SOVIET PHYSICS JETP VOLUME 36, NUMBER 4 APRIL, 1973

EXCHANGE INTERACTIONS AND CANTED SPIN CONFIGURATIONS IN $MnFe_{2-x}Cr_xO_4$

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Submitted April 25, 1972

Zh. Eksp. Teor. Fiz. **63**, 1343–1352 (October, 1972)

The system of ferrite-spinels $MnFe_{2-x}Cr_xO_4$ ($0 \le x \le 1.75$) are studied by the nuclear γ-resonance technique at temperatures between 78 and 700°K. The cation distribution in the A- and B-lattices is determined. The temperature dependence of the A- and B-sublattice magnetization is studied and the values of the exchange interaction integrals are estimated. For Mn-ferrite, $J_{Mn(A)-Fe(B)} = -(12.8 \pm 0.2)$°K and $J_{Fe(A)-Fe(B)} = -(15.4 \pm 0.2)$°K. Measurements in an external magnetic field show that the magnetic moments of the Fe^{3+} and Cr^{3+} ions in the B-sublattice are ordered noncollinearly at low temperatures. A peculiar type of compensation point is detected in ferrite and is related to the temperature dependence of the noncollinearity angle Θ. The ferrite magnetic moments are analyzed by taking into account the angular spin structure and statistical distribution of the Fe^{3+} and Cr^{3+} ions in B-sites. The angles Θ corresponding to various local environments are estimated approximately.

INTRODUCTION

THE system of ferrites $MnFe_{2-x}Cr_xO_4$, henceforth abbreviated $\mathscr{F}_x$, constitutes a series of solid solutions of the spinels $MnCr_2O_4$ and $MnFe_2O_4$. The magnetic structure and the properties of the initial compounds differ strongly from each other. $MnCr_2O_4$ is a normal spinel having a magnetic structure of the conical-helix type[1]. The magnetic moment of the spinel $MnFe_2O_4$ at 0°K is somewhat lower than predicted by the Néel theory, although no deviation of the magnetic structure from collinear was observed[2].

The main feature of the ferrites of the $\mathscr{F}_x$ system are the low magnetic moment at 0°K and the anomalous dependence of the moment on the degree of substitution x[3]. A high susceptibility of the paraprocess in strong magnetic fields was also observed[4]. To explain the magnetic properties of these ferrites it was proposed[3-5] that some of the magnetic moments of the chromium ions are antiparallel to the total moment of the B-sublattice or lie at an angle to it. However, no angular configurations of the magnetic moments were revealed by a neutron-diffraction study of this system[5].

We have investigated the $\mathscr{F}_x$ system with the aid of the Mössbauer effect. We obtained the distribution of the cations over the sublattices and studied the temperature dependence of the magnetizations of the A and B sublattices. The exchange interactions between the different magnetic ions were determined, and certain data were obtained on the magnetic structures of these ferrites.

EXPERIMENTAL PROCEDURE, SAMPLES

Ferrites of the system $\mathscr{F}_x$ (x = 0,0; 0,2; 0,6; 0,8; 1,0; 1,2; 1,4; 1,6; 1,75) were synthesized by the method of simultaneous precipitation of the hydroxides of the initial components with subsequent annealing in vacuum at 1400°C for six hours. The iron in the samples was enriched with Fe^{57}, from 10 to 85 at.%. The x-ray phase analysis of the ferrites was performed with a DRON-1 diffractometer. The Mössbauer spectra of the Fe^{57} nuclei were obtained with a previously described setup[6]. The Co^{57} source in a platinum matrix was at room temperature. The measurements were performed in the temperature interval 78–700°K. To analyze the magnetic structure and to determine more accurately the cation distribution in the ferrites, the measurements were performed in a 20 kOe external magnetic field perpendicular to the γ-quantum flight.

