



# Quantifying structural disorder in spinels by X-ray diffractometry through constrained–restrained Rietveld refinements

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## ABSTRACT

Accurate determination of the structural disorder (*i.e.*, cation misplacement, anionic and cationic vacancies, and reduced cations) of spinels is crucial to understanding the properties of this technologically attractive sub-family of ceramics, but it is very difficult to do in practice. Here, constrained–restrained Rietveld refinements of the experimentally measured X-ray diffraction patterns are proposed to tackle the challenging quantification of the structural disorder in spinels. First, it is demonstrated that the constraints–restraints to be imposed during the Rietveld refinements can be formulated by mathematical modelling through the linear inverse problem whose framework is first presented generically and then particularised to the different types of possible normal, inverse, and mixed spinels, namely, stoichiometric perfect spinels, stoichiometric and non-stoichiometric imperfect spinels, and non-stoichiometric imperfect spinels with oxidation state changes. And second, by way of example this type of constrained–restrained Rietveld refinement is successfully applied to the experimental quantification of the structural disorder in two custom-made spinels (*i.e.*, zinc-ferrite and nickel-ferrite spinels).

## 1. Introduction

Computational methods, based on the use of computer-implementable mathematical tools/algorithms, are playing a fundamental role in solving numerous problems in Materials Science, to the point that a new sub-discipline called Computational Materials Science has been coined. This is currently an emerging approach to handling complicated Materials Science problems when analytical solutions or experimental empirical solutions cannot be obtained, or are intractable, as is the case for those involving complex relationships between variables and/or large combinational spaces. One of these problems is the challenging quantification of the structural disorder (*e.g.*, cation misplacement, anionic and cationic vacancies, and reduced cations) in spinels.

The spinel-type cubic crystal structure is typical of many natural minerals and many modern synthesized structural and functional compounds [1,2]. Most spinels are given by the general formula  $AB_2X_4$ , where  $A$  and  $B$  are divalent ( $A^{2+}$ ) and trivalent ( $B^{3+}$ ) cations, respectively, and  $X$  are anions which are normally chalcogens ( $X^{2-}$ ) and most frequently  $O^{2-}$ , so that the prototypical spinel is the oxy-spinel  $A^{2+}B_2^{3+}O_4^{2-}$  (hereafter referred to simply as spinel). Spinel typically crystallize in the space group  $Fd\bar{3}m$  (sometimes incorrectly assigned to

$F\bar{4}3m$ ) [3–5], and the so-called normal spinels (*i.e.*,  $(A^{2+})^{tet}(B^{3+})_2^{oct}O_4^{2-}$ ), in which the tetrahedral sites are fully occupied by  $A^{2+}$  cations and the octahedral sites by  $B^{3+}$  cations, have a crystal structure comprising a hetero-polyhedral framework of four-fold coordination polyhedra ( $AO_4$ ) isolated from each other and sharing corners with neighbouring six-fold coordination polyhedra ( $BO_6$ ), the latter in turn sharing six of their twelve O–O edges with nearest  $BO_6$  neighbours. The so-called inverse spinels are those in which the tetrahedral sites are however fully occupied by  $B^{3+}$  cations instead of by  $A^{2+}$  cations, and the octahedral sites by  $A^{2+}$  and  $B^{3+}$  cations in equal proportions instead of only by  $B^{3+}$  cations, thus resulting in a spinel  $(B^{3+})^{tet}(A_{0.5}^{2+}B_{0.5}^{3+})_2^{oct}O_4^{2-}$ . Finally, the so-called mixed spinels, or partially inverse spinels, are cases intermediate between the normal and inverse spinels, with formulation  $(A_{1-y}^{2+}B_y^{3+})^{tet}(A_{y/2}^{2+}B_{1-y/2}^{3+})_2^{oct}O_4^{2-}$ . Here  $y$  is termed the inversion degree, which takes the value 0 for normal spinels, 1 for inverse spinels, and a number in the range 0–1 for mixed spinels. Spinel can also be classed as perfect if they exhibit only cation misplacement (*i.e.*,  $(B^{3+})^{tet}$  and  $(A^{2+})^{oct}$ ), or as imperfect if there are also other point defects (particularly vacancies in the cationic (*i.e.*,  $(V^C)^{tet}$  and/or  $(V^C)^{oct}$ ) and anionic (*i.e.*,  $V^O$ ) sub-lattices as well as oxidation state changes (*i.e.*, in particular

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$B^{3+} \rightarrow B^{2+}$  and in general  $A^{2+} \rightarrow A^{p+}$  (with  $p \neq 2$ ) and  $B^{3+} \rightarrow B^{n+}$  (with  $n \neq 3$ ) at both tetrahedral and octahedral sites). Moreover, spinels can also be classed as stoichiometric if the atomic ratios are 4O:1A, 4O:2B, and 2B:1A, or as non-stoichiometric otherwise. Therefore, it is evident that spinels can have very varied configurations of structural disorder, whose quantification is of fundamental importance to understanding their properties. Unfortunately however, the accurate evaluation of the structural disorder in spinels, that is, the determination of set of occupancies and vacancies of the crystallographic Wyckoff positions, is extremely difficult and tedious to do [1].

With the above in mind, the aim of the present work was to develop an experimentally simple procedure to accurately quantify the structural disorder in spinels using X-ray diffractometry (XRD), in particular by performing constrained–restrained Rietveld refinements of their XRD patterns [6,7]. While the restrained Rietveld refinements in perfect spinels with only cation misplacement are not unusual because it is a common practice to impose (i) that the occupancies of the different Wyckoff positions necessarily take values in the range 0–1 and (ii) that there exists only one simple linear relationship between the occupancies of the tetrahedral and octahedral Wyckoff positions, the truth is that the constrained–restrained Rietveld refinements required in imperfect spinels with other point defects are not common but rather occasional because in these cases (i) a wider set of constraints plus restraints is needed and (ii) the multiple relationships between different occupancies and other point defects are more, or much more, complex. Also, while the inversion parameter determined by restrained Rietveld refinements can provide a full description of the structural disorder in perfect spinels with only cation misplacement, this is insufficient for imperfect spinels with other point defects. In general, a series of constraints–restraints must be imposed during the Rietveld refinement to ensure its convergence with crystallographic coherence and therefore reliability of the resulting spinel crystal structure, and here will be formulated by mathematical modelling through the well-known linear inverse problem (LIP) [8]. Therefore, in what follows the basics of LIP are first briefly described (Section 2), then LIP is applied to various types of spinels to formulate the corresponding sets of constraints–restraints to be imposed in each case (Section 3), and finally constrained–restrained Rietveld refinements of the XRD patterns of custom-made zinc-ferrite and nickel-ferrite spinels (*i.e.*, nominally  $ZnFe_2O_4$  and  $NiFe_2O_4$ , respectively) are performed by way of examples to illustrate their practical utility in the experimental characterisation of spinels (Section 4).

