

Application of a Monte Carlo Method to the Determination of Cation Distribution in Spinel by Powder Diffractometry

C. OTERO AREÁN AND J. M. RUBIO GONZÁLEZ

Departamento de Química Inorgánica, Facultad de Química, Oviedo, Spain

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Use of a Monte Carlo method is proposed for assessing the reliability of the experimental determination of cation distribution in spinels as deduced from X-ray powder diffraction data. The method is demonstrated on the ternary spinels $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{Al}_2\text{O}_4$ and $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$, which present the complication of having two cations with very close X-ray scattering power. It is shown that the proposed method tests out the precision of the cation distribution results with greater detail than what can be obtained by simple consideration of a residual function. © 1986 Academic Press, Inc.

Introduction

Determination of cation distribution (among tetrahedral and octahedral sites) in spinels is of considerable interest, since the theoretical interpretation or the magnetic and semiconducting properties of spinel-type compounds leans heavily on the lattice sites assigned to the cations. Control of these properties can be exerted by using cations with marked coordination preference. To this end, many systems involving two (or more) spinels have been investigated, and it has been shown (1) that in ternary spinels (i.e., spinels having three different cations) cation distribution is a function of chemical composition.

Experimental determination of cation distribution in spinels is usually carried out by X-ray powder diffraction, since the materials are very often obtained in polycrystalline form. The neutron diffraction technique, although potentially more accurate, is not easily available, which makes it less suitable for routine work.

Determination of cation distribution by X-ray diffraction involves comparison between the experimentally determined diffraction intensities and those calculated for a number of simulated structures, where ionic partition is gradually changed. To this end, an *R*-factor method (2-4) can be utilized. However, in the standard use of such a method, the accuracy and reliability of the numerical results obtained cannot be assessed beyond the simple indication given by the value of the residual function, for which a minimum is sought. The present paper reports on the application of a Monte Carlo method which provides an independent estimation of the reliability of the results.

The use of the method is demonstrated by its application to the ternary spinels $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{Al}_2\text{O}_4$ and $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$. These are particularly severe cases. Since, besides the simultaneous presence of three different cations (as compared with only two cations in binary spinels), two of them: $\text{Cu}^{2+}/\text{Zn}^{2+}$ in the former system and $\text{Mg}^{2+}/$

Al^{3+} in the latter, have very close X-ray scattering powers, which poses a further complication.

Basis of the Calculation Method

As stated above, experimentally measured X-ray diffraction intensities can be used to determine cation distribution in spinels applying standard methods of X-ray crystallography where the best proposed structure is selected so as to minimize the value of a residual function, R , of the form

$$R = \sum_{hkl} \left| I_{hkl}^{obs} - I_{hkl}^{calc} \right| / \sum_{hkl} I_{hkl}^{obs} \quad (1)$$

where I_{hkl}^{obs} are the experimentally observed intensities and I_{hkl}^{calc} are the corresponding calculated values for a hypothetical structure. However, stochastic fluctuations in the I_{hkl}^{obs} values set an upper limit to the precision with which cation distribution can be determined. It is the uncertainty due to this factor which is statistically evaluated in the proposed calculation method. This method is based on the fact that the random fluctuations intrinsically inherent to the phenomena of X-ray excitation, diffraction, and detection are known to maintain a normal distribution (5) where the mean value equals zero and the standard deviation equals the square root of the counter reading. Knowledge of this statistics allows computer simulation of the diffraction intensity fluctuations which can thus be taken into account to evaluate their effect on the accuracy of the cation distribution results. Moreover, the statistical nature of the process renders it well suited to the application of a Monte Carlo method (6).

The calculation procedure we have devised runs as follows. From each individual value of an experimentally observed diffraction intensity, I_{hkl}^{obs} a Monte Carlo computer program generates a set of pseudorandom values, $I_{hkl}^1, \dots, I_{hkl}^n$, al-

lowing for stochastic fluctuations which follow the above-mentioned statistics.¹ Since the mean value of such fluctuations is set equal to zero, the mean of the $I_{hkl}^1, \dots, I_{hkl}^n$ equals I_{hkl}^{obs} . There is no limitation to the number of I_{hkl}^n values which can thus be generated, and it must necessarily be large enough to carry statistical significance. However, practical considerations (computer time) do set an upper limit. For the present work we have taken $n = 50$. Thus, 50 values $I_{hkl}^1, \dots, I_{hkl}^n$ are generated for every experimentally determined diffraction intensity.

The computer program proceeds now to carry out a cycle of operations where a series of hypothetical structures (with different ionic distribution) are simulated and the corresponding I_{hkl}^{calc} values computed.² Due account is taken of the corrections for anomalous scattering and for the Lorentz, polarization and multiplicity factors. Using Eq. (1), substituting I_{hkl}^n for I_{hkl}^{obs} , the best structure is selected so as to minimize the residual function R .

The whole cycle is repeated over 50 times, one for each set of pseudorandom I_{hkl}^n values, and the individual values of the cation distribution obtained in each calculation cycle (see Tables I and II) are then statistically analysed to determine the corresponding mean value and standard deviation. This standard deviation bears out the stability, and reliability, of the results.

The difference with the standard methods of crystal structure determination rests in the fact that the I_{hkl}^{calc} values are not directly compared with I_{hkl}^{obs} , but with the corresponding pseudorandom values instead.

