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### Reply to “Structural and magnetic behavior of the cubic oxyfluoride SrFeO<sub>2</sub>F studied by neutron diffraction”

Clemens, Oliver; Berry, Frank; Wright, Adrian; Knight, Kevin S.; Perez-mato, J.m.; Igartua, J.m.; Slater, Peter

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# Author's Accepted Manuscript

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## Reply to “Structural and magnetic behavior of the cubic oxyfluoride SrFeO<sub>2</sub>F studied by neutron diffraction”

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## Abstract

In this article we comment on the results published by Thompson et al. (Thompson, C. M.; Blakely, C. K.; Flacau, R.; Greedan, J. E.; Poltavets, V. V., *J. Solid State Chem.* **2014**, *219*, 173-178.) on the crystal structure of SrFeO<sub>2</sub>F, who claim the compound to crystallize in the cubic space group *Pm-3m*. We give a more detailed explanation of the determination of our previously reported structural model with *Imma* symmetry (Clemens, O.; Berry, F. J.; Wright, A. J.; Knight, K. S.; Perez-Mato, J. M.; Igartua, J. M.; Slater, P. R., *J. Solid State Chem.* **2013**, *206*, 158-169.), with addition of variable temperature XRD measurements with high counting time to provide unambiguous evidence for the *Imma* model being correct for our sample.

## Keywords

SrFeO<sub>2</sub>F; neutron diffraction; perovskite; magnetic scattering

## 1. Introduction

SrFeO<sub>2</sub>F is a perovskite compound which can be made by low temperature fluorination of SrFeO<sub>3-d</sub> using polyvinylidenedifluoride (PVDF) [1-4] or by low temperature fluorination of SrFeO<sub>2</sub> using XeF<sub>2</sub> [5, 6]. The detailed crystal structure has been subject to vivid discussion in literature. First reports on the compound by Berry et al. [2, 3] as well as Clemens et al. [1, 4] reported the material to crystallize in the cubic perovskite structure (space group *Pm-3m*). This structural arrangement was revised by Clemens et al. who studied the series La<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3-x</sub>F<sub>x</sub> by means of neutron diffraction, which was shown to be in agreement with a mode analysis of the obtained structural data [7]. Based on those analyses, the authors concluded that SrFeO<sub>2</sub>F is best described with an orthorhombic perovskite structure with space group *Imma*. In a recent article, Thompson et al. [5] contradict this structural description based on an analysis of temperature dependent neutron powder diffraction data (NPD) and report the compound to crystallize in the cubic space group *Pm-3m*. They state: "On the subject of different crystal symmetries, as mentioned in the Introduction, it has been proposed that *Imma* is the true space group for SrFeO<sub>2</sub>F [7]. ... Nonetheless, as mentioned earlier, the evidence for this symmetry is not strongly supported by the diffraction data as the unit cell is metrically cubic." Here, we would like to comment on the results published by Thompson et al. [5] and will give a more detailed description of our previous evaluation of the neutron

diffraction data recorded for SrFeO<sub>2</sub>F, showing that the compound cannot be appropriately described within the cubic structural model and that the *Imma* structural model is well supported by the powder diffraction data. This was in principle already mentioned in our previous article [7], but here we will highlight explicitly the differences in refinement quality of the different structural models, explaining in detail why the *Imma* structural must be considered to be correct. Additionally, we will present high counting time temperature dependent X-ray diffraction measurements, which indicate the structural transition from orthorhombic to cubic taking place at a temperature between 473 – 523 K. We will also comment on the structure refinements performed by Thompson et al. [5], which we also think to indicate that the use *Imma* model could give rise to a significant improvement of their refinement.

## 2. Experimental

The experimental details for the preparation of the compound SrFeO<sub>2</sub>F can be found in our previous article. For clarity, we would like to give the measurement conditions for the diffraction data and also give details about how the refinements have been performed.

X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 diffractometer with Bragg-Brentano geometry and a fine focus X-ray tube with Cu anode. A primary beam monochromator was attached. A LYNX eye detector and fixed divergence slit were used. The total scan time was 16 hours for the angular range between 5 and 140° 2 $\theta$ .

Time of flight neutron powder diffraction (NPD) data were recorded on the high resolution diffractometer (HRPD) at the ISIS pulsed spallation source (Rutherford Appleton Laboratory, UK). 4g of powdered SrFeO<sub>2</sub>F loaded into 8mm diameter thin-walled, cylindrical vanadium sample cans and data collected at ambient temperature for 75  $\mu$ Ah proton beam current to the ISIS target (corresponding to ~2 hours beamtime) for each sample.

