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INVESTIGATION OF INTERNAL MAGNETIC FIELDS AT Fe^{57} *NUCLEI IN* Ni—Zn *FERRITES BY MEANS OF NUCLEAR GAMMA RESONANCE*

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The Mossbauer spectra of the Ni—Zn series of ferrites were obtained; the values of the internal magnetic fields at Fe^{57} nuclei were determined for zinc concentrations x from 0 to 1 (for T = 300°K and T = 78°K). Two values of the field were identified with two different positions of the ions. It was shown that for Ni—Zn spinels the lesser value of the field corresponds to the tetrahedral positions of the iron ions. A simultaneous increase of the positive H_e component (a diminution of the resulting field at the nucleus) and of the electron density in the $|\psi(0)|^2$ region of the nucleus is observed. From the experiments it clearly follows that the field on iron nuclei in the tetrahedral sublattice, as well as in the octahedral, diminishes with the growth of x, which contradicts the data of Abe, Matsuura et al.[5]

1. INTRODUCTION

A considerable quantity of work of great interest for the understanding of magnetic phenomena is devoted to the investigation of the internal magnetic fields on the nuclei of magnetic and nonmagnetic atoms.

It follows from the theoretical treatments of Freeman and Watson[1] and Marshall[2] et al. that the magnetic field on a nucleus can arise as a result of various interactions. It is considered that the basic contribution to the magnetic field is brought about by the Fermi contact interaction of the nucleus with the s-electrons of the ionic core, "unpaired" because of the polarization of the core by the uncompensated spin, for example of the 3d-electrons for the transition elements of the iron group. The degree of polarization of the core and its associated contribution to the magnetic field of the nucleus depends substantially on the effective magnetic moment of the ion. A very considerable field on the nucleus can arise also as a result of dipole-dipole interaction of the nucleus with 3d-electrons, because of the unquenched orbital angular momentum of the 3d-electrons, because of mixing of 4s-electrons or their polarization in the 3d-band, etc. Measurements of the magnetic field on the nuclei of Fe^{3+} ions in different compounds afford a possibility of evaluating the contributions of the individual factors enumerated above.

In the series of Ni—Zn ferrite-spinels which we investigated the trivalent iron ions were disposed in positions of various symmetry: tetrahedral (sublattice A) and octahedral (sublattice B). The general structural formula of the compounds has in standard symbols the form

$$(Zn_x^{2+}Fe_{1-x}^{3+})[Ni_{1-x}^{2+}Fe_{1+x}^{3+}]O_4.$$

In samples having a greater zinc content and a correspondingly smaller iron content in the tetrahedral sublattice, the magnitude of the exchange magnetic-ordering interaction between sublattices is weaker. In the limiting case where the tetrahedral positions are filled with nonmagnetic zinc ions only, the material passes into the paramagnetic state.

Our investigations were carried out in order to establish the connection between the fields on the iron nuclei and the exchange interaction between sublattices A and B, and also to determine the difference in the fields on the nuclei for the two sublattices. The structure and magnetic properties of the Ni—Zn ferrites have been well studied.[3,4]

The method of nuclear gamma resonance (NGR) without recoil (Mossbauer effect) is employed for investigating the internal fields on atomic nuclei. Abe, Matsuura, et al.[5] carried out an experiment to determine the fields on the iron nuclei in these same compounds by means of nuclear magnetic resonance. However as a result of specific difficulties arising from the application of this method, the values of the internal magnetic fields were determined only within a small range of variation of x (from 0 to 0.3 for T = 300°K and from 0 to 0,5 for T = 78°K). Using the NGR method, we carried out investigations at two temperatures (78 and 300°K), varying x from 0 to 1.

