THE INFLUENCE OF THERMAL TREATMENT ON THE MAGNETIC STRUCTURE OF THE FERRITE $Fe_xLi_{1-x}[Li_{x-0.5}Fe_{0.9-x}Cr_{1.60}]O_4$

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In order to determine the influence of thermal treatment on the magnetic structure of the ferrite $Fe_xLi_{1-x}[Li_{x-0.5}Fe_{0.9-x}Cr_{1.60}]O_4$ a neutron diffraction study was carried out. The thermal treatment of the sample in the initial state consist in heating it to 1000°C and plunging it in a water-ice mixture.

Neutron diffraction measurements were performed with the powdered sample at 4.2K and 77K and in a magnetic field order of magnitude H = 13kOe. The Broglie wave length of the neutron was 1.137Å. It was found, that thermal treatment causes diffusion of ions between sublattices without changing the type of magnetic structure.

1. Introduction

The ferrite $Fe_xLi_{1-x}[Li_{x-0.5}\ Fe_{0.9-x}\ Cr_{1.60}]\ O_4$ is a typical one among the mixed lithium ferrites-chromites series described by the general formula $Li_2O(5-2t)\ Fe_2O_3\ 2t\ Cr_2O_3$. The results of the studies [1], [2] and [3] leads to the conclusion that for compositions with the parameter $t > 1.25$ there is a discrepancy between the values of magnetic moment obtained experimentally by using macroscopic methods and those calculated from the distribution of cations by assuming Neel's model.

The investigated ferrite has a composition which exhibits this divergence of magnetic moments.

Moreover, in the papers [2], [3] and [4] it was reported that the ferrite depends

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strongly on the thermal treatment which consists in quenching the samples in the initial state from adequately high temperatures.

Besides, it was found that after quenching the magnitude of the saturation magnetization for the sample increases. The papers [4] and [5] demonstrate the influence of thermal treatment on the crystallographic structure of this ferrite. It was established that thermal treatment causes Li and Fe ions to diffuse between sublattices.

It has also established that in contradistinction to samples in the initial state a sample quenched from 1000°C does not show the longe range ordering of cations in the tetrahedral sublattice. The distribution of cations in that case is described by the space group Fd3m No 227 [7].

The anomalous dependence of magnetic moment of Cr concentration can be explained by the following effects:

noncollinear structure inside one of the sublattices

I of the Yafet-Kittel type [8]

II of the ferrimagnetic spiral type [9]

collinear structure

I with antiferromagnetic coupling of spins in the sublattice B [10]

II with decreased value of Cr magnetic moment because of the low spin state admixture, nonreduced value of the moment of orbital momentum by the crystal field in the case of the Cr ion [12].

As a result of investigations [5] and [13] the magnetic structure of ferrites in the initial state was found to be collinear in structure with a reduced spin value for Cr ions.

The object of this work is two fold

1. to ascertain whether thermal treatment changes the type of magnetic structure in comparison with that of the initial state.

2. and to find a quantitative interpretation of the relationship between the magnetic saturation moments of the sample in the initial state and after quenching from 1000°C, denoted $t = 1.60$ and $t = 1.60_{1000}$ respectively.

2. Experimental procedure

The sample of ferrite $Fe_xLi_{1-x}[Li_{x-0.5}\ Fe_{0.9-x}\ Cr_{1.60}]\ O_4$ in the initial state was prepared by the ceramic method by mixing twice sintered oxides Li_2CO_3, Fe_2O_3 and Cr_2O_3 (pure) at temperatures of 1000°C and 1150°C in an air atmosphere.The sample in the quenched state was obtained by heating the ferrites at 1000°C for 6 hours and then quickly cooling in a mixture of water and ice.

The composition of the sample was checked by making a quantitative chemical analysis. It revealed an insignificant decrease of Li during the thermal treatment.

A neutron diffraction study was carried out with the use of a spectrometer at the Institute of Nuclear Technology of the Academy of Mining and Metallurgy positioned at Channel No 1 of the "EWA" nuclear reactor in Świerk ($\lambda = 1.12$ Å).

