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MÖSSBAUER EFFECT ON Fe^{57} *NUCLEI IN* $Y_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$ *COMPOUNDS*

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The effective magnetic fields H_{eff} acting on Fe^{57} nuclei in the octahedral and tetrahedral sublattices of substituted yttrium iron garnets (YIG) $Y_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$ ($0 \le x \le 2$) are investigated by means of the Mössbauer effect. The experimental dependence of the field strength H_{eff} on x is compared with the corresponding dependence of the Fe^{3+} ion magnetic moment calculated theoretically on the basis of Gilleo's model. The causes of the differences between the concentration dependences of H_{eff} and the magnetic moment for the a-sublattice of the substituted iron garnets are discussed. It is shown that in iron garnets the contribution of dipole interactions between neighboring magnetic ions to H_{eff} is insignificant. The principal reason for the different fields H_{eff} in the a- and d-sublattices of iron garnets is that the chemical bond of Fe^{3+} to the tetrahedral sublattice is partially covalent. The quadrupole splitting for both Fe^{3+} positions is found for $T > \Theta$. On the basis of the line intensities it is shown that the Sn^{4+} ions replace the Fe^{3+} ions only in the octahedral sites up to x = 2.0. The concentration dependences of the quadrupole splitting and isomer shifts for both of the ferrite sublattices are discussed. It is shown that below the Curie temperature the quadrupole effects in polycrystalline yttrium iron garnets cannot be observed experimentally.

IT is known that in the structure of iron garnets the ions of trivalent iron are distributed in different amounts among two crystallographically nonequivalent kinds of sites. In a formula unit of an YIG, $\{Y_3\}[Fe_2](Fe_3)O_{12}$, three Fe^{3+} ions occupy tetrahedral sites (of the d-sublattice) and two Fe^{3+} ions occupy octahedral sites (of the a-sublattice). The structure of iron garnets permits extensive substitutions of nonmagnetic ions for magnetic ions, thus altering the exchange interactions between the sublattices and the magnitudes of their magnetic moments. Recent work[1-4] has shown that studies of the effective magnetic fields acting on the nuclei in the given compounds enables us to understand more thoroughly the nature of effective fields acting on nuclei and to investigate how exchange coupling in a ferrimagnet is modified when nonmagnetic ions are substituted for magnetic ions.

In the case of the tin-substituted YIG $Y_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$ we have a favorable opportunity to measure the Mössbauer effect simultaneously for Fe^{37} magnetic and Sn^{119} nonmagnetic ions and to investigate the effective magnetic fields H_{eff} acting on these nuclei in the different sublattices of the ferrite. This system has become especially interesting since it was discovered that strong effective magnetic fields act on Sn^{119} nuclei.[1-4] In[3] the origin of the fields H_{eff} acting on the nuclei of the nonmagnetic tin ions in the given compounds were analyzed by comparing H_{eff} with the magnetic properties of the substances. It was shown that the principal source of the field is the exchange interaction between the iron ions in the d-lattice and the tin ion in the a-sublattice of the ferrite, in the chain

$$Fe^{3+}(d) — O^{2-} — Sn^{4+}(a) — O^{2-} — Fe^{3+}(d).$$

The present work investigates the Mössbauer effect for Fe^{57} nuclei in the same system of substituted yttrium iron garnets, $Y_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$.

1. EXPERIMENTAL TECHNIQUE

The Mössbauer resonant absorption spectra were measured with electrodynamic apparatus having a constantly accelerated vertical vibrator. The registering system consisted of a scintillation γ spectrometer and a multichannel analyzer. The Co^{57} source in a chromium host remained at room temperature. The spectrometer was calibrated by means of standard compounds: α-Fe_2O_3, Armco iron, and stainless steel. The internal line widths were 0.35 mm/sec for the Armco iron and α-Fe_2O_3, and 0.45 mm/sec for the stainless steel.

Polycrystalline samples of the iron garnets $Y_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$ were synthesized by conventional ceramic technology, with x having the values 0.0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0, 1.1, 1.2, 1.5, and 2.0. A careful x-ray analysis revealed no extraneous phase. Measurements were performed in the range from 80° to 600°K.

2. HYPERFINE MAGNETIC INTERACTIONS OF Fe^{57}

A. Figure 1 shows the Mössbauer absorption spectra of Fe^{57} in the substituted iron garnets for different values of x at liquid nitrogen temperature. The experimental spectra up to x = 1.1 can be interpreted as consisting of two Zeeman patterns for iron nuclei in the a- and d-lattices that were subjected to effective magnetic fields of different strengths. The stronger lines pertain to the d-sublattice,[5] which contains more Fe^{3+} ions than the a-sublattice.

