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Three Different Methods of Determining the Cation Distribution in Spinels: A Comparison

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$MgIn_2S_4$ crystallizes in the $Fd3m$ (O_h^7) space group with $a = 10.7108(8)$ Å. The cation distribution (x) and the deformation parameter (u) have been determined by means of three methods: Bertaut, Furuhashi, and Baltzer. A critical discussion about the coupled use of the three methods is presented.

I. Introduction

The unit cell of the ideal spinel structure (1) is given in Fig. 1.

The general formula of a 2–3 spinel may be written as

$$M_x^{+2}M_{1-x}^{+3}[M_{1-x}^{+2}M_{1+x}^{+3}]X_4^{-2}, \qquad 0<x<1$$

(the practice of writing the octahedral ions between square brackets will be followed). The spinel crystal structure is characterized by three quantities: a, the unit cell constant, u, the deformation parameter, and x, the degree of inversion parameter.

A precise determination of x, u, and a in spinels is a necessary step toward a reliable explanation of the thermodynamic, magnetic, and other properties of this class of compounds. Several methods have been used (2–7) to solve the spinel structure.

The present paper analyzes the three more popular methods: Bertaut's (*2*), Furuhashi's (*3*), and the R factor (*4*). The exploration of the x, u space has to be carried out by means of a grid comparable with the expected error on the x, u values. As a consequence, a large number of hypothetical crystal structures have to be generated and compared with the experiment in order to cover conveniently a suitable range in x and u.

Hence, the three methods have been wholly computerized and new "agreement indicators" used to ensure the most objective search of the best x and u values.

Examining the outcome of the three different and independent ways of determining x and u in parallel allows the elimination of the particular drawbacks of each method and increases the precision of the values obtained.

$MgIn_2S_4$ was chosen as the test compound.

II. Experimental

The $MgIn_2S_4$ was synthesized from a stoichiometric mixture of Mgs and In_2S_3 at 900°C in a sealed quartz tube for 60 hr and annealed.

The compound crystallizes in the $Fd3m$ (O_h^7) space group, and it has been characterized by Hahn (*8*). Iron-filtered Co$K\alpha$ radiation was used both for the cell parameter determination and for the intensity collection.

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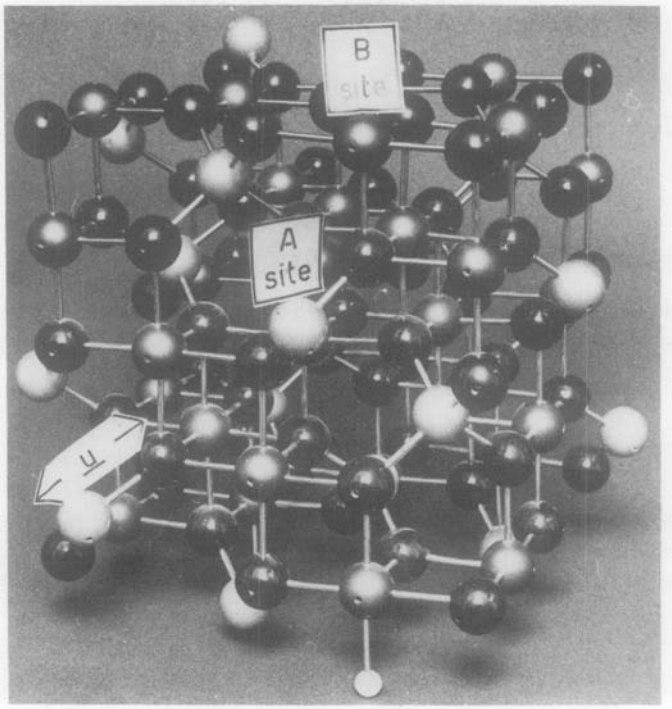

FIG. 1. Spinel unit cell.

The cell constant of the compound was calculated by the least-squares intercept of the Nelson–Riley plot using the α_1 and α_2 reflections (973), (866), (880), (775) at room temperature.

The a obtained was 10.7108 (8) Å and this value was assumed in the remaining part of the work.[1]

The X-ray reflection intensities were collected with a Philips scintillation counter up to $2\Theta = 110°$ using a flat-plate sample.

