SOVIET PHYSICS – CRYSTALLOGRAPHY VOL. 13, NO. 4 JAN.-FEB., 1969

REFINEMENT OF THE STRUCTURE OF THE SPINEL Al_2MgO_4

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Translated from Kristallografiya, Vol. 13, No. 4, pp. 703-705, July-August, 1968
Original article submitted April 12, 1967; revision submitted October 20, 1967

If a sufficient number of reliable nonsystematic extinctions can be established on the x-ray diffraction patterns of a crystal, then, in principle, the equations in which $F_{hkl} = 0$ worked out for these reflections can permit the determination of the coordinates of all atoms of the crystal. However, the mathematical difficulties associated with the solution of a system of transcendental equations, and the highly probable ambiguity of the answer, render the general case hardly surmountable in practice. Nevertheless, the nonsystematic extinction method may prove to be useful for the refinement of simple structures with a very small number of parameters.

As the object of this study we selected a spinel with a structure determined entirely by one parameter. The refinement of this parameter is of interest. In the unit cell of the spinel Al_2MgO_4 (space group $O^7_h = Fd3m$, $a = 8.075$ Å, z = 8), 8 magnesium atoms occupy positions (b), 16 aluminum atoms occupy positions (c), and 32 oxygen atoms occupy positions (e) determined by the one parameter x. The original structure determinations were carried out in 1915 [1, 2]. In information contained in literature, the parameter x is carried through from [1] and is given as 3/8, under conditions such that the origin of coordinates occurs at a point of intersection with a third-order axis. This parameter x becomes 1/4 if the origin is shifted to the center of symmetry.

This value of the parameter allows description of the positions of the oxygen atoms as forming a cubic close-packing with the edge of the cube as half the edge of the unit cell of the spinel. The radius of the magnesium ion is 0.74 Å, and the radius of the aluminum ion is 0.57 Å. Nevertheless, the magnesium ions are found to be located in the tighter tetrahedral interstices and the aluminum ions in the looser octahedral ones. This incongruity causes one to wish to interchange the atomic positions of aluminum and magnesium (inverted spinel). The problem of inversion of this or that spinel can be resolved by neutron diffraction [3]; however, in this case it is also expedient to make a preliminary, precise location of the oxygen by x-ray diffraction methods.

To obtain experimental data, a crystal in the shape of a sphere 0.5 mm in diameter was rotated about the [112] axis in a KFOR camera. The pattern was made using molybdenum radiation with a zirconium filter. Five reciprocal lattice planes were deciphered. In this case, the presence of twelve [112] type axes guaranteed full coverage of the possible reflection field.

First of all, we turned to the analysis of those reflections with the 4m, 4p, and 4n + 2 types of indices. Among them, these weak, but positively identified, spots were observed: 442; 842; 882; 12, 4, 2; 12, 8, 2; 12, 12, 2; 886, 12, 4, 6; 12, 8, 6. The 446; 4, 4, 10; 8, 4, 10; 8, 8, 10; 12, 4, 10; 4, 4, 14; 8, 4, 14 reflections of these same types were found to be extinguished. Magnesium and aluminum do not contribute to the formation of any of the reflections enumerated. These spots are caused by scattering by oxygen atoms only, and their intensities are proportional to the square of the function

$$\sin 2\pi hx \cdot \sin 2\pi kx \cdot \cos 2\pi lx \qquad (1)$$

and decrease with increase of the sum of the squares of the indices. If x = 0.250, then the third factor in (1) is equal to −1, and the first two reduce to zero. Therefore, the presence of a rather great number of reflections of the types indicated above shows that $x \neq 0.250$.

For other values of x close to 0.250, the first two factors in (1) are larger the larger h and k become, and the third becomes less the greater l becomes. In view of this, the reflections with small first two indices (4, 8) and large third index (10, 14) and comparatively large sum of squares of indices remain very weak over a wide range of values of x near 0.250 and are not suitable for refinement of the value of the parameter.

Six more nonsystematic extinctions were found on the patterns, with indices 117; 375, 1, 5, 11; 3, 11, 9; 6, 10, 8, and 10, 10, 4. The 117 reflection, with the smallest sum of squares of indices, was of interest. The structure factor F_{117} was found to be equal to zero for the values x = 0.036, 0.083, 0.171, 0.236, 0.264, 0.329, 0.417, and 0.464. The structure factors of the spots for the extinguished reflections were close to zero at the same time only for x = 0.236, which allowed us to consider this the correct value of the parameter. It should be noted that two or three structure factors are also close to zero at the same time for the other values of x. Therefore, in this case, not fewer than four extinguished reflections were required in order to obtain an unambiguous answer.

In order to test the accuracy of the result obtained, the x parameter was evaluated by comparison of the intensities of specific reflections, approximately as was done by V. P. Glagoleva and G. S. Zhdanov [4]. In addition, by use of 157 independent reflections, a one-dimensional section of the electron densities along the body diagonal of the cube was constructed, since peaks of all three sorts of atoms appear on it. This allowed us to calculate the parameter by still another independent method. Both control calculations gave the very same value: x = 0.236 ± 0.001.

TABLE 1

Atoms	$x=0.250$	$x=0.236$	ΣR_{theor}	ΣR_{exp}
Mg—O	1,75	1,94	2.02	2,10
Al—O	2.02	1,91	1,87	1,93

Finally, the oxygen-magnesium and oxygen-aluminum distances were calculated. These distances are given in Table 1, where they are compared with the sums of the corresponding ionic radii calculated theoretically [5] and found experimentally [6]. The significant improvement in agreement can be seen from the table, which allows us to consider that, if the spinel Al_2MgO_4 is inverted, it is not inverted significantly.

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