

СООБЩЕНИЯ  
ОБЪЕДИНЕННОГО  
ИНСТИТУТА  
ЯДЕРНЫХ  
ИССЛЕДОВАНИЙ  
ДУБНА

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**A TEST FOR CRYSTALLOGRAPHIC STUDIES  
ON THE NSWR NEUTRON SPECTROMETER  
AT THE IBR-2 PULSED REACTOR:  
CATION DISTRIBUTION IN SPINELS**

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## INTRODUCTION

The new Neutron Spectrometer NSW installed at the powerful impulse reactor IBR-2 is a versatile Time-of-Flight (TOF) neutron-scattering tool which capability for complex texture studies, amorphous materials characterization and quasi-elastic scattering has been proved in practice<sup>1,2/</sup>.

To test this spectrometer in relation to the crystallographic problem of structure analysis, the task was undertaken to determine the cation distribution in Co-Fe spinels. This system is interesting from the methodical point of view due to the following:

a) As iron and cobalt scatter X-rays almost equally, neutron nuclear scattering is needed to separate the contributions from these atoms in a diffraction experiment.

b) The considered spinels are ferrimagnetic, and thus give rise to characteristic magnetic neutron scattering phenomena.

From the technological point of view the Fe-Co spinels represent a family of important materials related to the laterites of the north-eastern region of Cuba.

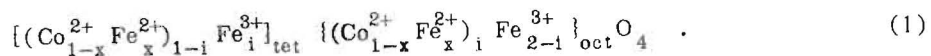
## THEORETICAL BACKGROUND

The general scheme of the spinel structure is well known<sup>3/</sup>. It's cubic cell (space group Fd3m) is built up on the frame of 32 oxygen anions, that determine the 16 octahedral and 8 tetrahedral sites among which the corresponding cations are distributed.

In a normal or direct spinel, as, for example, the mineral spinel  $MgAl_2O_4$ , the 16 trivalent cations occupy all the octahedral sites and the divalent cations occupy the tetrahedral sites. In inverse spinels, for example magnetite  $Fe_3O_4$ , a half of the trivalent cations occupy the tetrahedral sites, while the octahedral sites are fifty-fifty occupied by di- and trivalent cations. Between these extreme cases a continuous spectrum of states is, in principle, possible, so we have as the first problem in a structure analysis of a spinel that of the determination of the degree of inversion. For Cobalt-Iron spinels

$Co_{1-x}^{2+} Fe_x^{2+} Fe_2^{3+} O_4$ , with x characterizing the separation in relation to the stoichiometric  $CoFe_2O_4$ , this problem can be

stated as the determination of the inversion parameter  $i$  in the formula:



Evidently, for direct spinels  $i = 0$ , while for inverse  $i = 1$

Another problem to be solved in a spinel characterization is the measurement of the so-called oxygen parameter  $u$ , that describes the positions of the anions. For ideal cubic symmetry  $u = 3/8$ . In general, the oxygen ions are displaced from the ideal symmetric positions by an amount of  $\Delta = (u - 3/8)\sqrt{3} a_0$  in a cell diagonal direction.

The two above stated problems are to be solved by measuring the integral diffracted intensities of the Bragg peaks in the considered, in general polycrystal, sample. In our case the determination of cation distribution is associated with the magnetic scattering of neutrons by the ferrimagnetic order of this type of structure: the magnetic moments (spins) in tetrahedral sites are opposite to those in octahedral sites, thus leading to a phase-shift of  $180^\circ$  in the scattered neutron waves.

The fundamental equation relating the structure factor  $F^2$  to the integral intensity  $I$  measured in a neutron TOF polycrystal diffraction experiment is the following:

$$I = k F^2 \lambda^4 \phi L A N_c^2 p, \quad (2)$$

where:  $k$  is instrumental factor, constant in a given spectrum;  $\lambda$ , neutron wave-length;  $\phi = \phi(\lambda)$ , reactor spectrum;  $L$ , Lorentz factor. It depends on the scattering angle, so it is constant in a TOF spectrum.  $A$  is absorption factor. It depends on the absorption coefficient  $\mu$ , as described in the literature<sup>5/</sup>, with  $\mu$  proportional to  $\lambda$ ,  $N_c$  is number of unit cells per unit volume;  $p$ , multiplicity factor.

