

## MAGNETIC STRUCTURE OF LITHIUM FERRITES-CHROMITES

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The magnetic structure of some samples of a series of mixed lithium ferrites-chromites with spinel structure  $\text{Li}_2\text{O} (5-2t) \text{Fe}_2\text{O}_3 2t \text{Cr}_2\text{O}_3$  has been studied by means of the neutron diffraction method. The  $t$ -values varied from 0 to 1.70. The measurements were made at 4.2 and 77 K on powdered samples.

All the investigated samples exhibited collinear magnetic structure. The effective values of the spin  $S_A$  and  $S_B$  of the tetrahedric and octahedric sublattices have been determined. For samples with  $t$  greater than 1.25 the effective spin values of the octahedric sublattice were lower than those calculated from the distribution of cations upon the assumption of the Néel model. These results have been discussed on the basis of hypotheses existing in literature which explain such anomalous magnetic properties. They confirm the hypothesis of Baltzer and Wcjtowicz about the low spin state of a part of chromium ions.

A simple model is assumed which relates the number of chromium ions in low spin state with the degree of inversion and the parameter  $t$ . Agreement has been obtained between the calculated moments, the values determined from macroscopic measurements and those obtained by means of the neutron diffraction method.

*1. Introduction*

The molecular field theory which has been applied by Néel [1] for interpretation of the magnetic properties of ferrites gives good agreement with experiment for numerous compounds of this particular group of oxides.

It has been shown, however, by many authors [2—7] that this theory does not satisfactorily explain the magnetic properties of mixed ferrites containing chromium — which we shall call chromites.

For chromites containing much chromium there is a discrepancy between the magnetic moment of the sample determined from macroscopic measurements and that calculated on the basis of the Néel model from the distribution of ions with known spin values.

Neutron diffraction measurements for a series of spinels containing chromium have shown that the magnetic moment of the octahedric sublattice in which the Cr ions are located is lower than that predicted by the theory of Néel.

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Since the dominating interaction in ferrites is the negative  $AB$  interaction, the resultant magnetic moment per molecule can be written in the form:

$$M = M_B - M_A,$$

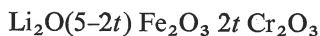
where  $M_B$  and  $M_A$  are the saturation magnetic moments of the sublattices  $B$  and  $A$ , respectively.

The smaller value of  $M_B$  compared to that predicted by the Néel theory results in a decrease in the resultant magnetic moment of the sample.

The papers published so far on this topic try to explain these anomalous magnetic moments by means of the following effects:

- a) Yafet-Kittel ordering in the sublattice  $B$  [11],
- b) helical ordering of spins in octahedric sites which leads to diminution in the resultant moment of this sublattice [12],
- c) antiferromagnetic coupling in the octahedric sublattice [13],
- d) non-cancellation of orbital angular momentum of magnetic ions by crystal field ( $g_{\text{eff}} \neq 2$ ) [14],
- e) existence of a low spin state of chromium ion [15].

The present paper presents the results of studies on the magnetic structure of a series of lithium ferrites-chromites with the general formula:



where  $t$  assumes the values from 0 to 1.70.

The comparison of the macroscopically measured saturation magnetic moments at 0 K (reported in Ref. [17] with those calculated from the Néel model indicates large discrepancies for  $t$ -values greater than 1.25.

It has been suggested in papers concerning the magnetic properties of this series of ferrites that the reason for this effect may be the occurrence of Yafet-Kittel ordering in the octahedric sublattice.

There were, however, so far no experimental data in literature which would confirm such hypothesis.

The present paper gives the results of the study of the magnetic structure by means of the neutron diffraction method as well as their discussion from the point of view of the above-mentioned possible interpretation of the anomalies of the magnetic moment in chromites.

## 2. Experimental

A series of lithium ferrites-chromites has been prepared by means of a simple ceramical method by mixing suitable proportions of  $\text{Li}_2\text{CO}_3$ ,  $\text{Cr}_2\text{O}_3$ , and pure  $\text{Fe}_2\text{O}_3$  and two-fold sintering at 1000°C and 1150°C in air atmosphere [19]. The samples thus obtained will be called samples in initial state. Analyses of these samples made by means of  $X$ -ray diffraction method, classical chemical analysis, and  $X$ -ray microanalysis have shown that pure spinel phase has been obtained as well as the desired iron-to-chromium ion ratio and good chemical homogeneity [19].

