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## LETTER TO THE EDITOR

# On the cationic distribution in $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$ spinels

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**Abstract.** A neutron powder diffraction refinement of the structure parameters of five samples of magnesium cobalt oxide spinels  $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$  ( $0 < x < 1$ ) has been carried out. It was found that all spinels under study are inverse and there is a limit to the occupancy of the tetrahedral sites by Mg.

Recently, the assumption that thermal decomposition of appropriate precursors with a specific layered structure derivative of that of brucite  $\text{Mg}(\text{OH})_2$  leads to formation of the oxide spinel phase via a topotactic mechanism requiring no long-range cationic diffusion transport has been verified for the  $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$  ( $0 < x \leq 1.0$ ) spinel system [1]. A neutron diffraction study yielded a statistical distribution (absence of any preference) of the  $\text{Cu}^{2+}$  cations in occupying the tetrahedral (A) sites and the octahedral (B) sites of the cationic sublattice, thus confirming the previous preliminary findings [2]. This result may be regarded as a direct confirmation of the suggestion that the cationic distribution of the final product is predetermined by the structure of the precursors and the mechanism of their thermal decomposition.

Results of a similar study on a set of samples with the general formula  $\text{Mg}_x\text{Co}_{3-x}\text{O}_4$  are presented here. The samples are prepared by thermal decomposition of a mixture of layered hydroxide nitrate precursors  $\text{Mg}_x\text{Co}_{2-x}(\text{OH})_3\text{NO}_3$  in which the magnesium content varies extensively within the spinel phase homogeneity limits. The procedure for sample preparation, which is essentially the same as the one used for the  $\text{Cu}_x\text{Co}_{3-x}\text{O}_4$  spinels, is presented in detail elsewhere [3]. X-ray diffraction analyses were carried out for phase control of the precursors and final products. The content of cobalt and magnesium in the resulting fine black powders was determined by means of a Spectroflame spectrometer, Germany, which uses inductively coupled plasma.

Neutron diffraction patterns were first obtained on the DN-520 diffractometer of the steady-state research reactor IRT-2000 of INRNE and later completed using the DN-2 time-of-flight apparatus equipped with a one-dimensional position-sensitive detector on beam 6B of the IBR-2 pulsed reactor of JINR, Dubna [4]. A thin-walled vanadium container for the powder sample was used.

The room temperature diffraction patterns consisted of Bragg peaks in positions given by the spinel structure and of a smooth background. No other phase was observed. There is a nuclear neutron scattering contribution to the measured intensity only because the magnesium cobalt oxides are not magnetically ordered at room temperature.

Since the intensity of neutron diffraction lines is related to the square of the coherent neutron scattering amplitude, which reflects the isotope concentration alone and is independent of the atomic valence state of the scatterer, the magnesium cobalt oxides should be considered as containing only two cationic components and the cationic distribution over the two spinel sites is expressed by the formula



where  $\alpha$  depends on  $x$  and denotes the degree of inversion defined as the fraction of octahedral sites occupied by  $\text{Mg}^{2+}$  ions, and the cations in B sites are given in brackets. Of special note is the completely random cationic distribution described by  $\alpha = (2/3)x$ . The average scatterer amplitudes  $b_A$  and  $b_B$  of the effective scatterers in the tetrahedral (A) and the octahedral (B) sites of the spinel structure should be written as

$$\begin{aligned} b_A &= (x - \alpha)b_{\text{Mg}} + (1 - x + \alpha)b_{\text{Co}} \\ 2b_B &= (2 - \alpha)b_{\text{Co}} + \alpha b_{\text{Mg}} \end{aligned} \quad (2)$$

where  $b_{\text{Co}}$  and  $b_{\text{Mg}}$  are the neutron scattering lengths of cobalt and magnesium taken from [5].

From (2) it follows that the relation

$$b_A + b_B = xb_{\text{Mg}} + (3 - x)b_{\text{Co}} \quad (3)$$

may be used as a constraint during the crystal structure refinement. On the other hand, the accuracy of the chemical composition and the stoichiometry of the sample under study may be checked.

The spinel structure refinement was done by the full profile Rietveldt method implemented in the computer code MR1A [6]. The origin of the spinel unit cell was chosen at the centre  $\bar{4}3m$ , the tetrahedral, octahedral and oxygen sites being in 8(a), 16(d) and 32(e) positions of the space group  $Fd\bar{3}m$ , number 227 in the *International Tables*. The structural parameters taken as variables in the profile analysis were the effective scattering amplitudes  $b_A$  and  $b_B$ , the oxygen parameter  $u$  and the lattice constant. The estimates of the temperature factor B were found unreliable and were left out of consideration due to the strong correlation between B and some structurally independent refinement parameters. The conventional profile reliability factors

$$\begin{aligned} R &= \sum_i |I_i^{\text{exp}} - I_i^{\text{calc}}| / \sum_i I_i^{\text{exp}} \\ R_w &= \left( \sum_i w_i (I_i^{\text{exp}} - I_i^{\text{calc}})^2 / \sum_i w_i (I_i^{\text{exp}})^2 \right)^{1/2} \end{aligned} \quad (4)$$

with  $I_i^{\text{exp}}$ ,  $I_i^{\text{calc}}$  the observed and calculated profile intensity, respectively, and  $w_i$  the corresponding weight ( $w_i = 1/(\Delta J_i)^2$ , where  $\Delta J_i$  is the estimated standard deviation of  $I_i^{\text{exp}}$ ), and with the summation carried out over all measured profile intensity points, were used as a criterion for the convergence of the theoretically calculated profile to the experimental one.