The integrated intensities of the 14 diffraction lines chosen were obtained by subtracting the background intensity from the intensity counted over a sufficiently wide range of diffraction angles, scanning the counter at $\frac{1}{8}°$ min^{-1}.

A FORTRAN IV program was written in order to automatically vary the x and u parameters and compute the "agreement indicators" for the three different methods of analysis. The program treats cationic solid solutions of up to five different atomic species per site as well as anionic solid solutions.

All the atomic scattering factors were taken from the "International Tables of Crystallography", Vol. IV (1974).

Final programs were run on the HP 2100 (under BCS) of the Research Area of Montelibretti and on the IBM 370/168 (under VM/CMS) of the CNUCE, Pisa.

III. Results

Bertaut's Method

According to Bertaut (*2*), in the $Fd3m$ space group, it is possible to identify five different classes of reflections that are influenced in a different way by changes in the parameters x and u, as shown in Table I.

[1] Preliminary results were presented at the XIth IUC Conference, Warsaw, August 3–12, 1978. The abstract of the communication contains two major printing errors concerning the a and u values.

TABLE I

CLASSES OF REFLECTIONS IN $Fd3m$ S.G. AND THEIR DEPENDENCE BY x AND u

Class	$h^2+k^2+l^2$	Dependence u	Dependence x
a	$32n$	$2^{o[a]}$	0^{b}
b	$16n+11$	1^{oc}	$-^{d}$
c	$16(2n+1)$	2^{o}	$+^{e}$
d	$32n+12$	2^{o}	+
e	$16n+8$	2^{o}	−
f	$16n+3$	1^{o}	+

[a] Influence of the second order.
[b] The intensity is not influenced by x.
[c] Influence of the first order.
[d] The intensity decreases with x.
[e] The intensity increases with x.

The method consists of comparing experimental and calculated intensity ratios of some selected reflections at similar Θ has the advantage that it is almost independent of the values of the scale factor K and the average thermal factor B.

In addition, if one chooses reflections which vary in an opposite manner with x and are influenced by the variation of u, the ratios are a more sensitive measure of the cation distribution than the original intensities.

Seven ratios, following Bertaut's criteria, were selected from the 14 diffraction intensities measured and the mean-square deviation σ was mapped against the x and u parameters in order to obtain an overview of the variation of the agreement between the experimental ratios and those computed according to several possible structures. Contour lines were then plotted at different σ values as shown in Fig. 2. From the map it is possible to identify a single zone of minimum quite well delimited in x, but shallow in u. An absolute minimum exists at $u=0.383$ and $x=0.16$. Table II shows the ratios used in Bertaut's method and their final values at the minimum.

TABLE II

RATIOS USED IN THE BERTAUT METHOD AND THEIR FINAL VALUES AT THE MINIMUM

Ratio	Class	Obs	Calc
400/220	c/e	0.614	0.656
400/422	c/e	1.558	1.584
311/400	b/c	4.371	4.097
(333+511)/400	b/c	1.735	1.778
(553+731)/444	b/c	4.120	4.219
444/620	c/e	0.770	0.778
444/642	c/e	0.589	0.590

The Furuhashi et al. Method

The method (*3*) looks for the best structure among the various possible ones by examining the degree of linearity of the plot obtained by the well-known relation:

$$\ln(I_{obs}/I_{calc}) = \ln K - 2B \sin^2 \Theta/\lambda^2, \quad (1)$$

where $I_{calc} = |FF^*|Lp\, m$.

The best structure must give the plot with the best linearity. The linear least-squares analysis was applied according to Eq. (1) to the 14 diffraction lines collected. This fact ensures that the analysis is sensitive to both x and u through the dependence of the lines themselves on the two above parameters.

For each of the structures generated by varying u and x, the least-squares line, on the basis of the experimental I_{obs} and the calculated I_{calc}, was computed and the correlation coefficient G was mapped against the two parameters. G ranges between +1 and −1 and its value is 0 for the worst fit. The use of G allows a more objective and rapid analysis of the degree of linearity of the plots corresponding to the large number of hypothetical structures needed for an accurate and complete examination of the x and u ranges. Contour lines are plotted in Fig. 3; a well-defined minimum is present with a good value of G (−0.78) at $x=0.16$ and $u=0.383$.

In Fig. 4 the final linear plot at the minimum is shown.

