Local magnetic structure and anomalies of magnetic hyperfine interactions of the $^{57}$Fe and $^{119}$Sn nuclei in lithium iron aluminates

1. INTRODUCTION

A special feature of the magnetic properties of the lithium iron aluminates Li$_3$Fe$_{2+x}$Al$_x$O$_4$ system is an anomalous temperature dependence of the magnetization. In the case of pure Li ferrite the direction of magnetization $\theta$ coincides with the direction of the magnetic moment of the octahedral $B$ sublattice. As iron is replaced with aluminum, the "normal" temperature dependence of the magnetization by the tetrahedral $A$ sublattice, the "normal" temperature dependence of the magnetization. Li, As iron is replaced with aluminum, the "normal" temperature dependence of the magnetization. The observed anomalies of the temperature dependence of the magnetization were attributed to changes of the various contributions made to the $H'$ field because of transformation of the local canted magnetic structure into a collinear one.

2. EXPERIMENTAL METHOD

A system of tin-doped Li$_3$Fe$_{2+x}$Al$_x$O$_4$ ferrites (-0.01 at. % Sn; 0.8, 0.9, 0.955, and 1.0) was synthesized by the ceramic technology using a method of simultaneous deposition of hydroxides. X-ray diffraction confirmed that the samples with the cubic spinel structure consisted of a single phase. The unit cell parameters $a_0$ and the Néel temperatures $T_N$ obtained in the present study for the Li$_3$Fe$_{2+x}$Al$_x$O$_4$ Sn system were as follows:

- $a_0$: 8.206(3), 8.208(3), 8.213(3)
- $T_N$: 801(3), 768(3), 767(3), 768(3)

An ordered distribution of univalent and trivalent cations in the ratio 1:3 was found at the octahedral positions (this was similar to the distribution found in pure lithium ferrite Li$_3$Fe$_2$O$_4$).

The Mössbauer spectra determined for the $^{57}$Fe and $^{119}$Sn nuclei in the temperature range 80-650 K. The gamma radiation sources were $^{57}$Co in a Cr matrix and $^{119}$Sn in the compound BaSnO$_3$.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Spectra of the $^{57}$Fe nuclei

The Mössbauer spectra of the $^{57}$Fe nuclei recorded in the range $T < T_N$. (Fig. 1) exhibited a "paramagnetic" doublet in the central part of the spectrum against the background of the hyperfine magnetic splitting. In contrast to Ref. 7, the intensity of the paramagnetic doublet far from $T_N$ did not vary with temperature or with the external magnetic field. We therefore concluded that this doublet appeared not because of relaxation, but because of the presence of the iron ions excluded from participation in the exchange interaction.

3.1.1. Magnetically disordered Fe$^{3+}$ ions. We used the cation distribution of Ref. 2 to calculate for each sample the fraction of the iron ions with a weaker exchange coupling. In the case of the ordered structure of the spinel the immediate environment of an iron ion in the $A$ sublattice consists of $B$ ions distributed as follows:

$$3 \text{Li}^3(9-a)\text{Fe}^{3+} + a\text{Al}^{3+}$$

where $a = 0, 1, ... , 9$. Then, the probability $P(m)$ that an
Fe\(^{3+}\) (A) ion has \(m\) magnetic neighbors in the B sublattice is

\[
P_r(m) = C_r k_r^m (1-k_r)^n,
\]

where \(k_r\) is the fraction of the nonmagnetic ions in the B sublattice. Consequently, in the case of the Fe\(^{2+}\) (B) ion the probability of the presence of \(m\) magnetic neighbors in the A sublattice is

\[
P_r(m) = C_r' k_r'^m (1-k_r')^n,
\]

where \(k_r'\) is the fraction of the nonmagnetic ions in the A sublattice.

Figure 2 shows the experimentally determined (at \(T = 300\) K) relative intensities of the paramagnetic doublet, proportional to the number of the Fe\(^{2+}\) ions which did not participate in the magnetic ordering and the corresponding calculated values. Our calculations were carried out for three cases: a) \(m = 0\); b) \(m < 1\); c) \(m < 2\). A good agreement between the experimental and calculated data in case b indicated that the paramagnetic doublet exhibited by our samples could be explained satisfactorily by the Gilleo model, i.e., on the assumption that only the Fe ions with at least two adjacent-sublattice magnetic ions in the immediate cation environment can be magnetically ordered.