The figure shows that as x increases the magnitude of Zeeman splitting decreases for both sublattices; this result is associated with weakening of the effective magnetic field. At x = 1.1 the background of the Zeeman pattern reveals a strong doublet caused by the fraction of the iron ions that have become paramagnetic. When the magnetic splitting has almost vanished the spectra merge into an asymmetric doublet rather than into a sin-

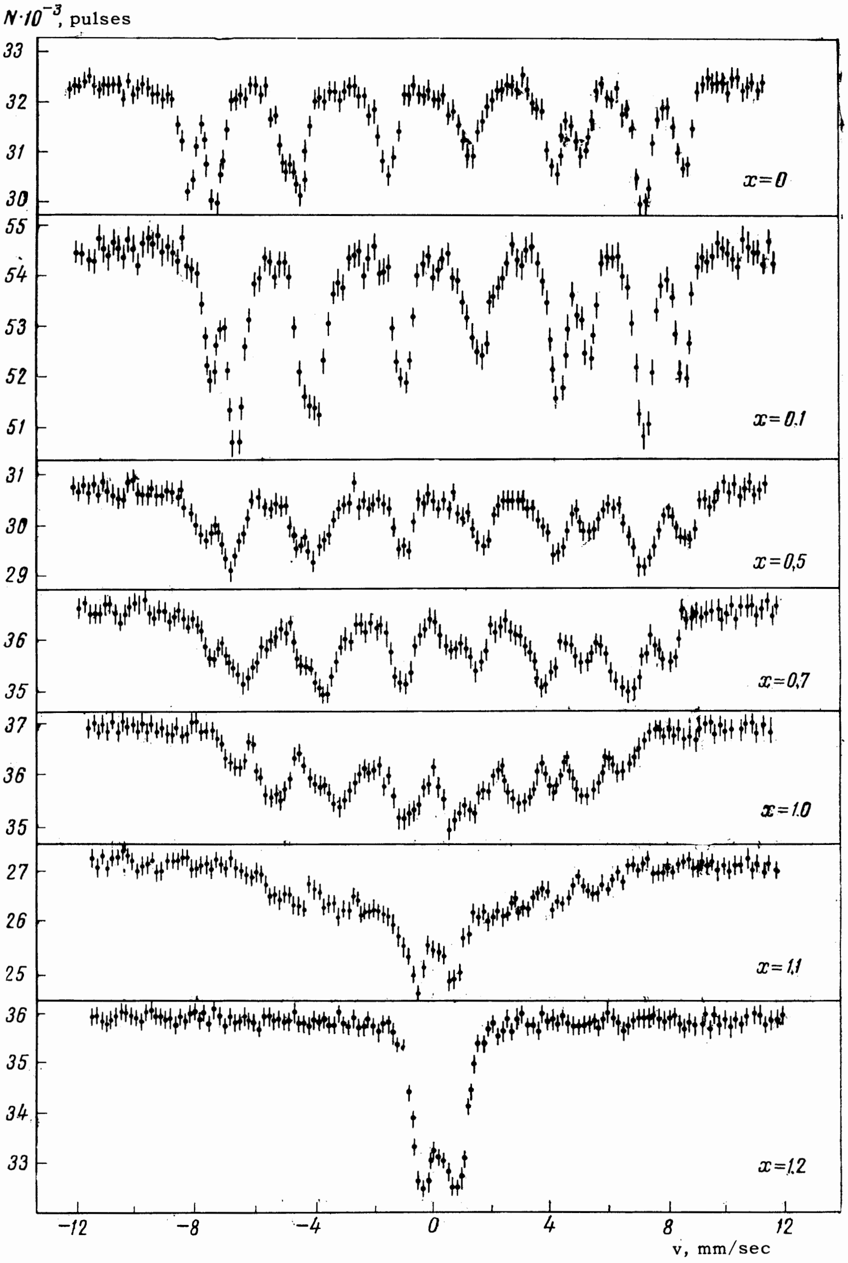

FIG. 1. Mössbauer absorption spectra of the iron garnets $Y_{3-x}Ca_xCe_{5-x}O_{12}$ for different values of x at 80°K.

