PARAMAGNETISM OF LITHIUM FERRITE-CHROMITES

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(Received June 5, 1972; Revised paper received July 18, 1972)

The results of investigations of a series of lithium ferrite-chromites in the paramagnetic region are shown. Temperature dependences of magnetic susceptibility, reciprocal susceptibility are given for samples in initial state as well as the values of Curie constants calculated from these curves. These values are significantly different from those calculated on the basis of the knowledge of the magnetic ion distributions in the samples. Hence it is found that while the chromium contents in the sample increases the effective magnetic moment of chromium ions becomes smaller. This fact confirms the hypothesis about the spin quenching in this type of compounds. The results of similar investigations are also given for samples subjected to quenching. The influence of quenching on Néel's temperature for the particular samples are given as well as the influence on the shape of the susceptibility and reciprocal susceptibility curves.

1. Introduction

The compounds studied in the present work were lithium ferrite-chromites described by the formula:

$$(Li_{1-x}Fe_x)\,[Li_{x-0.5}Fe_{2.5-x-a}Cr_a]O_4 \tag{1}$$

where the values of a were: 0.95, 1.15, 1.25, 1.45, 1.60, 1.75.

Basic information about these ferrites is given in the paper of Gorter [1]. The magnetic properties of these compounds below the Néel temperature were investigated by various methods [1–5]. Strong influence of heat treatment on the magnetic properties of these ferrites has been found in the same temperature range [2, 4]; in particular the quenching process gives rise to vanishing compensation point and the decrease in Néel's temperature for the particular samples. These changes can be explained in terms of migration of iron and lithium cations between tetrahedric and octahedric sublattices of the spinel structure of these compounds.

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The purpose of the present paper was the study of the properties of lithium ferrite-chromites in the paramagnetic region, in particular, the temperature dependence of magnetic susceptibility and reciprocal susceptibility, determination Néel's temperatures and effective magnetic moments and mean spins of chromium ions for samples in initial state and after quenching.

2. *Results and their discussion*

The measurements of magnetic susceptibility of the investigated ferrites were carried out using a magnetic balance [6, 7]. In the initial state the samples were preparated using a method described in Ref. [1]. They were quenched by immersion in ice-water mixture after previous heating at 1520 °K for two hours.

Figs 1–6 show the curves of magnetic susceptibility and its reciprocal value as a function of temperature for samples both in initial state and quenched. It follows from the figures that the curves of the $\frac{1}{\chi}$ *versus* temperature dependence for initial state samples are hyperbolic what is consistent with Néel's theory [8]. The process of quenching gives rise to the decrease in Néel's temperature. This decrease is the greater the greater the

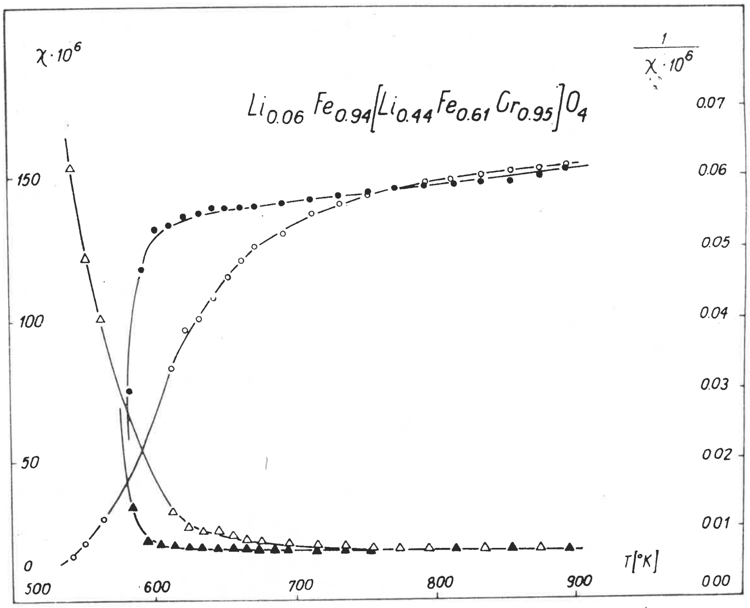

Fig. 1. Temperature dependence of magnetic susceptibility and reciprocal susceptibility for a sample with $a = 0.95$ in initial state and after quenching. Black points correspond to quenched samples

value of the parameter "*a*" which defines the number of chromium ions in the molecule. The dependence of the Néel temperature on the parameter "*a*" is shown in Fig. 7.

