity primarily reflects instrument resolution. As Al content increases, the oscillations extend to progressively shorter distances, reflecting a decrease in the size of the coherent scattering domains, as low as ~60 Å for $x_{\text{Al}} = 0.33$. At $r$ values ranging from 12 - 26 Å, where peaks from atom pairs in different Me hydroxide sheets contribute to the pattern, the PDFs also show very distinct differences with increasing $x_{\text{Al}}$ (Figure 4). Peak positions are offset to lower $r$ for the Al-LDH, reflecting contraction of the crystal structure, and some peaks show very large changes in intensity, whereas others do not, suggesting that the progressive structural alterations are anisotropic. Given the appearance of the $I(Q)$ (Fig. 1), this most likely reflects disarray of the arrangement of hydroxide sheets in the $c$ direction because of stacking disorder. To assess the impact of stacking disorder along the $c$ axis on PDFs at $r > 11$ Å, the PDF of a single Fe(II)-Fe(III) hydroxide sheet with a diameter of 6 nm was calculated with the software DiffPy-CMI, based on the structure by Christiansen et al. and subtracted by the PDF calculated for a bulk GR crystal (red line with superposed fat dashed line in Fig. 4). This calculated differential PDF (i.e., single sheet - bulk crystal) corresponds well with the difference in PDFs between experimental samples with $x_{\text{Al}} = 0.33$ and $x_{\text{Al}} = 0$. Thus, both intra- and intersheet structural coherence decreases as $x_{\text{Al}}$ increases. At $x_{\text{Al}} = 0.33$, the sample has very little structural coherence between layers and the coherence within the metal hydroxide layer is on the order of 6 nm.

### 3.2 Interpreting the changes in structural coherence

Several aspects of the material could lead to the observed decrease in structural coherence. Particle size, for example, might be very small, with dimensions similar to those determined for the coherent scattering domains. TEM images of the materials are shown in Figure 5. GR samples show well developed hexagonal particles with an average width of ~300 nm. With increasing $x_{\text{Al}}$, average particle width decreases to about ~40 nm for $x_{\text{Al}} = 0.33$. At this Al
content, particles were sometimes observed in an upright position in the images (example in insert of Fig. 5D), allowing measurement of particle thickness, which ranges from about 4 to 10 nm. Clearly, the width and thickness of particles are much larger than the dimensions of the coherent scattering domains from PDF.

Pair distribution function analysis of glassy carbon has shown that sheet bending in layered solids can result in significant decrease in the dimensions of the coherent scattering domains within the sheets. Upright particles in TEM images sometimes display bending with a radius of curvature of about 100 nm (example in insert in Fig. 5D). To determine if such bending could explain our observations, PDFs were calculated for variably curved, 18 nm wide single Me hydroxide sheets with $x_{\text{Al}} = 0.33$, using the nikischerite structure. Appreciable changes in the calculated PDF occur only at a radius of curvature of about 12.5 nm (Figure SI5). Such a radius of curvature would mean that the average particle, if composed of a domain as wide as the particles, would have to curl back on itself to produce a nanotube. Although GR has been observed to form nanotubes, we did not observe them in these experiments. Thus, particle curvature cannot explain the observed decrease in structural coherence within the metal hydroxide sheet.

Previous studies using PDF have shown that static disorder in crystals results in broader peaks and more extensive decay of peak intensity with increasing $r$, than would be expected from ideal materials. To probe if the peaks in measured PDFs are different in width from those expected for an ideal structure, calculated PDFs based on three structural models with ordered distribution of Me(II) and Me(III) were fit to the data for the end member samples, i.e. where $x_{\text{Al}} = 0$ and $x_{\text{Al}} = 0.33$, using the software PDFgui and DiffPy-CMI. Details about the structures and the fitting are given in the Supplementary Information, Section 2.

