The electron configuration of the iron ions in the $NiFe_{2-x}Cr_xO_4$ ferrites

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The paper reports the results of a Mössbauer-effect investigation of the Fe^{57} nuclei in the $NiFe_{2-x}Cr_xO_4$ ferrites in a wide range of variation of the composition at temperatures above the magnetic-transition point. The results of x-ray structural studies of the same ferrites are also presented. On the basis of the obtained data, a number of conclusions are drawn about the distinctive features of the electron configuration of the iron ions and the nature of their immediate surroundings.

1. The substitution of iron by chromium in the $NiFe_{2-x}Cr_xO_4$ ferrites leads to a significant change in their magnetic properties [1]. In some region of x values the ferrites of this system have a magnetic-compensation point. This circumstance alone indicates that the magnetic properties of the nickel ferrite chromites are not only extremely diverse, but are also rather complicated for interpretation. The main difficulty encountered in the interpretation is due to the presence in the ferrite sublattices of three kinds of magnetically active ions. Attempts have been made before to ascertain the distinctive features of the electron configuration of these ions [1]. The urgency of such attempts is due to the fact that knowledge of the electron configuration (or even some distinctive features of it) can significantly facilitate the elucidation of the exchange and magnetic interaction mechanisms.

In the present investigation we attempted to ascertain how the gradual substitution of iron by chromium influences the electron configuration of the Fe^{3+} ions. Such an experiment is made possible by the fact that iron has a Mössbauer isotope Fe^{57} that is very convenient for these purposes.

For the analysis of the obtained Mössbauer spectra, it was necessary to know the cation distribution over the sublattices. The data available on this problem are inconsistent. The majority of investigators agree with Miyahara and Tsushima [2] that for $x \leq 1$ the $NiFe_{2-x}Cr_xO_4$ ferrites have a completely inverted structure, and that as x is increased further, the structure gradually changes from the inverse to the normal, the inversion parameter α depending linearly on x: $\alpha = x - 1$ (idealized case). Such a dependence $\alpha(x)$ needs, however, to be refined. This (need) is indicated by the data for the ferrites with $x = 1.7$ [3] and $x = 1.2$ [4] (in which the iron nuclei were found not only at the tetrahedral, but also at the octahedral sites), as well as by the data obtained by Belov et al.[5]. For this reason, we also attempted to find the dependence $\alpha(x)$ with the aid of x-ray structural studies.

2. The experimental samples were prepared by the standard ceramic technology. About 25% of the iron used was made up of the Fe^{57} isotope. Samples with x in the range from 0 to 2 were synthesized. The quality of the obtained samples was monitored with the aid of thermal magnetic measurements, as well as from the data of the x-ray structural analysis. The x-ray structural investigations were carried out in filtered copper radiation, using Debye chambers of diameter 57.3 and 114.6 mm.

In the Mössbauer-effect experiments, the radiation source was the isotope Co^{57} in a stainless-steel matrix (at room temperature). The main attention was given to the paramagnetic temperature region. This was done for the following reasons. In the first place, at temperatures below the Curie point the quadrupole-interaction-induced shift of the spectral components can be veiled by the hyperfine magnetic interaction [6]. Meanwhile, the magnitude of the quadrupole splitting (together with the data on the isomeric shift) is of great interest in connection with the formulated problem. Secondly, as has been established for a number of samples of the ferrite system [7,8], a structural phase transition is observed in the region of the Curie point.

The Mössbauer spectra were analyzed with the aid of an electronic computer by the least-squares method (in the Lorentz approximation for the line shape). We assumed, in doing this, that the relation between the intensities of the spectra for the ions at the A and B sites is determined only by the cation distribution (this is in complete agreement with the observed comparatively high effective Debye temperatures for the two types of sites). It was also assumed that the quadrupole dublets are completely symmetric about their center of gravity.

3. The cation distribution in the obtained samples was determined on the basis of the dependence of the lattice constant a on the parameter x at room temperature. This dependence (shown in Fig. 1) is in good agreement with similar data obtained by Miyahara and Tsushima [2]. In analyzing the x-ray patterns, we took into consideration the fact that the tetragonal distortions of the lattice (which are observed for $x \geq 1.2$) can be neglected in the entire interval of x values [1,8].