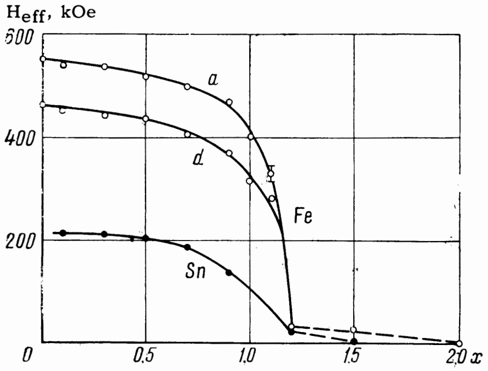

FIG. 2. Effective magnetic field acting on Fe^{3+} in the a- and d-sublattices of the iron garnets vs. x at 80°K. Also, the dependence of H_{eff} on Sn^{119} concentration.

gle line. Investigations of this effect for all concentrations in the paramagnetic region showed that the doublet observed in Fig. 1 is associated with quadrupole splitting of the Fe^{57m} energy levels, although quadrupole splitting is not observed in the magnetic spectra; the causes of this effect will be discussed.

B. Figure 2 shows the dependence on x that is manifested by the effective magnetic field acting on Fe^{3+} in the a- and d-sublattices at 80°K. In the pure ferrite ($x = 0$) H_{eff} then equals 553 ± 10 and 464 ± 10 kOe for the a- and d-sublattices, respectively, and decreases to 488 ± 10 and 391 ± 10 kOe, respectively, at room temperature. These results are in good agreement with the Mössbauer measurements in[5] and with the work on nuclear magnetic resonance in[6].

Figure 2 shows that H_{eff} decreases monotonically with increasing content of nonmagnetic tin ions in the a-sublattice. The field changes in about the same way for both sublattices in the interval $0 \leq x < 1.1$, and drops sharply to zero in the small interval $1.1 < x \leq 1.2$. Only the broadening of the doublet lines at 80°K when compared with their widths in the paramagnetic temperature region proves that an effective magnetic field of the order 30—40 kOe still acts on the iron nuclei in $Y_{1.8}Ca_{1.2}Fe_{3.8}Sn_{1.2}O_{12}$ ($\Theta = 290$°K) and $Y_{1.5}Ca_{1.5}Fe_{3.5}Sn_{1.5}O_{12}$ ($\Theta = 140$°K). This field vanishes only at $x = 2.0$.

The existence of the long tail extending to $x = 2.0$ can apparently be accounted for by the formation of superparamagnetic regions with concentrations $1.2 \leq x < 2.0$. Ishikawa recently predicted a superparamagnetic transition in $Y_{1.5}Ca_{1.5}Fe_{3.5}Sn_{1.5}O_{12}$ at 180°K.[7] Our results appear to confirm this theoretical prediction qualitatively. It is interesting that tails have been observed even when $x < 1.2$, on the magnetization-temperature curves of the same compounds.[8] This result can evidently also be associated with the formation of superparamagnetic regions, because the Mössbauer spectra do not reveal lines associated with extraneous magnetic phases.

Figure 2 also shows the concentration dependence of the effective magnetic field acting on the nonmagnetic tin nuclei at 80°K.[3] The curves of H_{eff} vs. x are alike for the tin and iron ions in the a- and d-sublattices, respectively; differences exist only with respect to absolute values.

C. It is of great interest to compare the effective fields with the magnetic moments. Magnetic measurements ordinarily enable us to determine only the total magnetic moment of a ferrite; for any comparison with H_{eff} we must also know the magnetic moment of each sublattice. To determine the latter we used Gilleo's theoretical model,[9] from which the magnetic moments of ferrite sublattices can be calculated.

In Gilleo's model the only magnetic ions of substituted iron garnets that are considered to be magnetically active are those ions that interact with two or more other magnetic ions in different coordinations (two bonds). The ions that are linked only to nonmagnetic ions or have only a single bond with magnetic ions are excluded from participation in ferrimagnetism. For a substituted yttrium iron garnet represented by

$$\{Y_{3-y-z}Me_{y+z}\}\,[Fe_{2-y}M_y]\,(Fe_{3-z}M_z)\,O_{12}$$

Gilleo's formulas for the magnetic moments n_B^a and n_B^d of the magnetic moments of a- and d-sublattices near 0°K become

$$n_B{}^a = 2\mathscr{M}^a(1-k^a)[1-E^a(k^d)],$$
$$n_B{}^d = 3\mathscr{M}^d(1-k^d)[1-E^d(k^a)], \qquad (1)$$

where k^a and k^d are the respective fractions of the nonmagnetic ions in octahedral and tetrahedral sites; $1-k$ is the corresponding fraction of magnetic ions of which $1-E(k)$ ions are magnetically active; $\mathscr{M}^a$ and $\mathscr{M}^d$ are the magnetic moments of the ions in terms of Bohr magnetons. Experiments in which Fe^{3+} ions in yttrium iron garnet were replaced by the nonmagnetic ions Zr^{4+}, Si^{4+}, Sn^{4+}, In^{3+}, and Hf^{4+},[10,11] have shown that Gilleo's theory accounts satisfactorily for the behavior of the total magnetic moment and for the Curie point, although some discrepancies exist.