Other measurements were carried out by means of the neutron spectrometer M 12 of CEN in Saclay, France ($\lambda = 1.137$ Å).

The investigations on the powdered sample of ferrite were made at temperatures of 4.2 K and 77 K in a magnetic field of intensity 12.6 kOe parallel to the scattering vector.

Macroscopic measurements of the magnetic moments for the lithium ferrite-chromite series were carried out at the Laboratory of Solid State Physics of the Institute of Metallurgy (Academy of Mining and Metallurgy).

Data relating to the investigated ferrite is adopted from the papers [3] and [4]. According to these autors the magnetization of the sample $t = 1.60_{1000}$ is 1.38 times than that of sample $t = 1.60$.

3. *Choice of magnetic structure model*

The magnetic structure of ferrites in the initial state has been determined in papers [5] and [13].

Figure 1 presents the neutron diffraction patterns of ferrite $t = 1.60$ which have been obtained at 4.2 K and the room temperature, without any magnetic field and in a 13.5 kOe magnetic field.

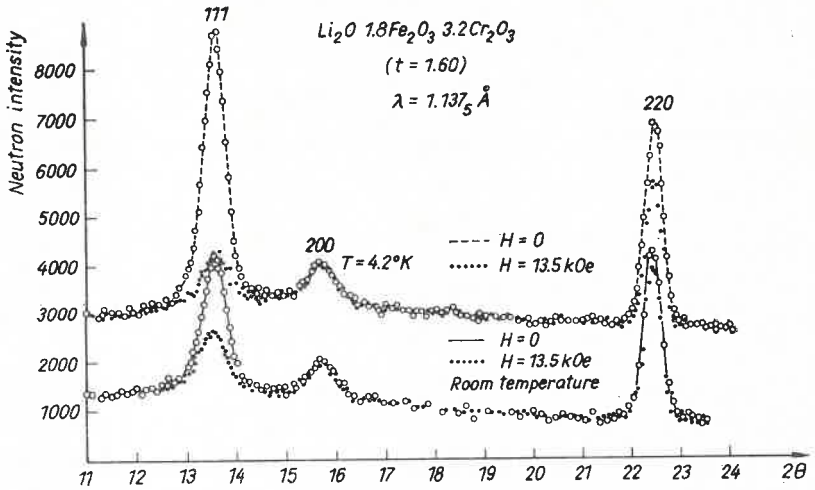

Fig. 1. Sample with $t = 1.60$ at room temperature. The measurement was made without field and in a 13.5kOe magnetic field

The lack of additional magnetic lines in Fig. 1 indicates that no exists a noncollinear magnetic structure or antiferromagnetic coupling inside one of the sublattices. Using the results of Ref. [12] it was assumed that the abnormally small value of magnetic moment is not connected with an admixture of orbital momentum to the magnetic moment of the Cr ion.

Taking into account all information from these studies it was determined that the investigated ferrite has in the initial state $t = 1.60$ a collinear magnetic structure.

Neel's model of magnetic structure was proposed in Ref. [13] by assuming the existence of an admixture of the low-spin state in the magnetic moment of the Cr ion [11]. The number of Cr ions in the low spin state 1/2 has been related to the inversion parameter x and to a parameter defines the contents of Cr. A resultant spin of Cr, measured by the neutron diffraction method shows there is a mixture of low and high spin states.

In Fig. 2 is presented a pattern of the ferrite quenched at 1000°C, $t = 1.60$. The measurements were performed at 4.2 K without and the 12.6 kOe magnetic field.

There are no additional reflections in the neutron diffraction patterns, which would be evidence of a change of magnetic structure type in consequence of the thermal treatment.

