TEMPERATURE DEPENDENCE OF THE SUBLATTICE MAGNETIZATION OF LITHIUM FERRITE–CHROMITES

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The Mossbauer effect for Fe^{57} nuclei in the ferrite $Li_{0.5}Fe_{1.1}Cr_{1.4}O_4$ has been investigated in the temperature interval from 77 to 500°K. The purpose of the present work was to elucidate the character of the correlation between the temperature dependences of the effective magnetic field acting on the atomic nucleus and of the magnetization of its "own" sublattice. Within the limits of experimental accuracy the effective magnetic fields for both the ferrite sublattices were found to be proportional to the sublattice magnetizations. A ferrite with a compensation point was specially chosen as the subject of the investigation. The magnetizations of the ferrite sublattices were obtained from data on the measurements of the effective field and the magnetization of the sample. It is shown that the temperature dependence of the sample magnetization is described by the Néel model. For both sublattices the temperature dependence of the magnetic moment has the Weiss form; this indicates strong AB-interaction. In spite of the presence of a magnetic compensation point in the ferrite, it is only with considerable reservations that we can distinguish the "weaker" of the two sublattices (which is found to be an octahedral sublattice).

1. MUCH attention has been given recently to the question of the character of the temperature dependence of the effective magnetic field acting on an atomic nucleus in a magnetically-ordered spin system. In the majority of the papers on this problem, it is tacitly assumed that the field H_n is proportional to the magnetization J_S of the sublattice in which the given atom is situated:

$$H_n = aJ_s. \tag{1}$$

The basis for such an assumption is the fact that the function $H_n(T)$ usually has the Weiss form and in a rough approximation can be described by the Brillouin function. The essential point is that the accuracy of this approximation is roughly the same as that for the spontaneous magnetization $J_S(T)$. This, however, is no more than an indirect confirmation of the fact that relation (1) can be found to be true. A direct comparison of the experimental data on H_n and J_S at different temperatures is necessary.

An elucidation of the question of the correlation of the dependences $H_n(T)$ and $J_S(T)$ and of the limits of applicability of relation (1) to specific types of magnetically ordered substances would enable us to give a more complete interpretation of the experimental data on the dependence $H_n(T)$ in a number of cases. In the first place, this applies to multi-sublattice magnetic systems, for which the neutron-diffraction method is up to now practically the only reliable method for determining the temperature dependence of the magnetization of the sublattices, in spite of its comparatively low accuracy. Methods based on nuclear magnetic resonance and the Mossbauer effect would evidently be able to supplement appreciably the data from temperature measurements of the magnetization of a substance, if only it were clear to what extent relation (1) is true.

One can point immediately to a case for which relation (1) does not hold. This is the case of sufficiently fast relaxation of an atomic spin, in which the spectral line shape is determined not so much by the extent of magnetic ordering as by the relaxation properties of the spin. The problem thus reduces to the question of the correlation of the functions $H_n(T)$ and $J_S(T)$ in the absence of relaxation phenomena.

2. An interesting opportunity to elucidate this is presented in the study of ferrite-spinels with a compensation point. The very existence of magnetic compensation of the sublattices at a certain temperature enables us, in principle, to make a simple check of the validity of relation (1) for this type of substance (as will be shown below). For this, it is true, one more condition must be satisfied: the nuclei at which the nuclear magnetic resonance or Mossbauer effect is investigated must occur in both magnetic sublattices. Such a condition is satisfied by the ferrite of the system $Li_{0.5}Fe_{2.5-x}Cr_xO_4$ with $x = 1.4$ as regards the isotope Fe^{57}, on which we undertook investigations of the Mossbauer effect in a wide range of temperatures. This ferrite is a very suitable object of investigation from the point of view of the problem we have posed. The x-ray and magnetic characteristics of this ferrite system were studied in [1-3]. In the crystal lattice of this ferrite spinel the iron atoms all have the same valency and are distributed in comparable quantities between the two sublattices. The compensation point T_{comp} and the Curie point T_C of the ferrite $Li_{0.5}Fe_{1.1}Cr_{1.4}O_4$ lie in an easily attainable temperature region.

According to [2,3], the structural formula of the investigated ferrite can be written in the form

$$Li_{0,15}Fe_{0,85}[Li_{0,35}Fe_{0,25}Cr_{1,4}]O_4, \tag{2}$$

where, as usual, the ions written in the square brackets occupy the B-sites.

In our experiments we used a polycrystalline ferrite sample, prepared by the usual powder process by the so-called "dry" method. The reagents used were Li_2CO_3, Cr_2O_3, and Fe_2O_3 (of analytically pure quality).