## 2. The methodological approach proposed

Generally speaking, in science a direct problem is the process of transforming causes into effects, and consequently an inverse problem is the process of calculating the causal factors that produced a set of observations, using linear algebra in the case of LIPs. Applied to the determination of structural disorder in crystals, the LIP can be defined in general form by the following matrix notation:

$$\mathbf{A} \times \mathbf{X} = \mathbf{a}, \quad (1)$$

where  $\mathbf{X}$  would be the column vector of order  $n$  with the occupancies and vacancies of the Wyckoff positions,  $\mathbf{A}$  is a known  $m \times n$  matrix (with  $m \leq n$  being the number of constraints), and  $\mathbf{a}$  is a known column vector of order  $n$ . The order  $n$  is the sum of occupancies and vacancies describing the crystallographic lattice of the crystal (spinel in this case), and therefore varies from one case to another. Individually, each component of the column vector  $\mathbf{X}$  varies from 0 to 1, a condition that could be written formally as:

$$\mathbf{0} \leq \mathbf{I} \times \mathbf{X} \leq \mathbf{1}, \quad (2)$$

where  $\mathbf{I}$  is the  $n \times n$  identity matrix,  $\mathbf{0}$  is a column vector of order  $n$  with all its elements equal to 0, and  $\mathbf{1}$  is the column vector of order  $n$  with all its elements equal to 1.

As can be seen above, in general terms there are two possible sets of linear equations that can be formulated, namely (i) equalities (*i.e.*, Eq. (1)), that must be satisfied exactly, as are the cases with the relations of stoichiometry if preserved, the relations of full occupation of the Wyckoff positions including vacancies if present, and the condition of charge neutrality, and (ii) inequalities (*i.e.*, Eq. (2)), as is the case with the different occupancies and vacancies of the Wyckoff positions, which necessarily take values in the range 0–1. Equation (1) gives rise to constraints, and Eq. (2) to restraints. In the case of the spinels, the total number of unknowns (*i.e.*, the occupancies and vacancies) is greater than the set of possible independent linear equations, and therefore the linear system to be solved is mathematically classed as consistent and dependent (which in fact gives rise to the different possible varieties of spinels). The linear system formulated can be solved “by hand” using classical algebraic procedures, or with the help of free software such as the LIMSOLVE package. Also, because there is no target function to minimise/maximise, whether linear or non-linear, unfortunately LIP cannot be used alone to find a single solution (*i.e.*, the set of occupancies and vacancies of the Wyckoff positions) but rather the feasible solution space, including at least the free unknowns, the ranges for all unknowns, and the incompatibilities. This information is nonetheless extremely important because it can be used as input in a possible constrained–restrained Rietveld refinement of the experimentally measured XRD pattern, which does seek to minimise the sum of weighted squares of the differences between the observed and calculated intensities [6]. By doing so, the number of refinable crystallographic parameters is greatly reduced while ensuring that the Rietveld refinement converges with physical meaning.

## 3. Particularisation of LIP to spinels

In what follows, LIP will be applied to the different types of possible spinels to obtain their set of constraints – restraints, namely, to (i) perfect spinels, which are also stoichiometric, and to (ii) imperfect spinels, which in turn can be stoichiometric, non-stoichiometric, and non-stoichiometric with oxidation state changes.

### 3.1. Perfect spinels

By definition, perfect spinels may have only cation misplacement at tetrahedral and octahedral sites, with no cationic or anionic vacancies, and are therefore always stoichiometric. Consequently, in these spinels the Wyckoff position 32e is fully occupied by  $O^{2-}$  and the Wyckoff positions 8a and 16d by a certain combination of  $A^{2+}$  and  $B^{3+}$  depending on whether the perfect spinel is normal, inverse, or mixed. The following linear system of 4 equations can thus be formulated for stoichiometric perfect spinels (see Appendix A for the derivation):

$$(A^{2+})^{oct} + (B^{3+})^{oct} = 1, \quad (3)$$

$$(A^{2+})^{tet} + (B^{3+})^{tet} = 1, \quad (4)$$

$$4(A^{2+})^{oct} - 2(B^{3+})^{oct} + 2(A^{2+})^{tet} - (B^{3+})^{tet} = 0, \quad (5)$$

$$4(A^{2+})^{oct} + 6(B^{3+})^{oct} + 2(A^{2+})^{tet} + 3(B^{3+})^{tet} - 8 = 0. \quad (6)$$

Physically, these equations are the conditions of full occupation of positions 16d (Eq. (3)), of full occupation of positions 8a (Eq. (4)), of stoichiometry (Eq. (5)), and of charge neutrality (Eq. (6)). Of those 4, only 3 are however linearly independent, which is expected because otherwise the linear equation system would be consistent and independent with a unique solution, in turn implying the falsehood that all perfect spinels always have identical cation disorder. The solution to this consistent and dependent linear equation system is that the only refinable occupancy during the Rietveld refinement is actually  $(B^{3+})^{tet}$  (*i.e.*, the inversion degree), and that the others are necessarily given by:

$$\begin{pmatrix} (A^{2+})^{oct} \\ (B^{3+})^{oct} \\ (A^{2+})^{tet} \\ (B^{3+})^{tet} \end{pmatrix} = \begin{pmatrix} \frac{1}{2}(B^{3+})^{tet} \\ 1 - \frac{1}{2}(B^{3+})^{tet} \\ 1 - (B^{3+})^{tet} \\ (B^{3+})^{tet} \end{pmatrix}. \tag{7}$$