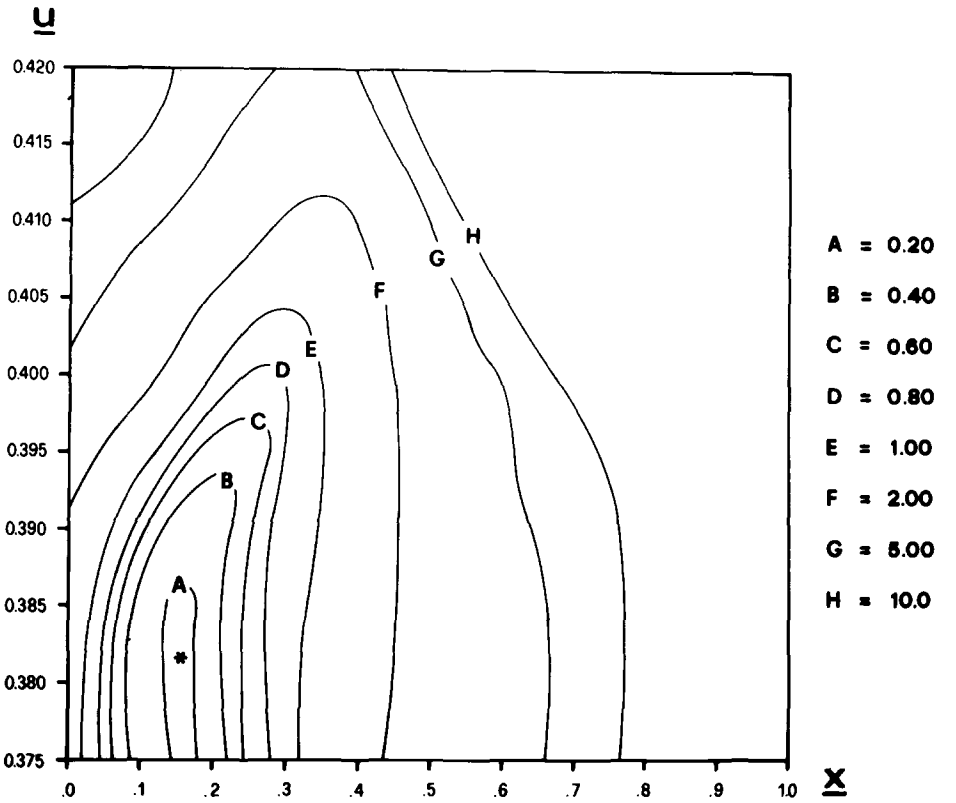

FIG. 2. σ map and contour line values.

This method gives an estimate of the average thermal factor B which is an important physical quantity in the spinel (*9*). At the minimum the values of B and K are 0.77 Å^2 and 3.9×10^{-4}, respectively.

R-factor Method

Following Baltzer *et al.* (*4*), the R-factor function has been mapped against the parameters u and x:

$$R = \frac{\sum|I_{obs} - I_{calc}|}{\sum I_{obs}}, \qquad (2)$$

where

$$I_{calc} = K\, e^{-2B(\sin\Theta/\lambda)^2} |FF^*| Lp\, m. \qquad (3)$$

At each point of the map, the R was optimized with respect to the average thermal factor B and the scale factor K. Because of the great correlation between K and B a Newton–Raphson procedure was applied in order to minimize satisfactorily the R function.

The analysis was applied to all of the 14 diffraction lines collected. The contour lines, reported in Fig. 5, show a single minimum at $x = 0.16$ and $u = 0.383$ with an $R = 0.026$.

The final optimized values of B and K at the minimum are 0.70 Å^2 and 0.4×10^{-3}, respectively.

In Table III the final calculated intensities at the minimum are shown together with the corresponding experimental values.