The iron in the Fe_2O_3 was 20% enriched by the isotope Fe^{57}. Measurements of the sample magnetization in the temperature interval 77–500°K were carried out by means of a vibration magnetometer. The values obtained $T_C = 424 \pm 1$°K and $T_{comp} = 279 \pm 1$°K agree well with data from other work.[1-3]

The Mossbauer-effect measurements were carried out by means of an automatic single-channel spectrometer of the electrodynamic type. The Co^{57} isotope in stainless steel served as the radiation source. The thickness of the investigated sample amounted to 0.37 mg/cm² of the isotope Fe^{57}. During the measurements the sample temperature was maintained constant with an accuracy not worse than 0.1°K (within limits of 1° over the sample).

3. In the whole temperature interval investigated (from 77 to 500°K) we did not observe clear resolution of the spectral components corresponding to the A- and B-sites in the ferrite lattice (Fig. 1). Only the distortion of the fronts of the spectral lines indicated that each of the six lines consists in fact of two lines of different intensity, as required by the structural formula (2). To resolve each of the spectra obtained into two Zeeman sextets, a special technique was developed, based on the use of a "reference" sample with one Zeeman sextet. The essence of this technique consists in the fact that the spectrum of the investigated sample can be represented in the form of a superposition of the reference-sample spectra at two optimally chosen temperatures corresponding to the two values H_n of the field for the complex spectrum. The integrated intensities of the two reference sample spectra being combined were chosen in accordance with the distribution of the Fe^{3+} ions among the A- and B-sites. Among the characteristic special features of this technique are the following:

a) The investigated and standard samples must be as homogeneous as possible in composition; this requirement is especially important for the temperature region close to the magnetic transition, where the effect on the shape of the spectrum of the dependence of the Curie point on the composition of the investigated system is greatest.

b) The calculation of the relative intensities of the two reference sample spectra being combined from data on the distribution of the Mossbauer isotope in the sublattices is not, generally speaking, completely rigorous; it is necessary to bear in mind that the temperature dependence of the probability of the effect can be slightly different for different crystallographic sites; however, we can neglect the corresponding correction if it is known from the Mossbauer effect data that the effective Debye temperature for ions at sites of both types is sufficiently great (as was the case for our sample).

c) The technique obviates the need to introduce assumptions about the actual shape of the components of the Zeeman sextet.

In our case we chose as the standard a nickel ferrite–chromite with a compensation point $Fe[NiCr]O_4$, investigated previously in [4]. The homogeneity of the composition of the reference sample and the investigated sample was estimated in the Gaussian approximation from the magnitude of the magnetic moment at the compensation point, taking account of known data on the dependence of T_{comp} on the ferrite composition.

Using the technique described, we obtained the temperature dependence of the effective fields H_n^A and H_n^B acting on the iron nuclei in the A- and B-sublattices of the lithium ferrite-chromite.

4. The temperature dependences of the fields H_n^A and H_n^B are shown in Fig. 2. If relation (1) holds, the two curves obtained for $H_n^A(T)$ and $H_n^B(T)$ represent, essentially, the temperature dependences, in relative units, of the magnetizations $J_S^A(T)$ and $J_S^B(T)$ of a tetrahedral and an octahedral sublattice. This fact can, however, be verified directly.

It is clear that the dependences $H_n^A(T)$ and $H_n^B(T)$, treated as curves for the magnetization of the ferrite sublattices against the temperature, have a different scale along the magnetic moment coordinate axis. This is clear from the fact that the curves do not intersect at temperature T_{comp}. To reduce them to the same scale it is necessary to make the curves coincide at $T = T_{comp}$, thereby obtaining "magnetic compensation." We note that at the compensation point $H_n^A/H_n^B = 1.130 \pm 0.002$.

In accordance with the Néel model, the difference in the "magnetic moments" of the sublattices in Fig. 2 is the "spontaneous magnetization" of the ferrite J_S. If relation (1) holds for each of the sublattices, the dependence "J_S"(T) must be described by precisely the same function as that given by direct measurements of the ferrite magnetic moment at different temperatures.

Figure 3 leaves us in no doubt that within the limits of experimental accuracy this is really so (at least at temperatures up to 0.9 T_C). In this figure, the continuous line shows the values of the specific magnetization of the ferrite, obtained by the usual magnetic measure-

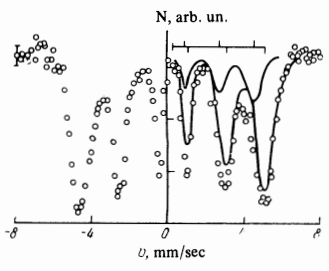

FIG. 1. Mossbauer spectrum of Fe^{57} nuclei in the ferrite $Li_{0.5}Fe_{1.1}Cr_{1.4}O_4$ at T = 293°K.