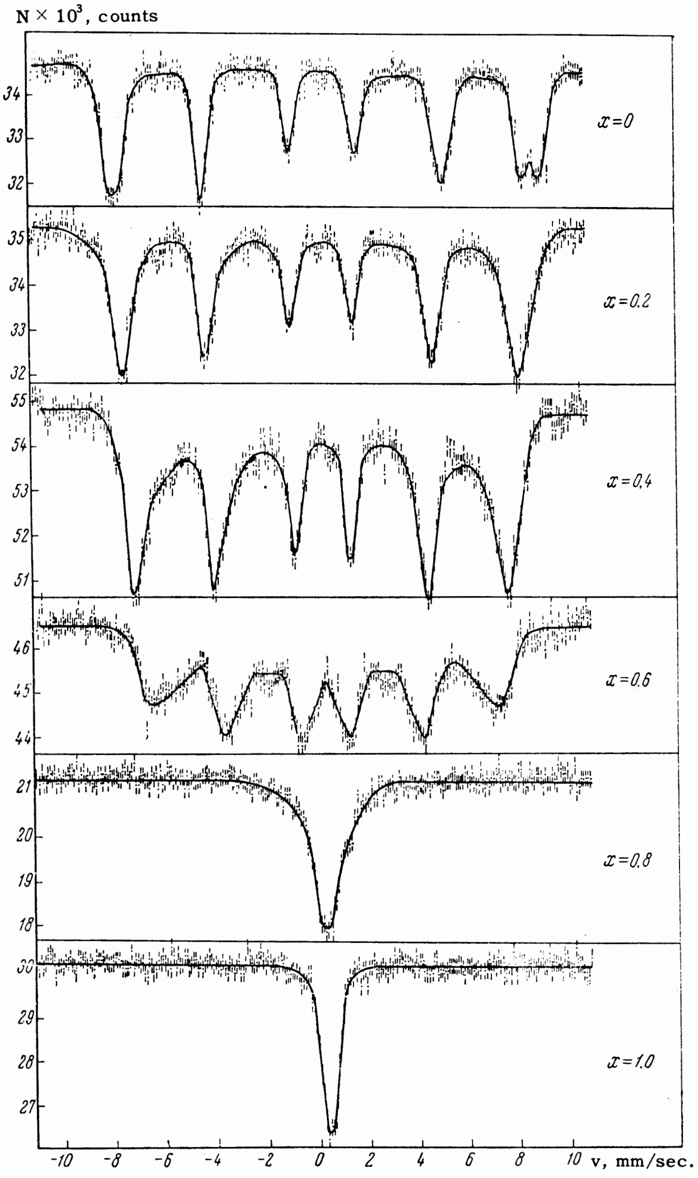

FIG. 1. Mossbauer spectra of Ni-Zn ferrites for various zinc contents (T = 300°K).

2. EXPERIMENTAL PROCEDURE

The investigations of Ni—Zn ferrites were carried out on a Mossbauer apparatus of the electrodynamic type with uniformly accelerated motion. The recording system comprised a scintillating gamma spectrometer with a multichannel analyzer (AI-2048). The output data were produced in digital form on the tape of an automatic recorder. A detailed description of the apparatus is given in [6].

The Ni—Zn ferrites were prepared by the usual ceramic method. The annealing was carried out in air at 1350°C over a period of three hours. X-ray data confirmed the presence of one spinel structure. For control, measurements were carried out of the saturation of magnetization of the samples, which exhibited good agreement with the data in the literature.

3. THE FORM OF THE MOSSBAUER SPECTRA AND THEIR INTERPRETATION

Figure 1 shows the Mossbauer spectra of the Ni—Zn ferrites for various zinc contents at room temperature. In the region of values of $x \leq 0.6$, a distinct Zeeman splitting into six components is evident. The distance between lines diminishes with increasing zinc content, thus testifying to the diminution of the effective magnetic field H_e at the iron nuclei.

When $x = 0.8$ one broadened line appears (half-width $\Gamma = 1.15$ mm/sec). When $x = 1$ the half-width of the line is 0.8 mm/sec. Usually the experimental half-width of the line, obtained with the same source on a calibration sample of Fe_2O_3 of equal density (in terms of Fe^{57}), does not exceed 0.5 mm/sec. No detailed investigation of the broadening of the isolated line in the zinc ferrite was carried out.

The presence of an isolated line in the spectrum is characteristic of the paramagnetic state of iron ions in the case when the spin-lattice relaxation time is much less than the nuclear transition time, and the nucleus "sees" a zero time-averaged spin.