Besides these constraints, one further restraint to also be imposed during the Rietveld refinement is logically that:

$$0 \leq (B^{3+})^{tet} \leq 1. \tag{8}$$

### 3.2. Imperfect spinels

By definition, imperfect spinels may have cation misplacement at tetrahedral and octahedral sites plus cation (i.e.,  $(V^C)^{tet}$  and/or  $(V^C)^{oct}$ ) and anion (i.e.,  $V^O$ ) vacancies, and even reduced cations. Consequently, in these spinels the Wyckoff position 32e is only partially occupied by  $O^{2-}$  and the Wyckoff positions 8a and 16d only partially by  $A^{2+}/A^{p+}$  (with  $p \neq 2$ ) and  $B^{3+}/B^{n+}$  (with  $n \neq 3$ ), depending on whether the imperfect spinel is normal, inverse, or mixed. Besides, imperfect spinels can be stoichiometric or non-stoichiometric depending on the particular combination of the populations of cation and anion vacancies. If any at all, the deviations from stoichiometry will in any case be moderate because the vacancy populations cannot be very large.

#### 3.2.1. Stoichiometric imperfect spinels

This spinel sub-type comprises imperfect spinels with no oxidation state charges that preserve the stoichiometry. The following linear system of 6 equations can thus be formulated for stoichiometric imperfect spinels:

$$O^{2-} + V^O = 1, \tag{9}$$

$$(A^{2+})^{oct} + (B^{3+})^{oct} + (V^C)^{oct} = 1, \tag{10}$$

$$(A^{2+})^{tet} + (B^{3+})^{tet} + (V^C)^{tet} = 1, \tag{11}$$

$$O^{2-} - 2(A^{2+})^{oct} - (A^{2+})^{tet} = 0, \tag{12}$$

$$2O^{2-} - 2(B^{3+})^{oct} - (B^{3+})^{tet} = 0, \tag{13}$$

$$8O^{2-} - 4(A^{2+})^{oct} - 6(B^{3+})^{oct} - 2(A^{2+})^{tet} - 3(B^{3+})^{tet} = 0. \tag{14}$$

Physically, these equations are the conditions of full occupation of positions 32e (Eq. (9)), of full occupation of positions 16d (Eq. (10)), of full occupation of positions 8a (Eq. (11)), of stoichiometry (Eq. (12)–(13)), and of charge neutrality (Eq. (14)). Of those 6, only 5 are however linearly independent. Therefore, the solution to this consistent and dependent linear system is that the only 3 refinable occupancies during the Rietveld refinement are actually  $O^{2-}$ ,  $(A^{2+})^{tet}$ , and  $(B^{3+})^{tet}$  (i.e., the inversion degree), and that the others are necessarily given by:

$$\begin{pmatrix} O^{2-} \\ V^O \\ (A^{2+})^{oct} \\ (B^{3+})^{oct} \\ (V^C)^{oct} \\ (A^{2+})^{tet} \\ (B^{3+})^{tet} \\ (V^C)^{tet} \end{pmatrix} = \begin{pmatrix} O^{2-} \\ 1 - O^{2-} \\ \frac{1}{2}(O^{2-} - (A^{2+})^{tet}) \\ 1 - \frac{1}{2}(B^{3+})^{tet} \\ 1 - \frac{1}{2}(3O^{2-} - (A^{2+})^{tet} - (B^{3+})^{tet}) \\ (A^{2+})^{tet} \\ (B^{3+})^{tet} \\ 1 - (A^{2+})^{tet} - (B^{3+})^{tet} \end{pmatrix}. \tag{15}$$

Besides these constraints, 3 further restraints to also be imposed during the Rietveld refinement are logically that:

$$(i) 0 \leq O^{2-} \leq 1, (ii) 0 \leq (A^{2+})^{tet} \leq 1, \text{ and } (iii) 0 \leq (B^{3+})^{tet} \leq 1. \tag{16}$$

#### 3.2.2. Non-stoichiometric imperfect spinels

This spinel sub-type comprises imperfect spinels with no oxidation state changes that do not preserve the stoichiometry. A linear system of 4 independent equations constituted only by Eqs. (9)–(11) and (14) above can thus be formulated for non-stoichiometric imperfect spinels (that is, as above for the stoichiometric imperfect spinels except for the two equations of stoichiometry (i.e., Eqs. 12 and 13)). Therefore, the solution to this consistent and dependent linear system is that the only 4 refinable occupancies during the Rietveld refinement are actually  $O^{2-}$ ,  $(A^{2+})^{oct}$ ,  $(A^{2+})^{tet}$ , and  $(B^{3+})^{tet}$  (i.e., the inversion degree), and that the others are necessarily given by:

$$\begin{pmatrix} O^{2-} \\ V^O \\ (A^{2+})^{oct} \\ (B^{3+})^{oct} \\ (V^C)^{oct} \\ (A^{2+})^{tet} \\ (B^{3+})^{tet} \\ (V^C)^{tet} \end{pmatrix} = \begin{pmatrix} O^{2-} \\ 1 - O^{2-} \\ (A^{2+})^{oct} \\ \frac{1}{3} + \frac{4}{3}O^{2-} - \frac{2}{3}(A^{2+})^{oct} - \frac{1}{3}(A^{2+})^{tet} - \frac{1}{2}(B^{3+})^{tet} \\ \frac{2}{3} - \frac{4}{3}O^{2-} - \frac{1}{3}(A^{2+})^{oct} + \frac{1}{3}(A^{2+})^{tet} + \frac{1}{2}(B^{3+})^{tet} \\ (A^{2+})^{tet} \\ (B^{3+})^{tet} \\ 1 - (A^{2+})^{tet} - (B^{3+})^{tet} \end{pmatrix}. \tag{17}$$

Besides these constraints, 4 further restraints to also be imposed during the Rietveld refinement are logically that:

$$(i) 0 \leq O^{2-} \leq 1, (ii) 0 \leq (A^{2+})^{oct} \leq 0.5, (iii) 0 \leq (A^{2+})^{tet} \leq 1, \text{ and } (iii) 0 \leq (B^{3+})^{tet} \leq 1. \tag{18}$$