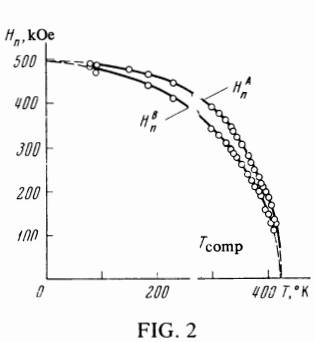

FIG. 2

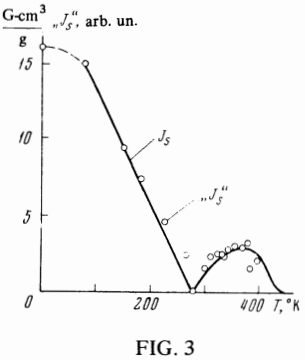

FIG. 3

FIG. 2. Temperature dependence of the effective magnetic field at iron nuclei in the A- and B-sublattices of the ferrite $Li_{0.5}Fe_{1.1}Cr_{1.4}O_4$ (at 77°K, $H_n^A = 488 \pm 4$ kOe and $H_n^B = 484 \pm 4$ kOe).

FIG. 3. Dependence $J_S(T)$ and "J_S"(T) for the ferrite $Li_{0.5}Fe_{1.1}Cr_{1.4}O_4$.

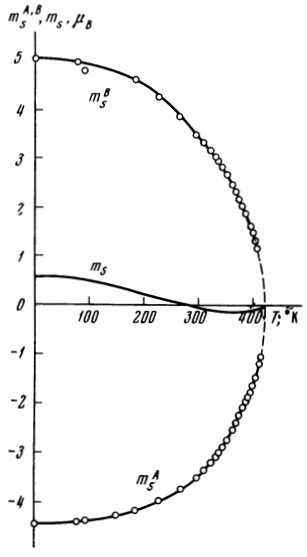

FIG. 4. Dependences $m_s^A(T)$ and $m_s^B(T)$ from data of Mossbauer effect measurements) and $m_s(T)$ (from data of measurements of the magnetic moment) for $Li_{0.5}Fe_{1.1}Cr_{1.4}O_4$.

ments (the data from [1,2] were used for the region of temperature below 77° K). The points indicated in the figure were obtained from the Mossbauer effect experiments.

We note that it is not only with ferrites with a compensation point that we have such an opportunity for a direct check of the validity of Eq. (1) for magnetic sublattices (without using data from neutron-diffraction experiments). It is important that the temperature dependence of the total magnetization of the system should, as far as possible, be substantially different from that of the magnetization of the sublattices, i.e., that it should be, in this sense, anomalous. However, a ferrite with a compensation point is the most suitable substance of such a type for investigation. The presence of a magnetic compensation point increases its "sensitivity" as regards possible deviations of the effective field data from relation (1). Not the least important role in this is played by the magnitude of the resultant moment at 0° K, which must, clearly, be the largest possible.

5. Thus, for our sample it is possible to obtain absolute values for the magnetization of the sublattices at different temperatures, using data on the effective magnetic field.

In Fig. 4 are shown curves for the temperature dependence of the sublattice magnetic moments m_s^A and m_s^B per "molecule" of $Li_{0.5}Fe_{1.1}Cr_{1.4}O_4$.

Gorter,[1] starting from measured data on the saturation magnetization, pointed out the anomalously low magnetic moment of lithium ferrite-chromites with large Cr^{3+} content. To explain the experimental data he suggested that at low temperatures the magnetic moments of ions in the B-sublattice are aligned at an angle.

The existence of a triangular configuration of magnetic moments in the crystalline lattice was predicted by Yafet and Kittel[5] for the case when the exchange AB interaction becomes comparable with the BB (or (AA) interaction. One of the special features of a triangular configuration of moments is its temperature instability.[6] It is just this fact which enables us to assert that in the ferrite we have investigated the triangular configuration hardly occurs. In fact, according to the data obtained, the temperature dependence of the ferrite magnetization is fairly well described by the relation

$$m_s(T) = k_B H^B{}_n(T) - k_A H_n{}^A(T). \qquad (3)$$

The instability of the triangular configuration would manifest itself in the fact that the coefficients k_A and k_B would depend on temperature. In fact these coefficients do not change with temperature, and this corresponds to the usual Néel model.

It seems that we cannot definitely state that the magnetic moments of the sublattices are accurately colinear with each other. The experimental error in the determination of the coefficients k_A and k_B and also of the effective field values results in a corresponding error in the sublattice magnetic moments. At 0° K, the magnetic moments m_s^A and m_s^B are found to be 4.4 ± 0.1 μ_B and 5.0 ± 0.1 μ_B respectively. From these data it is easy to estimate the probable value of the angle α which the magnetic moments of one of the sublattices (in this case the octahedral) can make with the direction of the magnetization vector of the domain, if the triangular configuration does occur. The required angle α turns out to be approximately 13°.

