X-Ray Diffraction Determination of the Cation Distribution and Oxygen Positional Parameter in Polycrystalline Spinels

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A critical assessment is made of the calculation procedures currently used for determining the cation distribution in spinels from *X*-ray powder diffraction data. Both binary and ternary spinels are considered. It is shown that *X*-ray powder diffraction, in conjunction with appropriate computational methods, has enough sensitivity to determine the cation distribution and oxygen positional parameter. A difference of one electron between two different cations can be enough to render them distinguishable.

Structural characterization of solids with a spinel-type structure involves determination of the unit-cell length, a_0, the oxygen positional parameter, u, and the distribution of the different cations present among the tetrahedral and octahedral interstices of the anion close-packed lattice. The oxygen parameter quantifies the degree of distortion of the anion sub-lattice, and may be defined by making the product ua_0 equal to the distance from a (001) cation plane of the tetrahedral sub-lattice to the next-nearest-neighbour (001) plane of the anion sub-lattice. For an ideal close-packed cubic oxide lattice, $u = 0.375$, but significantly higher values (in the range 0.380—0.390) are very often found in spinels.

Determination of the cation distribution is of considerable relevance to the solid-state chemistry of spinels, since theoretical interpretation of the chemical and physical properties (*e.g.* magnetic, semiconducting, catalytic, *etc.*) of these compounds rests on the sites assigned to the cations. Also, it is very useful for investigating the balance between the various factors which determine tetrahedral and octahedral preferences in the structural chemistry of oxides. In both of these contexts ternary spinels (which may be regarded as solid solutions between two binary spinels) are particularly amenable, since they enable the effects of gradual compositional changes to be studied.[1] However, the presence of more than two kinds of cations complicates the determination of the corresponding distribution, thereby demanding more rigorous methods.

Most work on the crystal chemistry of spinels is currently being done on polycrystalline materials, using *X*-ray powder diffraction measurements combined with appropriate calculation methods; among these, the *R*-factor method[2–4] and the methods proposed by Furuhashi *et al.*[5] and by Bertaut and co-workers[6,7] are in common practice. A comparative study of these three methods has been carried out by Gastaldi and Lapiccirella[8] with particular reference to the binary spinel $MgIn_2S_4$. However, these authors did not consider more complex situations such as those arising from the presence of a third cation (in ternary spinels) or two cations with similar scattering power.

The present paper reports on the reliability of *X*-ray powder diffraction methods with respect to the solution of the cation distribution and oxygen parameter in both binary and ternary spinels. Cases where the cations have only a small difference in atomic scattering factors are also considered. The emphasis is placed on a comparison of the above-mentioned calculation procedures in order to draw conclusions about their relative merits, but attention is also paid to the application of a Monte Carlo method for testing the reliability of the cation distribution and oxygen parameter. The computer programs involved have long been used in our laboratory, and applied to a large number[9–13] of both binary and ternary spinels. Examples of spinels which typify particularly relevant situations have been selected; $CuGa_2O_4$, $Cd_{0.75}Zn_{0.25}Fe_2O_4$, and $Cu_{0.6}Zn_{0.4}Al_2O_4$.

Experimental

Sample Preparation.—Spinels were prepared in polycrystalline form by solid-state reaction, in an electric furnace, of the parent oxides mixed in the appropriate proportions. To facilitate reaction the samples were periodically removed from the furnace and ground. This also allowed the progress of the reaction to be followed by *X*-ray diffraction. When a reaction was completed the sample was rapidly cooled to quench the cation-distribution equilibrium.

X-*Ray Diffraction Measurements.*—Experimental diffraction intensities were determined with a Philips powder diffractometer equipped with a graphite-crystal monochromator (for the diffracted beam) and scintillation counter; Cu-K_α radiation was used in all cases. Prolonged grinding of samples and back loading of the (flat) specimen holder were performed in order to minimize (possible) preferred orientation effects. Diffraction lines were scanned at a speed of 0.125° min^{-1} (2θ), accumulating the corresponding number of pulses. Allowance for background intensity was made by setting the goniometer at each side of every diffraction line and accumulating enough pulses to determine the background intensity with only a very small statistical error. Sixteen to nineteen diffraction lines were measured for each spinel.