The PDFgui fits for a bulk crystal for the sample with $x_{\text{Al}} = 0$ are shown in Figure 6 and Table SI2. Residuals of the fit are presented in Figure SI8. Both models yield realistic values for fitting
parameters, including larger displacement parameters, \( U_{\text{iso}} \), for interlayer atoms. This has also been observed for intercalated iodide\(^{42} \) and the calculated and measured patterns agree reasonably well, with a simpler P 3 model achieving better agreement for low \( r \) peaks and slightly poorer agreement for higher \( r \) compared to the model by Christiansen et al.\(^{39} \). For the sample with \( x_{\text{Al}} = 0.33 \), which showed very little structural coherence across interlayers, fitting was performed in two steps. First, the Huminicki and Hawthorne\(^{40} \) and the P 3 bulk structures were fit in PDFGui to the data, ranging from 1.7 - 10 Å, where correlations across interlayers did not contribute. Based on these results, the structure for single Me-hydroxide sheets, 6 nm wide were constructed and fit using DiffPy-CMI. For both structures, the calculated patterns were very similar, agreed reasonably with the measurements and gave realistic values for the fitting parameters (Fig. 6 and Table SI2). Although both patterns showed some discrepancy from the measured PDF, measured peaks are not systematically broadened as \( r \) values increased compared with those expected for the ideal, calculated structures. Thus, the PDF showed no resolvable signs of disorder in the atomic arrangement within the Me hydroxide sheet, that could explain the observed decrease in the length scale of the structural coherence.

### 3.3 Structural coherence: Implications and causes

Modelling suggests that electrons are mobile in GR, hopping as thermally activated, small polarons between Fe atoms.\(^{33} \) Alternatively, intervalence charge transfer has been proposed to be responsible for the green-blue colour of LDH,\(^{53} \) as for other iron bearing minerals.\(^{54} \) Regardless of whether electron transfer is caused thermally or by absorption of light, Fe(II) and Fe(III) might rearrange to give an ordered Me(II)-Me(III) distribution within the metal hydroxide layer. Indeed, high resolution AFM shows a pattern with superstructures, where periodicities are consistent with an ordered arrangement of Fe(II) and Fe(III) in the hydroxide layer.\(^{39} \) In contrast, for Al-bearing samples, reordering of Me(II)-Me(III) would require
diffusion of Al(III) if initial ordering is not achieved. Thus, a hypothesis at the outset of our work was that incorporation of Al in the Me hydroxide layer might give rise to disorder in cation distribution. Our PDF data indicate increased Me-Me distances at intermediate $x_A$, but short distances for the endmembers with $x_{Al} = 0$ and 0.33 (Figure 2). Given that AFM data indicate Fe(II) and Fe(III) ordering for GR$_{Na,SO_4}$, the variation of Me-Me distances suggests that both endmembers are ordered but that coexistence of both Fe(III) and Al(III) causes structural relaxation. The satisfactory fitting of the endmember PDFs substantiates this interpretation. Thus, we interpret that both GR$_{Na,SO_4}$ and nikischerite have a high degree of cation ordering at local and intermediate range. Hence, our data neither confirms nor contests that electrons are mobile in green rust.

Our data indicate that structural coherence decreases both within layers and between them as the Al content increases. Lack of structural coherence between layers, i.e., stacking disorder, arises easily in layered materials, such as silicate clays and carbon, which have strong bonds within layers and much weaker bonds between layers. For LDH, the translation of structure from one hydroxide layer to the next is generally considered to occur largely through hydrogen bonds between the hydroxyl groups of the metal hydroxyl layer, the water and ions in the interlayer. Mapping the strength and directionality of the hydrogen bond network is no simple task. As a first approximation, the smaller size of Al(III) should render it more polarising, resulting in stronger hydrogen bonds from the hydroxyl groups. Using the dynamics of water shells coordinating to Me ions as an analogue, Al(III) possesses slower exchange kinetics for water in the first shell than Fe(III) and it is among the highly polarising Me(III) that have strong hydrogen bonding from the first shell water to those of the second shell. Based on modelling, this results in approximately 4 times longer residence time for second shell water bonding to Al(III) than for Fe(III). Thus, it is not clear that substitution of Al(III) in the hydroxide sheets would weaken hydrogen bonding and facilitate disarray in the stacking order,
nor that it would cause concomitant decrease in the length for the structural coherence within the hydroxide layers.