The results of the studies of the crystallographic structure are given in Refs [19] and [20].

If one introduces the parameter  $x$  — the degree of inversion, the distribution of cations in samples of the investigated series can be written in the form:



where before the square bracket are written the ions located in the sublattice  $A$  and inside the brackets those in the sublattice  $B$ . It has been found in Refs [6], [19] and [20] that with changing chromium contents there is a change in the type of long range ordering in the sublattices  $A$  and  $B$ . Namely, for samples with  $t$ -values between 0 and 0.35 ordering is established in the sublattice  $B$ , while for  $t$  greater than 1.60 in the sublattice  $A$ . Samples with  $t$ -values between 0.40 and 1.55 do not exhibit long range ordering in either sublattice. The cation distributions are described, respectively, by the following space groups:  $P4_332$  (No 208 in Ref. [21]),  $F\bar{4}3m$  (No 216 in Ref. [21]), and  $Fd3m$  (No 227 in Ref. [21]).

The macroscopic measurements of the magnetic properties of lithium chromite (the saturation magnetic moment at 0 K, the Curie and compensation temperatures) are given in Refs [6] and [16] and above all in [17] and [18]. The authors of the above papers find that for samples with  $t$ -values greater than 1.25 there is a discrepancy between the experimental saturation magnetic moment at 0 K and the value calculated from the known distribution of cations under the assumption of the Néel model. The dependence of the values of the magnetic moment on  $t$  is shown in Fig. 1. The experimental data from macro-

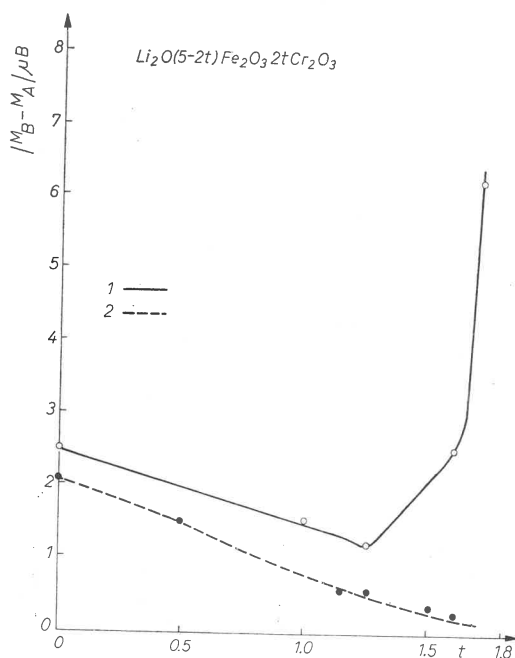


Fig. 1. Dependence of the magnetic moment on the composition for the series of lithium ferrites-chromites, 1 — magnetic moment calculated from the Néel model, 2 — magnetic moment determined in macroscopic measurements

scopic measurements have been taken from Ref. [17] while the calculated values have been obtained on the basis of the cation distribution given in Refs [18] and [20].

The X-ray diffraction measurements were made using a HZG1 counter-goniometer adapted for operation together with a TUR M61 X-ray apparatus (manufactured in East Germany). The measurements were made using the  $K_\alpha$  line of Co ( $\lambda = 1.79021 \text{ \AA}$ ) with an iron filter and the  $K_\alpha$  line of Cr ( $\lambda = 2.2902 \text{ \AA}$ ) with a vanadium filter.

The neutron diffraction measurements were made thrice: with the spectrometer of the Institute of Nuclear Research operating at channel No 2 of the EWA-reactor at Świerk, with the spectrometer of the Institute of Nuclear Techniques operating at channel No 1 of this reactor, and with the  $H_{12}$  spectrometer of the Centre d'Etudes Nucleaires at Saclay (with the kind cooperation of Dr P. Meriel). The monochromatic neutron beams used in these measurements were  $\lambda = 1.18 \text{ \AA}$ ,  $1.12 \text{ \AA}$  and  $1.1375 \text{ \AA}$ , respectively.