Calculations

The Bertaut, Furuhashi *et al.*, and *R*-factor methods are all based on a comparison between the diffraction intensities observed experimentally and those calculated for a large number of hypothetical (simulated) crystal structures, which are generated to cover a suitable range of the cation distribution and u parameter. The criterion used for such a comparison is the most distinctive feature of each method.

In the Bertaut method[6,7] experimental and calculated diffraction intensities for a few pairs of reflections are compared according to expression (1) where $I^{\mathrm{obs.}}_{hkl}$ and $I^{\mathrm{calc.}}_{hkl}$ are,

$$I^{\mathrm{obs.}}_{hkl}/I^{\mathrm{obs.}}_{h'k'l'} = I^{\mathrm{calc.}}_{hkl}/I^{\mathrm{calc.}}_{h'k'l'} \qquad (1)$$

respectively, the observed and calculated intensities for reflection *hkl*. If an agreement factor, *R*, is defined as in equation (2), the simulated structure which best matches the actual

$$R = \left|(I^{\mathrm{obs.}}_{hkl}/I^{\mathrm{obs.}}_{h'k'l'}) - (I^{\mathrm{calc.}}_{hkl}/I^{\mathrm{calc.}}_{h'k'l'})\right| \qquad (2)$$

Table 1. Cation distribution and oxygen parameter for $CuGa_2O_4$ obtained by computational methods which take into account the full set of intensity values[a]

	Cation distribution					
	Fraction on tetrahedral sites		Fraction on octahedral sites			
Method	Cu^{2+}	Ga^{3+}	Cu^{2+}	Ga^{3+}	Oxygen parameter	Agreement factor[b]
Furuhashi *et al.* [equation (3)]	0.163(27)	0.837(27)	0.837(27)	1.163(27)	0.384 5(9)	0.73
R-factor						
[equation (4)]	0.146(49)	0.854(49)	0.854(49)	1.146(49)	0.382 5(4)	0.06
[equation (5)]	0.178(43)	0.822(43)	0.822(43)	1.178(43)	0.383 2(10)	0.04

[a] Standard deviations, given by the Monte Carlo method, are shown in parentheses. [b] Linear regression coefficient (r^2) in equation (3), R_1 or R_2 in equation (4) or (5) respectively.

Table 2. Cation distribution in $CuGa_2O_4$ calculated by following the Bertaut method [equation (2)]

		Cation distribution			
		Fraction on tetrahedral sites		Fraction on octahedral sites	
u value used	Intensity ratio used	Cu^{2+}	Ga^{3+}	Cu^{2+}	Ga^{3+}
0.3821	220/400	0.016	0.984	0.984	1.016
	400/422	0.000	1.000	1.000	1.000
0.3823	220/400	0.021	0.979	0.979	1.021
	400/422	0.000	1.000	1.000	1.000
0.3841	220/400	0.067	0.933	0.933	1.067
	400/422	0.000	1.000	1.000	1.000
0.3855	220/400	0.110	0.890	0.890	1.110
	400/422	0.000	1.000	1.000	1.000

structure of the sample will lead to a minimum value of *R*. One such minimum (and corresponding cation distribution) is obtained for each *hkl*, *h'k'l'* reflection pair considered.

According to Bertaut[6] and to Weil *et al.*[7] the best information on cation distribution is achieved when comparing experimental and calculated intensity ratios for reflections whose intensities (*i*) are nearly independent of the oxygen parameter, (*ii*) vary with the cation distribution in opposite ways, and (*iii*) do not differ significantly. These requirements impose severe limitations on the number of diffraction lines which can be used; those most suitable are the reflections (220), (400), and (422). Besides, requirement (*i*) precludes determination of the oxygen parameter; a value of *u* has to be assumed for the determination of $I^{calc.}_{hkl}$ values. In the case of ternary spinels it has been common practice[14–16] to assume a linear variation of *u* over the whole range of composition. Some experimental results,[17,18] however, show that this assumption lacks general validity.