It is worth to note the change in the shape of the reciprocal susceptibility plots which occurs after quenching. In case of not quenched samples the corresponding plots are

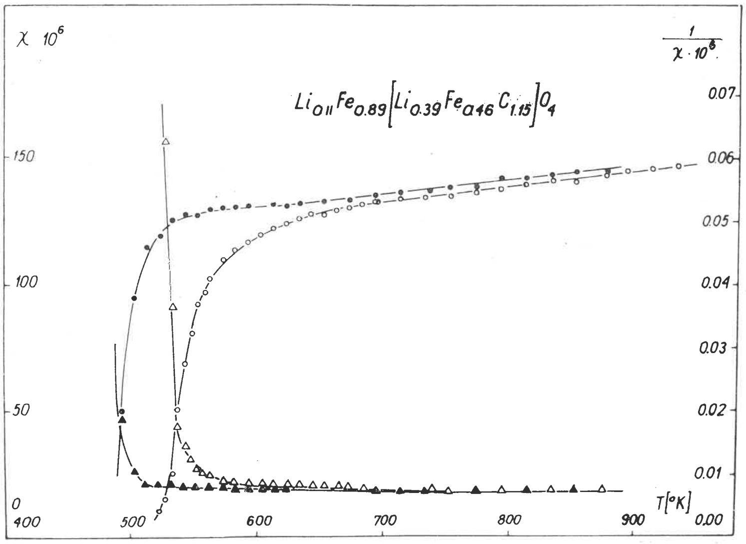

Fig. 2. Same for a sample with a = 1.15

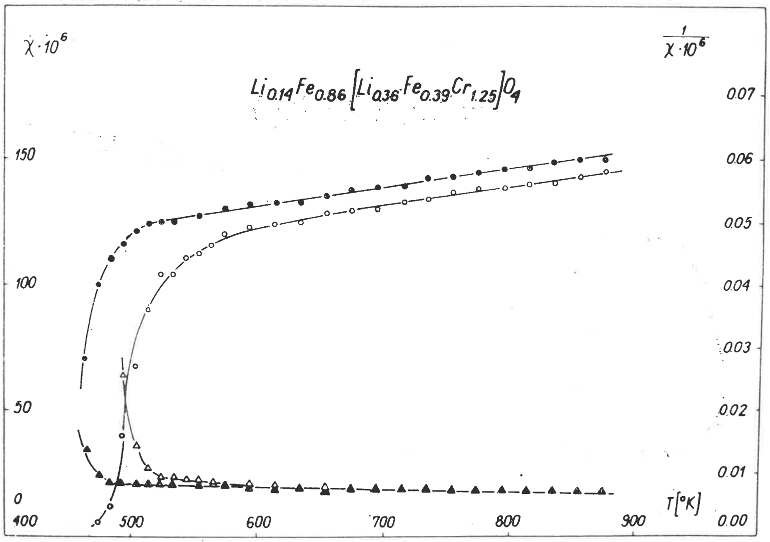

Fig. 3. Same for a sample with a = 1.25

hyperbola-like which after quenching the $\frac{1}{\chi} = f(T)$ plot is a straight line up to the Néel point where it rapidly falls down.

This is consistent with Néel's theory which predicts such behaviour for cases when $\frac{M_A}{M_B} = \frac{1+\beta}{1+\alpha}$, where M_A and M_B are the magnetizations, and α, β the reduced molecular field coefficients of the tetrahedral and octahedral sublattices, respectively. It is most