The measurements of the magnetic structure were made for chosen samples at the temperatures 4.2 and 77 K using magnetic fields of the order of 13 kOe applied in the direction parallel to the scattering vector.

### 3. Determination of the type of magnetic structure

Detailed studies of the type of magnetic structure have been made for two representative samples of the investigated series, one from the region of good agreement with the Néel model and the other the region of large discrepancy with this model. The respective  $t$ -values amounted to 0.70 and 1.60 (Fig. 1).

To check the first three types of magnetic structure proposed, namely: Yafet-Kittel structure, ferrimagnetic spiral structure, antiferromagnetic ordering in sublattice  $B$ , the neutron diffraction measurements have been made at 4.2 K, with and without magnetic field.

It is known that the evidence for the existence of Yafet-Kittel ordering is the appearance of an additional magnetic line (200) [8] with simultaneous extinction of the magnetic scattering contributions in the lines (111) and (220) by external magnetic field or only the second effect alone [22]. On the other hand ordering of the type of ferrimagnetic spiral results in the appearance of additional magnetic lines around the principal reflections of the magnetic structure [23].

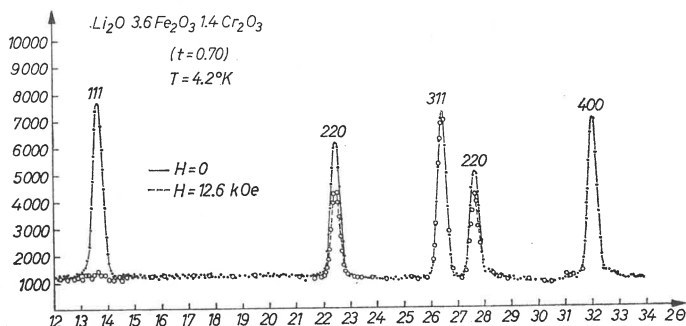


Fig. 2. Neutron diffraction patterns for  $H = 0$  and 12.6 kOe at 4.2 K;  $t = 0.70$

After applying external magnetic field parallel to the scattering vector of principal reflections the intensity of the satellite lines increases.

Antiferromagnetic ordering of spins inside the sublattice *B* results in the appearance of lines of magnetic superstructure.

Fig. 2 shows the results of measurements for a sample with the *t*-value of 0.70. For this composition one has to reject the possibility of the occurrence of the magnetic structure of one of these types, since no additional lines appear in the diffraction pattern.

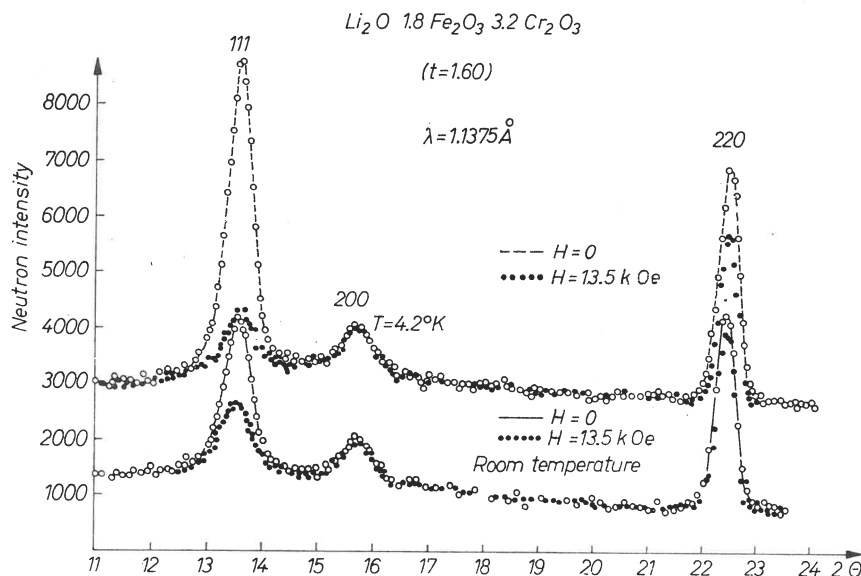


Fig. 3.  $t = 1.60$ . Temperatures 4.2 K and room temperature. Measurements for  $H = 0$  and 13.5 kOe

The results of measurements for the sample with  $t = 1.60$  are shown in Fig. 3. It has been mentioned before that the cation distribution is described by the space group  $F\bar{4}3m$  (No 216 in Ref. [21]).