The method proposed by Furuhashi *et al.*[5] selects the best simulated structure by examining the degree of linearity of the well known relation[19] (3), where *k* is a scale factor, $B_{eff.}$ is the

$$\ln (I^{obs.}_{hkl}/I^{calc.}_{hkl}) = \ln k - 2\,B_{eff.}\,\sin^2\theta_{hkl}/\lambda^2 \qquad (3)$$

thermal parameter, θ_{hkl} is the diffraction angle, and λ is the *X*-ray wavelength. In this method as many diffraction lines as experimentally possible are taken into account, and the best simulated structure is chosen so as to maximize the linear regression coefficient for equation (3). When enough diffraction lines are considered, the analysis is sensitive to both the cation distribution and oxygen parameter, which are simultaneously determined. At the same time, the corresponding values of *k* and $B_{eff.}$ are also determined.

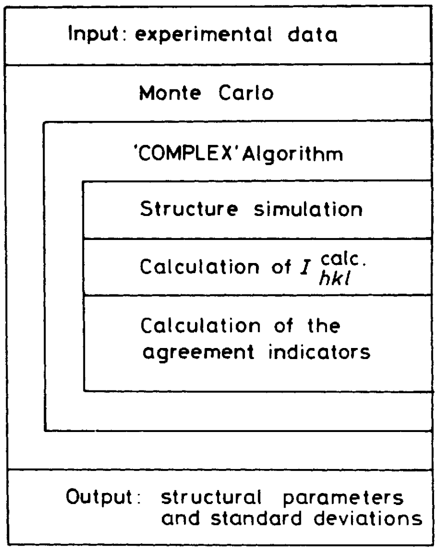

Figure. Logic scheme of the calculation program. The sequence of operations goes from top to bottom. Rectangles enclosed in others correspond to operations performed under control of the immediately external rectangle

In the *R*-factor method[2–4] the best structure is selected so as to minimize the value of a residual function, *R*. Several expressions for *R* have been proposed;[2–4] those used in the present work are presented in equations (4) and (5). This

$$R_1 = \sum_{hkl} | I^{obs.}_{hkl} - I^{calc.}_{hkl} | / \sum_{hkl} I^{obs.}_{hkl} \qquad (4)$$

$$R_2 = \sum_{hkl} | \sqrt{I^{obs.}_{hkl}} - \sqrt{I^{calc.}_{hkl}} | / \sum_{hkl} \sqrt{I^{obs.}_{hkl}} \qquad (5)$$

method enables (as in the previous case) simultaneous determination of the cation distribution and the oxygen parameter, as well as the thermal (and scale) factor.

In the standard use of the calculation methods hitherto outlined the reliability of the numerical results obtained cannot be assessed beyond the simple indication furnished by the value of either the linear regression coefficient for equation (3) or the residual functions R_1 or R_2. We have developed a statistical analysis, based on a Monte Carlo method, which enables the

Table 3. Cation distribution and oxygen parameter for $Cd_{0.75}Zn_{0.25}Fe_2O_4$ obtained by computational methods which take into account the full set of intensity values; details as in Table 1

	Cation distribution							
	Fraction on tetrahedral sites			Fraction on octahedral sites				
Method	Cd^{2+}	Zn^{2+}	Fe^{3+}	Cd^{2+}	Zn^{2+}	Fe^{3+}	Oxygen parameter	Agreement factor
Furuhashi *et al.* [equation (3)]	0.74(3)	0.04(6)	0.22(6)	0.01(3)	0.21(6)	1.78(6)	0.387(3)	0.84
R-factor								
[equation (4)]	0.72(2)	0.02(4)	0.26(3)	0.03(2)	0.23(4)	1.74(3)	0.390(2)	0.03
[equation (5)]	0.72(2)	0.02(3)	0.26(3)	0.03(2)	0.23(3)	1.74(3)	0.390(2)	0.02

Table 4. Cation distribution in $Cd_{0.75}Zn_{0.25}Fe_2O_4$ calculated by following the Bertaut method [equation (2)]