RESULTS AND DISCUSSION

1. Paramagnetic Region of Temperatures ($T > T_C$)

In the paramagnetic state, the Mössbauer spectra of ferrites with x = 0.0–0.8 are each a superposition of a symmetrical doublet and a low-intensity single line (Fig. 1), with isomeric shifts δ equal to +0.19 and +0.11 mm/sec respectively relative to stainless steel (at 670°K). One can conclude from the line intensity that the doublet pertains to Fe^{3+} ions at the B-points, and the single peak to Fe^{3+} ions at the A-points. The quadrupole splitting in the B sublattice is apparently due to distortion of the oxygen environment of the Fe^{3+}(B) ions as a result of filling of A sites by cations of two types, iron and manganese. The single line decreases in intensity with increasing x, and vanishes completely at x = 1.0.

At $x \ge 0$, an additional single line appears in each spectrum (Fig. 1) and corresponds in accordance with the isomeric shift to divalent iron ions (δ = +1.2 mm/sec at room temperature). Since this line has no quadrupole splitting, we assume that the observed Fe^{2+} ions are in the A sublattice, since it is precisely the tetrahedral environment in spinels that has a strictly cubic symmetry.

From the ratio of the areas of the Mössbauer spectra pertaining to the ions Fe^{2+} and Fe^{3+} we determined the number of Fe^{2+} ions in each sample. It is interesting that the absolute content of the Fe^{2+} turns out to be constant (equal to 0.07 per formula unit of O_4) and does not depend on x within the limits of the measurement accuracy.

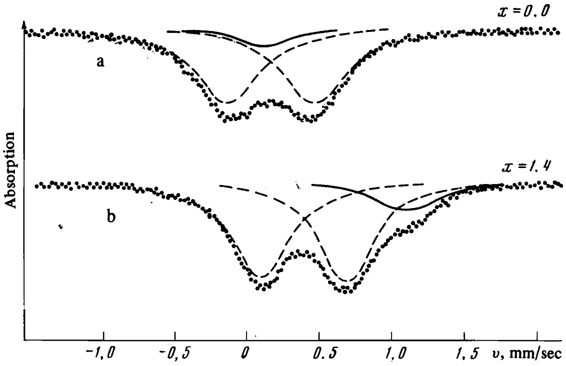

FIG. 1. Mössbauer spectra of the nuclei Fe^{57} for the ferrites $MnFe_{2-x}Cr_xO_4$ ($\mathscr{F}_x$) in the paramagnetic temperature region: a—T = 670°K; b—T = 351°K. The dashed and solid lines show the resolution of the spectrum into components.

Figure 2 shows the x-dependence of the quadrupole splitting Δ of the Fe^{3+} ions at the B sites. This dependence has an unusual form with a clearly pronounced minimum at $x \approx 0.5$. It can be assumed that the minimum of $\Delta(x)$ corresponds to a situation wherein the redistribution of the cations causes almost all the A sites to be occupied by Mn^{2+} ions, and the distortions of the oxygen octahedra are minimal. With increasing chromium content, the inhomogeneity of the filling of the B sublattice sites with Fe^{3+} and Cr^{3+} ions comes into play and the leads to further distortion of the oxygen surrounding of the Fe^{3+} (B) ions.

2. Ferrimagnetic Region of Temperatures (T/T_C)

A. Cation distribution. The Mössbauer spectra of samples with x = 0.0, 0.2, 0.6, 0.8, and 1.0 at room temperature are each a superposition of two six-line Zeeman components (Fig. 3). The components with the more intense lines pertain to the Fe^{3+} ions in the B sublattice, while the less intense ones pertain to the iron ions in the A sublattice. The intensity of the lines belonging to the A sublattice decreases with increasing x. At x = 1.0 one observes only one Zeeman component pertaining to the B sublattice, thus indicating complete normalization of the spinel.