In Fig. 3 the solid lines are the theoretical curves of the magnetic moment per Fe^{3+} ion in the a- and d-sublattices. We calculated these values from (1) for substituted iron garnets $\{Y_{3-x}Ca_x\}\,[Fe_{2-x}Sn_x] \cdot (Fe_3)O_{12}$ assuming that all Sn^{4+} ions are in the a-sublattice.

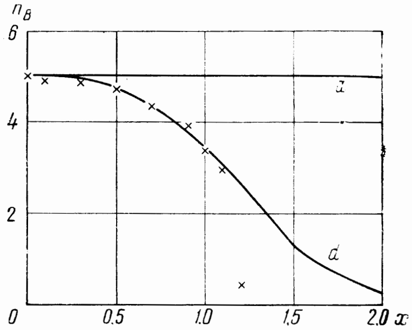

FIG. 3. Solid lines – theoretical dependence on x for the Fe^{3+} magnetic moment in the a- and d-sublattices; crosses – magnetic moments derived from the experimental values of H_{eff} vs. x. (For the system $Y_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$.)

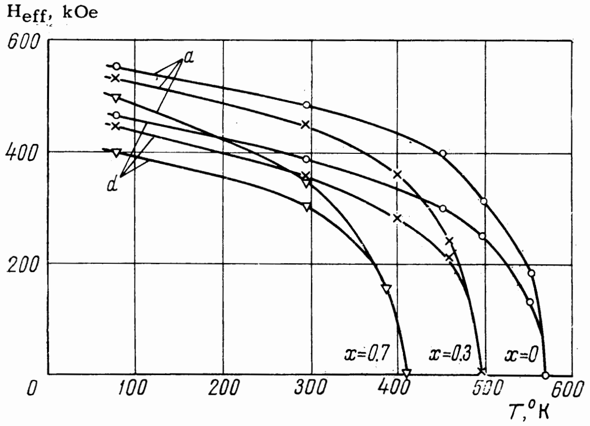

FIG. 4. Temperature dependence of H_{eff} in the a- and d-sublattices of tin-substituted iron garnets for different values of x.

The effective magnetic field acting on an Fe^{3+} nucleus results mainly from the polarization of the core electrons through an exchange interaction with uncompensated spins in the 3d shell.[12] The degree of polarization and, therefore, the magnitude of H_{eff} depend largely on the effective magnetic moment of the ion. Assuming that the effective magnetic field H^d_{eff} in the d-sublattice is proportional to the magnetic moment of an Fe^{3+} ion in this sublattice, we calculated the magnetic moment $\mathscr{M}^d(x)$ of the d-sublattice for different concentrations x from the measured values of $H^d_{eff}(x)$. In Fig. 3 the crosses represent the Fe^{3+} magnetic moment in the d-sublattice, derived from

$$\mathscr{M}^d(x) = \mathscr{M}^d(0) H^d_{eff}(x) / H^d_{eff}(0),$$

where $\mathscr{M}^d(0) = 5\ \mu_B$ is the magnetic moment of Fe^{3+} and $H^d_{eff}(0)$ is the field acting on the nucleus of this ion in the d-sublattice of a substituted yttrium iron garnet. Good agreement with the theory is observed for x from 0 to 1.0.

For the octahedral a-sublattice the theoretical magnetic moment of Fe^{3+} is independent of the degree of substitution; its value is $5\ \mu_B$ for all x (Fig. 3). However, our experimental values of H_{eff} in the a-sublattice at 80°K decrease as x is enhanced exactly as in the case of the d-sublattice (Fig. 2). This result evidently cannot be attributed exclusively to thermal effects, i.e., to an approach to the Curie point.

The temperature dependences of H_{eff} in the two sublattices (Fig. 4) near 80°K do not differ significantly. The concentration dependences of the d-sublattice magnetic moment at 0°K and H_{eff} at 80°K are identical for $0 \le x \le 1.0$. They begin to differ only when $x > 1.0$; the d-sublattice then begins to exhibit temperature dependence. We can therefore assume in first approximation that the discrepancy between the theory (at 0°K) and experiment (at 80°K) for the a-sublattice is not attributable solely to the temperature difference.