Structure refinements reported here were performed on both the XRD and NPD data using the Rietveld method with the program TOPAS Academic V5 [8]. The instrumental intensity distribution for the X-ray data was determined empirically from a sort of fundamental parameters set [9], using a reference scan of LaB<sub>6</sub>, and the microstructural parameters were refined to adjust the peak shapes for the XRD data.

For the neutron diffraction data, a corresponding TOF shape model was used. Lattice parameters were allowed to be slightly different for neutron- and XRD- data ( $\Delta \sim 0.01\text{-}0.02\%$ ); this difference can be reasonably explained by a slightly different temperature during measurement at the ISIS facilities. The same positional parameters were used and refined for both data sets. Independent thermal displacement parameters were refined for each type of atom, but those for O and F were constrained to the same value. While these parameters were also constrained to be the same both for X-ray- and neutron- powder diffraction data, an additional B overall value was refined for the XRD data accounting for further effects such as absorption or surface roughness.

Refinements of the magnetic structures of  $\text{SrFeO}_2\text{F}$  was performed by introducing a second phase, with magnetic symmetry  $Pm'ma'$ , for which scaling parameter, lattice parameters as well as the position of the Fe atom were restrained to the same values as used for the nuclear phase and for which only the magnetic scattering was refined. This strategy allows for easier depiction of the magnetic scattering compared to the nuclear scattering. Since the cell lengths are pseudocubic, and the determination of the direction of the magnetic moment within a (pseudo)cubic is not possible [10], only the z-axis component of the magnetic moment was refined and  $M_x / M_y$  were set to zero.

Variable temperature X-ray powder diffraction (VT-XRD) patterns of  $\text{SrFeO}_2\text{F}$  were recorded on a Bruker D8 diffractometer with Bragg-Brentano geometry and a fine focus X-ray tube with Cu anode using an Anton Paar HTK 1200N High-Temperature Oven-Chamber. No primary beam monochromator was attached. A VANTEC detector, a step size of  $0.00785^\circ$ , and a fixed divergence slit ( $0.1^\circ$ ) were used. The patterns were recorded at variant temperatures in the order 291, 473, 373, 573, 673, 523, 423 and 323 K to highlight reversibility of the phase transition. At each temperature two patterns have been recorded: one in the angular range between  $36.5$  and  $40.5^\circ 2\theta$  using a total scan time of 2 hours, and one in the angular range between  $30$  and  $60^\circ 2\theta$  using a total scan time of 4 minutes.

Analysis of the VT-XRD diffraction patterns was performed using the method of Pawley. For this analysis, a coupled refinement of the two scans was performed. Again, the instrumental intensity distribution for the X-ray data was determined empirically from a sort of fundamental parameters set [9], using a reference scan of

LaB<sub>6</sub>. Lattice parameters of the orthorhombic phase were constrained to be pseudocubic (i. e.  $a_{\text{ortho}} = b_{\text{ortho}} / 2^{0.5} = c_{\text{ortho}} = 2^{0.5} a_{\text{cub}}$ ). Microstructural parameters were refined to adjust the peak shapes for the XRD data, but same parameters were used for both partial scans. The short time scan between 30 and 60 ° 2 $\theta$  served to determine the pseudocubic lattice parameter as well as the sample height displacement, allowing for calculation of the correct peak position of the (2 1 1)<sub>ortho</sub> superstructure reflection. The long-time scan of the angular range between 36.5 and 40.5 ° 2 $\theta$  was used to determine the intensity ratio of the (2 1 1)<sub>ortho</sub> to the (2 2 0)<sub>ortho</sub> (resp. (2 1 1)<sub>ortho</sub> to (1 1 1)<sub>cubic</sub>) reflection.

### 3. Discussion

#### Validation of the structural model of SrFeO<sub>2</sub>F with space group *Imma* on our own data [7]

The possible incorrectness of the cubic model for SrFeO<sub>2</sub>F was first proposed by Perez-Mato from a mode analysis of the structural data (from XRD experiments only) reported by Clemens et al. [4] on the system La<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3-x</sub>F<sub>x</sub> in the form of a private communication (provided as Electronic Supplementary Material). This analysis motivated us to perform neutron diffraction measurements on selected compounds of the system which then resulted in the revised structural descriptions reported in [7]. Those reported structures then agree well with a subsequent mode analysis. However, the *Imma* structure for SrFeO<sub>2</sub>F has by no means been derived from a mere comparison to the other compounds of the La<sub>1-x</sub>Sr<sub>x</sub>FeO<sub>3-x</sub>F<sub>x</sub> system ( $x < 1$ ), but is accurately reflected in the room temperature NPD data recorded on SrFeO<sub>2</sub>F. In addition, we will show that the reduced symmetry is even reflected in the XRD data (see later in this section).