3.1.2. Magnetically inequivalent cation positions. The different environments of the iron ions in the two sublattices give rise to a complex hyperfine splitting pattern because of the superposition of the subspectra due to the Fe\(^{3+}\) ions at specific local environments.

FIG. 1. Mössbauer spectra of the "Fe nuclei at 80 K, recorded for samples with different aluminum concentrations in the Li\(_2\)Fe\(_x\)Al\(_{1-x}\)O\(_4\):Sn system: 1) \(x = 0.8\); 2) 0.9; 3) 0.955; 4) 1.0.

FIG. 2. Experimental (points) and calculated (dashed lines) values of the number of the iron ions that do not participate in the magnetic ordering. The calculated dependences are plotted for \(m = 0\) (a), \(m < 1\) (b), and \(m < 2\) (c).

The parameters of the individual components were determined by analyzing the spectra of all the samples recorded at temperatures 80 and 300 K in accordance with a special program. In the initial approximation the statistical regularization method was used to reduce the individual lines in the spectrum to zero width. Then, the individual lines in the spectrum were resolved into 6–8 peaks subject to the following assumptions:

1) the ratio of the intensities of the individual subspectra is described by Eqs. (1) and (2);
TABLE I. Parameters of the Mössbauer spectra of the $^{57}$Fe nuclei of iron ions with different magnetic environments in Li$_x$Fe$_{1-x}$Al$_2$O$_4$ Sn ferrite.

<table>
<thead>
<tr>
<th>T, K</th>
<th>A sublattice</th>
<th>B sublattice</th>
<th>A sublattice</th>
<th>B sublattice</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_{\text{A}}$, kOe</td>
<td>$\Delta H_{\text{A}}$, mm/s</td>
<td>$H_{\text{B}}$, kOe</td>
<td>$\Delta H_{\text{B}}$, mm/s</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td></td>
<td>6</td>
<td>-0.26</td>
</tr>
<tr>
<td>80</td>
<td>516</td>
<td>-0.24</td>
<td>536</td>
<td>-0.25</td>
</tr>
<tr>
<td>4</td>
<td>402</td>
<td>-0.28</td>
<td>403</td>
<td>-0.26</td>
</tr>
<tr>
<td>3</td>
<td>459</td>
<td>-0.27</td>
<td>459</td>
<td>-0.17</td>
</tr>
<tr>
<td>2</td>
<td>450</td>
<td>0</td>
<td>450</td>
<td>0</td>
</tr>
<tr>
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<td>450</td>
<td>0</td>
<td>450</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>401</td>
<td>0.04</td>
<td>401</td>
<td>-0.24</td>
</tr>
<tr>
<td>6</td>
<td>402</td>
<td>0.12</td>
<td>403</td>
<td>0.26</td>
</tr>
<tr>
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<tr>
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<td>421</td>
<td>0.23</td>
<td>423</td>
<td>0.97</td>
</tr>
<tr>
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<td>0.04</td>
<td>450</td>
<td>0.83</td>
</tr>
<tr>
<td>2</td>
<td>300</td>
<td>0.04</td>
<td>200</td>
<td>0.53</td>
</tr>
<tr>
<td>1</td>
<td>200</td>
<td>0.15</td>
<td>200</td>
<td>0.53</td>
</tr>
</tbody>
</table>

2) the isomeric shifts are the same for the paramagnetic doublet and the magnetically split part of the spectrum;
3) the cation distribution is the same as that postulated in Ref. 2.

This analysis enabled us to resolve the experimental spectra into the components representing the iron ions with different magnetic environments. The parameters of the iron ions for the $x = 1.0$ case are listed in Table I.