IV. Discussion

Comparing the σ, G, and R maps, it is obvious that the three zones giving minima in

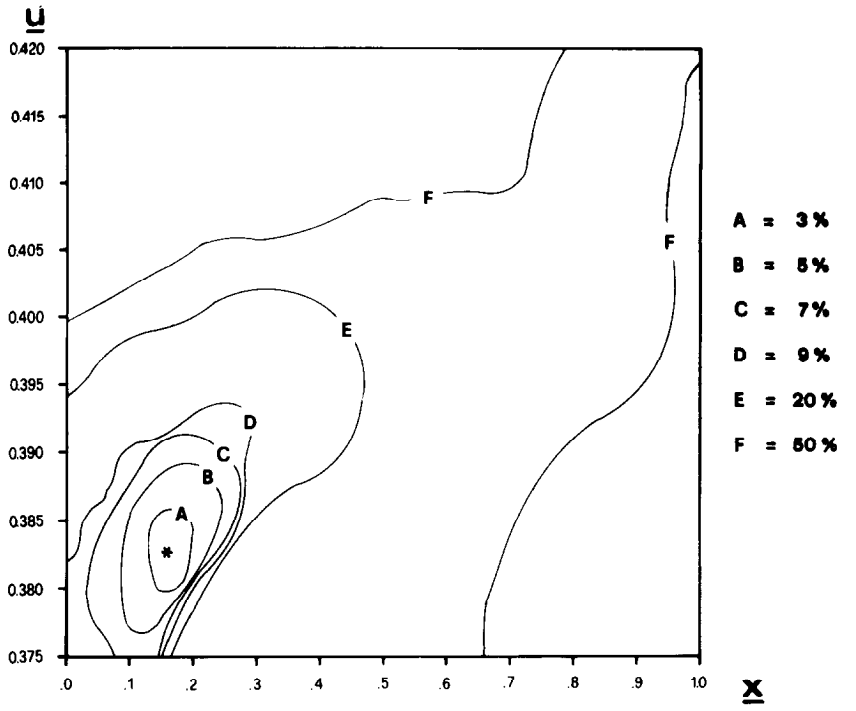

FIG. 3. G map and contour line values.

x and u are superimposed on the three maps; the three absolute minima coincide. The three "minimum" zones are shallow in the variable u and much narrower in x.

TABLE III

EXPERIMENTAL AND COMPUTED INTENSITIES AT THE R MINIMUM

hkl	Class	I_{obs}	I_{calc}
220	e	14,740	14,852
311	b	39,569	39,549
400	c	9,053	9,506
422	e	5,812	5,855
333+511	b	15,705	16,339
440	a	26,768	25,990
602	e	2,170	2,334
444	c	1,672	1,772
642	e	2,837	2,929
553+731	b	6,889	7,229
800	a	3,512	3,786
751+555	b	5,128	4,748
840	c	2,108	2,390
844	a	10,064	10,195

In the present case, the G map, which gives the smallest "minimum" zone, was chosen as a basis for the indication of the final values of x and u and their errors. In other cases, where more ambiguity is present in the final map (e.g., scattering factors of the cationic species not sufficiently different), only those regions having a minimum in x and u that are overlapping in all three maps can be chosen as a basis for the location of the final results; this decreases the uncertainty in each of the methods.

The multidimensional mapping technique will show its power when applied to compounds with more physical variables, and it avoids the multiple-minima problem that is a bad feature of the refinement procedures.

In order to make σ, G, and R as sensitive as possible to x and u, the highest number of X-ray intensities of all classes must be collected with high precision (*10*).