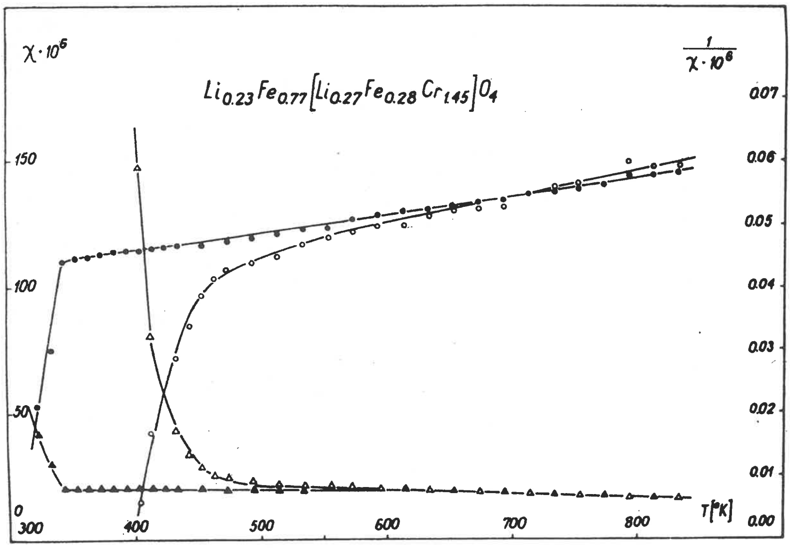

Fig. 4. Same for a sample with $a = 1.45$

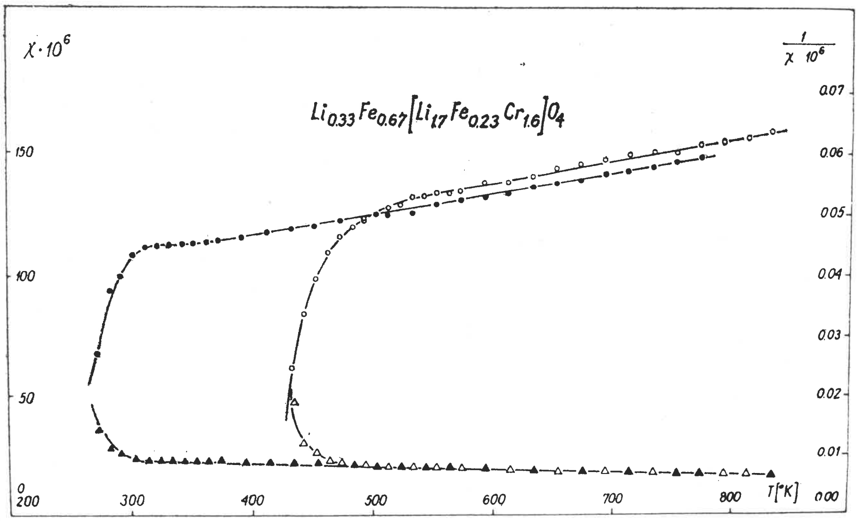

Fig. 5. Same for a sample with $a = 1.60$

probable that quenching freezes another distribution of cations than that which is characteristic for the initial state samples, and in consequence the reciprocal susceptibility curves are changed. Curves of such shape have been observed by Blasse *et al.* [9] in case of some $NiFe_{2-x}V_xO_4$ spinels.

The Aléonard method [10] has been used to determine the Curie constants C' which are equal to the reciprocal slopes of the asymptotes of the hyperbolas $\frac{1}{\chi}(T)$. The values of these constants obtained in this way are, in general, greater than those which can be