The structure factor, as described in<sup>6/</sup>, is built up of its nuclear and magnetic contributions:

$$F^2 = F_{\text{nuc}}^2 + q^2 F_{\text{mag}}^2 \quad (3)$$

with

$$F_{\text{nuc}}^2 = \left| \sum b \exp 2\pi i \left( \frac{hx}{a_0} + \frac{ky}{b_0} + \frac{lz}{c_0} \right) \right|^2 e^{-2w} \quad (4)$$

$$F_{\text{mag}}^2 = \left| \sum p \exp 2\pi i \left( \frac{hx}{a_0} + \frac{ky}{b_0} + \frac{lz}{c_0} \right) \right|^2 e^{-2w} \quad (5)$$

$$q^2 = \sin^2 \alpha. \quad (6)$$

Here  $b$  and  $p$  are, respectively, the nuclear (isotropic) and magnetic (form-factor dependent) scattering amplitudes;  $h, k, l$ , miller indices;  $x, y, z$ , atomic coordinates;  $a_0, b_0, c_0$ , cell parameters;  $\exp(-2W)$ , temperature factor; and  $\alpha$ , angle between scattering and magnetization vectors.  $q^2$  is the "magnetic interaction vector" squared.

In comparison with angle dispersive neutron or X-ray diffraction, the neutron TOF measurements have the following peculiarities. As the plotted spectra are  $I$  vs  $\lambda$ , the factor  $\lambda^4$  varies strongly within one spectrum. Also significantly vary  $\phi(\lambda)$  and  $A$ . Specific contrast with X-rays is found in the amplitudes  $b$  and  $p$ . Nuclear amplitudes appreciably differ between Fe and Co, although the corresponding values for X-rays are almost the same. Neutron magnetic amplitudes are composed in dependence on the magnetic moment orientation. In our ferrimagnets opposite spins have opposite signs for  $p$  in Eq. (5).

For calculating the magnetic interaction vector one needs to know the relative orientation of scattering and magnetization vectors. In spinels the magnetic equivalence of the cell diagonals as easy directions leads to a mean value of  $\langle q^2 \rangle = 2/3$  for all reflections<sup>7/</sup>.

With these elements, the determination of cation distribution in spinels is carried out by fitting the crystallographic and magnetic structures to minimize the disagreement between experimental and calculated intensities.

## EXPERIMENTS AND RESULTS

Two samples were prepared at the Laboratory of Magnetism of the Havana University (Physics Faculty). Sample 1 is the stoichiometric  $\text{CoFe}_2\text{O}_4$ . Sample 2 has the composition  $\text{Co}_{0.8}\text{Fe}_{2.2}\text{O}_4$ . Suitable amounts of  $\text{Co}(\text{SO}_4)_2(\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2 \cdot 6\text{H}_2\text{O}$  were dissolved in water and then coprecipitated in acetone. The resulting salt was decomposed at  $840^\circ\text{C}$ , sifted and pressed at 250 MPa. For sintering the obtained blocks were heated in Argon atmosphere at a temperature increase rate of  $5^\circ\text{C}/\text{min}$  to a final  $T = 1300^\circ\text{C}$ . At this temperature the process was completed after 2 hours. The dimensions of the cylinders thus prepared were: diameter = 12 mm, height = 5 mm. They were examined by X-ray diffraction and showed only the spinel lines.

The TOF spectra for the considered samples were obtained at NSW with the texture configuration, as described in<sup>1/</sup>. The neutron flight-path was 34.20 m and the scattering angle was fixed at  $2\theta = 60^\circ$ . Two cylindrical samples were glued at both sides of a paper foil conforming a roughly "spherical" sample that was bathed in the neutron beam.