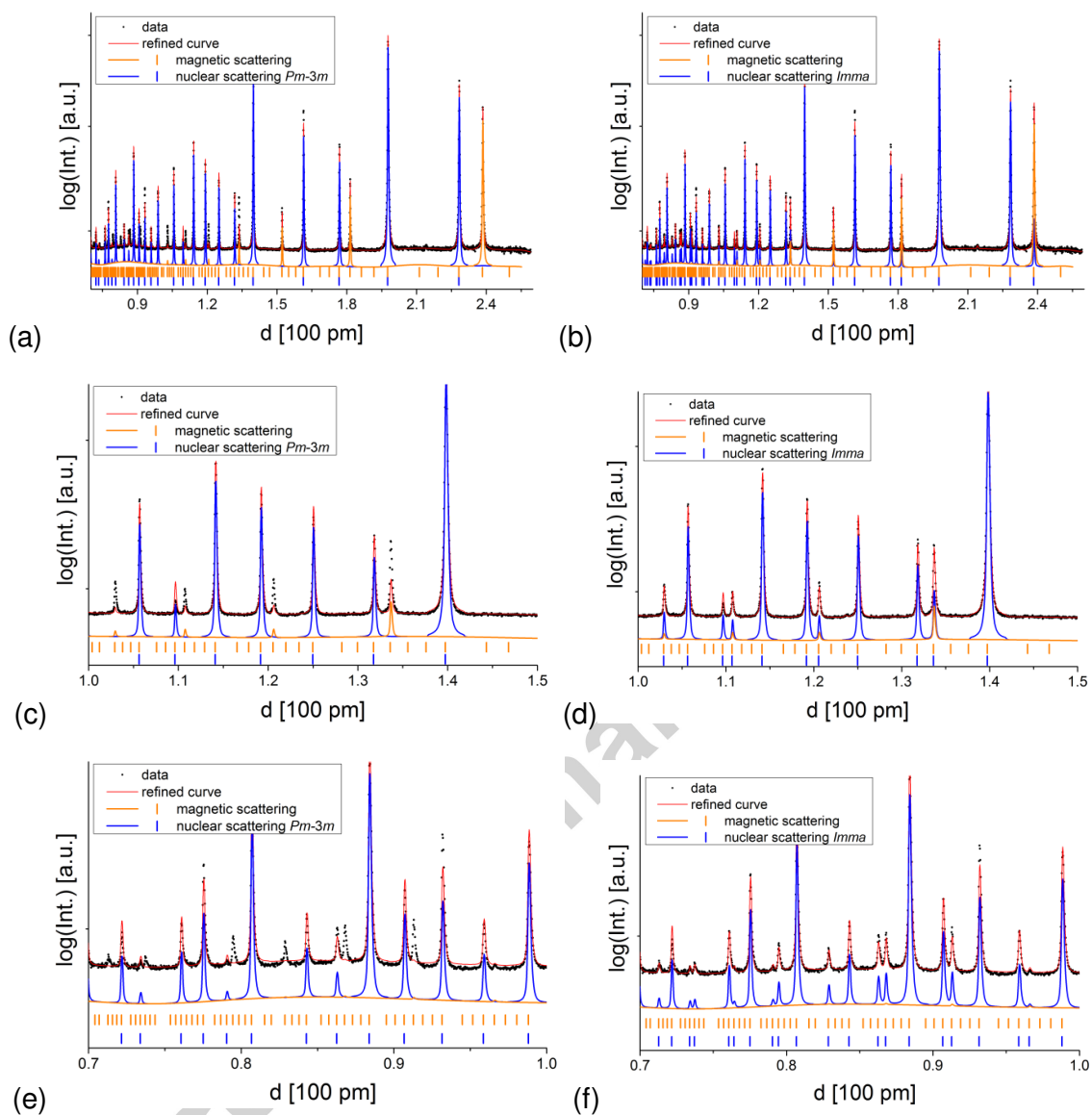
As reported in our previous article [7] and also stated by Thompson et al. [5], the cell metric of SrFeO<sub>2</sub>F is basically cubic. The lattice parameters reported by Clemens et al. [7] for the *Imma* type structure correspond to a pseudocubic cell arrangement with

$$a_{\text{Imma}} / 2^{0.5} = b_{\text{Imma}} / 2 = c_{\text{Imma}} / 2^{0.5} = a_{Pm-3m}$$