		Cation distribution					
		Fraction on tetrahedral sites			Fraction on octahedral sites		
u value used	Intensity ratio used	Cd^{2+}	Zn^{2+}	Fe^{3+}	Cd^{2+}	Zn^{2+}	Fe^{3+}
0.385	220/400	0.73	0.11	0.16	0.02	0.14	1.84
	400/422	0.68	0.18	0.14	0.07	0.07	1.86
0.386	220/400	0.70	0.23	0.07	0.05	0.02	1.93
	400/422	0.67	0.24	0.09	0.08	0.01	1.91
0.390	220/400	0.70	0.15	0.15	0.05	0.10	1.85
	400/422	0.67	0.20	0.13	0.08	0.05	1.87

reliability of the calculated values of the cation distribution and oxygen parameter to be more precisely evaluated.

The experimentally determined values of *X*-ray diffraction intensities are intrinsically affected by statistical fluctuations inherent to the phenomena of *X*-ray excitation, diffraction, and detection.[20] The reiterative measurement (under fixed experimental conditions) of any diffraction intensity over a sufficiently large number of times would result in a set of intensity values which, to a good approximation, would follow a normal distribution[21] with a maximum value corresponding to the mean value of the experimental determinations and with a standard deviation equal to the square root of the mean value.[20] This is, therefore, a statistical process well suited to the application of a Monte Carlo method.[22,23]

The calculation procedure devised carries out the following cycle of operations; (*i*) from the experimentally determined values of both line and background diffraction intensities the Monte Carlo program generates a new set of values, $I_{hkl}^{\text{obs.}}$, which are then used in the subsequent calculation; (*ii*) a series of hypothetical structures are simulated and the corresponding values of $I_{hkl}^{\text{calc.}}$ computed, taking into account corrections for the anomalous scattering and the Lorentz, polarization and multiplicity factors;[24] and (*iii*) by comparing $I_{hkl}^{\text{calc.}}$ with $I_{hkl}^{\text{obs.}}$, using the appropriate mathematical expression [equation (3), (4), or (5)], the simulated structure which best matches the set of $I_{hkl}^{\text{obs.}}$ values is selected. Steps (*ii*) and (*iii*) are carried out using the Box COMPLEX algorithm.[25] The whole cycle is repeated over a sufficiently large number of times (70 in all the examples examined in this paper) to confer statistical value to the Monte Carlo method. Each cycle leads to individual values of the cation distribution and oxygen parameter which are then statistically analysed to determine the corresponding mean values and standard deviations. These standard deviations provide a quantitative indication of the statistical stability of the results.

The logic of the computer program (FORTRAN 66) developed to accomplish the described calculations is shown in the Figure. Inspection of this scheme may help to visualize the calculation procedure. Apart from the values of the structural parameters, and their standard deviations, the program also prints out the reflections which show the largest difference between experimental and calculated diffraction intensities. This is a convenient feature which helps to diagnose possible errors in the data-acquisition process or in the data input to the computer.

Results and Discussion

(*a*) *Binary Spinel* $CuGa_2O_4$.—The determination of the cation distribution in spinels by *X*-ray diffraction increases in difficulty as the scattering powers of the cations approach one another. The $3d^9$, $3d^{10}$ pair Cu^{2+}, Ga^{3+} in $CuGa_2O_4$ provides a good opportunity to ascertain the sensitivity of the method since these cations, differing in only one electron, show very similar scattering powers. The compound $CuGa_2O_4$ is also one of the few spinels where the cation distribution has been determined by neutron diffraction,[26–28] thus providing a standard against which *X*-ray-derived results can be tested.

A sample annealed at 1 223 K and rapidly quenched[29,30] has been used for the present investigation. The results of applying different computational procedures to the experimentally determined intensities of 16 diffraction lines are shown in Tables 1 and 2. For Table 1 the full set of intensity data has been used. In the Bertaut method (Table 2) only the diffraction lines (220), (400), and (422) were used. Since in this method a value of the oxygen parameter (*u*) has to be assumed prior to calculation, it was interesting to determine the effect of utilizing different *u* values. Table 2 shows the results for a set of *u* values covering the range of fluctuation found with the other calculation methods.