For a more distinct separation of the Mössbauer lines pertaining to the A and B sublattices, we plotted the spectra of the samples in an external magnetic field of 20 kOe (Fig. 3). From the ratios S_A/S_B of the areas under the lines of the spectra belonging to the Fe^{3+} ions in the A and B sites, we determined the degree of inversion λ of the spinel in the formula[1)]

$$(Fe^{3+}_{1-\lambda}Mn_\lambda{}^{2+})[Fe^{3+}_{1-x+\lambda}Cr_x{}^{3+}Mn^{2+}_{1-\lambda}]O_4. \quad (1)$$

The distribution of the Fe^{3+} ions among the A and B sublattices in the $\mathscr{F}_x$ ferrites is as follows:

x:	0.0	0.2	0.6	0.8	1.0
S_A/S_B:	0.14	0.12	0.09	0.04	0.02
λ:	0.75±0.03	0.81±0.03	0.89±0.03	0.95±0.02	0.98±0.02

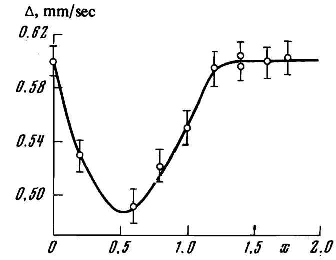

FIG. 2. Dependence of the quadrupole splitting Δ on the degree of substitution x in $\mathscr{F}_x$ ferrites at $T > T_C$.

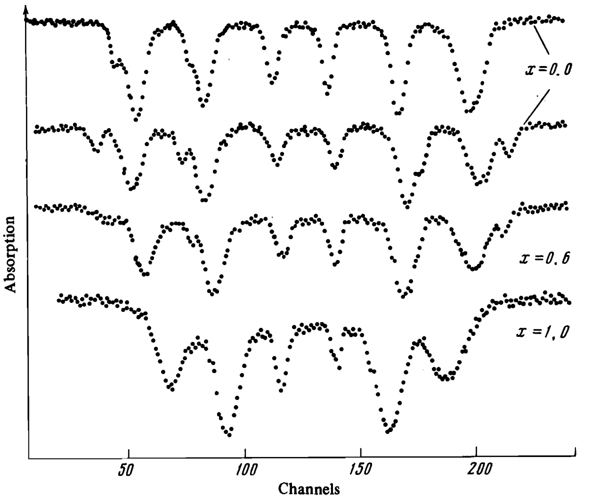

FIG. 3. Mössbauer spectra of the Fe^{57} nuclei for $\mathscr{F}_x$ ferrites at T = 295°K in an external magnetic field H_0 = 20 kOe; the upper spectrum was obtained at H_0 = 0.

B. Temperature dependence of sublattice magnetization. From the Mössbauer spectra obtained at different temperatures we found the temperature dependence of effective magnetic fields H^A_{eff} and H^B_{eff} at the Fe^{3+} ion nuclei in the A and B sites (Fig. 4) and determined the Curie points T_C of the ferrites (Fig. 5). We note that the lowering of the Curie point following replacement of iron ions by chromium ions indicates that the inter-sublattice interactions of the type Mn(A)—Cr(B) are weaker than Mn(A)—Fe(B) interactions.

We have plotted the relative effective fields h_A and h_B against the relative temperature τ (Fig. 6), where $h = H_{eff}(T)/H_{eff}(0)$ and $\tau = T/T_C$. The values of $H_{eff}(0)$ were determined by extrapolating the $H_{eff}(T)$ curves to 0°K. It is interesting that the character of the $h(\tau)$ dependence is the same for all x.

Within the framework of the molecular-field theory, we have estimated the integrals of the inter-sublattice exchange interactions for the ferrite $MnFe_2O_4$. The estimates were made under the following assumptions:

1) The effective field at the ion nucleus in the i-th sublattice, as a function of the temperature, is proportional to its magnetic moment, i.e.,

$$h_i(T) = m_i(T), \quad (2)$$

where $m_r(T) = \langle S_i^Z\rangle/S_i$, S_i is the ion spin, and $\langle S_i^Z\rangle$ is the average value of its Z component.

2) Only inter-sublattice interactions between the nearest neighboring ions are taken into account.

3) Only iron ions are present in the B sublattice.