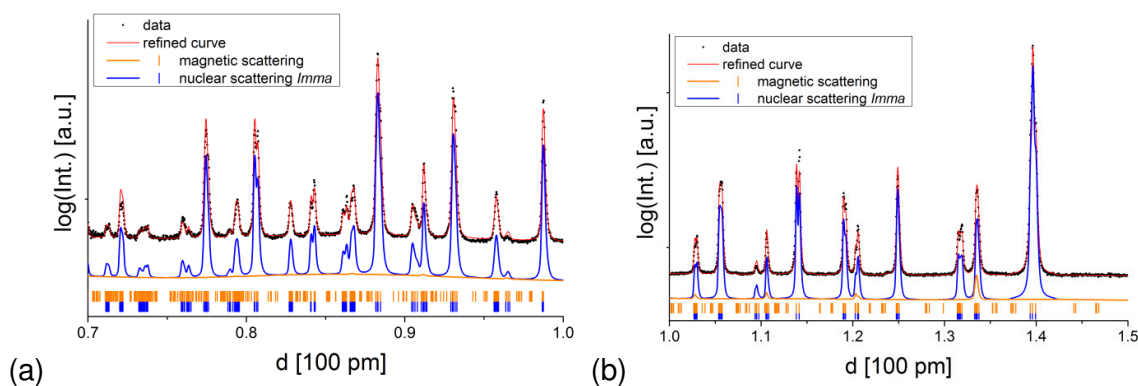
Therefore, the reduced symmetry cannot be deduced from a splitting or asymmetry of the reflections, even though the high resolution neutron powder diffractometer HRPD

at ISIS, UK, had been used. However, a reduced symmetry will not only be reflected in splitting of reflections but also in the appearance of superstructure reflections due to the loss of translational symmetry. Those superstructure reflections will coincide with the reflections from a magnetic cell, which implies that a detailed analysis of the reflection intensities down to low d-spaces will be required to prove the correctness of the *Imma* model. This is explained by the strong decrease of the magnetic form factor for lower d-spaces, and so the relative contribution to these reflections from the magnetic superstructure will rapidly fall off at these d-spacings, thus illuminating the nuclear contribution. The backscattering detector bank at HRPD allowed us to use reflections with d-spacings down to 0.67 Å for the structural analysis, whereas the measurement conditions for neutron diffraction used by Thompson et al. [5] (Canadian Neutron Beam Centre, Ontario,  $\lambda = 1.33025$  Å,  $2\theta$  from 12 ° to 92 °) are limited to a lower d-spacing range between 6.36 and 0.92 Å. The Rietveld analysis on bank 1 data show that the reflections at low d-spacings cannot be described by the common magnetic form factor of  $\text{Fe}^{3+}$  as included in GSAS [11] or TOPAS V5 [8] using the nuclear structural model of *Pm-3m* with G-type antiferromagnetic ordering (see Figure 1a/c/e). This can also not be significantly improved by allowing for an independent refinement of the thermal parameter B for the Fe atom of the magnetic phase, which then gives a physically non sensible value of  $\sim -3$  Å<sup>2</sup>. This inability to accurately describe these low d-spacing reflections is despite the fact that from our experience, the magnetic form factor provided by the above programs has served well to describe the magnetic scattering of several  $\text{Fe}^{3+}$  containing phases [12-15]. This validity of the magnetic form factor of  $\text{Fe}^{3+}$  provided by the two programs can also easily be verified by comparison to the fits obtained for the other compounds of the system  $\text{La}_{1-x}\text{Sr}_x\text{FeO}_{3-x}\text{F}_x$  ( $x < 1$ ), for which deviation from cubic symmetry can additionally be verified from the splitting of the reflections (see Figure 2). Again, for those compounds effectively no intensity contribution from magnetic scattering can be observed for reflections with d-spacings below 1 Å.





**Figure 1.** Rietveld analysis of HRPD bank 1 data recorded at ambient temperature on SrFeO<sub>2</sub>F using the structural models with space group  $Pm-3m$  (a,c,e) and  $Imma$  (b,d,f) together with a G-type arrangement of the magnetic moments. (a) and (b) show the full range of the detector banks, and (c) – (f) show blow-ups of the low d-spacing regions.



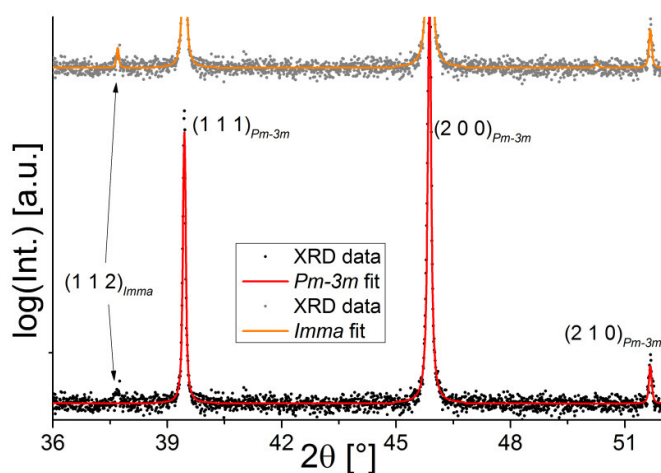
**Figure 2. Rietveld analysis of HRPD bank 1 data recorded at ambient temperature on  $\text{La}_{0.2}\text{Sr}_{0.8}\text{FeO}_{2.2}\text{F}_{0.8}$  using the structural models with space group  $Imma$  together with a G-type arrangement of the magnetic moments.**