In the absence of obvious causes from crystallography and crystal chemistry for the coupled loss of coherence along all crystallographic axes, we turned to aspects of how the materials formed, i.e. nucleation and growth. These processes are controlled by several aspects of the system, such as the surface free energy at the interfaces and the presence of foreign ions and particles, e.g. 60 but they depend critically on the supersaturation, $\Omega$:

$$\Omega = \frac{IAP}{K_{sp}},$$

where $K_{sp}$ refers to the solubility product and $IAP$ to the product of the actual activities of the ions, both with reference to the reaction:

$$\text{Na}^+ + 6\text{Fe}^{2+} + x\text{Fe}^{3+} + (3-x)\text{Al}^{3+} + 18 \text{OH}^- + 2\text{SO}_4^{2-} + 12 \text{H}_2\text{O} \rightleftharpoons \text{NaFe(II)}_6 \text{Fe(III)}_x \text{Al(III)}_{3-x} (\text{OH})_{18} (\text{SO}_4)_2 \cdot 12 \text{H}_2\text{O}$$

A study of the relative stability of a range of Fe(III) and Al(III) LDH with interlayer chloride indicates that the Al(III) versions are more stable than the Fe(III) counterparts with respect to their Me(III) hydroxides. 61 For a simplified reaction equation:

$$2\text{Me}^{2+} + \text{Me(III)(OH)}_{3(s)} + 3 \text{OH}^- + \text{Cl}^- \rightleftharpoons \text{Me(II)}_2 \text{Me(III)(OH)}_6 \text{Cl}_{(s)},$$

they determined equilibrium constants for LDH that were ~1000 fold higher on average for the Al(III) LDH, reflecting higher solubility for Al(III) hydroxides. In our experiments, the source of Al(III) is nanocrystalline basaluminite and the Fe(III) activity is unlikely to have greatly exceeded ferrihydrite solubility. Given that the bulk pH and Fe(II) concentration in all our experiments are the same, these considerations indicate that the Al-rich LDH most likely formed at significantly higher saturation state, $\Omega$. A higher stability of Al(III)-bearing LDH with respect
to Me(III)-(oxyhydr)oxides should entail lower aqueous Fe(II) concentrations, i.e. a shift in
equilibrium toward products in Eq. 3. Consistent with this, the Fe(II) concentration determined
during LDH formation and subsequent oxidation to Me(III)-(oxyhydr)oxides was lower for the
material produced at $x_{Al} = 0.12$ than for $x_{Al} = 0$ (Figure SI9).

Higher $\Omega$ in experiments containing Al(III) and the presence of nanocrystalline basaluminite
would be expected to have had several implications:

1. Nucleation rate for crystals increases with increasing supersaturation e.g., $60, 62, 63$; details on the
rates of nucleation in the Supplementary Information, Section 3). Thus, LDH with smaller
particle sizes should have formed in experiments with higher $x_{Al}$, where $\Omega$ was most likely
higher. Moreover, nucleation in the experiments with Al(III) occurred in the presence of
basaluminite particles, which could act as a substrate for faster heterogeneous nucleation of
LDH, if interfacial tension is favourable. If so, even more, smaller LDH particles would have
formed. These considerations are consistent with our TEM images (Figure 5), which show
decreasing particle size with increasing $x_{Al}$.

2. The manner by which crystals grow is also affected by the value of $\Omega$. The Kossel model of a
crystal surface consists of flat terraces, steps linking adjacent terraces and kinks on the steps. $64$
At these three types of growth sites, attachment of ions to produce growth occurs progressively
faster and requires decreasing values of $\Omega$. e.g., $60$ Hence, growth at kinks and steps occurs quickly
until the active sites here are depleted. Establishment of growth on top of a terrace requires
nucleation of a new layer through a process akin to regular nucleation (termed 2D nucleation;
details in SI Section 3). Similar to crystal nucleation, the rate of 2D nucleation increases with $\Omega$.
The process can also be favoured by the presence of foreign particles on the surface of a growing
crystal when surface free energies favour wetting of the foreign particle by the 2D nucleus.
Thus, the presence of nanocrystalline basaluminite might well have decreased the energy barrier
(and rate) for 2D nucleation.
3. In general, increased $\Omega$ means that formation of metastable, and sometimes disordered phases, become possible. Examples of disordered phases include dense liquids e.g., and amorphous solids (e.g. amorphous calcium carbonate). For Mg-Al LDH, high temperature oxide melt solution calorimetry indicates that stacking faults produce a solid that is metastable with respect to the ordered material, with faults originating from kinetic reasons. Thus, the faster reaction rates that are expected as $\Omega$ increases with $x_{Al}$, could mean that lack of structural coherence in the direction of stacking would develop.