[1)] If we take into account the small number of Fe^{2+} ions in samples with $x \leqslant 1.0$, then the cation distribution for these ferrites should be written in the form

$$(Mn^{2+}_{0.93}Fe^{2+}_{0.07})[Mn^{3+}_{0.07}Fe^{3+}_{1.93-x}Cr_x{}^{3+}]O_4.$$

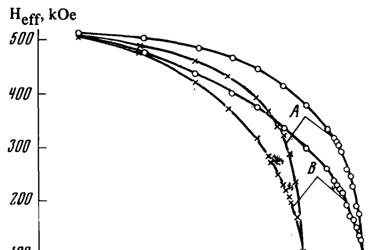

FIG. 4. Temperature dependence of the effective magnetic fields Heff at the nuclei of the iron ions in the A and B sublattices for the $\mathscr{F}_x$ ferrites.

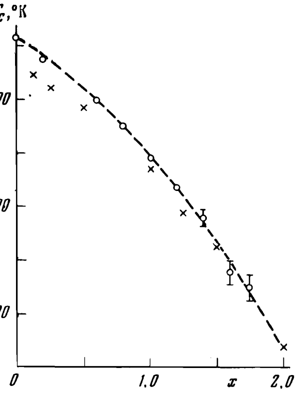

FIG. 5

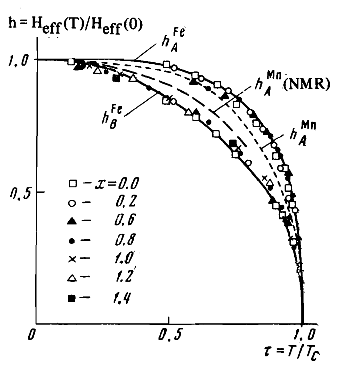

FIG. 6

FIG. 5. Dependence of the Curie temperature on the degree of substitution x for $\mathscr{F}_x$ ferrites. The crosses show Gorter's data [3].

FIG. 6. Relative fields h = Heff(T)/Heff(0) vs the relative temperature τ for $\mathscr{F}_x$ ferrites. The points represent experimental data for iron ions; the solid lines are the theoretical curves for iron ions. The figure shows also the experimental [7] (dash-dot) and theoretical (dashed) curves for manganese ions.

The molecular field acting on an ion in the i-th sublattice is then

$$H_i(T)=\frac{2}{g_i\mu_B}\sum_j z_{ij}J_{ij}\langle S_j^z\rangle, \tag{3}$$

where $\langle S_j^Z\rangle = S_jh_j(T)$, z_{ij} is the number of neighbors in the j-th sublattice for an ion situated in the i-th sublattice, J_{ij} is the exchange integral, g is the Landé factor, and μ_B is the Bohr magneton. The temperature dependence of the effective field at the nucleus of an ion in the i-th sublattice, under assumption (2), is described by the Brillouin function

$$h_i(T)=B_{S_i}[g_i\mu_B S_i H_i(T)/kT]. \tag{4}$$

Combining (3) and (4), we obtain

$$h_i(T)=B_{S_i}\left[\frac{2S_i}{kT}\sum_j z_{ij}J_{ij}S_jh_j(T)\right]. \tag{5}$$

Using formula (3), we obtain the following system of equations for the description of the inter-sublattice interactions in a manganese ferrite:

$$h_A^{\mathrm{Mn}}(T)=B_{5/2}\left[\frac{150}{kT}J_{\mathrm{Mn}(A)-\mathrm{Fe}(B)}\,h_B^{\mathrm{Fe}}(T)\right], \tag{6}$$

$$h_A^{\mathrm{Fe}}(T)=B_{5/2}\left[\frac{150}{kT}J_{\mathrm{Fe}(A)-\mathrm{Fe}(B)}\,h_B^{\mathrm{Fe}}(T)\right],$$

$$h_B^{\mathrm{Fe}}(T)=B_{5/2}\left[\frac{75}{kT}(0.75J_{\mathrm{Mn}(A)-\mathrm{Fe}(B)}\,h_A^{\mathrm{Mn}}(T)+0{,}25J_{\mathrm{Fe}(A)-\mathrm{Fe}(B)}\,h_A^{\mathrm{Fe}}(T))\right].$$