Table 1 shows that the three computational methods which use the full set of intensity data give consistent results, when the standard deviations are taken into account. These standard deviations also show that the one-electron difference between Cu^{2+} and Ga^{3+} is enough to render both cations distinguishable by the *X*-ray diffraction method.

The average of the results shown in Table 1 gives an inversion parameter γ (fraction of bivalent ions in octahedral sites) of 0.84(4), implying the structural formula $Cu_{0.16}Ga_{0.84}[Cu_{0.84}Ga_{1.16}]O_4$, where the square brackets enclose octahedral ions. This is consistent with the value $\gamma = 0.79(1)$ obtained by neutron diffraction,[26,27] hence testifying to the validity of the *X*-ray powder diffraction method. The high degree of inversion in this spinel is a consequence of the tetrahedral preference of Ga^{3+}. Such a preference is a general feature among d^{10} ions in spinels, due to the strong covalent contribution which can be

Table 5. Cation distribution and oxygen parameter in $Cu_{0.6}Zn_{0.4}Al_2O_4$ obtained by computational methods which take into account the full set of intensity values; details as in Table 1

	Cation distribution							
	Fraction on tetrahedral sites			Fraction on octahedral sites				
Method	Cu^{2+}	Zn^{2+}	Al^{3+}	Cu^{2+}	Zn^{2+}	Al^{3+}	Oxygen parameter	Agreement factor
Furuhashi *et al.* [equation (3)]	0.37(5)	0.39(4)	0.24(1)	0.23(5)	0.01(4)	1.76(1)	0.388(1)	0.916
R-factor								
[equation (4)]	0.35(3)	0.37(3)	0.28(1)	0.25(3)	0.03(3)	1.72(1)	0.387(1)	0.020
[equation (5)]	0.36(2)	0.38(2)	0.26(1)	0.24(2)	0.02(3)	1.74(1)	0.388(1)	0.016

Table 6. Cation distribution in $Cu_{0.6}Zn_{0.4}Al_2O_4$ calculated by following the Bertaut method [equation (2)]

		Cation distribution					
		Fraction on tetrahedral sites			Fraction on octahedral sites		
u value used	Intensity ratio used	Cu^{2+}	Zn^{2+}	Al^{3+}	Cu^{2+}	Zn^{2+}	Al^{3+}
0.3875	220/400	0.35	0.40	0.25	0.25	0.00	1.75
	400/422	0.33	0.39	0.28	0.27	0.01	1.72

developed in the bond between a four-co-ordinated cation and an anion.[31]

The average value of the oxygen parameter (Table 1) is $u = 0.383(1)$, which is consistent with the neutron-diffraction value, $u = 0.381(1)$,[27,28] when the experimental uncertainties are taken into account.

The Bertaut method (Table 2) gives an inversion parameter which is slightly dependent upon the *u* value used. When the reflection pair 220, 400 is considered, γ is seen to decrease systematically from 0.98 to 0.89 as *u* is increased. However, the most relevant feature of the results shown in Table 2 is that, when both intensity ratios (220/400 and 400/422) are taken into account, the Bertaut method gives an inversion parameter very close to 1.00. This value can be used as a first approximation, but it should be clear that the computational procedures considered above provide more accurate results.

(*b*) *Ternary Spinel* $Cd_{0.75}Zn_{0.25}Fe_2O_4$.—This spinel was prepared in polycrystalline form by solid-state reaction at 1 273 K of the parent oxides (CdO, ZnO, and Ga_2O_3) mixed in the appropriate proportion. The compound was then rapidly quenched to room temperature and the *X*-ray diffraction intensities of the 16 most intense lines determined.

Table 3 shows the cation distribution and oxygen parameter obtained applying the Furuhashi and *R*-factor methods. They all give entirely consistent results, which have good precision. The standard deviations for the distributions for Cd^{2+} are smaller than for the corresponding data for Zn^{2+} and Fe^{3+}. This is a consequence of the larger difference in *X*-ray scattering power between Cd^{2+} ($4d^{10}$) and Fe^{3+} ($3d^5$) and Zn^{2+} ($3d^{10}$).