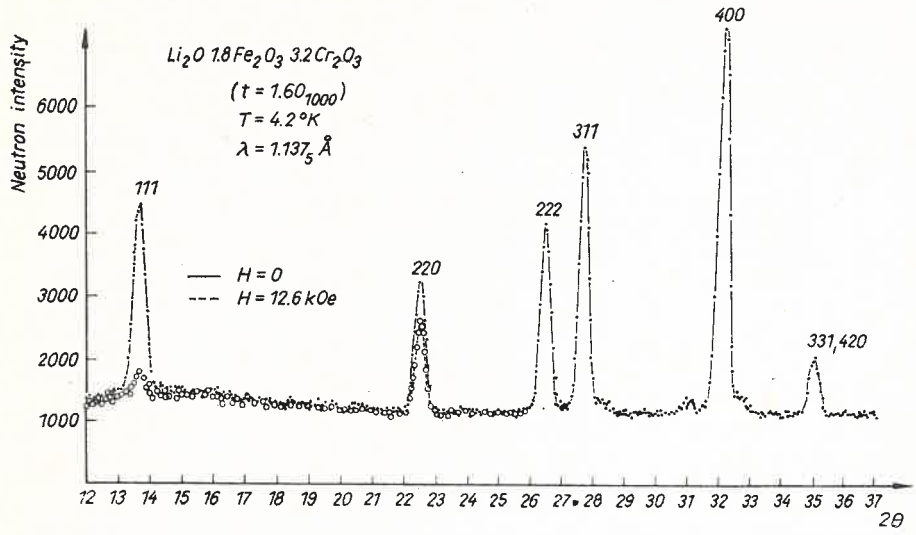

Fig. 2. Sample with $t = 1.60_{1000}$ at 4.2 K. The measurement was made without field and in a 12.6 kOe magnetic field

The disapperance of the (200) line in the neutron diffraction patterns of the sample $t = 1.60_{1000}$ is associated with the cation disorder in the tetrahedric sublattice and the transformation of the space group describing of cation distribution from $F\bar{4}3m$ No 216 to Fd3m No 227 [7].

So it was assumed that thermal treatment does not alter magnetic structure. By making use of the fact that the intensities of the (220) and (200) lines are derived from diffraction on atoms located in the sublattice A, whereas the intensity of the (222) line from the sublattice B, it was possible to determine the average values of spins S_A and S_B of these sublattices from the magnetic part of the line intensities. The magnetic formfactor $2/3\ jF^2m$ was calculated by subtracting from the total form factor jF^2_{tot} the nuclear part jF^2n.

The average value of the magnetic form factor of these sublattices was evaluated by considering the occupation of its sites by the individual types of magnetic ions, because in the sublattice B there are two magnetic ions, Fe and Cr. The errors of the magnetic part of the form factor $2/3\ jF^2m$ were evaluated from statistical errors of the total form factors

divided into two parts proportional respectively to the values of nuclear and magnetic form factors. Determination of the errors of the appriopriate form factors allow the errors of the found spins S_A and S_B to be determined. The value of spin for Cr was obtained from the average S_B values. All values obtained in this manner have been verified by calculations of the form factors $2/3\ jF^2m$ for different lines and comparing them the corresponding values.

TABLE I

Parameters defining the magnetic structure of the ferrite $Fe_xLi_{1-x}[Li_{x-0.5}Fe_{0.9-x}Cr_{1.60}]O_4$ in the initial and hardened states. The values for the various *hkl* correspond to intensities $2/3\ jF^2m \exp^2 \frac{\sin^2\theta}{\lambda^2}$