Substituting here the experimentally obtained values of $h_A^{Fe}(T)$ and $h_B^{Fe}(T)$, we solve this system of equations relative to the unknowns $J_{Mn(A)-Fe(B)}$, $J_{Fe(A)-Fe(B)}$, and h_A^{Mn}. As a result we obtain

$$J_{\mathrm{Mn}(A)-\mathrm{Fe}(B)} = -(12.8\pm 0.2)\ ^\circ\mathrm{K},\quad J_{\mathrm{Fe}(A)-\mathrm{Fe}(B)} = -(15.4\pm 0.2)\ ^\circ\mathrm{K}.$$

Figure 6 shows plots of the calculated $h_A^{Fe}(T)$, $h_B^{Fe}(T)$, and $h_A^{Mn}(T)$. For comparison, the figure shows the values of $h_A^{Mn}(T)$ obtained for a manganese ferrite by the NMR method[7].

An attempt was made to estimate the exchange integrals in the MnCrFeO$_4$ ferrite with allowance for the intra-sublattice interactions Fe(B)—Cr(B) and Cr(B)—Cr(B). The system of equations for a ferrite containing magnetic ions of three different types has too many free parameters and is difficult to solve with sufficient accuracy. However, even the roughest estimates point to the presence of noticeable negative intra-sublattice interactions Fe(B)—Cr(B).

C) Measurements in an external magnetic field. To determine the magnetic structure of ferrites of the $\mathscr{F}_x$ system, we investigated the Mössbauer spectra in an external magnetic field H$_0$ = 20 kOe at 120 and 296°K. The following features were observed for the ferrite Mn[FeCr]O$_4$:

1) At 120°K, the field H_{eff} at the nucleus of the Fe^{3+} ion in the B sublattice turns out to be positive, i.e., it increases when an external field is applied (Fig. 7). This means that the ferrite magnetization direction coincides with the direction of the magnetic moment of the manganese ion Mn^{2+} in the A sublattice.

2) When the temperature is increased, the field H_{eff} reverses sign and becomes negative at 296°K (Fig. 7). This indicates that the ferrite magnetization at room temperature coincides in direction with the magnetic moment of the B sublattice.

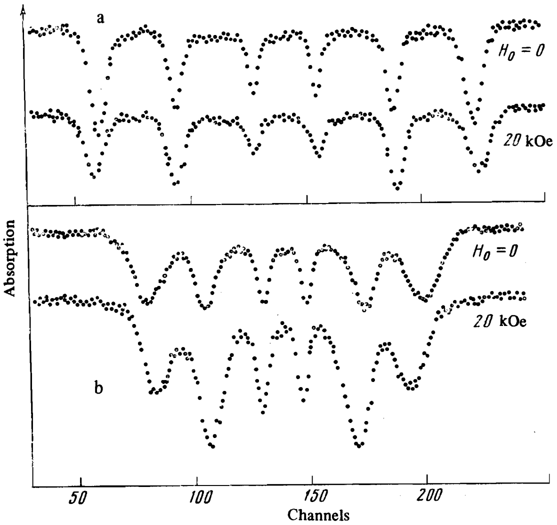

FIG. 7. Mössbauer spectra of the Fe^{57} nuclei for the ferrite MnCrFeO$_4$ in an external magnetic field H$_0$ = 20 kOe and in the absence of an external field, at 120°K (a) and 296°K (b).

The feature (1) offers direct evidence that the magnetic moments in the B sublattice of the ferrite Mn[FeCr]O$_4$ are not collinear. Indeed, if the ordering were collinear, the magnetic moment of the B sublattice would exceed the moment of the A sublattice ($M^B = M^{Fe} + M^{Cr} = 8\mu_B$, and $M^A = M^{Mn} = 5\mu_B$), and the total magnetization of the ferrite would coincide in direction with the moment of the B sublattice.

At low temperatures and under definite conditions, the direct intra-sublattice exchange interactions Fe(B)—Cr(B) and Cr(B)—Cr(B) apparently become comparable with the inter-sublattice interactions Fe(B)—Mn(A) and Cr(B)—Mn(A). In this case the minimum interaction energy corresponds to a noncollinear arrangement of the magnetic moments of the Cr^{3+} and Fe^{3+} ions in the B sublattice, and they can be disposed at a certain angle θ to the total magnetization of the B sublattice, or may even be antiparallel to the latter. Only then can the magnetization of the B sublattice become smaller than the magnetization of the A sublattice.