The (200) line is not extincted in this space group and is of nuclear origin.

In order to investigate whether there any contribution of magnetic scattering in the intensity of the (200) line and whether the contribution of this scattering in the (111) and (220) lines is extincted by external magnetic field measurements of the intensities of the above-mentioned reflections have been made as a function of the magnetic field. These measurements were made at 4.2 K. These results are shown in Fig. 4.

As it follows from Fig. 4 the intensity of the (200) line does not change with the magnetic field and is equal to the intensity of nuclear scattering and the intensities of the two remaining lines also reach this level. This fact and the lack of additional lines on the neutron diffraction patterns of this sample (see Fig. 3) suggest that the possibility of application of the above-mentioned first three models of magnetic structure must be rejected.

Thus in the investigated series of samples we thus deal with collinear magnetic structure.

Therefore there remain the last two of the proposed hypotheses which explain the anomalous values of the magnetic moment, namely incomplete cancellation of orbital angular momentum by the crystal field and thus its influence on the magnetic moment of

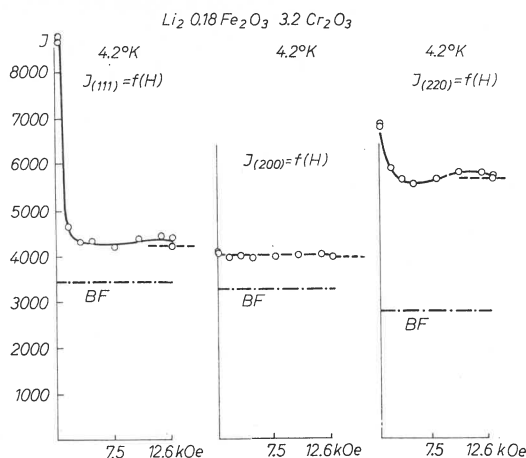


Fig. 4.  $t = 1.60$ . Influence of magnetic field on the intensities of reflections (111), (200) and (220)  
 - - - - nuclear scattering level, · - · - · - BF counter background

chromium ions, and existence of a contribution of low spin state to the magnetic moment of chromium ions.

The results of measurements of  $g_{\text{eff}}$  in Ref. [14] for the sample with  $t = 1.50$  which is already in the region of anomalous magnetic moment permit the rejection the hypothesis of the diminution of the magnetic moment of chromium ions due to non-cancellation of orbital angular momentum by the crystal field.

Finally the last possibility considered is the combination of a model of structure of Néel's type with the concept of the existence of a contribution from a low-spin state to the magnetic moment of the chromium ion [15].

The above-mentioned idea of Baltzer and Wojtowicz [15] about the existence of spin  $\frac{1}{2}$  chromium ions has been developed here to a simple model which explains the possibility of the formation of a strong crystal field in the octahedral sublattice.

As it follows from Eq. (1) in the tetrahedral sublattice there are iron and lithium ions in amounts defined by the degree of inversion  $x$  in each sample.

The sublattice  $A$  can be divided into two lattice complexes, one occupied by ions with the mean valency two and the other by ions with the valency three.

These complexes are occupied by the ions:  $\text{Li}_{1-x}^+ \text{Fe}_{1-x}^{3+}$  and  $\text{Fe}_{2x-1}^{3+}$ , respectively.

Basing on the results of Ref. [24] the possibility of the formation of the  $\text{Fe}_{2(1-x)}^{2+}$  complex has been accepted. The latter is electrostatically equivalent to the first of the above-mentioned ion systems.

As it follows from considerations of the theory of the ligand field the  $\text{Fe}^{2+}$  ions in tetrahedral sides produce distortion of their environment. The distortion of a part of tetrahedron results in the distortion of surrounding octahedrons [15]. The decrease in

field symmetry in octahedrons leads to partial cancellation of the degeneracy of the  $t_{2g}$  orbitals of ions located in this particular sublattice. In the field of the deformed octahedron the triplet  $t_{2g}$  becomes split into a doublet and a singlet.

Fig. 5 shows the influence of the symmetry of the crystal field into orbitals  $t_{2g}$  and  $e_g$ .