Composition *hkl*	1.60 F$\bar{4}$3*m*			1.60_{1000}Fd3*m*		
	I_{exp}	I^a_{calc}	I^b_{calc}	I_{exp}	I^a_{calc}	I^b_{calc}
111	257.46±14.57	257.60	319.12	249.39±8.38	240.70	523.43
200	41.66±8.20	41.66	34.27			
220	142.16±8.50	142.16	237.60	114.13±14.59	114.13	220.34
311	3.17±45	62.99	147.42	0.04±30.62	0.41	7.44
222	153.85±6.0	158.51	113.04	86.91±37.80	132.71	345.58
400	203.85±8.0	155.71	322.82	0. ±4.92	22.02	500.86
331	27499±26	348.16	400.75	240.26±55.58	239.68	525.28
temperature of measurement in deg. Kelvin	4.2					
I^a_{calc}	$S^{1A}_{Fe} = 2.19\pm0.13$; $S^{2A}_{Fe} = 2.06\pm0.55$ $S^{B}_{Fe} = 2.50\pm0.01$; $S_{Cr} = 0.73\pm0.58$			$S^{A}_{Fe} = 1.92\pm0.12$; $S^{B}_{Fe} = 2.50\pm0.04$ $S_{Cr} = 0.76\pm0.08$		
I^b_{calc}	$S^{1A}_{Fe} = 2.50$; $S^{2A}_{Fe} = 2.50$; $S_{Cr} = 1.50$ $S^{B}_{Fe} = 2.50$			$S^{A}_{Fe} = 2.50$; $S^{B}_{Fe} = 2.50$; $S_{Cr} = 1.50$		

Experimental and calculated values of magnetic intensities for the investigated ferrite in the initial state and after quenching from 1000°C are given in Table I. It also contains the intensities $2/3\ jF^2m$ for the respective lines calculated for the assumed model I^a_{calc} and I^b_{calc} for Neel's structure with the spin of free ions. The value of Cr spin S_{Cr} calculated from the assumed model is also include for comparison.

A comparison of the data in Table I with experimental values shows that Neel type structure does not explain the experimental data in the case of the investigated ferrite. There is good agreement between the spin value of Cr of the assumed model and the experimental one.

By making use of neutron diffraction data the ratios of saturation moments per mole of ferrite were determined in the initial state and after quenching from 1000°C. The value of this ratio was compared with analogous values computed for a) the model assumed here,

TABLE II

Comparison of saturation moment ratios for the samples $t = 1.60$ and $t = 1.60_{1000}$

Method	Results
neutron diffraction	1.53 ± 0.12
magnetic weight measurements	1.39 ± 0.07
Neel's model	1.12
model assumed in present work	1.32

b) Neel's model, and c) the value obtained from magnetic weight measurements[1]. The results of this comparison is given in Table II.

The obtained results suggest that the magnetic structure model described in Ref. [13] can be applied to the ferrite in the initial state and after quenching.

4. Conclusions

A thermal treatment process bears an influence on the type order of cations and on the diffusion of cations between sublattices.

However, the thermal treatment process does not change the magnetic structure. As in a case of a sample in the initial state the magnetic structure of quenched sample is collinear with a reduced value of Cr ion spin.

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REFERENCES

[1] E. W. Gorter, *Philips Rev.*, **9**, 419 (1954).
[2] K. P. Belov, K. M. Bolshova, T. A. Elkine, M. A. Zaitseva, *Izv. Akad. Nauk SSSR, Ser. Fiz.*, **10**, 1283 (1958).
[3] Z. Obuszko, *Ph. D. Thesis*, Cracow 1965.
[4] Z. Obuszko, A. Kołodziejczyk, *Acta Phys. Polon.*, **35**, 857 (1969).
[5] L. Dargel, *Thesis*, Cracow 1971.
[6] L. Dargel, W. Kubeł, K. Olkiewicz, *Acta Phys. Polon.*, **A41**, 689 (1972).
[7] *International Tables for X-Ray Crystallography*, Birmingham 1962.
[8] Y. Yafet, C. Kittel, *Phys. Rev.*, **87**, 290 (1952).
[9] D. M. Lyons, T. A. Kaplan, K. Dwight, N. Menyuk, *Phys. Rev.*, **126**, 540 (1962).
[10] D. G. Wickham, J. B. Goodenough, *Phys. Rev.*, **115**, 1156 (1959).
[11] P. K. Baltzer, P. J. Wojtowicz, *J. Appl. Phys.*, **30**, 27S (1959).
[12] J. S. Van Wieringe, *Phys. Rev.*, **30**, 488 (1953).
[13] L. Dargel, *Acta Phys. Polon.*, **A43**, 673 (1973).

[1] Weight measurements were carried out at a temperature of 77K.