#### 3.2.3. Non-stoichiometric imperfect spinels with oxidation state changes $B^{3+} \rightarrow B^{2+}$

This spinel sub-type comprises imperfect spinels with a certain fraction of reduced cations  $B^{2+}$ . Note that the oxidation state change  $B^{3+} \rightarrow B^{2+}$  generates additional oxygen vacancies, and therefore necessarily entails the loss of stoichiometry (see Appendix B for the derivation). The following linear system of 4 equations can thus be formulated for non-stoichiometric imperfect spinels with oxidation state changes:

$$O^{2-} + V^O = 1, \tag{19}$$

$$(A^{2+})^{oct} + (B^{3+})^{oct} + (B^{2+})^{oct} + (V^C)^{oct} = 1, \tag{20}$$

$$(A^{2+})^{tet} + (B^{3+})^{tet} + (B^{2+})^{tet} + (V^C)^{tet} = 1, \tag{21}$$

$$8O^{2-} - 4(A^{2+})^{oct} - 6(B^{3+})^{oct} - 4(B^{2+})^{oct} - 2(A^{2+})^{tet} - 3(B^{3+})^{tet} - 2(B^{2+})^{tet} = 0. \tag{22}$$

Physically, these equations are the conditions of full occupation of positions 32e (Eq. (19)), of full occupation of positions 16d (Eq. (20)), of full occupation of positions 8a (Eq. (21)), and of charge neutrality (Eq. (22)). The solution to this consistent and dependent linear system is that the only 6 refinable chemical occupancies are actually  $(A^{2+})^{oct}$ ,  $(B^{3+})^{oct}$ ,  $(B^{2+})^{oct}$ ,  $(A^{2+})^{tet}$ ,  $(B^{3+})^{tet}$  and  $(B^{2+})^{tet}$ , and that the others are necessarily given by:

$$\begin{pmatrix} O^{2-} \\ V^O \\ (A^{2+})^{oct} \\ (B^{3+})^{oct} \\ (B^{2+})^{oct} \\ (V^C)^{oct} \\ (A^{2+})^{tet} \\ (B^{3+})^{tet} \\ (B^{2+})^{tet} \\ (V^C)^{tet} \end{pmatrix} = \begin{pmatrix} \frac{3}{4}(B^{3+})^{oct} + \frac{1}{2}(B^{2+})^{oct} + \frac{1}{4}(A^{2+})^{tet} + \frac{3}{8}(B^{2+})^{tet} \\ 1 + \frac{3}{4}(B^{3+})^{oct} - \frac{1}{2}(B^{2+})^{oct} - \frac{1}{4}(A^{2+})^{tet} - \frac{3}{8}(B^{2+})^{tet} \\ (A^{2+})^{oct} \\ (B^{3+})^{oct} \\ (B^{2+})^{oct} \\ 1 - (A^{2+})^{oct} - (B^{3+})^{oct} - (B^{2+})^{oct} \\ (A^{2+})^{tet} \\ (B^{3+})^{tet} \\ (B^{2+})^{tet} \\ 1 - (A^{2+})^{tet} - (B^{3+})^{tet} - (B^{2+})^{tet} \end{pmatrix} \quad (23)$$

$$8O^{2-} - 4(A^{2+})^{oct} - 6(B^{3+})^{oct} - 2p(A^{p+})^{oct} - 2n(B^{n+})^{oct} - 2(A^{2+})^{tet} - 3(B^{3+})^{tet} - p(A^{p+})^{tet} - n(B^{n+})^{tet} = 0. \quad (28)$$

Physically, these equations are the conditions of full occupation of positions 32e (Eq. (25)), of full occupation of positions 16d (Eq. (26)), of full occupation of positions 8a (Eq. (27)), and of charge neutrality (Eq. (28)). The solution to this consistent and dependent linear system is that the only 8 refinable chemical occupancies are actually  $(A^{2+})^{oct}$ ,  $(B^{3+})^{oct}$ ,  $(A^{p+})^{oct}$ ,  $(B^{n+})^{oct}$ ,  $(A^{2+})^{tet}$ ,  $(B^{3+})^{tet}$ ,  $(A^{p+})^{tet}$ , and  $(B^{n+})^{tet}$ , and that the others are necessarily given by:

$$\begin{pmatrix} O^{2-} \\ V^O \\ (A^{2+})^{oct} \\ (B^{3+})^{oct} \\ (A^{p+})^{oct} \\ (B^{n+})^{oct} \\ (V^C)^{oct} \\ (A^{2+})^{tet} \\ (B^{3+})^{tet} \\ (A^{p+})^{tet} \\ (B^{n+})^{tet} \\ (V^C)^{tet} \end{pmatrix} = \begin{pmatrix} \frac{1}{2}(A^{2+})^{oct} + \frac{3}{4}(B^{3+})^{oct} + \frac{p}{4}(A^{p+})^{oct} + \frac{n}{4}(B^{n+})^{oct} + \frac{1}{4}(A^{2+})^{tet} + \frac{3}{8}(B^{3+})^{tet} + \frac{p}{8}(A^{p+})^{tet} + \frac{n}{8}(B^{n+})^{tet} \\ 1 - \frac{1}{2}(A^{2+})^{oct} - \frac{3}{4}(B^{3+})^{oct} - \frac{p}{4}(A^{p+})^{oct} - \frac{n}{4}(B^{n+})^{oct} - \frac{1}{4}(A^{2+})^{tet} - \frac{3}{8}(B^{3+})^{tet} - \frac{p}{8}(A^{p+})^{tet} - \frac{n}{8}(B^{n+})^{tet} \\ (A^{2+})^{oct} \\ (B^{3+})^{oct} \\ (A^{p+})^{oct} \\ (B^{n+})^{oct} \\ 1 - (A^{2+})^{oct} - (B^{3+})^{oct} - (A^{p+})^{oct} - (B^{n+})^{oct} \\ (A^{2+})^{tet} \\ (B^{3+})^{tet} \\ (A^{p+})^{tet} \\ (B^{n+})^{tet} \\ 1 - (A^{2+})^{tet} - (B^{3+})^{tet} - (A^{p+})^{tet} - (B^{n+})^{tet} \end{pmatrix} \quad (29)$$