When the above-mentioned splitting is high enough the Hund rule is violated in the built-up of the electron shells of ions located in the octahedric sublattice. In case of the

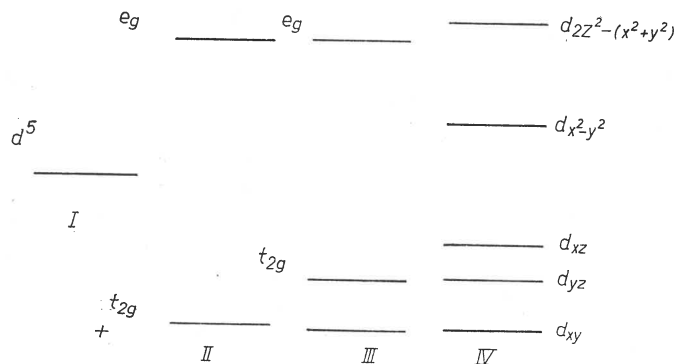


Fig. 5. Influence of crystal field of different symmetries on the  $3d$  orbitals. I free ion, II cubic field, III tetragonal distortion, IV trigonal distortion

$\text{Cr}^{3+}$  ion with electron configuration  $d^3$  which is in the field of a deformed octahedron the result of the violation of the above-mentioned rule is the reduction of the spin of this ion to  $\frac{1}{2}$ .

The effective spin measured by means of the neutron diffraction method is due to a mixture of the low and high spin states.

According to the distribution of cations given by Eq. (1) in the octahedric sublattice there are ions of lithium, chromium and iron in numbers defined for each sample by two parameters  $x$  and  $t$ . The percentage of the occupation of deformed octahedrons by the above-mentioned ions is proportional to their contents in the sublattice  $B$ . Besides it is assumed that the deformed octahedrons are randomly distributed inside the cell and do not result in any distortion of the whole lattice. The decrease in the symmetry of the octahedric field will also influence the decrease in the effective spin of iron. For samples with high chromium contents the amount of iron in the octahedrons is small so that the influence of this effect on the decrease in the magnetic moment of the sublattice  $B$  can be neglected.

#### 4. Determination of the spins $S_A$ and $S_B$

Measurements of the spins of the sublattices  $A$  and  $B$  were made for  $t$  equal to 0.70, 1.25, 1.50, 1.60 and 1.70. These measurements were made at the temperatures 4.2 and 77 K which are much lower than the Curie temperature which for all these samples was of the order of 373 K. The values of  $S_A$  and  $S_B$  have been calculated from the magnetic contributions of the intensity of the lines (220) and (222), respectively.

TABLE I

Parameters defining the magnetic structure of lithium ferrites-chromites in initial state. The values given at the particular  $hkl$  correspond to the intensities  $\frac{2}{3} J^2 m \exp - \frac{2W \sin^2 \theta}{\lambda^2}$

