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MAGNETIC FIELDS AT TIN NUCLEI IN SUBSTITUTED NICKEL FERRITE

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Series of local fields were discovered at tin nuclei in a substituted nickel ferrite by γ-resonance Mössbauer spectroscopy. Relatively high values of the fields ($H_{e\,max} > 250$ kOe at T = 80°K) were attributed to two complementary mechanisms: indirect exchange A–B and direct B–B interactions. The differences between the values of the fields were governed by the number of Ni^{2+} ions in the sphere of the immediate B environment of tin. It was concluded that local inhomogeneities of the cation distribution existed in the B sublattice and an explanation was given of the broadening of the Fe^{57} Mössbauer lines in unsubstituted $NiFe_2O_4$.

CONTINUING our investigations of the mechanisms inducing local magnetic fields at the nuclei of nonmagnetic atoms, we carried out the following experiments.

We prepared a series of tin-substituted nickel ferrites $Ni_{1+t}Fe_{2(1-t)}Sn_tO_4$ with t = 0.05, 0.125, 0.2, 0.25, and 0.3. Samples were prepared by the ceramic technique and the original oxides Fe_2O_3 and SnO_2 were enriched with the Fe^{57} and Sn^{119} nuclides. In all the cases, the formation of a single-phase spinel-type structure was checked by x-ray diffraction analysis. Preliminary magnetic measurements were also carried out between room temperature and 80° K.

The magnetic moment per formula unit of a sample with t = 0.125 was $(1.5 \pm 0.1)\,\mu_B$. The Fe^{57} Mössbauer spectra were recorded. These measurements confirmed the inversion of this spinel structure on the assumption that all Sn^{4+} ions occupied octahedral sites.

The γ-resonance spectra of Sn^{119} for the compound with t = 0.125 are shown in Fig. 1. The spectrum in Fig. 1a was recorded at T = 80° K in the absence of external magnetic fields. The spectra in Figs. 1b and 1c were recorded at room temperature in the presence of external fields: in the first case, the field $H_{ext\,\parallel} \approx 12$ kOe was parallel to the direction of propagation of the γ quanta; in the second case, $H_{ext\,\perp} \approx 17$ kOe was perpendicular to that direction. Each of the spectra in Fig. 1 represents a fairly complex pattern of several superimposed Zeeman sextets, which indicate the presence of strong local magnetic fields at the tin nuclei ($H_{e\,max} > 250$ kOe at T = 80° K). The peak in the center of the spectrum in Fig. 4a may be attributed to traces of unreacted stannic oxide SnO_2.

We attributed the differences between the values of the fields to the inequivalence of the positions of tin in the B sublattice. Since the number of tin ions in the sample with t = 0.125 was relatively small, we could ignore the possibility of Sn neighboring with other Sn atoms and we assumed that the neighbors of Sn^{4+} in the octahedral lattice were either Ni^{2+} or Fe^{3+} ions. Thus, the possible variants of the environment could be expressed as $(Ni^{2+})_n(Fe^{3+})_{6-n}$, where n = 0, 1, ..., 6. The different values of n correspond to inequivalent positions of tin. X-ray structure investigations of the unsubstituted nickel ferrite $NiFe_2O_4$[1] showed that the Ni^{2+} and Fe^{3+} ions were distributed at random in the B sites. In the case of a purely random distribution of these ions in our sample, the probabilities of various combinations should be given by the binomial law:

$$P(n, x) = \binom{6}{n} x^n (1-x)^{6-n},$$

where n is, as before, the number of the Ni^{2+} ions in the immediate B environment of a given tin ion; x is the fraction of such ions in the total number of possible B neighbors. For x = 0.6 (t = 0.125), we obtained the

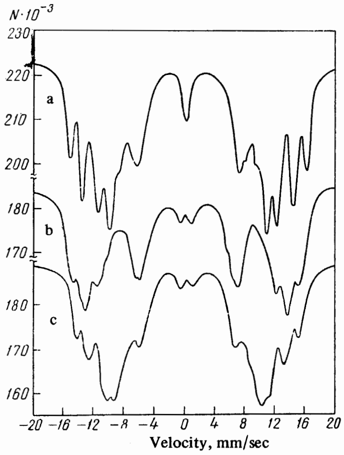

FIG. 1

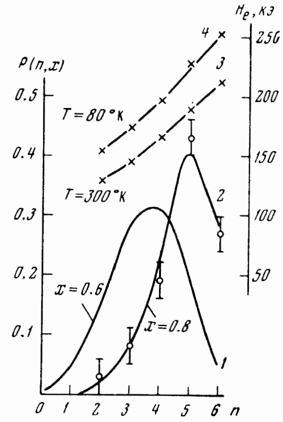

FIG. 2

FIG. 1. Gamma-resonance spectra of $Ni_{1.25}Fe_{1.75}Sn_{0.125}O_4$: a) at T = 80° K; b) in an external parallel field $H_{ext\parallel} \approx 12$ kOe; c) in an external transverse field $H_{ext\perp} \approx 17$ kOe.