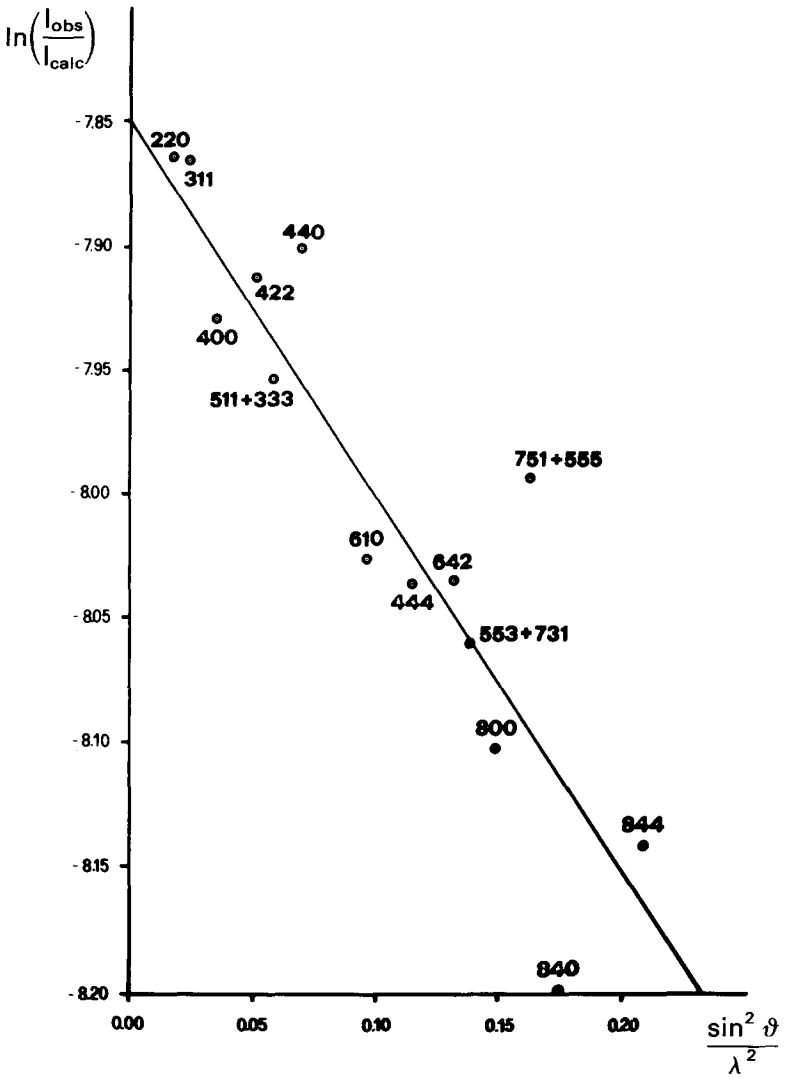

FIG. 4. Linear plot according to Eq. (1) at the minimum of the G map.

TABLE IV

FINAL CRYSTAL DATA: $MgIn_2S_4$

Space group	$Fd3m$
Unit cell constant	$a = 10.7108(8)$ Å
Inversion degree	$x = 0.16(3)$
Deformation parameter	$u = 0.383(2)$
Radiation	Co$K\bar{\alpha}$ $\lambda = 1.7903$ Å
Final value of R	0.026
B average	0.70 Å^2
K	0.4×10^{-3}

The final results for $MgIn_2S_4$ are shown in Table IV where the error in x is assigned on the basis of Ref. *(11)* and the error on u is assigned considering the broadness of the "minimum" zone of the G map.

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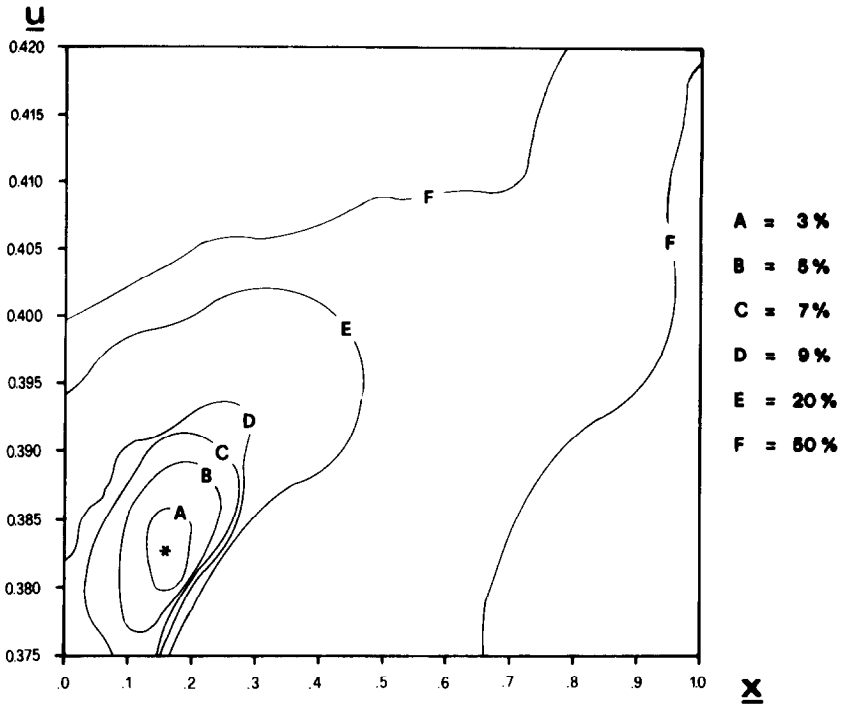

FIG. 5. R map and contour line values.

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