For  $\text{SrFeO}_2\text{F}$ , the  $Imma$  model together with G-type antiferromagnetic ordering gives a superior description of the reflection intensities even down to very low d-spacings (see Figure 1b/d/f), strongly indicating the validity of the  $Imma$  model. The  $R_{wp}$  for the fit of the bank 1 NPD data decreases substantially from 3.50 % to 2.22 % for changing to the  $Imma$  structural model, and according to Hamilton's significance test [16], the  $Pm-3m$  model can therefore be rejected at the 0.5 % significance level.

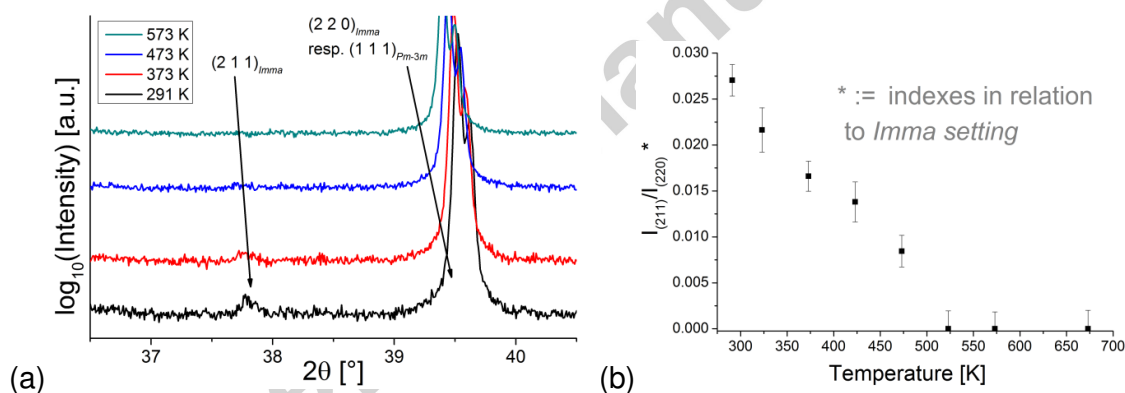
To further facilitate the verification of the correctness of the  $Imma$  model to the reader, our raw neutron diffraction data are provided in the Electronic Supplementary Material, and we encourage scientists who mistrust this structural model to verify our analysis using the provided data.

A further strong proof of the validity of the correctness of a symmetry lower than cubic is given by the observation the weak  $(2\ 1\ 1)_{Imma}$  superstructure reflection (appearing at the same position than the  $(1\ 1\ 2)_{Imma}$  as well as the  $(0\ 3\ 1)_{Imma}$  reflections, with all three carrying intensity) in the XRD data, even without the use of synchrotron radiation (see Figure 3). This reflection (group) is predicted to be the most intense superstructure reflection for XRD from the structure with  $Imma$  symmetry reported in [7]. Additionally, we performed VT-XRD measurements (see Figure 4a) in the temperature range between 291 and 673 K. The  $(2\ 1\ 1)_{Imma}$  superstructure reflection appears exactly at the position where it would be expected from the lattice parameter and sample height displacement. The reflection disappears on heating above 473 K and reappears when cooling down to temperatures below 473 K. From this fact the assignment to a possible impurity phase can be basically ruled out. From the intensity ratio of the  $(2\ 1\ 1)_{Imma}$  superstructure reflection to the

$(2\ 2\ 0)_{Imma}$  ( $= (1\ 1\ 1)_{Pm-3m}$ ) reflection (see Figure 4b), the phase transition from orthorhombic to cubic is between 473 and 523 K.



**Figure 3.** XRD part of the coupled structural analysis of XRD and NPD data recorded at ambient temperature on  $\text{SrFeO}_2\text{F}$ . Fits are shown comparing the structural models with space group  $Pm-3m$  and  $Imma$ . The  $(1\ 1\ 2)_{Imma}$  superstructure reflection is indicated with an arrow.



**Figure 4.** Results of VT-XRD measurements recorded on  $\text{SrFeO}_2\text{F}$ . (a) VT-XRD patterns of the angular range between  $36.5$  and  $40.5^\circ 2\theta$  recorded with high counting time. (b) Intensity ratio of the  $(2\ 1\ 1)_{Imma}$  to  $(2\ 2\ 0)_{Imma}$  reflection vs. temperature, indicating a phase transition temperature from orthorhombic to cubic between 473 and 523 K.