It is clear from this table that the replacement of one Fe$^{3+}$ ion in the polycrystalline sample with an Al$^{3+}$ ion from the immediate environment of the B iron ion reduces the local magnetic field $H(B)$ at the nucleus by an amount $\Delta H$ amounting to 12-13 kOe at 80 K and 17-22 kOe at 300 K. These values are in agreement with the results reported for the Li-Zn and Li-Ga systems in Refs. 10 and 11. Removal of one Fe$^{3+}$ ion from the immediate environment of Fe$^{3+}$ (A) reduces the local magnetic field $H(B)$ by $13$ kOe, which is close to the results reported for the Li-Ti system in Ref. 12. It should be pointed out that at temperatures $T = 0$ the value of $\Delta H$ should consist mainly of two contributions: firstly, due to the hyperfine magnetic field transferred from the Fe$^{3+}$ ion via oxygen to the central cation (indirect hyperfine interaction field $H_{\text{A2}}$) and, secondly, the temperature-dependent contribution due to the weakening of the exchange interaction on removal of one of the magnetic neighbors of the central ion (equivalent to lowering of the Néel point).

The values of the parameters (Table I) obtained by solving the spectra of the samples with $x = 0.8, 0.9,$ and 0.955 agreed within the limits of the experimental error with those found for $x = 1.0$ if we allowed for the intensities of the individual components. The average values of the fields $H = 2P\cdot H_1$ (here, $P_1$ is the ratio of the area under the ith subspectrum to the total area under the spectrum; $P_1$ represents the probabilities $P(m)$ in Eqs. (1) and (2)), calculated from the data of Table I, are as follows:

$H_A = 410$ kOe, $H_B = 652$ kOe at 300 K;
$H_A = 481$ kOe, $H_B = 506$ kOe at 80 K.

The temperature dependences of the average magnetic hyperfine fields for the $A$ and $B$ sublattices were used to find the Néel temperatures $T_N$ for all the samples (see Sec. 2).

1.1.3. Quadrupole splitting. The quadrupole splitting of the paramagnetic doublet $\Delta E_0$ was $0.55 \pm 0.01$ mm/s at room temperature, in agreement with the values calculated using the model of point charges.

It is worth noting the behavior of the quadrupole shift in the spectra determined below the magnetic ordering temperature. Table I gives the values of $\Delta E$ obtained when the spectra were resolved into the components representing different local environments. The weighted average $\Delta E$ was $-0.26$ mm/s at 80 K and $-0.17$ mm/s at 300 K. This behavior of the quadrupole shift can be explained as follows.

The magnetic moment of each domain in lithium aluminum spinels is directed along a specific axis of the $(111)$ type (which is the easy magnetization axis). The principal electric-field gradient (EFG) axis is just as likely to be oriented along one of the four directions of the $(111)$ type. Then, in the absence of an external magnetic field each sublattice should have two types of sites differing in aspect of the angle $\alpha$ between the EFG axis and the magnetization: one-quarter of the ions have $\alpha = 0$, whereas for the remaining three-quarters of Fe$^{3+}$ ions, we have $\alpha_1 = 70.32'$. Since $\Delta E = \Delta E_0(3 \cos^2 \alpha - 1)$, where $\Delta E_0$ is the true value of the quadrupole shift and $\Delta E$ is the observed value, it follows that in the case of the Mössbauer spectrum one-quarter of the ions is characterized by $\Delta E_1 = \Delta E_0$, whereas in the case of the remaining three-quarters we have $\Delta E_2 = -\Delta E_0/3$. Consequently, the Mössbauer spectrum of such a sample should exhibit two six-line components ( sextets), one with positive values of $\Delta E$, and the other with negative values.

In the case of a real spectrum of a polycrystalline sample the pattern is averaged out and we have

$$\overline{\Delta E} = 0.25\Delta E_0(1 + 0.75\cos \alpha/3) = 0.$$

When the magnetic moment of the iron ion is tilted from the $(111)$ axis by an angle $\alpha$ the positive part of $\overline{\Delta E}$ decreases and the negative one increases. Therefore, the average value of $\overline{\Delta E}$ becomes negative and its absolute value increases on increase in $\alpha$.

Our experimental data thus allow us to draw the following conclusions.

1. The deviation of the average value of $\overline{\Delta E}$ from zero demonstrates that the magnetic moments of the iron ions are
not collinear, i.e., a canted magnetic structure occurs in both sublattices.

2. The reduction in the average value of $\Delta E$ on increase in temperature means that the canting angle decreases on increase in temperature, i.e., that thermal vibrations destroy the canted magnetic structure.