We see thus from the behavior of the Mossbauer spectra, as shown in Fig. 1, that with increasing zinc content, right up to the stage where it replaces all the iron ions in the tetrahedral sublattice, the material goes over from a state of ferromagnetic ordering to a paramagnetic state.

We note that in the pure nickel ferrite ($x = 0$) there is observed a complex picture of splitting, which can be explained by the superposition of two Zeeman sextuplets corresponding to two different values of the magnetic fields at the iron nuclei: 500 ± 8 and 520 ± 8 kOe. In the remaining spectra the two sextuplets merge, which leads to asymmetry of the lines: their internal slopes are less steep than the external ones. A similar asymmetry of the lines is possible in the case when the smaller value of the effect corresponds to a smaller field value.

For more distinct confirmation of the presence of a second magnetic field at the iron nuclei in nickel-zinc ferrites supplementary investigations were carried out with thickened samples. For example, the sample with $x = 0.5$ (Fig. 2) exhibits clearly peaks corresponding to the smaller value of the field.

Since only one type of iron ion (Fe^{3+}) was present in the ferrites which we have investigated, it is natural to suppose that the difference in fields is caused only by the different positions of the ions, namely by the presence of tetrahedral and octahedral positions. A similar difference in H_e at the nuclei of trivalent iron was previously observed in iron garnets[7,8], where it was shown that the smaller value of the field corresponds to iron ions disposed in tetrahedral positions.

A direct comparison of the relative magnitude of the effect for the two sublattices, at various degrees of replacement of nickel by zinc, leads to an analogous conclusion for spinels in our case. In the pure nickel ferrite $(Fe^{3+})[Ni^{2+}Fe^{3+}]O_4$ an identical quantity of iron ions is located in the various sublattices. From Fig. 1 ($x = 0$) it is evident that the magnitudes of the effect in the two sublattices are also identical here. On the introduction of zinc, according to the data of [3,4,9], the population of the tetrahedral sublattice by iron ions diminishes. In the Mossbauer spectra which we have observed, the replacement of nickel by zinc leads to the lessening of the effect for the sublattice characterized by the smaller absolute value of the magnetic field. Inasmuch as the sign of the local magnetic field at the iron nuclei, as is currently generally accepted, is negative[1], a decrease of the absolute magnitude of the field means an increase in the contribution to the positive component of the iron ions in tetrahedral positions A in comparison with octahedral positions B.

We note that the iron ions in positions A are characterized by smaller chemical shifts in comparison with B: $\delta \approx 0.3$ mm/sec for A and $\delta \approx 0.5$ mm/sec for B, i.e.,

$$|\psi(0)|_A^2 > |\psi(0)|_B^2.$$

It is interesting to note the simultaneous increase of the positive H_e component and of the

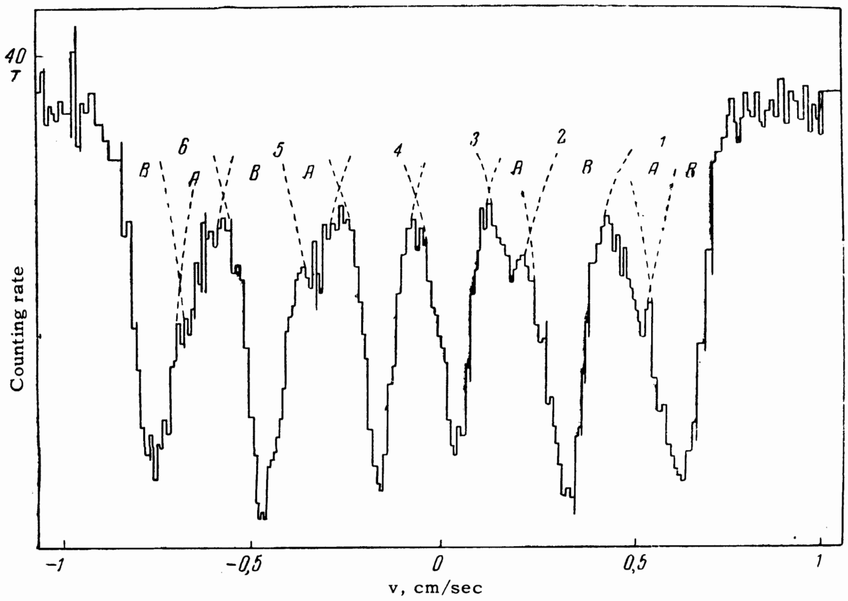

FIG. 2. Mossbauer spectrum of the Ni-Zn ferrite with $x = 0.5$ for $T = 300°K$.