Note that in this type of spinel the inversion degree is  $(B^{3+})^{tet} + (B^{2+})^{tet}$ . Besides these constraints, 6 further restraints to also be imposed during the Rietveld refinement are logically that:

$$\begin{aligned} (i) 0 \leq (A^{2+})^{oct} \leq 0.5, (ii) 0 \leq (B^{3+})^{oct} \leq 1, (iii) 0 \leq (B^{2+})^{oct} \leq 1, \\ (iv) 0 \leq (A^{2+})^{tet} \leq 1, (v) 0 \leq (B^{3+})^{tet} \leq 1, \text{ and } (vi) 0 \leq (B^{2+})^{tet} \leq 1. \end{aligned} \quad (24)$$

### 3.2.4. Non-stoichiometric imperfect spinels with any possible oxidation state change

This spinel sub-type comprises imperfect spinels with a certain fraction of cations  $A^{2+}$  and  $B^{3+}$  having changed their oxidation states to  $A^{p+}$  (with  $p \neq 2$ ) and  $B^{n+}$  (with  $n \neq 3$ ), respectively, and that they do not preserve the stoichiometry. The following linear system of 4 equations can thus be formulated for non-stoichiometric imperfect spinels with any possible oxidation state change:

$$O^{2-} + V^O = 1, \quad (25)$$

$$(A^{2+})^{oct} + (B^{3+})^{oct} + (A^{p+})^{oct} + (B^{n+})^{oct} + (V^C)^{oct} = 1, \quad (26)$$

$$(A^{2+})^{tet} + (B^{3+})^{tet} + (A^{p+})^{tet} + (B^{n+})^{tet} + (V^C)^{tet} = 1, \quad (27)$$

Note that in this type of spinel the inversion degree is  $(B^{3+})^{tet} + (B^{n+})^{tet}$ . Besides these constraints, 8 further restraints to also be imposed during the Rietveld refinement are logically that:

$$\begin{aligned} (i) 0 \leq (A^{2+})^{oct} \leq 0.5, (ii) 0 \leq (B^{3+})^{oct} \leq 1, (iii) 0 \leq (A^{p+})^{oct} \leq 0.5, \\ (iv) 0 \leq (B^{n+})^{oct} \leq 1, (v) 0 \leq (A^{2+})^{tet} \leq 1, (vi) 0 \leq (B^{3+})^{tet} \leq 1, \\ (vii) 0 \leq (A^{p+})^{tet} \leq 1, \text{ and } (viii) 0 \leq (B^{n+})^{tet} \leq 1. \end{aligned} \quad (30)$$

## 4. Experimental quantification of the point defects in zinc-ferrite and nickel-ferrite spinels

### 4.1. Methodology

Zinc-ferrite and nickel-ferrite spinels (i.e., nominally  $ZnFe_2O_4$  and  $NiFe_2O_4$ , respectively) were synthesized by the co-precipitation method as described elsewhere for  $NiFe_2O_4$  and cobalt-ferrite (i.e.,  $CoFe_2O_4$ ) spinels [9], and their XRD patterns were measured (D8 Advance, Bruker AXS, Germany) over the angular range  $20\text{--}90^\circ 2\theta$ , with step of  $0.05^\circ 2\theta$  and counting time of 2 s per step, using conventional  $CuK\alpha$  incident radiation (although  $CoK\alpha$  would have been more recommendable to minimise fluorescence).

The Rietveld refinements of the XRD patterns of both spinels were

performed using the software package FULLPROF (version September 2020), applying cubic spline interpolation to model the intensity background and the following refinable global, instrumental, and profile parameters: (i) the scale factor to capture the peak intensities; (ii) the zero-point, transparency, and off-centering parameters to account for possible instrumental shifts in the peak positions; (iii) the lattice parameter of the cubic crystal structure to model, together with the instrumental shifts, the peak positions; and (iv) the mixing parameter, the half-width parameters, and the asymmetry parameters of a pseudo-Voigt function to describe the peak shape. An approach based on the principle of parsimony was followed, therefore starting with the simplest spinel model and using gradually more complex spinel models only if the Rietveld refinement was unsatisfactory (as measured in terms of the conventional agreement indicator  $\chi^2_r$ ). The spinel crystal structure was described using the cubic space group  $Fd\bar{3}m$  (No. 227) in the second setting, with refinable lattice parameter  $a$ , refinable Wyckoff position  $32e$  (fractional coordinates  $u,u,u$ , with  $u$  being known as the oxygen parameter whose value is close to 0.25) for the anions  $O^{2-}$ , and fixed Wyckoff positions  $8a$  and  $16c$  (fractional coordinates  $0,0,0$  and  $\frac{5}{8}, \frac{5}{8}, \frac{5}{8}$ , respectively) for the cations  $A^{2+}$ ,  $B^{3+}$ , and  $B^{2+}$  or  $A^{p+}-B^{n+}$  if needed.

#### 4.2. The zinc-ferrite spinel

Fig. 1 shows the experimentally acquired XRD pattern of the  $ZnFe_2O_4$  spinel together with the plotted output from the constrained–restrained Rietveld refinement performed as described above using the stoichiometric perfect spinel model, which is the simplest one (i.e., Eqs. (7) and (8)). It can be seen that the Rietveld refinement shows an excellent fit between the experimental and calculated XRD patterns, with  $\chi^2_r$  being as low as only 1.24, indicating that the stoichiometric perfect spinel model describes well the structural disorder of the present  $ZnFe_2O_4$  spinel. The refinable occupancy  $(B^{3+})^{tet} = (Fe^{3+})^{tet}$  is thus determined to be 0.152 (6), in turn resulting in the following occupancies (note that there are no vacancies in this case):

$$\begin{pmatrix} (A^{2+})^{oct} \\ (B^{3+})^{oct} \\ (A^{2+})^{tet} \\ (B^{3+})^{tet} \end{pmatrix} = \begin{pmatrix} (Zn^{2+})^{oct} \\ (Fe^{3+})^{oct} \\ (Zn^{2+})^{tet} \\ (Fe^{3+})^{tet} \end{pmatrix} = \begin{pmatrix} \frac{1}{2}(Fe^{3+})^{tet} \\ 1 - \frac{1}{2}(Fe^{3+})^{tet} \\ 1 - (Fe^{3+})^{tet} \\ (Fe^{3+})^{tet} \end{pmatrix} = \begin{pmatrix} 0.076(3) \\ 0.924(6) \\ 0.848(6) \\ 0.152(6) \end{pmatrix}.$$