Feature (2) indicates that a unique compensation point exists in the ferrite Mn[FeCr]O$_4$. A compensation point usually appears in ferrites when one of the sublattices has a larger magnetic moment and has a stronger dependence of the moment on the temperature, while the other with the smaller magnetic moment has a weak temperature dependence of the magnetization. At a definite temperature, the magnetic moments of the sublattices cancel each other, and the total magnetization of the ferrite becomes equal to zero. In the ferrite Mn[FeCr]O$_4$, the situation is different: the magnetic moment of the ion in the sublattice with the smaller magnetization (B sublattice) has a stronger temperature dependence than in the A sublattice. This is evidenced by the temperature dependence of the effective magnetic field H_{eff} in the A and B sublattices (Fig. 4). In spite of this, the magnetization of the B sublattice begins to exceed the magnetization of the A sublattice with increasing temperature.

This effect can be due only to a decrease of the noncollinearity angle θ in the B sublattice. With increasing temperature, the intrasublattice interactions decrease more rapidly than the intersublattice interactions (the evidence is that ferrites containing magnetic ion in one sublattice have low Curie temperatures). This should lead to a decrease in the angle θ, and accordingly to an increase of the magnetization of the B sublattice. At a certain temperature, the magnetization of the B sublattice becomes larger than the magnetization of the A sublattice. This is indeed observed in the Mössbauer spectra at room temperature. Thus, the compensation point in Mn[FeCr]O$_4$ is the consequence of the temperature dependence of the noncollinearity angle θ in the B sublattice.

The loss of noncollinearity with increasing temperature was theoretically predicted by Kaplan et al.[8,9] for the structure of a conical ferrimagnetic helix and was experimentally observed by the neutron-diffraction method in certain spinels containing chromium[1,10,11]. It can be assumed that a conical-helix magnetic structure, which is more stable[8,9] than the Yafet-Kittel structure, is likewise realized in the ferrite MnFeCrO$_4$.

Similar measurements of the Mössbauer spectra in an external magnetic field were performed also for other ferrites of the $\mathscr{F}_x$ system. The measurement results are listed in the table. In the ferrite with x = 0.8, the compensation point T_{comp} is apparently close to 120°K, since H_{eff} remains practically unchanged in an external field at 120°K. For x = 1.2, we observe no change in the sign of the magnetization, and we assume therefore that T_{comp} in this ferrite is shifted towards lower temperatures ($T_{comp} < 120°K$). Finally, in the sample with x = 1.4, the inclination angles θ are apparently so large that the noncollinear structure is preserved up to the Curie point T_C, and T_{comp} is close to T_C.

Effective magnetic fields at the iron-ion nuclei in the B sublattices of the $\mathscr{F}_x$ ferrites in an external magnetic field and without a field

Measurement conditions		H_{eff}^{Fe} (B), kOe (± 4 kOe)			
		$x = 0,8$	1.0	1.2	1.4
$T = 120°$ K	$H_0 = 20$ kOe	494	499	455	481
	$H_0 = 0$	495	485	477	459
$T = 296°$ K	$H_0 = 20$ kOe	382	333	254	—
	$H_0 = 0$	398	350	275	—

D. Statistical magnetically-nonequivalent positions of the Fe^{3+} and Cr^{3+} ions. If the ions Fe^{3+} and Cr^{3+} are statistically distributed among the B sites, then for each x in the $\mathscr{F}_x$ system there exists a definite probability for the ion Fe^{3+}(Cr^{3+}) to have k Cr^{3+}(Fe^{3+}) ions among the nearest neighbors in the B sublattice ($0 \leq k \leq 6$). Since the canted spin configurations in the B sublattice are the results of competition between the intra-sublattice (B-B) and inter-sublattice (A-B) interactions, the angle θ can vary as a function of the local surrounding of the ion.