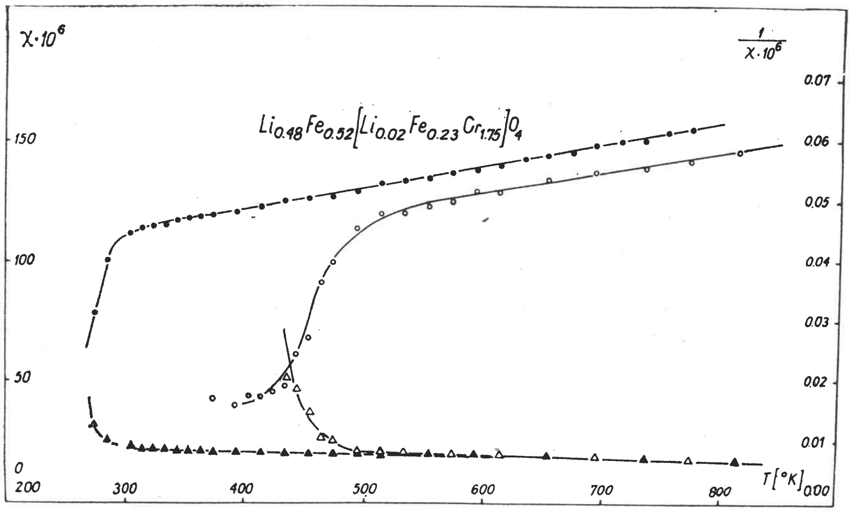

Fig. 6. Same for a sample with $a = 1.75$

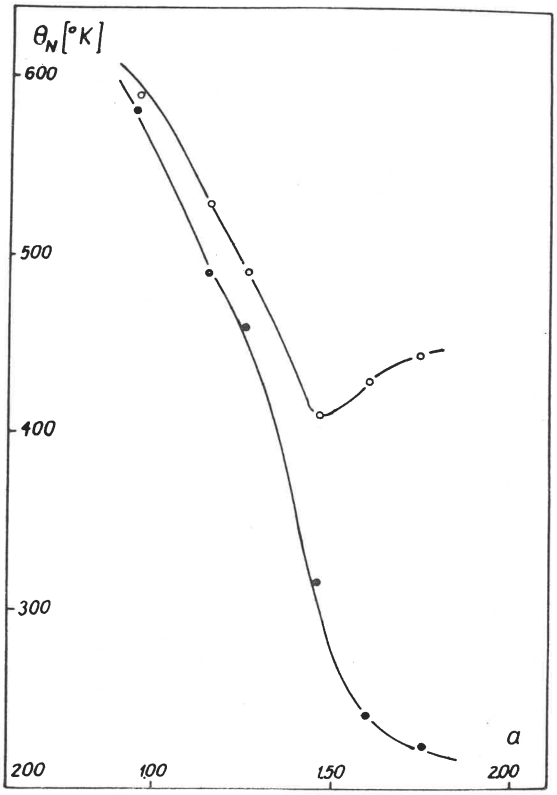

Fig. 7. Dependence of Néel temperature on the chromium contents for samples in initial state and after quenching (black points)

calculated from the knowledge of the distribution of ions in the particular sublattices and the ionic magnetic moments. This discrepancy can be eliminated by using the formula for the temperature dependence of the molecular field coefficients given by Néel [11]:

$$n_{ij} = n_{ij}(0)\,(1+\gamma \cdot T) \tag{2}$$

where n_{ij} is the molecular field coefficient at the temperature T, $n_{ij}(0)$ — the molecular field coefficient at 0°K, γ — temperature variation coefficient of the molecular field coefficient, T — absolute temperature, i, j — indices indicating the particular sublattices.

Eq. (2) leads to the following relationship:

$$\frac{1}{C} = \frac{1}{C'} - \gamma \frac{1}{\chi_0'} \tag{3}$$

where C is the Curie constant calculated from the known cation concentrations in the sublattices and C' the Curie constant determined from the asymptotic slope.

The method of determination of $\frac{1}{\chi_0'}$ which defines the experimental hyperbola is described in Ref. [10]. The constants C have been determined on the basis of X-ray diffrac-

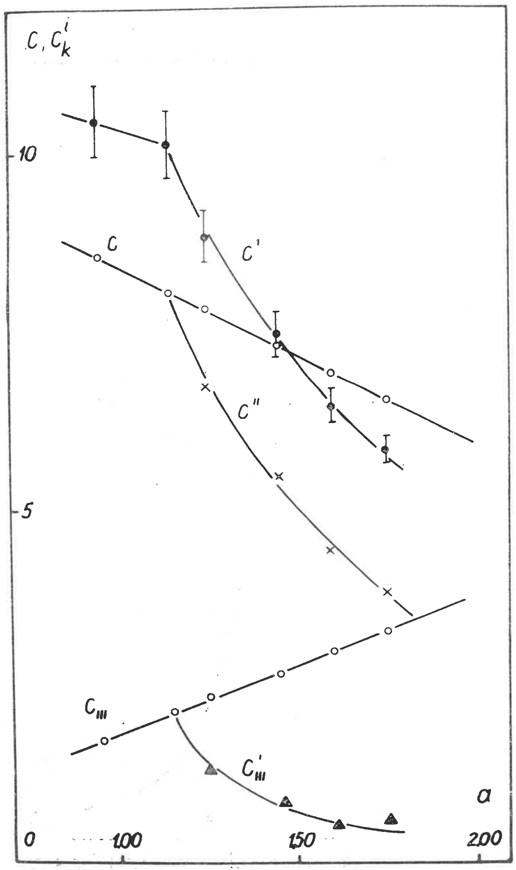

Fig. 8. Dependence of C, C', C'', C_{III} and C'_{III} on chromium contents for samples in initial state

tion measurements [12] for one fourth of a mole, *i. e.*, according to the formula (1) which defines the chemical composition. Table I gives the values of C and C' for one fourth of the mole.

Fig. 8 shows the dependence of these constants on the parameters "a". Here one can also see some discrepancies, *viz.*, for compositions for which $a = 0.95$, 1.15, 1.25 the value of C' is greater than C, while for $a = 1.45$ $C' = C$. However, for greater a-values $C' < C$.

Since $\frac{1}{\chi_0}$ is always positive and depends only slightly on the composition, the temperature variation coefficient (which amounts to about -1.1×10^{-4} for $a = 0.95$, and 1.15) decreases in absolute value according to Eq. (2), becomes zero at about $a = 1.45$ and again increases for $a > 1.45$. Therefore the difference between C and C' cannot be explained in terms of the dependence (2) only, as there is no obvious reason for such anomalous behaviour of γ in case of ferrites. Moreover, no similar examples are reported in literature. It is worth noting that the determined value of γ for $0.95 \leqslant a \leqslant 1.15$ is up to the order of magnitude in agreement with the values of γ for other ferrites given in literature [9, 10]. It is well known that Fe^{3+} ions occur in ferrites with the magnetic moment of 5 μ_B independently of the composition. If one assumes that in case of the investigated ferrites γ does not change with the composition and that its value is always the same as for samples the range $0.95 \leqslant a \leqslant 1.15$, the differences between C and C' can be explained by the occurrence of chromium ions with effective magnetic moments the smaller the greater the number of chromium ions in the molecule, *i. e.*, the greater the parameter a.