Therefore, the present  $ZnFe_2O_4$  spinel is a mixed stoichiometric perfect spinel with inversion degree 0.152, given by  $(Zn_{0.848}^{2+}Fe_{0.152}^{3+})^{tet}(Zn_{0.076}^{2+}Fe_{0.924}^{3+})^{oct}O_4^{2-}$ . For its complete description, the

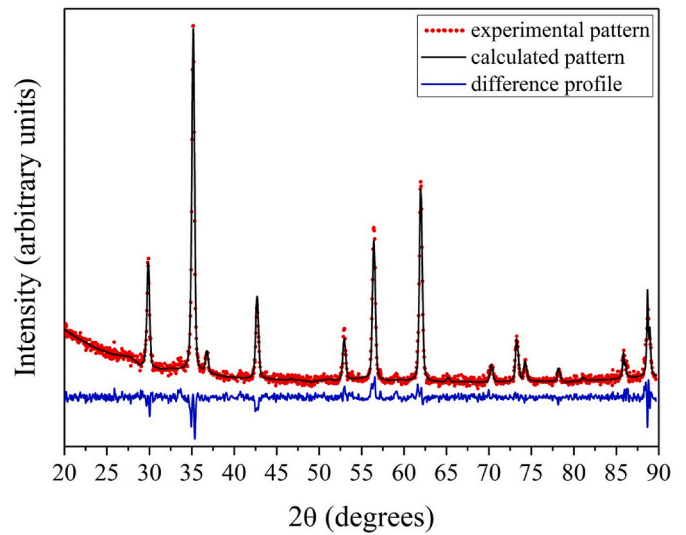


Fig. 1. Experimentally acquired XRD pattern of the present  $ZnFe_2O_4$  spinel together with the plotted output from the corresponding constrained–restrained Rietveld refinement performed using the stoichiometric perfect spinel model.

Rietveld refinement also indicated that the lattice parameter of this spinel is  $a = 8.4609(1)$  Å and that the oxygen parameter is  $u = 0.2580$  (2).

#### 4.3. The nickel-ferrite spinel

Fig. 2 shows the experimentally acquired XRD pattern of the  $NiFe_2O_4$  spinel together with the plotted outputs from the constrained–restrained Rietveld refinements performed as described above using first the stoichiometric perfect spinel model (Fig. 2A), which is the simplest one (i.e., Eq. (7)– (8)), and then the stoichiometric imperfect spinel model (Fig. 2B), which is the second simplest one (i.e., Eq. (15)– (16)). It can be seen that the former did not lead to a satisfactory fit (i.e.,  $\chi^2_r$  being as high as 2.71) while the latter already does (i.e.,  $\chi^2_r$  being as low as 1.37), indicating that the perfect spinel model does not describe well the structural disorder of the present  $NiFe_2O_4$  spinel while the stoichiometric imperfect spinel model already does. In this scenario the refinable occupancies  $O^{2-}$ ,  $(A^{2+})^{tet} = (Ni^{2+})^{tet}$ , and  $(B^{3+})^{tet} = (Fe^{3+})^{tet}$  are thus determined to be 0.960(1), 0.871(2), and 0.112(2), in turn resulting in the following occupancies (note that there are anionic and cationic vacancies in this case):

$$\begin{pmatrix} O^{2-} \\ V^O \\ (A^{2+})^{oct} \\ (B^{3+})^{oct} \\ (V^C)^{oct} \\ (A^{2+})^{tet} \\ (B^{3+})^{tet} \\ (V^C)^{tet} \end{pmatrix} = \begin{pmatrix} O^{2-} \\ V^O \\ (Ni^{2+})^{oct} \\ (Fe^{3+})^{oct} \\ (V^C)^{oct} \\ (Ni^{2+})^{tet} \\ (Fe^{3+})^{tet} \\ (V^C)^{tet} \end{pmatrix} = \begin{pmatrix} O^{2-} \\ 1 - O^{2-} \\ \frac{1}{2}(O^{2-} - (Ni^{2+})^{tet}) \\ 1 - \frac{1}{2}(Fe^{3+})^{tet} \\ 1 - \frac{1}{2}(3O^{2-} - (Ni^{2+})^{tet} - (Fe^{3+})^{tet}) \\ (Ni^{2+})^{tet} \\ (Fe^{3+})^{tet} \\ 1 - (Ni^{2+})^{tet} - (Fe^{3+})^{tet} \end{pmatrix} = \begin{pmatrix} 0.960(1) \\ 0.040(1) \\ 0.045(2) \\ 0.944(1) \\ 0.011(4) \\ 0.871(2) \\ 0.112(2) \\ 0.017(4) \end{pmatrix}.$$