The dashed lines in Fig. 1 represent the dependences $\alpha_0(x)$ and $a_0(x)$, corresponding to the idealized case [2]. The first dependence (which was actually obtained on the basis of the second) does not, generally speaking, take into account the possible appearance of spontaneous magnetostriction as a result of the presence of magnetic order. The data obtained by us in the thermal investigations for a number of compositions together with the results of other authors [8,9] (see Fig. 1) allow us to conclude that the magnitude of the spontaneous magnetostriction is at least an order of magnitude smaller than the value that would have allowed the explanation of the discrepancy between the dependences a(x) and $a_0(x)$. The values of the inversion parameter α for the investigated compositions were computed on the basis of these data. It was borne in mind that for

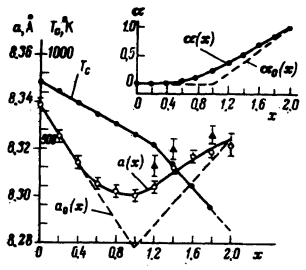

FIG. 1. The lattice parameter a (○–for T = 293°K, ▲–for T = 450°K), the inversion parameter α, and the Curie temperature T_C of the $NiFe_{2-x}Cr_xO_4$ ferrites as functions of x. The dashed lines represent the dependences for the "idealized" case.

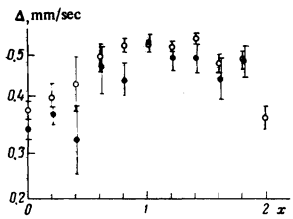

FIG. 2.

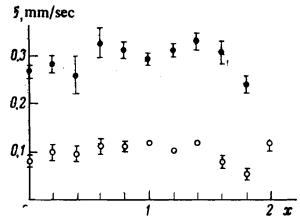

FIG. 3.

FIG. 2. The quadrupole splitting Δ of the Mössbauer line of the Fe^{57} nuclei of the $NiFe_{2-x}Cr_xO_4$ system in the paramagnetic temperature region: ○–for the A sites, ●–for the B sites.

FIG. 3. The isomeric shift δ of the Mössbauer line for T = 713°K (obtained from the data or the paramagnetic temperature region); ○–for the A sites, ●–for the B sites.

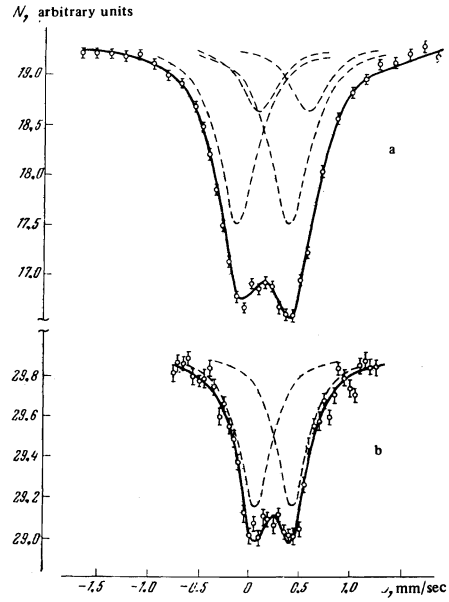

FIG. 4. The Mössbauer spectra of the Fe^{57} nuclei in the $NiFe_{2-x}Cr_xO_4$ ferrites: a) x = 0.80, T = 713°K; b) x = 1.99, T = 483 °K.

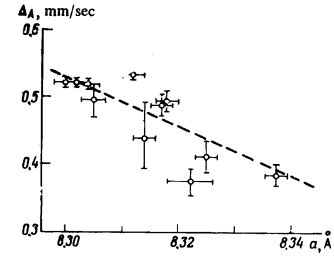

FIG. 5. The dependence of Δ_A on the lattice parameter a.

all values of x the Cr^{3+} ions occupy only the octahedral sites (the latter corresponds to the well-known neutron-diffraction data [10]). The results of the computations are presented in Fig. 1.