Taken together, these considerations indicate that the increased $\Omega$ and the presence of foreign particles in experiments with Al(III) could well result in rapid nucleation of particles and growth characterised by more numerous 2D nucleation events, producing 2D islands that i) are structurally incoherent with respect to the layer beneath and to each other and ii) grow until pinned by other islands. The outcome of this would be small particles, consisting of sheets with decreased structural coherence lengths, both internally and between sheets, as we observe.

Generally, the Kossel model for crystal growth predicts a shift from spiral growth, where steps and kinks are generated continuously at low supersaturation, to growth by 2D nucleation at higher saturation. Growth spirals have recently been observed for Zn-Al LDH grown at low supersaturation. Our results suggest that growth of LDH in general conforms to the expectation from the Kossel model, with 2D nucleation taking place at higher saturation. In addition, our results suggest that the weak bonding between sheets in LDH allows for nucleation and growth of 2D islands that are an isolated structurally coherent entity, leading to formation of mosaic crystals. Such crystals would have a high density of internal grain boundaries, where surface termination at the LDH edges could be highly reactive.

Acknowledgements
This work was partly funded by the European Union’s Horizon 2020 Research and Innovation Programme Metal-Aid (Marie Skłodowska-Curie grant agreement No. 675219). D.J.T. acknowledges financial support from MIRO (PIEF-GA-2013-624619), a Marie Curie Intra-European Fellowship (IEF). This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. D.J.T and K.D. are thankful for assistance provided during beam time from Olaf Borkiewicz and Kevin A. Beyer at APS beamline 11 ID-B, APS, and for financial support for travels to APS from the Danish Council for Independent Research (via DANSCATT).

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Figure captions

Figure 1. A) I(Q) of samples synthesised with variable Al content (xAl). B) Zoom of I(Q) to show peaks from Q = 2 to 4.5 Å. Peaks are assigned (hkl) based on the structure for GR(Na,SO₄) given by Christiansen et al.³⁹

Figure 2. A) PDF peaks in the r range 0-12 Å with indications of the atomic pairs contributing dominantly to peak intensity. B) The first neighbour Me-O and Me-Me peak and the Gaussian
fitting (grey: individual components; black: sum of components). C) Me-Me peak widths expressed as the full width at half maximum intensity as a function of $x_{Al}$. D) Fe(III)/Fe(II) ratio at varying $x_{Al}$ derived from fitting the PDF with Gaussian shaped contributions (B) and measured with MS.

Figure 3. PDFs for interatomic distance, $r$, ranging from 0-100 Å. The short, black lines indicate the approximate size of the coherent scattering domains.

Figure 4. Zoom of PDFs in the $r$ range 12-26 Å and differential PDFs between i) the patterns measured for $x_{Al} = 0.33$ and $x_{Al} = 0$ (grey line) and i) the calculated patterns for a single green rust sheet and a bulk green rust crystal (red striped line). The coordination number for Fe-Fe pairs within layers are given as black numbers and those between layers, as grey numbers. Measured and calculated patterns have been normalised to give same intensity for the first Me-Me peak at about 3.15 Å.

Figure 5. TEM of LDH with $x_{Al} = 0$, 0.03, 0.1 and 0.33. All scale bars represent 100 nm. Insert in Figure 5D showing bending particle. The uncertainty represents that associated with the average width of particles at 2 standard errors. One standard error equals the standard deviation divided by the number of observations ($n$).

Figure 6. Measured and calculated patterns after fitting crystal models to the data for A) GR(Na$_2$SO$_4$) ($x_{Al} = 0$) and B) nikisherite ($x_{Al} = 0.33$).
Figure 1
Figure 2
$G(r)$

$\alpha = 0$

$\alpha = 0.03$

$\alpha = 0.1$

$\alpha = 0.2$

$\alpha = 0.33$

Figure 3
Figure 4
Figure 5
Figure 6
SUPPLEMENTARY INFORMATION

Order and disorder in layered double hydroxides: Lessons learned from the green rust sulphate - nikischerite series.