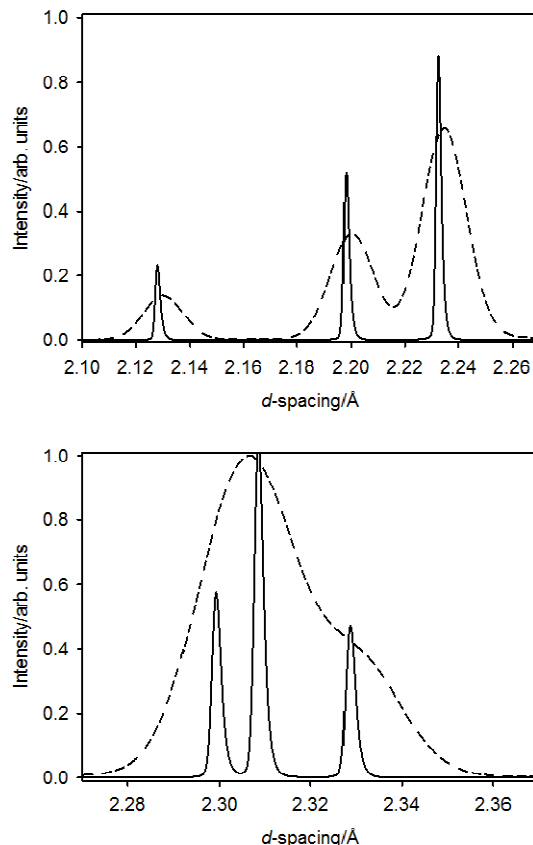
Also from an a posteriori point of view the validity of the  $Imma$  structural model is highly supported. On comparing the magnitude of shifts for the compounds with  $x < 1$  by mode analysis (as we've done in detail in our previous article, to which we would like the interested reader to refer to [7]), it is indicated that deviation from cubic symmetry would have to be expected for  $\text{SrFeO}_2\text{F}$ .

We therefore conclude that our structural model for  $\text{SrFeO}_2\text{F}$ , prepared by PVDF based fluorination of  $\text{SrFeO}_3$ , is indeed correct.

**Comments on the analysis of diffraction data and structural reports as reported by Thompson et al. [5]**

We would also like to comment on the structure refinements on a differently prepared SrFeO<sub>2</sub>F compound (made by XeF<sub>2</sub> based oxidative fluorination of SrFeO<sub>2</sub>) of Thompson et al. [5]. Albeit there might be a chemical difference for compounds prepared by different routes, in particular with regards to local O/F distributions, we think that a misinterpretation of their neutron diffraction data is more likely.

Firstly, it is worth comparing the performances of the two different neutron diffractometers used in our study (HRPD at ISIS, UK) [7] with the diffractometer used by Thompson et al. (C2, Chalk River, Canadian Neutron Beam Centre, Canada) [5]. The resolution of the C2 neutron diffractometer has already been shown to be lower by a factor of  $\sim 10$  (at  $d \sim 2.5 \text{ \AA}$ ) compared to the HRPD time-of-flight neutron diffractometer (see [17] and Figure 5). If having the same noise to integral intensity ratio, weak reflections can therefore be poorly evaluated. Therefore, this low resolution of course makes the detection and evaluation of reflections with low intensities at low d-spacings very difficult, indeed nearly impossible. Therefore, evaluation of such small structural features at low d-spacings using the C2 diffractometer can be at best called “challenging”.



**Figure 5.** Comparison of the instrumental resolution of the C2 diffractometer (Chalk River, Canadian Neutron Beam Centre, Canada; dashed curve) to the HRPD time-of-flight diffractometer (ISIS, UK, solid curve). The sample recorded is  $\text{NaMgF}_3$  and the full study of this compound is reported in [17].

Still, regarding the Rietveld analysis plots on  $\text{SrFeO}_2\text{F}$  of Thompson et al. [5] recorded at room temperature and 4 K, it is obvious that basically all superstructure reflections at low d-spaces / high angles, which the authors assumed to result from magnetic scattering, suffer from a significant misfit of intensity (see e. g. left part of Figure 2 as well as right part of Figure 3 in their article [5] or the respective reprint with assigned d-spaces shown in Figure 6a,b of this article). This intensity misfit is very similar to the one depicted in Figure 1c, where the  $Pm-3m$  model was used for  $\text{SrFeO}_2\text{F}$  prepared by polymer based fluorination. The neutron diffractometer used by Thompson et al. shows a reduced resolution, and reflections at d-spacings lower than  $0.92 \text{ \AA}$  have not been recorded. We therefore think that from the quality of their diffraction data and due to the limited angular range of measurement, a reduced symmetry of their  $\text{SrFeO}_2\text{F}$  cannot be ruled out. Going one step further, the  $Imma$  symmetry might even be indicated from the intensity misfit of their diffraction data regarding the Rietveld fit.