3. The difference between the values of $\Delta E$ for different local environments (see Table I) indicates that the angle $\theta$ varies with the number of the magnetic neighbors. 

3.1.4. Magnetic structure. Interesting results were obtained when the M"ossbauer spectra were recorded at $T = 300 \text{ K}$ in the presence of an external magnetic field $H_i = 20 \text{ kOe}$ directed at right-angles to the wave vector $k_i$ of the gamma rays. It is known that the ratio of the intensities $I_i$ of the lines in the M"ossbauer spectrum of a magnetically ordered crystal are in the ratio

$$I_1/I_2 = 3:q:1, \quad q = \frac{4 \sin^2 \beta}{1 + \cos \beta}.$$  \hspace{1cm} (3)

where $\beta$ is the angle between the magnetic moment and $k_i$. Therefore, the ratio of the intensities of the resonance lines can provide information on the magnetic structure of a crystal.

We shall now consider the two cases when this can be done.

1. In the first case the magnetic moments of the iron ions lie within a cone which makes an angle $\theta_0$ with an external magnetic field $H_i$, directed perpendicularly to the vector $k_i$ (Fig. 3). We then have $\cos \beta = AO/OC = \sin \theta \cos \varphi$.

We shall now calculate the average value of $\cos^2 \beta$ inside a cone with a vertex angle $\theta_0$:

$$\cos^2 \beta = \frac{\int_{0}^{\pi} \int_{0}^{\pi} \cos^2 \beta \sin \theta \, d\theta \, d\varphi}{\int_{0}^{\pi} \int_{0}^{\pi} \sin \theta \, d\theta \, d\varphi}.$$

$$= \frac{2 - \cos \theta_0 - \cos^2 \theta_0}{6}.$$ \hspace{1cm} (4)

Two known special cases follow from Eq. (4):

i) a collinear magnetic structure characterized by $H_{ik}, \theta_0 = 0$ and $q = 2$; ii) an analog of a polycrystalline sample or a homogene-ous distribution of the magnetic moments on a sphere: $\theta_0 = \pi$ and $q = 2$. It should be noted that when the magnetic moments are distributed on a hemisphere ($H_{ik}, \theta_0 = \pi/2$), we again obtain $q = 2$ as in the case of a polycrystalline sample when $H_i = 0$.

2) In the second case all the magnetic moments have the same fixed angle $\theta_0 = 0$ (helical magnetic structure). We then have

$$\cos^2 \beta = \frac{\int_{0}^{\pi} \cos^2 \beta \, d\beta}{2\pi} = \frac{1}{2} \sin^2 \theta_0.$$ \hspace{1cm} (5)

In particular, if $\theta_0 = \pi/2$ (when the magnetic moments lie in the $XY$ plane, spiral structure), we find that $\cos^2 \beta = \frac{1}{2}$, $\sin^2 \beta = \frac{1}{2}$, and $q = 6/3$.

Our experiments in an external magnetic field at $T = 300 \text{ K}$ showed that the values of $q$ found from the ratio of the areas under the M"ossbauer lines were approximately equal for all the samples and amounted to $3.8 \pm 0.1$. Using Eqs. (3)–(5), we then calculated the angle $\theta_0$ for the two cases discussed above.

In case 1, when the angle of tilt of the magnetic moments from the $Z$ axis varies continuously from $0$ to $\theta_0$, we obtain $\theta_0 = (18 \pm 5)^\circ$. In case 2, when the angle of tilt of all the magnetic moments relative to the $Z$ axis is the same and equal to $\theta_0$, we obtain $\theta_0 = (13 \pm 4)^\circ$.

These results agree well with the neutron diffraction data reported in Ref. 5, where a sample of $\text{Li}_2 \text{Fe}_5 \text{Al}_1 \text{O}_{0.5}$ was investigated at $T = 300 \text{ K}$ and a helical structure with a cone vertex half-angle $\theta = (14 \pm 6)^\circ$ was observed in the $B$ sublattice.