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⁵Department of Physics, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark

Content of the supporting information

The supporting information contains text with details about 1) the methods used for fitting the Mössbauer spectra and the results, 2) the crystal structures and methods employed in the fitting of the pair distribution functions as well as the results; and 3) a description of the theory for classical nucleation and 2D nucleation. In addition, it contains two tables and nine figures.
1. Mössbauer Spectroscopy (MS)

All MS spectra were fit with two doublets for Fe(II) (D$_1$) and Fe(III) (D$_2$) (Figure SI2), and their relative abundances, $R_A$, was used to determine the Fe(II):Me(III) ratio (Table SI1). In the pure GR sample, additional peaks from a magnetically ordered phase were observed, which were fitted with a sextet, S$_1$, yielding MS parameters characteristic of goethite (Table SI1). With increasing $x_{Al}$, a decrease in the spectral area for the D$_2$ component for Fe(III) was observed, showing a decrease in Fe(III) content with Al(III) substitution. Additionally, a broadening of the D$_1$ component (i.e. FWHM of Fe$^{II}$) was observed (Table SI1) with increasing Fe(II) content and Al(III) substitution. The Fe(III):Fe(II) ratio obtained for pure GR is 0.43 and compares well with the values reported in the literature for GR$_{SO_4}$, which range from 0.43 to 0.53. e.g., 2-4

2. Details about the fitting of the pair distribution functions (PDFs) for $x_{Al} = 0$ and $x_{Al} = 0.33$

For each PDF, we used 1) the corresponding model derived from structural refinement of powder or single crystal XRD$^{5,6}$ and 2) a simple common model based on P 3 symmetry. The structural model for nikischerite, NaFe(II)$_6$Al(III)$_3$(OH)$_{18}$(SO$_4$)$_2$$\cdot$12 H$_2$O, is rhombohedral, space group R-3, and has unit cell dimensions, $a \approx 9.35$ Å and $c \approx 33$ Å. $^6$ The unit cell encompasses three metal hydroxide layers and features distinct positions for interlayer SO$_4^{2-}$ and Na$^+$, reflecting a highly ordered material. Green rusts with sulphate show variation in both the spacing between hydroxide layer and the cation removability that depend on the identity of the monovalent cation, consistent with cations being placed in the interlayer. $^4$ The model for the Green rusts with sulphate and sodium (GR(Na,SO$_4$);
NaFe(II)$_6$Fe(III)$_3$(OH)$_{18}$(SO$_4$)$_2$·12 H$_2$O) was derived using the nikischerite model as a starting point. Because of stacking disorder of interlayer ions, the GR(Na,SO$_4$) model features a smaller trigonal cell, space group P-3, with $a \approx 9.53$ Å and $c \approx 11$ Å that encompass only a single hydroxide sheet. In this model, SO$_4^{2-}$ and Na$^+$ are placed in the interlayer space above and below all Fe(III) sites with an occupancy of 1/3, reflecting the lack of ordering of interlayer ions across metal hydroxide sheets. In addition, sulphate tetrahedra are rotated 30° compared to nikischerite structure, so that oxygen atoms at the tetrahedra base are oriented towards the neighbouring Fe(II) atoms, rather than being located almost directly above the top oxygens in the Me(III) octahedra (illustrated in Fig. SI6). To have a model where the positions of the O atoms in the metal hydroxide sheet could be more easily fitted, a simpler structure was constructed based on P 3 symmetry with either Fe(III) or Al(III) as the trivalent metal. In this model, the oxygens of the Me-hydroxide sheet are located in two planes (i.e., identical $z$ position) and the sulphate tetrahedra are located like for GR(Na,SO$_4$). Details about the P 3 structures are given below. For all models, the top and bottom oxygen triads of the Fe(II) octahedra are rotated with respect to each other to allow shorter Me(III)-O bonds (Fig. SI6).

The model parameters were fitted to decrease the squared residual between calculated and measured PDF using PDFGui (bulk crystals) and DiffPy-CMI (single sheets). For all fits, parameters included a scaling factor, a parameter to describe correlated atomic motion ($\delta^2$), the cell dimensions, and a set of isotropic displacement parameters ($U_{iso}$) for Fe(II), Me(III), O in the hydroxide sheet, O in the interlayer, Na, and S. For the P 3 models, the positions of the oxygens in the metal hydroxide sheet were also refined in both PDFGui and DiffPy-CMI fits, each top and bottom triad constrained to have
identical Me-O bond distance and O-O-O angles of 60 degrees. The P3 structure features two types of oxygen atoms, O1 and O2. To impose the three fold rotational symmetry operating on O1 and O2 in DiffPy-CMI calculations, two displacement vectors \((\nu)\) were fitted and imposed on the x and y positions of O1 and O2 as well as their symmetry equivalents after vector rotation by angle \(\theta\) equalling 120° and 240° (Fig. SI7).