Composition $hkl$	0.70 $Fd\bar{3}m$			1.25 $Fd\bar{3}m$			1.50 $Fd\bar{3}m$		
	$J_{\text{exper.}}$	$J_{\text{calc.}}^a$	$J_{\text{calc.}}^b$	$J_{\text{exper.}}$	$J_{\text{calc.}}^a$	$J_{\text{calc.}}^b$	$J_{\text{exper.}}$	$J_{\text{calc.}}^a$	$J_{\text{calc.}}^b$
111	$680.89 \pm 20.90$	753.50	760.50	$429.91 \pm 61.36$	429.91	150.29	$270.78 \pm 24.9$	345.58	533.30
220	$487.53 \pm 33.14$	487.53	490.10	$302.30 \pm 51.38$	302.30	234.30	$252.95 \pm 57.07$	252.95	286.08
331	$0 \pm 56.76$	9.69	9.10	0	17.31	10.25	$0 \pm 62.00$	21.90	0.28
222	$390.92 \pm 38.84$	390.92	395.10	$25.30 \pm 2.00$	22.50	305.22	$215.46 \pm 89$	134.39	439.28
400	$311.50 \pm 75.86$	471.72	480.10	$345.51 \pm 6$	399.60	609.21	$11.72 \pm 125$	249.00	487.00
331				$382.79 \pm 100$	454.21	690.14	$421.14 \pm 123.5$	337.12	576.00
422				$279.38 \pm 112.8$	276.96	375.00	$177.85 \pm 15.42$	176.32	294.96
511, 333				0	21.33	309.26	$36.24 \pm 20.7$	44.36	345.52
440	4.2			0	3.92	0.600	$0 \pm 55.3$	1.10	0.21
Meas. temp in K							77		
Values of $x$				$0.88 \pm 0.02$			$0.74 \pm 0.02$		
$J_{\text{calc.}}^a$	$S_{\text{Fe}}^A = 2.46 \pm 0.05; S_{\text{Fe}}^B = 2.50 \pm 0.08$ $S_{\text{Cr}} = 1.46 \pm 0.08;$			$S_{\text{Fe}}^A = 2.15 \pm 0.17; S_{\text{Fe}}^B = 2.50 \pm 0.14$ $S_{\text{Cr}} = 1.0 \pm 0.19$			$S_{\text{Fe}}^A = 2.35 \pm 0.25; S_{\text{Fe}}^B = 2.50 \pm 0.10$ $S_{\text{Cr}} = 0.84 \pm 0.16$		
$J_{\text{calc.}}^b$	$S_{\text{Fe}}^A = 2.50; S_{\text{Fe}}^B = 2.50$ $S_{\text{Cr}} = 1.50$			$S_{\text{Fe}}^A = 2.50; S_{\text{Fe}}^B = 2.50$ $S_{\text{Cr}} = 1.50$			$S_{\text{Fe}}^A = 2.50; S_{\text{Fe}}^B = 2.50$ $S_{\text{Cr}} = 1.50$		



TABLE II

Parameters defining the magnetic structure of lithium ferrites-chromites in initial state. The values given at the particular  $hkl$  correspond to the intensities  $\frac{2}{3}jF^2m \exp - \frac{2W \sin^2 \theta}{2}$

Composition $hkl$	1.60 $F\bar{4}3m$			1.70 $F\bar{4}3m$		
	$J_{\text{exper.}}$	$J_{\text{calc.}}^a$	$J_{\text{calc.}}^b$	$J_{\text{exper.}}$	$J_{\text{calc.}}^a$	$J_{\text{calc.}}^b$
111	$257.46 \pm 14.57$	257.60	319.12	$191.57 \pm 39.61$	187.70	532.70
200	$41.66 \pm 8.20$	41.66	34.27	$37.48 \pm 16.89$	34.12	58.08
220	$142.16 \pm 8.50$	142.16	237.60	$123.37 \pm 29.75$	121.42	176.00
311	$3.17 \pm 45$	62.99	147.42	$0 \pm 50.00$	58.45	41.60
222	$153.85 \pm 6.0$	158.51	113.04	$89.19 \pm 11.81$	62.75	410.33
400	$203.45 \pm 8.0$	155.71	322.82	$170.57 \pm 30.68$	146.40	475.24
331	$274.99 \pm 26$	348.16	400.75	$243.71 \pm 79.97$	282.02	619.84
422				$167.26 \pm 99.12$	112.35	162.88
511, 333				$250.83 \pm 38.20$	130.44	373.70
440				$0 \pm 110$	1.06	16.59
Meas. temp. in K	4.2			77		
$J_{\text{calc.}}^a, S_{\text{Fe}}^{1A} = 2.19 \pm 0.13; S_{\text{Fe}}^{2A} = 2.06 \pm 0.35$ $S_{\text{Fe}}^B = 2.50 \pm 0.01; S_{\text{Cr}} = 0.73 \pm 0.08$				$S_{\text{Fe}}^{1A} = 2.60 \pm 0.70; S_{\text{Fe}}^{2A} = 2.01 \pm 0.30$ $S_{\text{Fe}}^B = 2.50 \pm 0.10; S_{\text{Cr}} = 0.44 \pm 0.02$		
$J_{\text{calc.}}^b, S_{\text{Fe}}^{1A} = 2.50; S_{\text{Fe}}^{2A} = 2.50; S_{\text{Fe}}^B = 2.50$ $S_{\text{Cr}} = 1.50$				$S_{\text{Fe}}^{1A} = 2.50; S_{\text{Fe}}^{2A} = 2.50; S_{\text{Fe}}^B = 2.50$ $S_{\text{Cr}} = 1.50$		