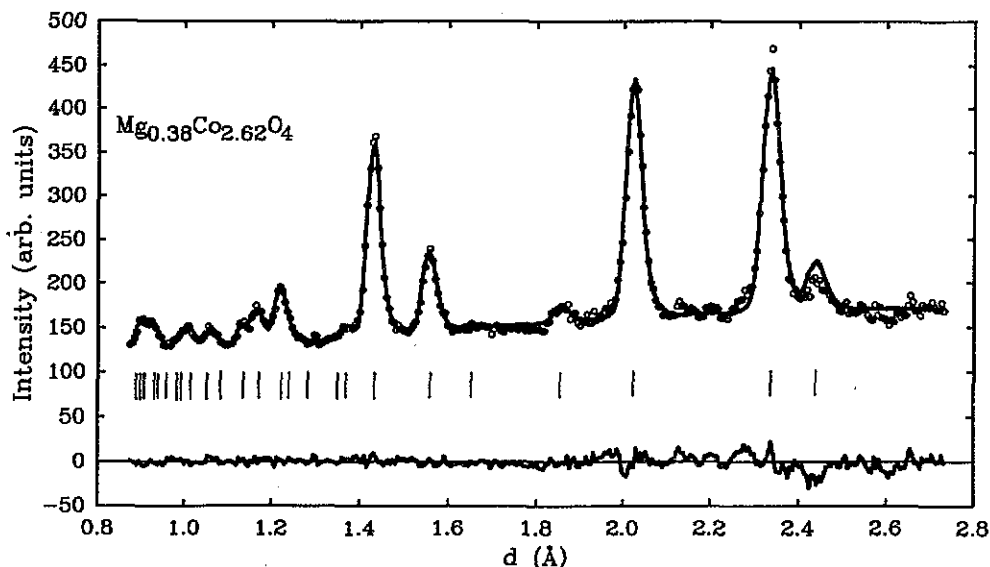


Figure 1. Neutron powder diffraction pattern of  $\text{Mg}_{0.379}\text{Co}_{2.621}\text{O}_4$  at  $T = 293\text{K}$  and the difference curve between the observed and calculated intensities obtained by the full profile analysis.

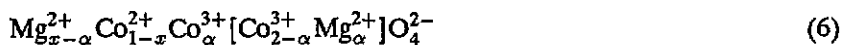
The refinement resulted in relatively low reliability factors of the order of 2–3%, and  $\chi^2$  values ranging from 1.5 to 2.2 for all samples investigated, which implies a quite satisfactory agreement between observed and calculated intensities. Figure 1 shows the neutron diffraction pattern of the sample with composition  $x = 0.38$  as a typical illustration of the final result of the refinement procedures with or without imposed constraints.

The values of the refined structure parameters are given in table 1. For the sake of completeness some published results on  $\text{Co}_3\text{O}_4$  are summarized and presented in the same table.

Here we should note that the supposition that the magnesium ions are distributed fully at random among the spinel lattice sites was not proved. As figure 2 shows, the actual variation of the amount of Mg(A) ions,  $x - \alpha$ , and Mg(B) ions,  $\alpha$ , with composition,  $x$ , does not correspond to what one would expect on the basis of the statistical distribution. The two sets of data fit straight lines described by

$$\begin{aligned} z - \alpha &= 0.20 + 0.0x & r &= 0.02 \\ \alpha &= -0.20 + 1.0x & r &= 0.996. \end{aligned} \quad (5)$$

Bearing in mind the condition for electrical neutrality and that the magnesium ions can only be bivalent, the ionic formula



is consistent with the partially inverse spinel structure and accounts for the formal valence of the cations. The resulting occupancies of lattice sites by the different cationic species according to (6) presented in table 1 are calculated from (2) using the refined values of the effective scattering amplitudes  $b_A$  and  $b_B$ .

Table 1. Dependences of the lattice cell parameter,  $a_0$ , oxygen parameter,  $u$ , tetrahedral (A) and octahedral (B) site occupancies of  $Mg_xCo_{3-x}O_4$  spinels on the magnesium content,  $x$ , in the formula unit. Conventional profile reliability factors  $R$  and  $R_w$  are shown† (see text).