On the other hand, the sublattice moments at 0° K can be calculated from the Hund rules, using electron configurations for the cations which are the same as for the free ions (as is also done in the majority of cases). The calculations give $m_s^A = 4.25\ \mu_B$ and $m_s^B = 5.4\ \mu_B$, whence $\alpha \approx 27°$. As we can see, the angle corresponding to the Hund rules is twice as large as the permissible value corresponding to experimental errors in the Mossbauer effect data.

We draw attention to the fact that there is a discrepancy between the calculated and experimental values of the magnetic moment for the B-lattice at 0° K. Clearly, we must seek the cause of this in peculiarities of the electron configuration of the Cr^{3+} ions, which occupy B-sites.

6. The functions $m_s^A(T)$ and $m_s^B(T)$ for the magnetizations of the ferrite sublattices, as is clear from Fig. 4, are of completely analogous character, although there are some differences, appearing, in particular, in the form of an anomaly in the curve $m_s(T)$. Only with considerable reservation is it possible to distinguish which is the "weaker" of the two sublattices, i.e., the sublattice for which the magnetic moment decreases rather faster on increase of T than it does for the other one. As the "weak" sublattice, we should have to take the B-sublattice. It is important, however, that even at temperatures rather close to T, both functions $m_s^A(T)$ and $m_s^B(T)$ have the Weiss form and the resultant magnetization $m_s(T)$ is noticeably less than either of the components. This enables us to state that, of the different types of exchange interaction in a ferrite crystal lattice, the dominant one is the AB interaction. As regards the AA and BB interactions, the former is found to be slightly the weaker (if both are negative). It is usually assumed that one of the criteria for the existence of magnetic compensation of sublattices is a significantly weaker exchange interaction in one sublattice than in the other.[7] For strong interaction between the

sublattices, such a condition is, clearly, unnecessary.

An entirely different situation occurs in the case of ferrite-garnets with a compensation point. In these ferrites the rare-earth sublattice has a characteristic "tail" of spontaneous magnetization, which is a result of the comparatively weak exchange interaction between the sublattices.[8]

7. A paper by Ritter[9] has recently been published, in which data are obtained,from Mossbauer effect experiments, on the temperature dependence of the effective field at Fe^{57} nuclei in sublattices of a ferrite of the same system (for x = 1.2). However, the question of the connection between the values of the field H_n and the magnetizations of the ferrite sublattices was not considered in [9]. The data published in [9] enable us to treat the results by our proposed technique (the ferrite $Li_{0.5}Fe_{1.3}Cr_{1.2}O_4$, like the one we have investigated, has a compensation point).

In Fig. 5 are shown curves for the temperature dependence of the magnetization of the sublattices of the ferrite $Li_{0.5}Fe_{1.3}Cr_{1.2}O_4$ obtained by treatment of the results of [9]. In obtaining these curves, we also used data from [1] for the spontaneous magnetization at different temperatures; the corresponding curve is also shown in the figure, for comparison with the data of the Mossbauer effect measurements.

The $H_n^B(T)$ dependence, shown in the figure by a dashed line, is obtained from relation (3) using the dependences $H_n^A(T)$ and $m_S(T)$. It is clear from Fig. 5 that the temperature behavior of the curve $m_S(T)$ for the ferrite with x = 1.2 is also well described within the framework of the assumption that the effective field

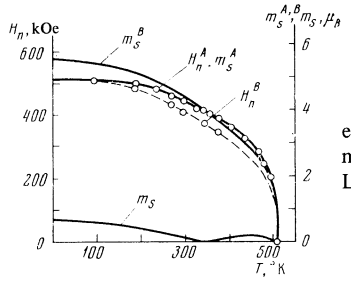

FIG. 5. Temperature dependence of the quantities H_n^A, H_n^B, m_S^A, m_S^B and m_S for $Li_{0.5}Fe_{1.3}Cr_{1.2}O_4$.

x	H_n^A (0 °K), kOe	H_n^B (0 °K), kOe	κ_A, $10^{-2}\frac{\mu_B}{kOe}$	k_B, $10^{-2}\frac{\mu_B}{kOe}$	m_s^A (0 °K), μ_B	m_s^B (0 °K), μ_B
1.2	503±7	508±7	0.96±0.03	1.08±0.03	4.8±0.2	5.4±0.2
1.4	494±4	494±4	0.90±0.02	1.01±0.02	4.4±0.1	5.0±0.1

is proportional to the magnetic moment of the "own" sublattice.

Values of the coefficients k_A and k_B for the lithium ferrite-chromites, and also a number of other data relating to them, are given in the table.

The values of the fields $H_n^{A,B}$ at 0°K are obtained by extrapolation of the data at 77°K using the "three-halves" law.

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