TABLE III

Comparison of chromium spin values measured and calculated from the present model

Composition $t$	exper. $S_{\text{Cr}}$	calc. $S_{\text{Cr}}$
0.70	$1.46 \pm 0.08$	1.44
1.25	$1.00 \pm 0.19$	1.26
1.50	$0.84 \pm 0.16$	0.98
1.60	$0.73 \pm 0.08$	0.84
1.70	$0.44 \pm 0.22$	0.66

The magnetic part of the structure factor  $\frac{2}{3}jF^2m$  has been obtained by subtracting from the total structure factor its part responsible for nuclear scattering.

The scale factor has been determined assuming that there is no contribution of magnetic scattering to the (311) line.

In the sublattice  $B$  there are two magnetic ions, *i. e.*, iron and chromium, and therefore the mean magnetic formfactor has been calculated taking into account the occupation of this sublattice by the particular types of magnetic ions.

The errors of the magnetic structure factors determined in this way have been calculated from the statistical errors of the total magnetic structure factors by splitting up this error proportionally to the values of the nuclear and magnetic factors. These errors permitted the determination of the errors of spins  $S_A$  and  $S_B$ .

Assuming that the value of spin of the iron ions is the same as that of the free ion the value of the spin of chromium has been calculated from the effective value of the spin of iron.

The values obtained in this manner have been checked by calculating  $J_{\text{calc}}^a$  for other lines and comparing the latter with the experimental values  $J_{\text{exp}}$ . Tables I and II give the results of these calculations compared with the experimental data, together with the

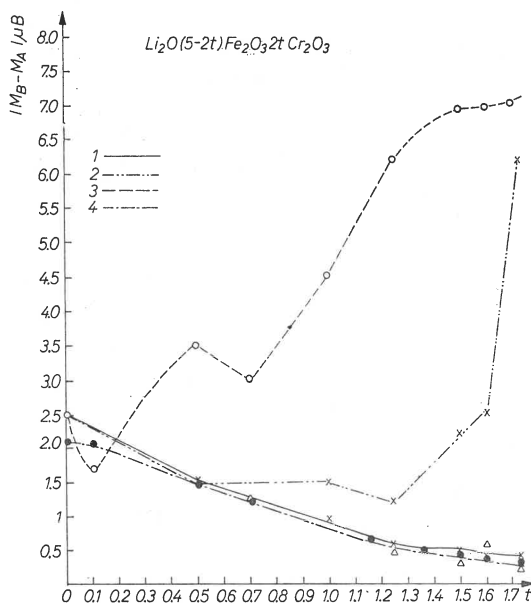


Fig. 6. Dependence of the magnetic moment on the composition for the series of lithium ferrites-chromites. 1 — magnetic moment determined in macroscopic measurements, 2 — calculated from the Néel model, 3 — calculated from the Néel model with antiferromagnetic coupling in the sublattice  $B$ , 4 — calculated from the present model,  $\Delta$  — determined from neutron diffraction measurements

values  $J_{\text{calc}}^b$  calculated from the Néel model for the particular lines. Table III presents the values of the spin of chromium determined from neutron diffraction patterns and those calculated on the basis of the present model. They seem to be in good agreement. Fig. 6 shows the dependences of the saturations magnetic moments on the  $t$ -value for the investigated series of samples calculated from the present model, that of Néel and the model of antiferromagnetic coupling in the sublattice  $B$ . For the sake of comparison the same dependences obtained from macroscopic measurements [17] and the neutron diffraction data are also indicated in the figure. Both macroscopic and neutron diffraction data are consistent and are in agreement with the curve obtained from the present model.

### 5. Conclusions

The neutron diffraction measurements permitted the fact to be established that irrespective of the chromium contents the lithium ferrites-chromites have collinear magnetic structure.

The values of the spin of chromium determined from these measurements deviate from the data for the free ion. This discrepancy increases with increasing chromium contents. The model of collinear magnetic structure with decreased value of chromium spin owing to the existence of an admixture of low spin state has been confirmed by the present investigations.

The model has also permitted to explain the dependence of the saturation magnetic moment on chromium contents determined in macroscopic measurements in the whole  $t$ -range.

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