An attempt has thus been made to calculate the effective magnetic moments of chromium ions for the investigated series of ferrites assuming that both γ and the magnetic moment of Fe^{3+} ion are constant with varying composition. The experimental results permit the assumption to be made that for compositions with $a = 0.95$ and 1.15 the difference between C and C' follows from the relationship (3). This difference $C = C' - C$ calculated for the $0.95 \leqslant a \leqslant 1.15$ range is subtracted from the corresponding C' values for all other a values. The resulting C'' values are thus free of temperature overestimate. Knowing the cation distribution [11] the Curie constants C_{I} and C_{II} have been calculated for Fe^{3+} ions in the tetrahedric and octahedric sublattices, respectively. Next, using the well-known additivity theorem for the Curie constant and by its virtue, subtracting from the C'' value the sum $C_{\mathrm{I}} + C_{\mathrm{II}}$ we have obtained the constants C'_{III} which are Curie constants for chromium ions for the subsequent compositions. The knowledge of the ion distribution and the chromium ions contents in the molecule for the particular samples permitted the calculation of the theoretical Curie constants C_{III} by assuming the magnetic moment of Cr^{3+} ions to be equal to 3 μ_B. The results of these calculations are given in Table I and Fig. 8. It is seen that there are significant differences between the values of C_{III} and C'_{III}.

From the relationship:

$$\mu_{\mathrm{eff}} = \left[\frac{3kC'_{III}}{N_{\mathrm{Cr}}\mu_B^2}\right]^{\frac{1}{2}} \tag{4}$$

$$\mu_{\mathrm{eff}} = 2[S(S+1)]^{\frac{1}{2}} \tag{5}$$

where μ_{eff} is the effective magnetic moment of chromium ions, k — the Boltzmann constant, N_{Cr} — the number of Cr ions in the molecule, μ_B — the Bohr magneton and S — the mean spin of Cr ions we have calculated the effective magnetic moment and the mean spin of Cr ions. These results are also given in Table I.

TABLE I

a	x	C_I	C_{II}	C_{III}	C	C'	C''	C'_{III}	μ_{eff}	S
0.95	0.94	4.11	2.66	1.78	8.56	10.43	8.56	1.78	3.87	1.50
1.15	0.89	3.89	2.01	2.15	8.06	10.13	9.06	2.15	3.87	1.50
1.25	0.86	3.76	1.70	2.34	7.81	8.77	6.77	1.30	2.88±0.30	1.02±0.13
1.45	0.77	3.36	1.22	2.71	7.31	7.45	5.45	0.86	2.17±0.35	0.70±0.15
1.60	0.67	2.95	0.98	3.00	6.93	6.47	4.47	0.53	1.62±0.40	0.45±0.16
1.75	0.50	2.18	1.09	3.28	6.56	5.89	3.98	0.61	1.67±0.40	0.45±0.17

Our results are in agreement with the neutron diffraction data [12]. The mean spins of Cr ions determined by means of the latter method are:

$$S = 1.46\pm0.08 \text{ for } a = 0.7 \text{ and } T = 4.2\text{ K}$$
$$S = 1.00\pm0.19 \text{ for } a = 1.25 \text{ and } T = 80\text{ K}$$
$$S = 0.84\pm0.16 \text{ for } a = 1.50 \text{ and } T = 80\text{ K}$$
$$S = 0.74\pm0.08 \text{ for } a = 1.60 \text{ and } T = 4.2\text{ K}$$
$$S = 0.44\pm0.02 \text{ for } a = 1.70 \text{ and } T = 80\text{ K}$$

The measurements were made at low temperatures, *i. e.*, in the ferrimagnetic region.

It follows from our data that also in the paramagnetic temperature range the effective magnetic moment of Cr ions decreases with increasing a in case of the investigated ferrites. For the temperature range below the Néel point this effect was interpreted in Refs [12] and [13] by partial quenching of Cr-ion spins by the crystal field of the lattice. Similar measurements and calculation made in case of quenched samples have shown that the quenching process does not change the mean spin value of Cr ions nor their effective magnetic moment.

The authors are indebted to Mrs E. Guła for the program of numerical computations.

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