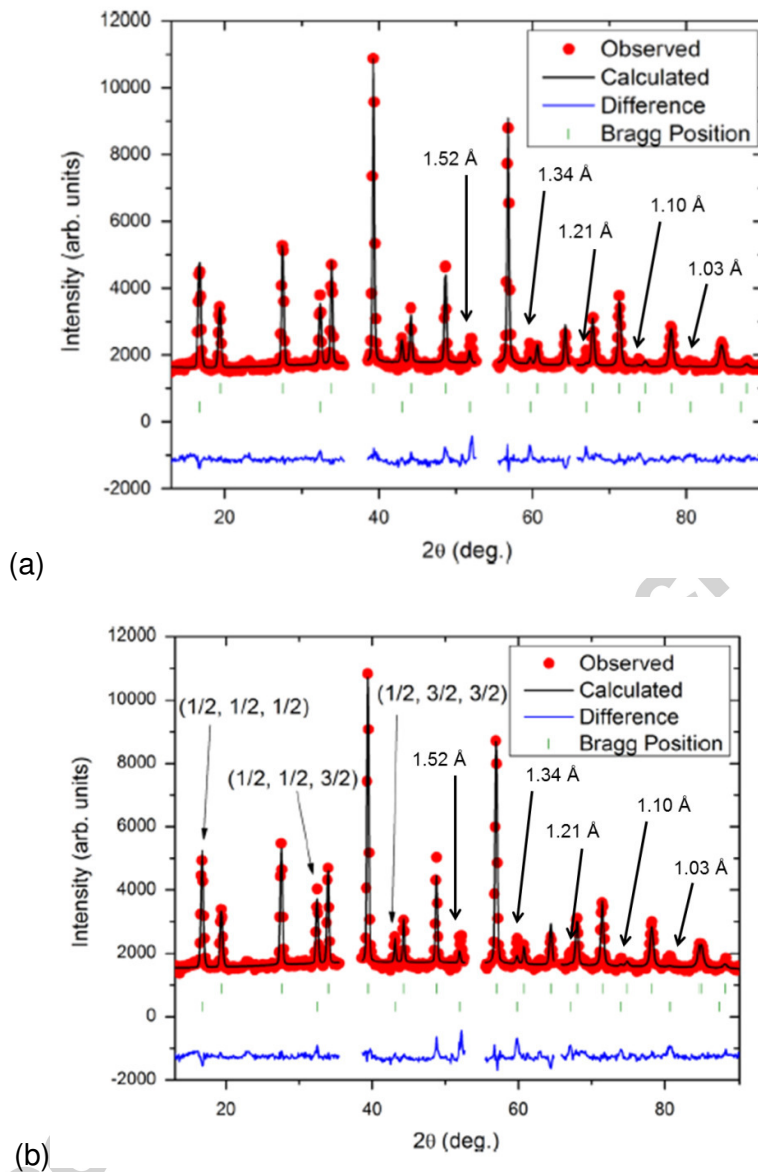


Figure 6. Rietveld analysis of NPD data of  $\text{SrFeO}_2\text{F}$  performed by Thompson et al. [5]. Recorded data red, refined curve black, difference curve blue, nuclear Bragg markers green (top), magnetic Bragg markers (bottom). The figure has been reprinted from their article, and d-spacings have been assigned to the magnetic reflections. The strong intensity misfit of the magnetic reflections with d-spacings below 1.6 Å can be seen from the difference curve. (a) ambient temperature, (b) 4 K.

Thompson et al. also performed temperature dependent NPD, and investigated the compound at an elevated temperature of 720 K, which is above the Néel temperature of the compound. No superstructure reflections could be observed at this higher temperature, and the authors conclude that this gives further proof of the correctness of the cubic space group  $Pm\bar{3}m$ . However, it is a well-known fact that the majority of distorted perovskite compounds transforms to the cubic structure at elevated temperature, and indeed our high temperature XRD measurements reported in the

previous section indicate a phase transition temperature between 473 and 523 K. Thus, the high temperature (720 K) study performed by Thompson et al. [5] is above the transition temperature so only suited to conclude that the compound is indeed cubic at this elevated temperature.

Finally, we also must comment on the conclusions made by Thompson et al. on the magnetic properties of SrFeO<sub>2</sub>F. Thompson et al. [5] correctly note that the *Pm-3m* symmetry would be prohibitive for magnetic canting. Since the *Imma* symmetry cannot be ruled out for SrFeO<sub>2</sub>F prepared by fluorination of SrFeO<sub>2</sub> using XeF<sub>2</sub>, and is furthermore valid for SrFeO<sub>2</sub>F prepared by polymer-based low-temperature fluorination, the spin canting model proposed by Berry et al. [2] still should be considered as a possible explanation for the small magnetic moment observed for SrFeO<sub>2</sub>F at temperatures below 150 K.