electron density in the nuclear region $|\psi(0)|^2$, since the growth of $|\psi(0)|^2$ in iron compounds of a given valence state is usually associated with the growth of the effective number of 4s-electrons[10], and according to data on the annihilation of polarized positrons[11,12] 4s-electrons give a negative contribution to H_e.

The change of the Mossbauer spectra with variation of the zinc content has at T = 78°K the same character as at room temperature, with a few exceptions: 1) the spectral lines come together in this case at high zinc contents (x ~ 1); 2) the internal magnetic fields at the nuclei have greater values; 3) the difference of internal fields produced at the nuclei by the different positions of the iron ions is larger than at room temperature, and comprises about 40 kOe.

4. THE DEPENDENCE OF THE EFFECTIVE MAGNETIC FIELD ON IRON NUCLEI IN NICKEL-ZINC FERRITES ON THE CONCENTRATION OF NONMAGNETIC ZINC IONS

On the basis of the energy separation between lines of the Mossbauer spectra we calculated the values of the effective magnetic fields on the iron nuclei situated in both sublattices. The results of the calculations are given in Figs. 3 and 4.

A. The octahedral sublattice B. Variation of the zinc content in the sample changes the number of active bonds between ions of the two different sublattices, leading to the ferromagnetic ordering in the crystal. From Fig. 3 it is clear that in the region x < 0.6 the breaking of one of the six active bonds of the octahedral ion (i.e. a variation of x by 0.167) leads on an average to a diminution of the field at the nucleus by roughly 20 kOe. As Gilleo has shown[13], the Curie temperature T_c may serve as a measure of the number of active bonds of magnetic ions.

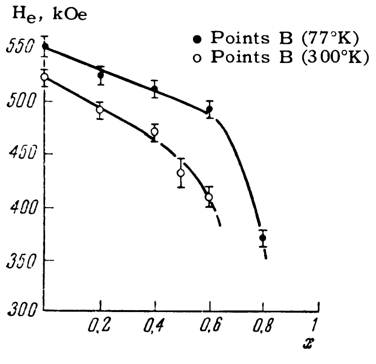

FIG. 3. Internal magnetic fields at Fe^{57} nuclei in the octahedral sublattice in the Ni-Zn series of ferrites vs. zinc content.

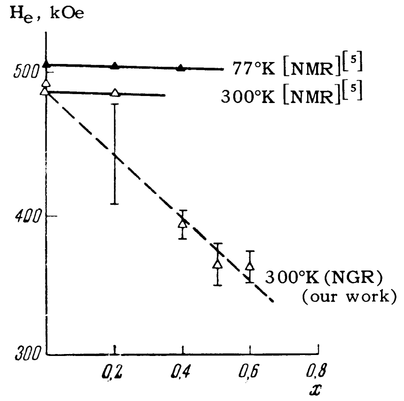

FIG. 4. Internal magnetic fields at Fe^{57} nuclei in the tetrahedral sublattice vs. zinc content x, obtained in the present work and in[5].

Figure 5 shows the dependence of the internal magnetic fields at the iron nuclei in the octahedral sublattice on the relative temperature T/T_c. The values of T_c for compounds with various zinc contents are taken from the work of Piskarev[4]. The identical numbers on Fig. 5 correspond to the same sample composition, i.e., to a single value of x and T_c. As is clear from Fig. 5, the relative temperature T/T_c is not a parameter that determines fully the magnitude of the field at the nucleus. The magnitude of the field depends to a considerably greater degree on the number of active bonds (Curie temperature) than on the temperature of the medium.

For example, for sample I, variation of the temperature of the medium (pure nickel ferrite) by about four times—from 78 to 300°K—brings about a variation of the field on the nucleus H_e by 30 kOe. An equal change in the field at the nucleus is brought about by maintaining the external temperature but increasing the zinc content and varying the Curie temperature of the sample by merely 15% (the transition from the first sample with T_c = 870°K to the second with T_c = 750°K).