Clearly, in the case of our samples the state was mixed, representing contributions of the variants 1 and 2, because the angle $\theta$ varied from $0$ to a certain maximum value, depending on the number of the nonmagnetic neighbors in the immediate cation environment. However, we found that this variation is not continuous but discrete, i.e., for each type of the local environment (and there are seven in the $B$ sublattice) there is a specific angle $\theta$. The average value of the angle $\theta$ depends on the statistical weight of each local environment configuration and, consequently, it varies with the aluminum concentration. Our value for the average angle $\theta$ agrees with the binomial nature of the distribution of the $\text{Al}^{3+}$ ions in the lattice.

This result is not in conflict either with the "spin semi-glass" structure proposed by Villain.\(^{14}\) In the case of this structure the $z$ components of the magnetic moments of the $\text{Fe}^{3+}$ ions at different inequivalent positions are parallel to the external field or to the easy magnetization axis, forming a long-range canted magnetic order, whereas the components normal to the field are distributed at random resembling a spin glass configuration.

3.2. Spectra of the $^{119}$Sn nuclei

The M"ossbauer spectra of the $^{119}$Sn nuclei were found to be split by the magnetic hyperfine interaction in all the samples and they represented strongly broadened sextets with a...
method of statistical regularization was used by us to find the distribution functions \( P(H^m) \) of the magnetic fields at the tin nuclei at various temperatures. The nature of the distribution \( P(H^m) \) shown in Fig. 4 demonstrated a considerable scatter of the magnetic field intensities at the tin nuclei within the range \( 0 < H^m < 200 \text{ kOe} \). It is worth noting a major change in the \( P(H^m) \) distribution with temperature and also a considerable "zero-field" contribution to \( P(H^m) \).

A detailed analysis of the function \( P(H^m) \) was made on the basis of the temperature dependences of the following quantities (Fig. 5): the average field \( \langle H^m \rangle \), the fields \( H^m \) and \( H^m \) corresponding respectively to the maximum and minimum of the distribution function \( P(H^m) \) (Fig. 5a), and the zero-field contribution \( P(0) \) (Fig. 5b). Extrapolation of the \( H^m(T) \) curves to 0 K in accordance with the law \( H = T^{-3/2} \) gives \( H^m(0) = 82 \pm 3 \text{ kOe} \) for all the compositions in the range 0.8 < x < 1.0. It is clear from Fig. 5 that the quantities \( H^m \), \( H^m \), and \( P(0) \) have singularities in the temperature range 150–200 K.

3.2. Temperature anomalies of \( H^m \). Usually the tin ions occupy the B sites in the spinel structure. It is shown in Ref. 15 that the field \( H^m \) at the tin nuclei in spinels is primarily due to two contributions: a negative one from the inter-sublattice indirect \( A-O-B \) exchange interaction (indirect transfer of the hyperfine magnetic field along the Fe(\( A \))-O-Sn(\( B \)) chain) and a positive one due to an intrasublattice direct \( B-B \) exchange (due to a direct Sn(\( B \))-Fe(\( B \)) overlap of the orbitals of the magnetic and diamagnetic ions). The competition between these two contributions determines

3.2.1. Magnetic hyperfine fields at the \( ^{119} \text{Sn} \) nuclei. The single central peak. The isomeric shift \( \delta \) of the central paramagnetic peak was equal to the isomeric shift of the magnetically split part of the spectrum and amounted to 0.2–0.3 mm/s (relative to SnO) at room temperature. The intensity of this peak increased on increase in temperature and on increase in the aluminum content.

3.2.2. Temperature anomalies of \( H^m \). Usually the tin ions occupy the B sites in the spinel structure. It is shown in Ref. 15 that the field \( H^m \) at the tin nuclei in spinels is primarily due to two contributions: a negative one from the inter-sublattice indirect \( A-O-B \) exchange interaction (indirect transfer of the hyperfine magnetic field along the Fe(\( A \))-O-Sn(\( B \)) chain) and a positive one due to an intrasublattice direct \( B-B \) exchange (due to a direct Sn(\( B \))-Fe(\( B \)) overlap of the orbitals of the magnetic and diamagnetic ions). The competition between these two contributions determines
largely the temperature dependences of the fields at the tin nuclei in spinels.