4. The results of the spectral analysis carried out with allowance for the found cation distribution are shown in Figs. 2 and 3. It is known that the quadrupole line splitting for the A sites in the case of the trivalent Fe^{3+} ion is equal to zero. This is connected with the fact that the A sites in the spinel structure have cubic symmetry with respect to the nearest cations, while the $3d^5$ electron configuration corresponds to a spherically symmetric charge distribution. The presence of the comparatively large quadrupole splitting Δ_A (0.4–0.5 mm/sec) indicates that these conditions are violated. In our experiments, we did not at all observe any variation of the quantity Δ_A with temperature right up to 1000–1300 °C. This means that the appearance of the electric-field gradient at the A sites cannot be due only to the change in the symmetry of the electron shell of the Fe^{3+} ion owing to the covalency of the bond and the addition of a sixth 3d electron, since a strong temperature dependence of Δ_A should be observed in that case [11]. Consequently, the electric-field gradient at the A sites is due to the external electrons surrounding the ionic nuclei. The nonequivalence of the Ni^{2+} and Cr^{3+} ions located at the B sites of the second coordination sphere is also not the main cause of the quadrupole line splitting for the sites. This is substantiated by the data for the ferrite with x = 1.99 (quite close in composition to $Ni[Cr_2]O_4$), since the order of magnitude of Δ_A for it is the same as for the other compositions of the system (see Figs. 2 and 4).

The main cause of the quadrupole line splitting at the A sites (in the case when the lattice as a whole has cubic symmetry) may be the oxygen vacancies, whose appearance during the sintering process is quite a probable circumstance [12]. It is evident that the appearance of oxygen vacancies will inevitably cause not only a sharp change in the symmetry of the crystal field at the A sites (as well as at the B sites), but also a deviation of the electron configuration of the cations from the configuration that is usually assumed for the spinel structure. In that case the electron configuration of the iron ions can be significantly different from the $3d^5$ configuration, and, besides, the sixth electron should contribute to the spin density in the d shell of the Fe^{3+} ion. The oxygen defects can lead to the quadrupole splitting of the Mössbauer line owing to the action of the crystal field of the "remaining" O^{2-} ions in the first coordination sphere and the removal of the d-shell degeneracy with respect to angular momentum.

5. Comparison of the dependences $\Delta_A(x)$ and a(x) reveals the correlation of Δ_A and a (Fig. 5). Since this relationship is well approximated by the equation of a straight line, the electron configuration of the iron ions at the A sites is quite stable against a change in the composition of the ferrite (it is characteristic that the magnitude of the isomeric shift depends extremely weakly on the composition, as can be seen from Fig. 2). Indeed, if the quantity Δ_A is largely determined by the point defects near the site in question, then it should, for slight variations in the unit-cell size, depend linearly on the lattice constant a, decreasing as a increases. The additional change in Δ_A due to the change in the overlap of the wave functions of the electrons participating in the Fe–O covalent bonds will then, in the first approximation, also depend linearly on a.

Since the magnitude of the quadrupole splitting turns out to be dependent on the lattice constant, a thermal expansion should lead to a decrease in the magnitude of

Δ. This effect is, however, too weak to be noticeable in the thermal measurements. Thus, for a thermal-expansion coefficient of 10×10^{-6} deg^{-1}, the thermal coefficient $\partial\Delta_A/\partial T$ is only equal to -3.5×10^{-4} mm sec^{-1} deg^{-1}. The increase in the oxygen parameter u upon the appearance of the magnetic order should lead to a more significant decrease in the magnitude of the quadrupole splitting Δ_A [7]. It is significant that for $T<T_C$ the quantity Δ_A is in fact less than for $T>T_C$ [13].

6. It is evident from the example of the trivalent iron ions in the $NiFe_{2-x}Cr_xO_4$ ferrites that the hyperfine electron-nucleus interaction in the ferrites may, to a large extent, be determined by the local distortions in the symmetry of the immediate surroundings (due, for example, to point defects). This fact is important from the point of view of the exchange-interaction mechanism in the ferrites. Thus, in the investigated $NiFe_{2-x}Cr_xO_4$ system, the presence of oxygen vacancies leads to the necessity for the consideration of the spin-orbit interaction, whose influence can, in the presence of a sufficiently large number of point defects, be appreciable. In particular, the iron ions at the A sites (together with the Ni^{2+} ions) can induce distortions in the crystal lattice, since the presence of a sixth electron in the 3d shell of an iron ion at an A site makes this ion a Jahn-Teller ion.

The question of the role of the oxygen vacancies in the electron-nucleus hyperfine interactions in the ferrites remains open. Of particular interest in this connection is the investigation of ferrite samples prepared by the nondiffusion method [12] and containing a known concentration of oxygen vacancies.

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