**P 3 structure for green rust \((x_{Al} = 0)\)**

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_audit_creation_method  'generated by CrystalMaker X for macOS'

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_cell_length_b  5.495000
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_cell_angle_alpha  90.000000
_cell_angle_beta  90.000000
_cell_angle_gamma  120.000000

_symmetry_space_group_name_H-M  'P 3'

loop_

_symmetry_equiv_pos_as_xyz

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'-y,+x-y,+z'

'-x+y,-x,+z'
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P 3 structure for nikischerite ($x_{Al} = 0.33$)

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_cell_length_b 5.436000
_cell_length_c 10.970000
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_symmetry_equiv_pos_as_xyz

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'-y,+x+y,+z'

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loop_

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_atom_site_type_symbol

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Table SI1: Parameters obtained by fitting MS spectra obtained at 80 K.

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$\delta$ isomer shift, $\Delta$ quadrupole splitting, RA relative abundance
Table SI2. Parameter value obtained from fitting of the PDFs for material from synthesis with $x_{\text{Al}} = 0$ and $x_{\text{Al}} = 0.33$.

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<td>P 3</td>
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<td>Bulk structure</td>
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<td>0.027</td>
</tr>
<tr>
<td>$U_{\text{iso} \text{Na}}$ $(\text{Å}^2)$</td>
<td>0.045</td>
<td>0.021</td>
</tr>
<tr>
<td>Reduced chi squared</td>
<td>0.11</td>
<td>0.12</td>
</tr>
</tbody>
</table>
3. Rates of crystal nucleation and 2D nucleation

The nucleation rate ($J$) of crystals is classically described by:

$$J = A \exp \left( \frac{\Delta G^\prime_{\text{nuc}l}}{kT} \right),$$

(SI 1)

where $A$ is a preexponential factor related to the addition rates of monomers, the site density for nucleation and the probability for growth of a nucleus at the top of the energy barrier ($\Delta G^\prime_{\text{nuc}l}$), whose magnitude for a simplified spherical nucleus is given by:

$$\Delta G^\prime_{\text{nuc}l} = \frac{16\pi \gamma_{cw}^3 V^2}{3(kT\ln(\Omega))^2}.$$  

(SI 2)

Here, $\gamma_{cw}$ signifies the surface energy between cluster and water, $V$, the molecular volume of the nucleating substance, $k$, the Boltzmann constant ($1.38*10^{-23}$ J K$^{-1}$), and $T$, absolute temperature. Eqs. SI 1 and SI 2 are such that nucleation rate increases with increasing supersaturation and that a threshold value for $\Omega$ exists, above which nucleation rates become significant.

In the presence of a foreign surface, nucleation may occur heterogeneously. For heterogenous nucleation of a hemispherical nucleus on a flat surface, the energy barrier ($\Delta G^\prime_{\text{nuc}l(het)}$) is given by:

$$\Delta G^\prime_{\text{nuc}l(het)} = \frac{8\pi \gamma^\prime V^2}{3(kT\ln(\Omega))^2},$$

(SI 3)

where $\gamma^\prime$, denotes the effective surface free energy of the nuclei, which is given by:

$$\gamma^\prime = \gamma_{cw} \left(1 - \frac{\gamma_{sw} - \gamma_{cs}}{2\gamma_{cw}}\right).$$

(SI 4)
Here, $\gamma_{SW}$ and $\gamma_{CS}$ denotes the surface free energy between substrate and water, and
cluster and substrate. Different geometries of the nucleus and the substrate results in
variation in the mathematical expression for nucleation, e.g., $^{10}$ but its dependence on
saturation remains unchanged. Depending on the values of the surface free energy of the
interfaces, heterogeneous nucleation may greatly increase nucleation rates.

Within the Kossel crystal growth model, establishment of a new layer on top of a terrace
requires 2D nucleation, the energy barrier for which is given by:

$$\Delta G'_{2Dnuc} = \frac{h\pi\gamma_{cw}^{2}V}{kTln(\Omega)},$$

(SI 5)

where $h$ is the step height of the new layer. e.g., $^{11}$ Inspection of this equation shows that
the energy barrier decreases with $\Omega$, meaning that rates of 2D nucleation increase.