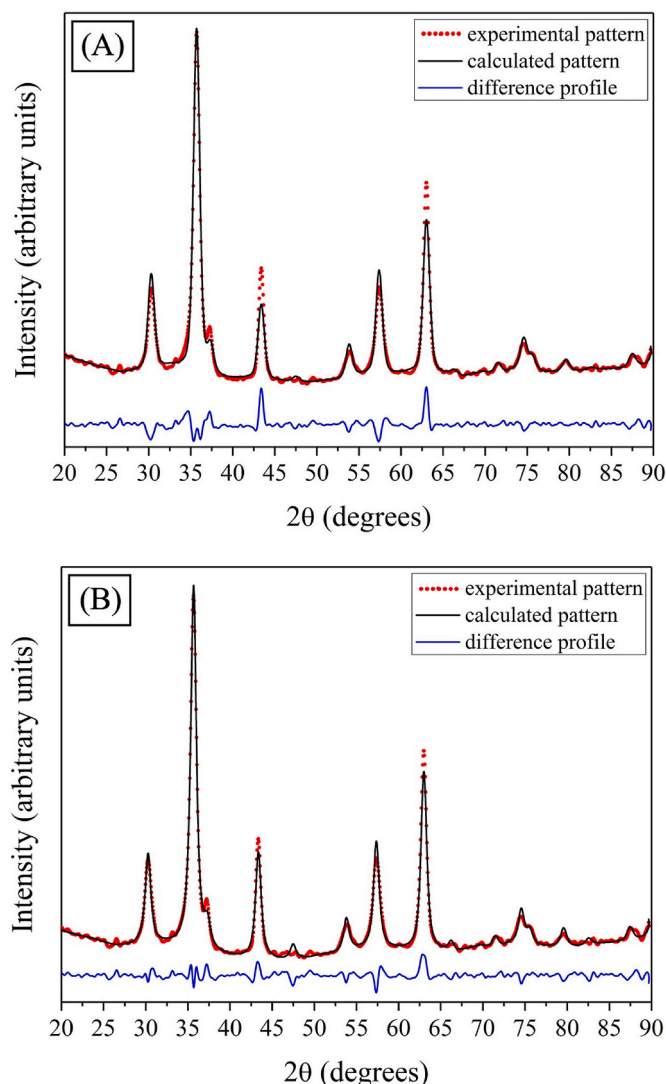


Fig. 2. Experimentally acquired XRD pattern of the present  $\text{NiFe}_2\text{O}_4$  spinel together with the plotted output from the corresponding constrained–restrained Rietveld refinement performed using (A) the stoichiometric perfect spinel model and (B) the stoichiometric imperfect spinel model.

Therefore, the present  $\text{NiFe}_2\text{O}_4$  spinel is a mixed stoichiometric

## Appendix A

The objective of this appendix is to show in more detail how the linear systems of equations to be solved are formulated, and the particularisation to the case of perfect spinels as a practical example (*i.e.*, derivation of Eq. (3)–(6)).

There are two general principles to be applied in all type of spinels:

1. The three Wyckoff positions in the spinel lattice (*i.e.*,  $8a$  of cations in tetrahedral positions,  $16d$  of cations in octahedral positions, and  $32e$  of anions) must be fully occupied, which is expressed mathematically by imposing that the sum of the occupancies by the different types of ions placed there plus the corresponding vacancies is 1.
2. The spinel crystal must be electrically neutral, which is expressed mathematically by imposing the condition of charge neutrality in the form that the sum of the positive charges of all cations (regardless of their type and Wyckoff position) plus the negative charges of all anions must be 0. In addition, there is also a third particular principle applicable only in the case of stoichiometric spinels:
3. Stoichiometric spinels must satisfy that, regardless of the Wyckoff positions occupied by the cations, they contain twice as many  $B^{3+}$  cations as  $A^{2+}$  cations, twice as many  $O^{2-}$  anions as  $B^{3+}$  cations, and four times as many  $O^{2-}$  anions as  $A^{2+}$  cations, which is expressed mathematically by imposing that  $B^{3+} = 2A^{2+}$ ,  $O^{2-} = 2B^{3+}$ , and  $O^{2-} = 4A^{2+}$ , respectively. However, one of them is always redundant.

In the particular case of the perfect spinels, given by the formula  $(A_{1-y}^{2+}B_y^{3+})^{tet}(A_{y/2}^{2+}B_{1-y/2}^{3+})^{oct}O_4^{2-}$ , where  $y$  is the inversion degree, it is

imperfect spinel with inversion degree 0.112, given by  $(\text{Ni}_{0.871}^{2+}\text{Fe}_{0.112}^{3+})^{tet}(\text{Ni}_{0.045}^{2+}\text{Fe}_{0.944}^{3+})^{oct}O_{0.960}^{2-}$ . For its complete description, the Rietveld refinement also indicated that the lattice parameter of this spinel is  $a = 8.3426(9)$  Å and that the oxygen parameter is  $u = 0.2626(2)$ .

## 5. Concluding remarks

Determining accurately the structural disorder in spinels, which are a very wide sub-family of ceramics with great technological interest in many different fields of application, is crucially important to understanding their properties, but it is very challenging to do in practice. Here, a simple procedure based on performing constrained–restrained Rietveld refinements of their XRD patterns has been proposed to that end, where the constraints–restraints required have in turn been formulated by mathematical modelling through the LIP. After a brief general description of the LIP, this was particularised to establish the set of constraints–restraints to be imposed during the Rietveld refinements for the different types of possible normal, inverse, and mixed spinels: stoichiometric perfect spinels, stoichiometric and non-stoichiometric imperfect spinels, and non-stoichiometric imperfect spinels with oxidation state changes. Finally, the applicability of this type of constrained–restrained Rietveld refinement was illustrated using as examples the XRD patterns of custom-made zinc-ferrite and nickel-ferrite spinels synthesized by co-precipitation.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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satisfied that:

1. There are no  $O^{2-}$  vacancies so that the Wyckoff position 32e is fully occupied by  $O^{2-}$ , a condition that is expressed mathematically as  $O^{2-} = 1$ .
2. There are no cation vacancies in octahedral positions but there can be cation misplacement so that the Wyckoff position 16d is fully occupied by  $A^{2+}$  and  $B^{3+}$  cations, a condition that is expressed mathematically expressed as  $(A^{2+})^{oct} + (B^{3+})^{oct} = 1$ . This is Eq. (3).
3. There are no cation vacancies in tetrahedral positions but there can be cation misplacement so that the Wyckoff position 8a is fully occupied by  $A^{2+}$  and  $B^{3+}$  cations, a condition that is expressed mathematically expressed as  $(A^{2+})^{tet} + (B^{3+})^{tet} = 1$ . This is Eq. (4).
4. The spinel is stoichiometric so that it contains twice as many  $B^{3+}$  cations as  $A^{2+}$  cations, a condition that is expressed mathematically as  $B^{3+} = 2A^{2+} \rightarrow [(B^{3+})^{tet} + 2(B^{3+})^{oct}] = 2[(A^{2+})^{tet} + 2(A^{2+})^{oct}] \rightarrow 4(A^{2+})^{oct} - 2(B^{3+})^{oct} + 2(A^{2+})^{tet} - (B^{3+})^{tet} = 0$ . This is Eq. (5). Note that one of the three stoichiometry equations is always redundant, and that in this case adding the other is redundant with the charge neutrality equation.
5. The spinel crystal is electrically neutral, with zero net charge. The molecular formula states that there are four  $O^{2-}$  anions, two cations in octahedral position (i.e.,  $(A^{2+})^{oct} + (B^{3+})^{oct} = 2$ ), and one cation in tetrahedral position (i.e.,  $(A^{2+})^{tet} + (B^{3+})^{tet} = 1$ ), so considering their valences it follows that the negative charge is 8, the positive charge in octahedral position is  $2[2(A^{2+})^{oct} + 3(B^{3+})^{oct}] = [4(A^{2+})^{oct} + 6(B^{3+})^{oct}]$ , and the positive charge in tetrahedral position is  $[2(A^{2+})^{tet} + 3(B^{3+})^{tet}]$ . Therefore, the charge neutrality condition is mathematically expressed as  $4(A^{2+})^{oct} + 6(B^{3+})^{oct} + 2(A^{2+})^{tet} + 3(B^{3+})^{tet} - 8 = 0$ , which is Eq. (6).