FIG. 2. Experimental (circles) and theoretical (curves 1 and 2) distributions P(n, x) of the relative occupancy of the B positions by tin, and the fields at the tin nuclei (curves 3 and 4) as a function of the number (n) of Ni^{2+} ions among the six cations in the immediate B environment in the compound $Ni_{1.125}Fe_{1.75}Sn_{0.125}O_4$. 1) P(n, x) for the ratio of Ni^{2+} and Fe^{3+} at the B positions given by chemical formula (x = 0.6); 2) P(n, x) obtained on the assumption of local inhomogeneities in the cation distribution ($x_{loc} = 0.8$); 3) internal fields at the tin nuclei at T = 300°K; 4) internal fields at the tin nuclei at T = 80°K.

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probabilities of possible combinations represented by curve 1 in Fig. 2.

The spectra shown in Fig. 1 were analyzed using an electronic computer, which was programmed to expand each of the spectra into five strongest Zeeman sextets. The values of the local field at the tin nuclei, corresponding to each of these five sextets, were determined. The intensity of a given sextet was assumed to be proportional to the population of a state with some value of n. However, it was not known in advance which sextet corresponded to which value of n. The attribution of the various sextets to particular values of n was based on the following considerations. Several of our experiments (cf., in particular,[2]) showed that when small amounts of tin were added to different ferrite spinels, the field at the tin nuclei increased due to the substitution of ions in the B environment in the following sequence: Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}. Therefore, we assumed that the maximum field corresponded to the case when all six positions of the immediate environment of tin were occupied by the nickel ions (n = 6). This assumption was confirmed also by an investigation of a batch of samples substituted to different degrees. We found that when t was increased, i.e., when the relative concentration of nickel at the B sites was increased, the intensity of the outer components, corresponding to higher values of the field at the tin nuclei, increased as well. The other sextets were attributed to particular values of n on the assumption that the field decreased monotonically with decreasing n.

When these assumptions were made, it was possible to plot the dependences of H_e (at 80 and 300°K) on n, represented by curves 3 and 4 in Fig. 2, as well as to plot the dependence P(n), representing the relative populations of states with different values of n (the error in the determination of the value of the field was less than ± 2 kOe and in the measurement of the relative population of states it was less than ± 0.3). It is evident from Fig. 2 that these experimental points did not fit curve 1, calculated on the assumption that the ratio of the Ni and Fe atoms in the B sublattice was given by the chemical formula. However, if we assumed that, when tin was introduced, electrostatic interactions in the sphere of the nearest B environment of a multiply charged Sn^{4+} ion produced local clusters of the Ni^{2+} ions and a corresponding reduction in the number of the Fe^{3+} ions, we found (by solving the inverse problem) that the best agreement with the experiment was obtained using a binomial formula with a local value $x_{loc} \approx 0.8$ (curve 2 in Fig. 2).

Obviously, in the unsubstituted nickel ferrites, the Fe^{3+} ions also had inequivalent positions both in the A and in the B sublattices. The observed broadening of the iron Mössbauer lines in $NiFe_2O_4$[3-5] were more likely due to this factor than to an angular distribution of spins or the powder state of the absorber. The broadening of the Mössbauer lines of Fe^{3+} at the A sites was due to an indirect A—B interaction because of a random distribution of the Ni^{2+} and Fe^{3+} ions in the sphere of the nearest B neighbors of the A ions. The broadening of the lines at the B sites was also due to a random distribution of Ni^{2+} and Fe^{3+} but in this case a direct B—B interaction existed. This conclusion was confirmed also by the observation that, for example, in lithium ferrite $Li_{0.5}Fe_{2.5}O_4$, in which the cation distribution was ordered, no such broadening of the Fe lines was observed.

To determine the sign of the effective magnetic fields at the tin nuclei, we recorded the spectrum in a transverse external magnetic field of 17 kOe (Fig. 1c) after careful calibration of the scale of the spectrum in terms of the velocities. It is evident from Fig. 1c that an external magnetic field reduced the separation between the Zeeman components. Consequently, the magnetic fields at the tin nuclei in the substituted nickel ferrite $Ni_{1.125}Fe_{1.75}Sn_{0.125}O_4$ had directions opposite to the resultant magnetic moment of the B sublattice, and the same sign as the fields at the iron nuclei at the same positions.

Such a situation is obtained in ferrite spinels when the Sn^{4+} ions are themselves at octahedral sites.[2] This confirms our initial assumption made in the determination of the cation distribution on the basis of magnetic measurements.

The calculated ratios of the intensities of the components in the spectra of magnetized samples, shown in Figs. 1b and 1c, do not provide evidence for the assumption of a noncollinear distribution of spins of the magnetic cations, which induce the fields at the tin nuclei. The magnitudes and signs of these fields allow us to conclude that, in the present case, we are dealing with two complementary mechanisms of the origin of these fields. One mechanism is an indirect exchange generation of these fields by the A (Fe^{3+}) cations via oxygen anions (similar to that discussed in[6]), and the other is a direct generation of the field by electrons of the nearest B (Ni^{2+}) cations. In the second case, it is obvious that delocalized t_{2g} electrons of Ni^{2+} should have spins opposite to the total spin of the cation and of the whole B sublattice, and they should be partly mixed in the s states of the Sn^{4+} ions in order that the fields induced by these electrons should have signs opposite to the moment of the sublattice without violating Hund's first rule for the Ni^{2+} ions.

It was remarkable that in external magnetic fields of 17 kOe a small peak at the center of the spectrum was split. This was due to the influence of the external field on the tin nuclei in SnO_2 which did not dissolve in the lattice. The degree of splitting corresponded to the value of the applied field.

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