For heterogeneous 2D nucleation the energetics have been derived for cylindrical foreign
particles oriented with the axis perpendicular to the terrace and with a radius $R^c$. $^{11}$ For
this geometry, the energy barrier is given by:

$$\Delta G'_{2Dnuc(Het)} = \Delta G'_{2Dnuc} f(m, x),$$

(SI 6)

where $f(m,x)$ is a function of the angle, $\theta$, by which the 2D nucleus wets the foreign
particle:

$$m = \cos(\theta) = \frac{\gamma_{CS}-\gamma_{SW}}{\gamma_{cw}}$$

(SI 7)

and the ratio, $x$, between the sizes of foreign particles and the critical size of the 2D
nucleus ($r_c$):
\[ x = \frac{R^s}{r_c} = \frac{R^s kT \ln(\Omega)}{V \gamma_{cw}}. \]  

(SI 8)

Values for \( f(m, x) \) range from 1 to 0, decreasing with increasing values for \( x \) and \( m \). The outcome of these relationships is that heterogeneous 2D nucleation is highly promoted when surface free energies favour wetting of the foreign particle by the nucleus and when the size of the foreign particle is similar to or larger than the critical size of the 2D nucleus.

References


Figure Captions

Figure SI1. PDF for precipitate formed by titrating an Al$_2$(SO$_4$)$_3$ solution to pH 7.

Figure SI2. Mössbauer spectra of LDH with $x_{Al} = 0, 0.03, 0.1$ and $0.2$ with fitted components. Patterns were scaled to yield identical absorption at $v = -0.1$ mm/s.

Figure SI3. The Me-Me peak position as a function of Fe(III)/Fe(II) molar ratio. Both values were derived from peak fitting with Gaussian shaped contributions.

Figure SI4. Heron's formula describing the relationship between height and side lengths for a right angled triangle.

Figure SI5. PDFs of variously curved single Me hydroxide sheets ($x_{Al} = 0.33$) calculated with DiffPy-CMI. A 18 nm sheet based on the structure of Huminicki and Hawthorne were produced and bent with the software CrystalMaker. In the DiffPy-CMI calculations, scale and cell dimension was first fit to the r range 1.7 to 8 Å of the measured PDF, to have reasonably correct local structure. Then, the cell dimensions were fixed and only scale were fitted to optimise agreement between measured and calculated data in the r range 1.7 to 60 Å.

Figure SI6. Illustration of the structure of interlayer ions (top most) and hydroxides sheets (located below interlayer ions) in A) GR(Na,SO$_4$) and B) nikisherite. Oxygens are placed at the apices of polyhedra.

Figure SI7. Illustration of the imposed displacement vector and its rotation.
Figure SI8. Measured and calculated patterns as well as the residual after fitting crystal models to the data for A) GR(Na$_2$SO$_4$) ($x_{\text{Al}} = 0$) and B) nikisherite ($x_{\text{Al}} = 0.33$).

Figure SI9. Aqueous Fe(II) concentration determined for LDH with $x_{\text{Al}} = 0$ and $x_{\text{Al}} = 0.12$. The red and black lines indicate the onset of oxidative transformation of LDH to Me(III)-oxyhydroxides based on changes in base addition rates.
Figure SI1
Figure SI2
$h = \frac{1}{2} \text{O-O}$

$h^2 = b^2 - \left( \frac{-a^2 + b^2 + c^2}{2c} \right)^2$

Figure SI4
Figure SI5
Figure SI6
Vector $v = \begin{pmatrix} X_0 - X_1 \\ Y_0 - Y_1 \end{pmatrix} = \begin{pmatrix} \Delta X \\ \Delta Y \end{pmatrix}$

Vector $v_\theta = \begin{pmatrix} \Delta X \cos(\theta) - \Delta Y \sin(\theta) \\ \Delta X \sin(\theta) + \Delta Y \cos(\theta) \end{pmatrix}$

Figure SI7
**Figure SI8**

(A) $x_{Al} = 0$
- Christiansen et al. Bulk crystal
- P 3 Bulk crystal

(B) $x_{Al} = 0.33$
- Huminicki et al. Single sheet
- P 3 Single sheet

Fit
Residuals

$G(r)$ vs $r$ (Å)
Onset of oxidative transformation to Me(III)-(oxyhydr)oxides

Figure SI9