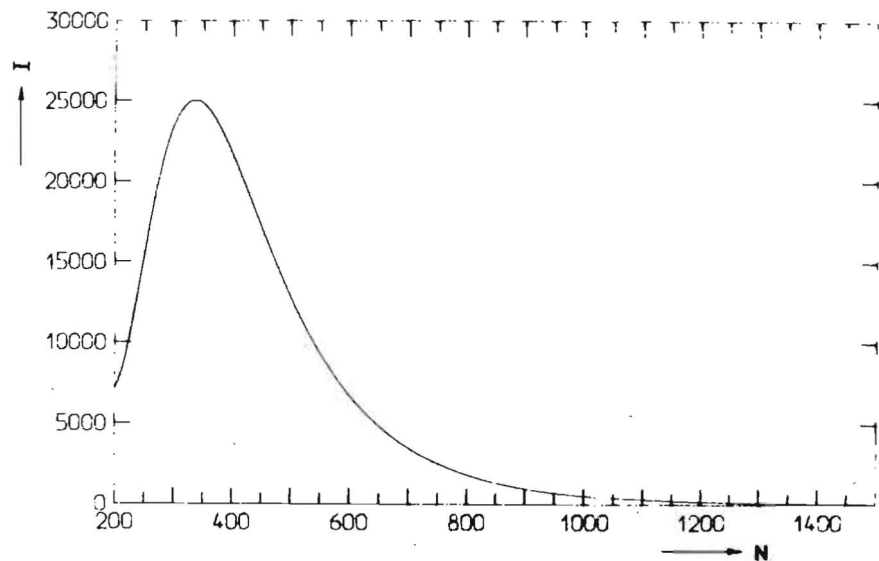


Fig. 1. Spectrum of the IBR-2 impulse reactor. Abscissae values on Figs. 1-3 are the TOF channel numbers. They could be converted to interplanar distances via eq. (7).

To check the possible influence of a texture on the diffracted intensities, the samples were rotated in the texture goniometer over a  $90^\circ$  interval about an axis perpendicular to the sample symmetry axis. No texture was detected.

Figure 1 shows the neutron intensity distribution of the incident beam in dependence of the wavelength, i.e., the reactor spectrum of the IBR-2. The drawing corresponds to a filtered mean-square fit to the experimental scattering spectrum from a vanadium sample. In this and in the following spectra, the horizontal axis represents the neutron wave-length, measured as "channel number"  $N$ . The relation among  $N$ ,  $\lambda$  and the interplanar distance  $d$  is given by the calibration:

$$d(\text{nm}) = \frac{N - 38}{2687} \quad (7)$$

for a Bragg angle  $2\theta = 60^\circ$  and a channel width of the time analyser  $32 \mu\text{s}$ . Vertical axes represent intensities in arbitrary scales.

Figure 2 is a plot of the TOF spectrum of sample 1 and Figure 3 shows the same spectrum divided point-by-point by the reactor spectrum of Fig. 1.