On the basis of the statistical model, we have analyzed the magnetic moments of the ferrites of the system $\mathscr{F}_x$ with allowance for the canted spin structure in the B sublattice. The following assumptions were made:

1) The negative intra-sublattice interactions Fe(B)—Cr(B) exceed all the other types of intra-sublattice interactions.

2) Deviation from collinearity is experienced both by the spins of the Cr^{3+} ions and by the spins of the Fe^{3+} ions. The latter circumstance is evidenced by the broadening of the Mössbauer lines in an external magnetic field.

3) There is a fixed value of the angle θ for each type of ion. The more bonds of the Fe(B)—Cr(B) are possessed by the given ion, the larger the angle.

Under these assumptions, the expression for the average magnetic moment $\overline{M}$ of the ferrite at 0°K can be written in the form

$$\overline{M} = xM^{Cr}\sum_{k=0}^{6} P^{Cr}(k)\cos\theta_k{}^{Cr} + (2-x)M^{Fe}\sum_{k=0}^{6} P^{Fe}(k)\cos\theta_k{}^{Fe} - M^{Mn}. \quad (7)$$

Here $P^{Cr}(k)$ is the probability that k of the nearest neighbors of Cr^{3+} in the B sublattice are Fe^{3+} ions:

$$P^{Cr}(k) = \frac{6!}{k!(6-k)!}\left(1-\frac{x}{2}\right)^k\left(\frac{x}{2}\right)^{6-k};$$

$P^{Fe}(k)$ is the probability that k of the nearest neighbors

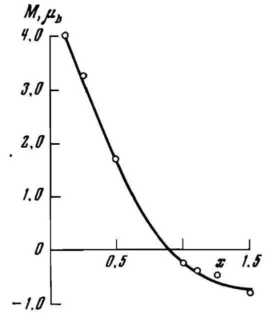

FIG. 8. Magnetic moment of $\mathcal{F}_x$ ferrites as a function of x at 0°K. The points are Gorter's experimental data [3], and the curve is calculated with the aid of formula (7).

of the Fe^{3+} ion in the B sublattice are Cr^{3+} ions:

$$P^{Fe}(k)=\frac{6!}{k!\,(6-k)!}\left(1-\frac{2-x}{2}\right)^{k}\left(\frac{2-x}{2}\right)^{6-k};$$

θ_k^{Cr} and θ_k^{Fe} are the angles of deviation of the magnetic moments of the Cr^{3+} and Fe^{3+} ions from collinearity, corresponding to the environment k; $M^{Cr} = 3\mu_B$, $M^{Fe} = 5\mu_B$, and $M^{Mn} = 5\mu_B$.

Using (7), we have estimated approximately the values of the angles θ at 0°K, by comparing the calculated values of the magnetic moments of the $\mathcal{F}_x$ ferrites for different substitutions with Gorter's experimental data[3]. It was assumed in the calculation that the deviation angles are somewhat larger than for the spins of the Cr^{3+} ions for Fe^{3+}, since the inter-sublattice interaction Cr(B)—Mn(A) is weaker than Fe(B)—Mn(A). Formula (7) agrees satisfactorily with the experimental data (Fig. 8) at the following values of the angles θ:

$\theta_6 = 180°$, $\theta_5 = \theta_4 = 90°$, and $\theta_3 = \theta_2 = \theta_1 = \theta_0 = 0°$ for the Fe^{3+} ions;

$\theta_6 = \theta_5 = 180°$, $\theta_4 = 90°$, $\theta_3 = \theta_2 = \theta_1 = \theta_0 = 0°$ for Cr^{3+} ions.

As seen from Fig. 8, the agreement between the experimental and calculated data is good enough even for such a simplified model. It is possible that actually the deviation angle differs from 0 at all k.

It is probable that in view of their statistical character, the angular configurations in the $\mathcal{F}_x$ system could not be observed by the neutron-diffraction method[5].

The authors thank L. M. Belyaev for interest in the work and A. P. Dodokin for a useful discussion of the results.

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Translated by J. G. Adashko
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