The temperature dependences of the magnetic moments of the sublattices cannot by themselves give rise to anomalies of $H^{\alpha}$ at the compensation point $T_c$ if there is no external magnetic field. Anomalies of the temperature dependences of the distribution parameters $H^{\alpha}_{Sn}$, $H^{\alpha}_{St}$, and $P(0)$ may be associated only with a rapid variation of the contributions made to the field $H^{\alpha}$ by some group of iron ions with a specific local environment. Clearly, the main reason for such anomalies is a change in the angular structure of the magnetic moments of the Fe$^{3+}$ ions in the A and B sublattices. It is shown in several papers (see, for example, Refs. 5, 16, and 17) that in the case of dilute ferrite spinels an increase in temperature reduces the canting angle and at some temperature $T_c$ the canted structure may "collapse" to form a linear one. The point $T_c$ can be regarded as the magnetic phase transition. In the case of a magnetically dilute system in the presence of local regions with different magnetic environments the temperature of such a transition to the collinear magnetic structure will be different for two different groups of atoms so that the transition itself will be smeared out.

In general, such a transition is unrelated to the compensation point and the range of temperatures where the anomalies of $H^{\alpha}$ are observed is accidentally close to $T_c$. However, it is shown in Ref. 6 that in the case of the spinel structure the actual compensation point can be a consequence of the temperature dependences of the canting angles of the sublattice moments.

A detailed investigation of the changes in the distribution $P(H^{\alpha})$ due to variation of temperature confirms that the canted structure is transformed into a collinear one. If we consider the function representing the difference between two distributions $P(H^{\alpha})$ for a pair in samples with the investigated concentrations $x_1$ and $x_2$ but at the same temperature, then in the collinear magnetic structure case we can easily determine theoretically such a function using the binomial distribution of cations around the Fe$^{3+}$ (A) ion and ignoring the B-B interaction. Figures 6 and 7 show the calculated experimental functions of these differences plotted for different compositions and temperatures. We can see that the experimental curve approaches the calculated one only at high temperatures. It therefore follows that the transition from the canted to the collinear structure occurs at these temperatures and it demonstrates once more that the canting angle decreases on increase in temperature.

It is particularly interesting to consider the origin of the zero-field contribution to $P(H^{\alpha})$. We shall assume that this contribution is created by two sources: the tin ions with only aluminum ions and/or magnetically disordered iron ions in the adjacent sublattice, and the tin ions surrounded by magnetically ordered Fe$^{3+}$ ions the contributions of which to $H^{\alpha}$ due to the A-O-B and B-B exchange interactions balance each other out. The former mechanism is confirmed by the rise of $P(0)$ on increase in the aluminum concentration in the samples. The second mechanism is clearly the reason for the temperature anomalies of $P(0)$.

4. CONCLUSIONS

Our investigations demonstrated that some of the Fe$^{3+}$ ions in Li$_{x}$Fe$_{y}$,Al$_{z}$O$_{x}$Sn ferrite spinels are in a mage-
tically disordered state at temperatures $T < T_c$. An estimate of the number of these ions confirms the validity of the model of dilute magnetic materials proposed by Gilleo. The $\text{Fe}^{2+}$ ions are located at magnetically inequivalent positions, differing in respect of the local environment. We determined the fields $H_{\text{Fe}^{2+}}$, corresponding to a reduction in the magnetic field at the $^{57}\text{Fe}$ nuclei when the nearest $\text{Fe}^{7+}$ ion was replaced with $\text{Al}^{3+}$.

The investigated compounds exhibited a canted magnetic structure and it was found that the canting angle $\theta$ was a function of temperature and of the magnetic environment. Local regions with a canted structure were distributed at random throughout a crystal and did not form a magnetic lattice. The nature of this canted magnetic structure was determined in greater detail and the average values of the canting angles $\theta$ were found for two variants of the structure.

Hyperfine magnetic fields were observed at the $^{119}\text{Sn}$ nuclei and they were characterized by a complex distribution $P(P_{\text{n}})$ which depended on temperature and on the aluminum concentration. Temperature anomalies of the dependence $P(P_{\text{n}})$ were attributed to a competition of the contributions made to the field $P_{\text{n}}$ by the magnetic moments of the $A$ and $B$ sublattices and by the transformation of the canted magnetic structure into a collinear one.

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