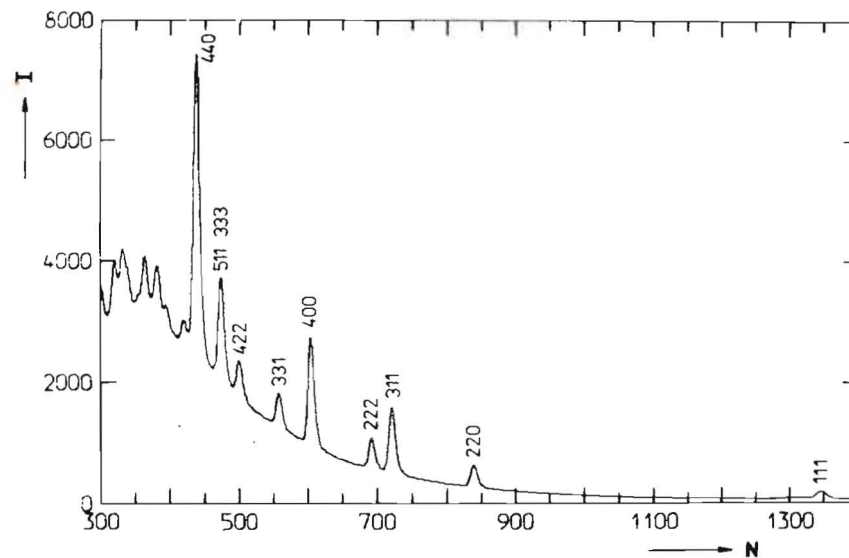


Fig. 2. Experimental TOF spectrum of sample 1.

The spectra of samples 1 and 2 were analyzed on a PDP 11/70 computer by means of a fitting program. Eighteen peaks were resolved and its integral intensities measured. The theoretical intensities to be compared with the experimental ones were calculated with the program SPINEL that computes the following. For a given sample, a set of constant data are taken that determine non-fit-table factors as composition and absorption. Then a set of structures is systematically generated to search for the best fitting among experimental and theoretical intensities. The minimized disagreement factor was:

$$R = \frac{\sum |I_{\text{teor}} - I_{\text{exp}}|}{\sum I_{\text{exp}}} \quad (8)$$

For calculations, nuclear amplitudes (scattering lengths) were taken from <sup>6/</sup>, magnetic form factors from <sup>8/</sup>, isotropic temperature and absorption corrections were treated, respectively, according to <sup>9/</sup> and <sup>7/</sup>, adequated to  $\lambda$ -dependence in the obtained TOF spectra.

Table 1 shows in detail the results for sample 1. The given theoretical intensities are optimized with respect to the inversion and oxygen parameters. The result of optimization is  $R = 6\%$  for  $i = 1$  and  $u = 0.376$ . For comparison let us consider

Calculated and Experimental Intensities for $\text{CoFe}_2\text{O}_4$						
NR	HKL	CHANNEL	MAGNETIC	NUCLFAK	TOTAL	EXPERIMENTAL
1	111	1342	535.2	0.3	534.5	530.6
2	220	837	37.7	49.0	86.7	84.5
3	311	720	2.8	94.6	102.4	115.0
4	222	690	36.6	19.8	56.4	44.4
5	400	604	28.4	50.5	78.9	83.6
6	331	557	22.0	0.2	22.2	18.4
7	422	500	3.4	12.8	16.2	14.4
8	511 + 333	474	0.4	25.9	26.3	34.3
9	440	439	0.8	81.8	82.6	81.9
10	531	421	5.1	0.0	5.1	5.9
11	620	397	0.4	4.8	5.2	4.9
12	533	384	0.1	7.5	7.6	6.6
13	622	380	1.4	5.0	6.4	5.4
14	444	365	0.6	8.2	8.8	4.0
15	711 + 551	356	0.8	0.0	0.8	3.2
16	642	341	0.1	4.9	5.0	3.7
17	731 + 553	334	0.0	11.7	11.7	10.8
18	800	322	0.0	10.4	10.4	7.8

Table 2

Calculated and Experimental Intensities for  $\text{Co}_{0.8}\text{Fe}_{2.2}\text{O}_4$ 

4KL	111	220	311	222	400	331	422	511/333	440	531
CALC.	709.5	169.5	232.0	104.8	197.8	55.1	42.3	91.2	243.5	14.4
EXPER.	715.2	167.9	229.1	102.5	195.7	45.8	37.8	92.7	250.4	28.0