¹ For computer generation of a pseudorandom variate with predetermined statistical distribution see, for instance, Refs. (6, 7).

² Atomic scattering factors, and corresponding anomalous scattering corrections, were taken from the International Tables for X-ray Crystallography.

Experimental

As stated in the Introduction, the calculation procedure is applied to the $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{Al}_2\text{O}_4$ and $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ ternary spinels. $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{Al}_2\text{O}_4$ was prepared in polycrystalline form by solid-state reaction at $1223(\pm 20)$ K of the parent oxides (CuO , ZnO , and Al_2O_3) mixed in the appropriate proportions. Further details were given elsewhere (8). Likewise, $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ was prepared from CuO , MgO , and Al_2O_3 , under the same experimental conditions. Both samples were rapidly quenched from the annealing temperature.

Diffraction intensities were determined with a powder diffractometer equipped with a graphite crystal monochromator (on the diffracted beam) and scintillation counter; $\text{CuK}\alpha$ radiation was used throughout. Diffraction lines were scanned at a speed of $0.125^\circ \text{ min}^{-1}$ (2θ), accumulating the corresponding number of pulses. Allowance for background was made by setting the goniometer at each side of every diffraction line and accumulating enough pulses to have only a small statistical error. In this way, the 19 most intense diffraction lines were measured for each sample.

Application and Discussion

Tables I and II show the results obtained for $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{Al}_2\text{O}_4$ and $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$, respectively. The first six columns display cation distribution, octahedral sites enclosed in square brackets. Column seven shows the value of the oxygen positional parameter, u . This parameter, which is calculated along with cation distribution, quantifies the distortion of the anion sublattice. When the anions form an ideal cubic close-packed array, $u = 0.375$. In most spinels, however, $u > 0.375$, as a result of small displacement of anions in the [111] direction, which allows expansion of the tetrahedral sites. The last column of Tables

I and II shows the value of the residual function in Eq. (1). Each row presents the results of an individual cycle of the computer program, as previously described. Finally, the last two lines (at the bottom of the tables) display the mean value and standard deviation of each structural parameter.

For $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{Al}_2\text{O}_4$ the mean values of cation distribution and oxygen parameter given in Table I are entirely consistent with previously reported results (8). In the case of $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ no comparative data were found in the literature.

The R -value resulted to be $R = 0.020$ in $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{Al}_2\text{O}_4$ and $R = 0.019$ in $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$. Small fluctuations of this parameter are not considered to be significant. However, it is important to realize that consideration of only the R -value conceals the fact that the precision with which cation distribution parameters are determined is not the same in both cases considered, as could be erroneously concluded from the similarity of the corresponding R -values. Consideration of the standard deviations, as evaluated by the proposed calculation procedure, shows that the results for $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{Al}_2\text{O}_4$ are far more accurate than those obtained for $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$. Thus, the maximum value of the standard deviation is 0.026 (for Cu^{2+}) in the former case, as compared to 0.168 (for Al^{3+}) in the latter (Tables I and II). The utility of the Monte Carlo method rests in its power to evaluate the relative precision with which the distribution of individual cations can be determined.

A related aspect, shown by the results in Tables I and II, is that for any particular sample the uncertainty in site-assignment may take quite different values for different cations. Thus, the corresponding standard deviations show that the uncertainty in the distribution of the ion pairs $\text{Cu}^{2+}/\text{Zn}^{2+}$ in $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{Al}_2\text{O}_4$ and $\text{Mg}^{2+}/\text{Al}^{3+}$ in $\text{Cu}_{0.2}\text{Mg}_{0.8}\text{Al}_2\text{O}_4$ is much greater than the corresponding uncertainty for the third cat-

ion present. Qualitatively this could be suggested in advance, since ions in the mentioned pairs have very close X-ray scattering powers. However, the advantage of the proposed calculation method resides in its ability to give a more quantitative evaluation of these differences, which would be completely overlooked in the standard calculation procedure where the value of the residual R -function is the only indicator of the reliability of the results.

We must stress that, since only stochastic fluctuations of the experimentally determined diffraction intensities have been taken into account, the calculated standard deviations of the results cannot be taken as a means to evaluate the ultimate accuracy of the calculated cation distribution; they are rather an upper limit of accuracy, since uncertainties due to possible systematic experimental errors are not evaluated in our calculation procedure.

It is also relevant to point out that (as suggested by the present results) X-ray power diffraction, coupled with appropriate computational methods, appears to have enough sensitivity to discriminate (at least in some cases) between ions with only one-electron difference, such as Cu^{2+} and Zn^{2+} in $\text{Cu}_{0.6}\text{Zn}_{0.4}\text{Al}_2\text{O}_4$. This has been further confirmed in recent studies on CuGa_2O_4 (9, 10), where it was shown that the distribution of the cations Cu^{2+} and Ga^{3+} (with only one-electron difference) determined by X-ray diffraction resulted to be consistent with the results obtained in previous neutron diffraction studies (11, 12). Iso-electronic ions, such as Mg^{2+} and Al^{3+} are much more difficult, or even impossible, to

discriminate, as shown by the large values of the corresponding standard deviations in Table II.

Finally, we suggest that application of a Monte Carlo method, in a similar way as shown in the present paper, may find a wider use in X-ray crystallography. In particular, it could be useful for studies of cation coordination in solids other than spinels, such as garnets, clays, or zeolites.

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