Derivation of the linear systems of equations for other types of spinels follows the same procedure.

### Appendix B

The objective of this Appendix is to show that the cation reduction  $B^{3+} \rightarrow B^{2+}$  necessarily breaks the spinel stoichiometry. Let us consider a hypothetical case of stoichiometric imperfect spinels with cation misplacement, cation (i.e.,  $(V^C)^{tet}$  and/or  $(V^C)^{oct}$ ) and anion (i.e.,  $V^O$ ) vacancies, and cation reduction (i.e.,  $B^{3+} \rightarrow B^{2+}$ ). In this scenario the Wyckoff position 32e is only partially occupied by  $O^{2-}$  and the Wyckoff positions 8a and 16d only partially by  $A^{2+}$ ,  $B^{2+}$ , and  $B^{3+}$  depending on whether the hypothetical stoichiometric imperfect spinel is normal, inverse, or mixed. The following linear system of 6 equations can thus be formulated for hypothetical stoichiometric imperfect spinels with oxidation state changes:

$$O^{2-} + V^O = 1, \tag{B1}$$

$$(A^{2+})^{oct} + (B^{3+})^{oct} + (B^{2+})^{oct} + (V^C)^{oct} = 1, \tag{B2}$$

$$(A^{2+})^{tet} + (B^{3+})^{tet} + (B^{2+})^{tet} + (V^C)^{tet} = 1, \tag{B3}$$

$$4(A^{2+})^{oct} - 2(B^{3+})^{oct} - 2(B^{2+})^{oct} + 2(A^{2+})^{tet} - (B^{3+})^{tet} - (B^{2+})^{tet} = 0, \tag{B4}$$

$$O^{2-} - 2(A^{2+})^{oct} - (A^{2+})^{tet} = 0, \tag{B5}$$

$$8O^{2-} - 4(A^{2+})^{oct} - 6(B^{3+})^{oct} - 4(B^{2+})^{oct} - 2(A^{2+})^{tet} - 3(B^{3+})^{tet} - 2(B^{2+})^{tet} = 0. \tag{B6}$$

Physically, these equations are the conditions of full occupation of positions 32e (Eq. (B1)), of full occupation of positions 16d (Eq. (B2)), of full occupation of positions 8a (Eq. (B3)), of stoichiometry (Eqs. (B4) – (B5)), and of charge neutrality (Eq. (B6)). The solution to this consistent and dependent linear system is that the only 4 refinable occupancies are actually  $(V^C)^{oct}$ ,  $(B^{3+})^{tet}$ ,  $(B^{2+})^{tet}$ , and  $(V^C)^{tet}$ , and that the others are necessarily given by:

$$\begin{pmatrix} O^{2-} \\ V^O \\ (A^{2+})^{oct} \\ (B^{3+})^{oct} \\ (B^{2+})^{oct} \\ (V^C)^{oct} \\ (A^{2+})^{tet} \\ (B^{3+})^{tet} \\ (B^{2+})^{tet} \\ (V^C)^{tet} \end{pmatrix} = \begin{pmatrix} 1 - \frac{2}{3}(V^C)^{oct} - \frac{1}{3}(V^C)^{tet} \\ \frac{2}{3}(V^C)^{oct} + \frac{1}{3}(V^C)^{tet} \\ -\frac{1}{3}(V^C)^{oct} + \frac{1}{2}(B^{3+})^{tet} + \frac{1}{2}(B^{2+})^{tet} + \frac{1}{3}(V^C)^{tet} \\ 1 - \frac{2}{3}(V^C)^{oct} - \frac{1}{2}(B^{3+})^{tet} - \frac{1}{3}(V^C)^{tet} \\ -\frac{1}{2}(B^{2+})^{tet} \\ (V^C)^{oct} \\ 1 - (B^{3+})^{tet} - (B^{2+})^{tet} - (V^C)^{tet} \\ (B^{3+})^{tet} \\ (B^{2+})^{tet} \\ (V^C)^{tet} \end{pmatrix}. \tag{B7}$$

Very importantly, because the only way to satisfy the relationship  $(B^{2+})^{oct} = -\frac{1}{2}(B^{2+})^{tet}$  is by imposing  $(B^{2+})^{oct} = (B^{2+})^{tet} = 0$ , Eq. (B7) reduces to:

$$\begin{pmatrix} O^{2-} \\ V^O \\ (A^{2+})^{oct} \\ (B^{3+})^{oct} \\ (B^{2+})^{oct} \\ (V^C)^{oct} \\ (A^{2+})^{tet} \\ (B^{3+})^{tet} \\ (B^{2+})^{tet} \\ (V^C)^{tet} \end{pmatrix} = \begin{pmatrix} 1 - \frac{2}{3}(V^C)^{oct} - \frac{1}{3}(V^C)^{tet} \\ \frac{2}{3}(V^C)^{oct} + \frac{1}{3}(V^C)^{tet} \\ -\frac{1}{3}(V^C)^{oct} + \frac{1}{2}(B^{3+})^{tet} + \frac{1}{3}(V^C)^{tet} \\ 1 - \frac{2}{3}(V^C)^{oct} - \frac{1}{2}(B^{3+})^{tet} - \frac{1}{3}(V^C)^{tet} \\ 0 \\ (V^C)^{oct} \\ 1 - (B^{3+})^{tet} - (V^C)^{tet} \\ (B^{3+})^{tet} \\ 0 \\ (V^C)^{tet} \end{pmatrix}. \tag{B8}$$

The implication is then that there are no stoichiometric imperfect spinels with reduced cations or, alternatively, that spinels with reduced cations are always non-stoichiometric. This is simply because additional anionic vacancies are required to compensate for the loss of positive charge deriving from the cation reduction  $B^{3+} \rightarrow B^{2+}$ , with the attendant loss of stoichiometry.

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