$x$	$a_0$	$u$	Occupancies, A			Occupancies, B			$R$ (%)	$R_w$ (%)	Reference
			$Mg^{2+}$	$Co^{3+}$	$Co^{2+}$	$Mg^{2+}$	$Co^{3+}$	$Co^{2+}$			
0.0	8.0835(6)	0.389(1)			1.00			2.00			[9]
	8.065	0.388			1.00			2.00			[10]
	8.0819(3)	0.388(1)			1.00			2.00			[11]
0.379(4)	8.1006(6)	0.3880(1)	0.18(2)	0.20(2)	0.62(2)			0.20(2)	1.80(2)	2.5	2.6
0.582(3)	8.1143(5)	0.3875(1)	0.23(2)	0.35(2)	0.42(2)			0.35(2)	1.65(2)	2.5	2.7
0.675(7)	8.1211(7)	0.3870(2)	0.22(3)	0.46(3)	0.32(3)			0.46(3)	1.54(3)	2.8	3.0
0.868(8)	8.134(1)	0.3865(2)	0.19(3)	0.68(3)	0.13(3)			0.68(3)	1.32(3)	2.7	3.0
0.925(6)	8.139(1)	0.3859(3)	0.20(4)	0.73(4)	0.07(4)			0.73(4)	1.27(4)	2.3	2.5

†Data refined using the following neutron nuclear scattering amplitudes:  $b_{Co} = 0.253$ ,  $b_{Mg} = 0.5375$ ,  $b_O = 0.5805$  ( $10^{-12}$  cm) [5]. Standard deviations referred to the last significant digit are given in parentheses.

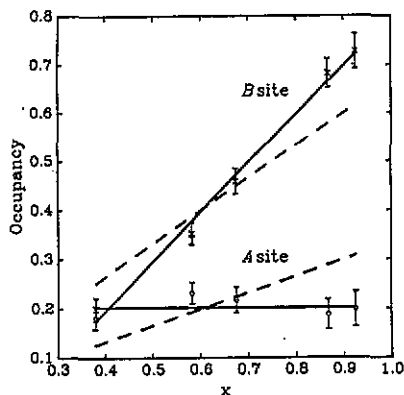


Figure 2. Dependence of the fraction of Mg ions in A sites and B sites on the total Mg content,  $x$ , per formula unit  $Mg_xCo_{3-x}O_4$ . Dashed lines correspond to the statistical distribution.

Linear regression analysis shows that the dependence of the unit cell parameter,  $a_0$ , on the magnesium content,  $x$ , in the formula unit is rather well fitted to a straight line

$$a_0 = c_1 + c_2x \quad (7)$$

with a slope  $c_2 = 0.00696(11)$  and a correlation coefficient near unity ( $r = 0.9996$ ). The intercept  $c_1 = 0.80740(8)$  nm compares favourably with the lattice parameter of  $Co_3O_4$  ( $x = 0$ ).

The linear relationship (7) has to be considered in correlation with the remaining structural parameters. The data (see table 1) show that all magnesium cobalt oxides under study are partially inverted spinels with oxygen parameters lower than that of  $Co_3O_4$  which is a normal spinel. With increasing content of bivalent magnesium the oxygen parameters gradually decreases towards the value  $u = 0.375$ , which corresponds to the ideal spinel structure. This behaviour can be understood bearing in mind that any deviation from  $u = 0.375$  implies a distortion from the ideal cubic close-packed arrangement of the oxygen ions. As  $u$  decreases the oxygen ions shift along the cube diagonals ([111] directions) causing the octahedral sites to enlarge at the expense of the tetrahedral sites. The decrease of  $u$  should be caused by the increased amount of  $Mg^{2+}$  ions in octahedral coordination, which are bigger than  $Co^{3+}$  ions, and the same quantity of  $Co^{3+}$  ions displaced by magnesium to the tetrahedral site, which are smaller than  $Co^{2+}$  and  $Mg^{2+}$  cations, whose effective ionic radii are almost equal (cf. table 2).

From this it follows that the increase in the lattice parameter with increasing magnesium content can be explained by accumulation of  $Mg^{2+}$  at the octahedral sites of the spinel lattice, which will outweigh the decrease in the unit cell parameter due to the appearance of  $Co^{3+}$  ions in tetrahedral sites.

In conclusion, for the mixed spinel system  $Mg_xCo_{3-x}O_4$  under study, evidence was obtained that practically a constant fraction of total Mg ions enters the tetrahedral sites of the spinel structure, i.e., there is a limit to the occupancy of A sites by magnesium.

Table 2. Effective ionic radii compiled by Shannon [7] and O'Neil and Navrotsky [8]. High-spin and low-spin states are denoted by HS and LS.

Cation type	Radius (Å)			
	Tetrahedral coordination		Octahedral coordination	
	[8]	[7]	[8]	[7]
Mg <sup>2+</sup>	0.585	0.57	0.715	0.72
Co <sup>2+</sup>	0.58	0.58	0.72	HS 0.745 LS 0.65
Co <sup>3+</sup>	0.45	—	0.53	HS 0.61 LS 0.545

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