The Bertaut method has been applied using three different values of the oxygen parameter, and the cation distributions obtained are given in Table 4. It is seen that these distributions are slightly dependent upon the *u* value, but no systematic trends are observed.

Comparison between Tables 3 and 4 evidences that for Zn^{2+} and Fe^{3+} the distributions obtained following the Bertaut method are significantly different from those given by the other computational procedures. The effect is most obvious for the Zn^{2+} ion which is found to occupy almost exclusively octahedral sites when the Furuhashi and *R*-factor methods are used, whilst the Bertaut method locates this ion mainly on tetrahedral sites.

(*c*) *Ternary Spinel* $Cu_{0.6}Zn_{0.4}Al_2O_4$.—This is an example of a ternary spinel in which two of the cations, Cu^{2+} ($3d^9$) and Zn^{2+} ($3d^{10}$), differ by only one electron. The sample used was prepared by solid-state reaction of the parent oxides (CuO, ZnO, and Al_2O_3) at 1 223 K, followed by rapid quenching in liquid nitrogen.[9]

In the case of the Furuhashi and *R*-factor methods, calculations of the cation distribution and oxygen parameter were performed using the experimentally determined intensities of 19 diffraction lines. The results are shown in Table 5. It is seen that the three methods give consistent results. The low values of the standard deviations for the cation distributions of Cu^{2+} and Zn^{2+} prove that these ions are clearly distinguished from one another, in spite of the small difference in their scattering powers. As might be expected, standard deviations corresponding to the parameters for Al^{3+} are even lower.

Table 6 shows that, for $u = 0.3875$, the Bertaut method leads to cation distributions which are consistent with those obtained using the other calculation procedures (Table 5). Good agreement has also been obtained for some other ternary spinels but, as in the previously discussed example, this is not always the case.

It should be pointed out that for spinels with more than two different cations computation of the cation distribution from the corresponding *X*-ray diffraction intensities can lead to a mathematically indeterminate set of equations, unless enough diffraction lines are taken into account. For ternary spinels (three different cations) the problem can be analysed, in simple terms, considering that the structure factor is given by an equation of the type (6) where, with reference to the tetrahedral

$$F_{hkl} = x f'_{hkl} + y f''_{hkl} + z f'''_{hkl} + f_{hkl} \qquad (6)$$

sites, *x*, *y*, and *z* represent the fractions of these sites occupied by each different cation. This provides the independent equation (7). In order to have a mathematically determinate, and

$$x + y + z = 1 \qquad (7)$$

compatible, system two independent equations of type (6) and equation (7) are needed. However, this is only the minimum (mathematical) requirement. In practice, the applicability of the *X*-ray diffraction method rests on the fact that the scattering powers of different cations vary in a slightly different way with the diffraction angle. Since these differences are small, a large number of equations of type (6) (*i.e.* a large number of *hkl* diffraction lines) must be taken into account to remove simultaneously the mathematical and experimental uncertainty.

The latter arises from the experimental uncertainties in the determination of diffraction intensities. The mathematical incompatibility which could stem from a multi-equation set is removed by the approximate character of the solution sought.

The above considerations shed new light on the relative reliability of different calculation procedures. It should be clear that the very limited number of diffraction lines usable in the Bertaut method can be a severe handicap, particularly for ternary spinels.

Conclusions

The application of *X*-ray powder diffraction methods to the structural characterization of polycrystalline spinels has been critically analysed. The results discussed, along with those obtained by the authors in the study of many other spinels, allow the following main conclusions to be drawn. (*i*) *X*-Ray powder diffraction, in conjunction with appropriate computational methods, has enough sensitivity to determine the cation distribution in both binary and ternary spinels. A difference of one electron between two of the cations present may be enough to render them distinguishable. (*ii*) The calculation method proposed long ago by Bertaut, and originally applied to binary spinels, had the merit of simplified computation. Its use, however, can hardly be justified nowadays, and even less in the case of ternary spinels. When computation facilities are available, other methods can be applied which, by using more information, are capable of yielding more reliable results. (*iii*) Appropriate statistical methods are a powerful tool which can be used to test the reliability of the calculated results.

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