#### 4. Supplementary Material

Supplementary Material associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.jssc>.

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#### Highlights

SrFeO<sub>2</sub>F was synthesized by polymer based fluorination of SrFeO<sub>3</sub>.

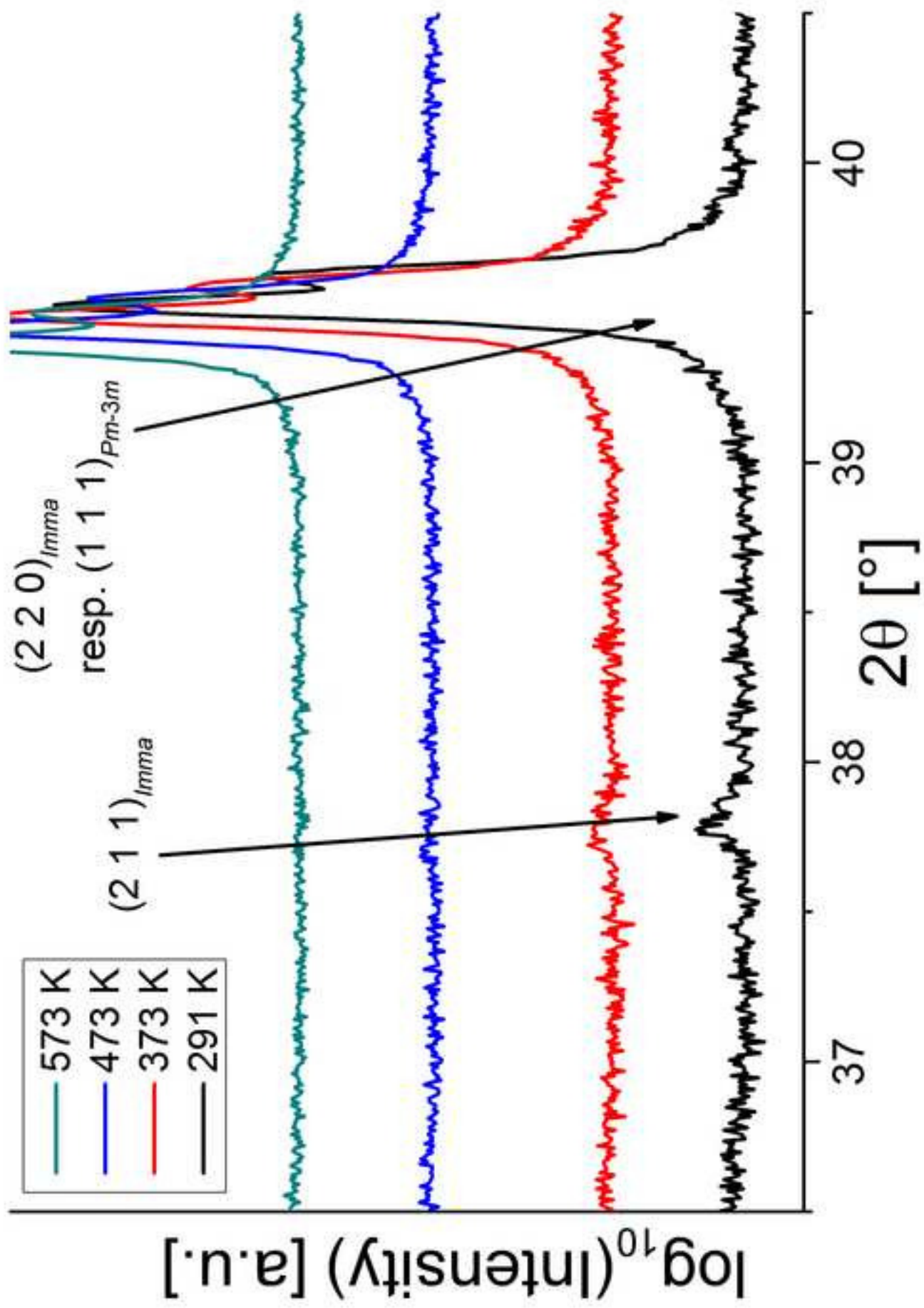
Evaluation of the diffraction data shows a pseudocubic cell metric.

Superstructure reflections at low d-spacings indicate deviation from cubic symmetry.

The phase transition temperature from orthorhombic to cubic was determined using variable temperature X-ray diffraction.

Results published by Thompson et al. are critically discussed with respect to those observations.





The crystal structure of SrFeO<sub>2</sub>F is discussed with regards to previous reports.

Accepted manuscript