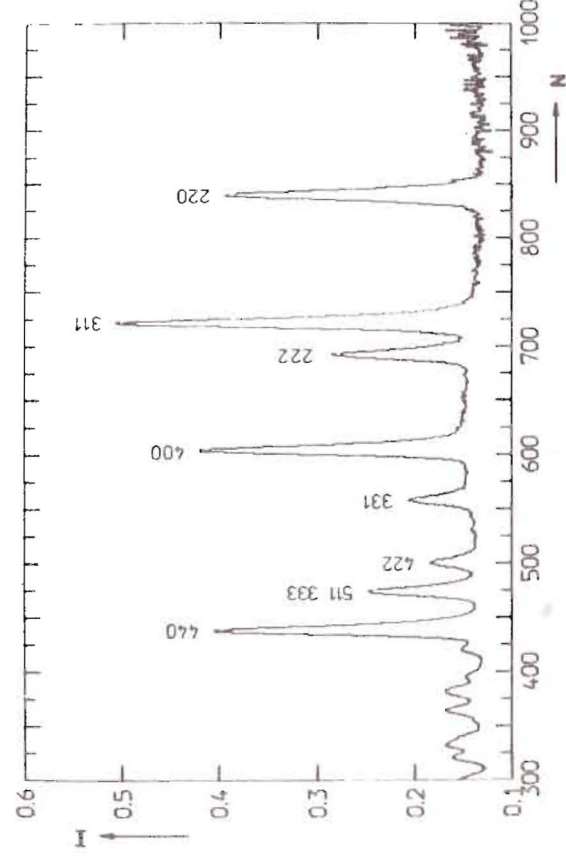


Fig. 3. Spectrum of sample 1, divided point-by-point by the reactor spectrum.

the following result. If  $i$  is fixed at  $i = 0$ , then independently of variations on  $u$  it is obtained  $R \geq 20\%$ . This shows the resolving power of the performed experiment and specifically the fully inverted character of the considered spinel.

For sample 2 the result is equivalent. Table 2 shows a more abstracted comparison of experimental and calculated data. For this sample the final  $R = 4\%$  for completely inverted structure ( $i = 1$ ) with  $u = 0.380$ .

#### CONCLUSIONS

The capability of the NSW neutron spectrometer for high-symmetry polycrystal structure analysis has been established. Pertinent methodical and computational means have been developed for spinel-type structures, with consideration of both nuclear and magnetic scattering. The cation distribution in  $\text{Co}_{1-x}\text{Fe}_{2+x}\text{O}_4$  spinels has been studied for  $x \leq 0.2$ , with the general result of inverse structures with oxygen parameter slightly larger than the ideal cubic-symmetry value.

#### ACKNOWLEDGEMENTS

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Фуентес Л., Гарсия-Тарахано Э., Вальтер К.  
Возможности спектрометра НСВР на реакторе ИЕР-2  
для кристаллографических исследований:  
распределение катионов в шпинелях

E14-85-474

Показаны возможности нейтронного спектрометра НСВР на импульсном реакторе ИЕР-2 для структурного анализа. Обсуждаются методические и математические вопросы интерпретации время-пролетных спектров с учетом ядерного и магнитного рассеяния нейтронов. Проведены исследования ферромагнитной структуры шпинелей Co-Fe. Для этих систем установлено одинаковое распределение катионов, которое образует обратную шпинельную структуру. Фактор расходимости составил 4-6%.

Работа выполнена в Лаборатории нейтронной физики ОИЯИ.

Сообщение Объединенного института ядерных исследований. Дубна 1985

Fuentes L., Garcia-Tarajano E., Walther K.  
A Test for Crystallographic Studies  
on the NSW Neutron Spectrometer at the IBR-2 Pulsed Reactor:  
Cation Distribution in Spinel

E14-85-474

The capability of the neutron spectrometer NSW at the impulse reactor IBR-2 for structure analysis is demonstrated. Methodical and mathematical problems in relation to the interpretation of time-of flight (TOF) spectra are discussed, taking into account nuclear and magnetic scattering of neutrons. Experimental application of the technique is performed on the ferrimagnetic structures of CO-Fe spinels. For this system the cation distribution has been determined, with the general result of inversed spinel structures. The disagreement factors  $R$  found were in the range 4-6%.

The investigation has been performed at the Laboratory of Neutron Physics, JINR.

Communication of the Joint Institute for Nuclear Research. Dubna 1985