For values of x > 0.6 with the further increase of zinc concentration (see Fig. 3) a sharp falling off

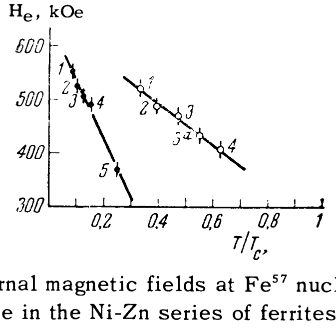

FIG. 5. Internal magnetic fields at Fe^{57} nuclei in the octahedral sublattice in the Ni-Zn series of ferrites, vs. the relative temperature T/T_c.

occurs in the magnitude of the magnetic field at the iron nuclei. For the description of the magnetic properties of matter for $x > 0.6$ various models have been proposed: those of Yafet-Kittel[14], of Kaplan[15], and of Gilleo[16]. In accordance with these models one should expect for such values of x a deviation from the Neel configuration, and a sharp change in the shape of the curve of magnetic saturation of the samples investigated.

The first two models start out from the relationship between the magnitudes of the exchange interactions of ions situated inside one sublattice (B – B) and in different sublattices (A – B). Our experiments were carried out at temperatures greatly exceeding the Curie temperature of pure zinc ferrite (9, 5°K), which determines the magnitude of the B – B interactions. Consequently the role of these interactions ought to be insignificant, and can be neglected. Evidently the most suitable model for interpreting our experimental data is the statistical model of Gilleo, which we have already partially employed. By way of a consequence of the statistical approach one sometimes employs, the concept of separate ferromagnetic clusters—islands in a paramagnetic matrix where there is a great dilution of the ferrite by nonmagnetic zinc ions[17]. The presence of clusters of various dimensions ought to lead to different magnetic fields at the iron nuclei and to "smear" the Mossbauer spectra. A similar Mossbauer spectrum of a Ni—Zn ferrite ($x = 0.6$; $T = 300$°K), in which discrete resonance absorption lines are totally absent, is given in the article of Ishikawa[17] as proof of the existence of clusters. However, our spectra have a sufficiently distinct structure, characteristic of one predominant value of the field in each sublattice right up to $x = 0.8$ ($T = 78$°K), which does not confirm the cluster model.

B. The tetrahedral sublattice A. From Fig. 3 it is clear that the magnitude of the magnetic field at the iron nuclei situated in the tetrahedral sublattice A, as in the case of sublattice B, diminishes with increasing zinc content.

If it is assumed that the basic parameter characterizing the magnitude of the magnetic field at the nucleus is the number of active bonds (as was done in the analysis of the fields at the nuclei in sublattice B), then such a dependence of the field strength on the zinc concentration seems somewhat strange. For any degree of replacement in the tetrahedral sublattice by the nonmagnetic zinc ions, the remaining iron ions will, as before, have twelve bonds with the neighboring magnetic ions of the octahedral sublattice. Varying the zinc concentration in no way affects the number of active tetrahedral ion interactions.

Although the experimental data obtained by a group of Japanese authors[5] seem to agree with these arguments, it is abundantly clear from our experiments that despite the data of the Japanese group[5] the field at iron nuclei in the tetrahedral sublattice does not remain constant as x is varied from 0 to 1 (see Fig. 5). It appears that the strength of the internal field at the nucleus is strongly effected not only by the number of bonds, but also by the character of the active bonds, which depends in turn on the degree of spin ordering in the octahedral sublattice.

In conclusion we note that the investigation of nuclear magnetic fields, even in the sufficiently simple and well studied compounds of the nickel-zinc type of ferrite-spinels, permits a new approach to already existing models used to explain the external magnetic properties of substances, making them more exact in some cases and proving their inapplicability in others.

The clarification of connections between the internal magnetic fields and the magnetic characteristics of substances undoubtedly contributes to a deeper understanding of the nature of magnetic ordering. Many of the questions arising here require further thorough experimental investigations and theoretical analysis.

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214