The lower values of H_{eff} in the a-sublattice as compared with the fields calculated theoretically from the Fe^{3+} magnetic moments can apparently be attributed to a "reaction" of the d-sublattice on the a-sublattice when substitutions are made in the latter. This influence is not considered in Gilleo's model, where, when magnetic ions are replaced with nonmagnetic ions in the a-sublattice as in the case of $\{Y_{3-x}Ca_x\}[Fe_{2-x}Sn_x](Fe_3)O_{12}$, the effective magnetic moment of Fe^{3+} in the d-sublattice diminishes because of the reduced number of exchange bonds with magnetic ions located in the a-sublattice. Since the number of magnetic bonds is not then altered for the magnetic ions in the a-sublattice, because the number of Fe^{3+} ions in the d-sublattice does not change, the effective magnetic moment of Fe^{3+} in the a-sublattice is taken to have the constant value $5\ \mu_B$. However, the theory neglects the fact that the reduction of the Fe^{3+} magnetic moment in the d-sublattice can also induce a reduction of this magnetic moment in the a-sublattice; this follows in first approximation from our experimental results.

The effective magnetic moment of a magnetic ion can change not only when the number of exchange bonds is diminished, but also probably as a result of a smaller effective magnetic moment belonging to a neighboring ion with which an exchange interaction takes place.[1]

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[1] A somewhat similar result even at 300°K, obtained by means of the Mössbauer effect, has been reported in [13] where the dependence of H_{eff} on the concentration of nonmagnetic ions in nickel-zinc spinel ferrites was studied. However, this result conflicts with the nuclear magnetic resonance findings for the same ferrites that were reported by Japanese investigators in [14].

D. Figure 2 has shown that the concentration dependence of the effective magnetic field on tin nuclei in $Y_{3-x}Ca_xFe_{3-x}Sn_xO_{12}$ compounds resembles the corresponding dependence of H_{eff} acting on iron nuclei. This confirms our earlier conclusion[3] that the effective magnetic field on Sn^{119} in the octahedral sublattice of $\{Y_{3-x}Ca_x\}[Fe_{2-x}Sn_x] \times (Fe_3)O_{12}$ results mainly from the exchange interaction between neighboring Fe^{3+} ions in the tetrahedral sublattice, effected through the exchange-bond chain

$$Fe^{3+}(d) — O^{2-} — Sn^{4+}(a) — O^{2-} — Fe^{3+}(d).$$

A similar conclusion was recently reached by Ofer and Nowik,[15] who investigated magnetic fields on Eu^{151} nuclei in a europium iron garnet. They found that about 90% of the exchange field acting on Eu^{3+} in this ferrite results from only the two nearest Fe^{3+} neighbors occupying tetrahedral sites.

E. We shall now consider the difference between the effective magnetic fields on Fe^{3+} at octahedral and tetrahedral sites of iron garnets. This difference is about 90 kOe for a pure yttrium iron garnet. Figure 2 shows that as the tin ion concentration changes the difference remains almost constant up to x = 1.0.

Watson and Freeman[12] have suggested two possible causes of reduced H_{eff} acting on Fe^{3+} in the d-sublattice as compared with the a-sublattice: 1) a distortion of cubic symmetry, whereby neighboring magnetic ions generate a dipole field, and 2) covalent bond effects. We shall now consider these effects in greater detail.

1) The larger quadrupole splitting for Fe^{3+} ions in d sites as compared with a sites (see Sec. 3 below) can serve as evidence that the tetrahedral sublattice departs more from cubic symmetry than the octahedral sublattice. Consequently, the dipole fields (generated by neighboring magnetic ions) that accompany diminished symmetry will also be greater for tetrahedral sites. Since these dipole fields are positive,[12] whereas the main contribution from the polarization of the ion core is negative, the combined experimentally observed field will have a smaller absolute value for d sites than for a sites.

It has been shown experimentally (Fig. 7a) that as x increases in substituted $Y_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$ the quadrupole splitting remains almost constant for both a and d sites. However, as x increases a decrease occurs in the number of magnetic ions in a sites that are nearest neighbors of d sites (since the former are replaced by tin ions). This reduction should diminish the dipole field in the d-sublattice and therefore decrease the difference between the fields acting on a and d sites. Since the experimental value of the field (H_{eff}) difference remains constant up to x = 1.0 (Fig. 2) despite the fact that for x = 1.0 the number of nearest-neighbor magnetic

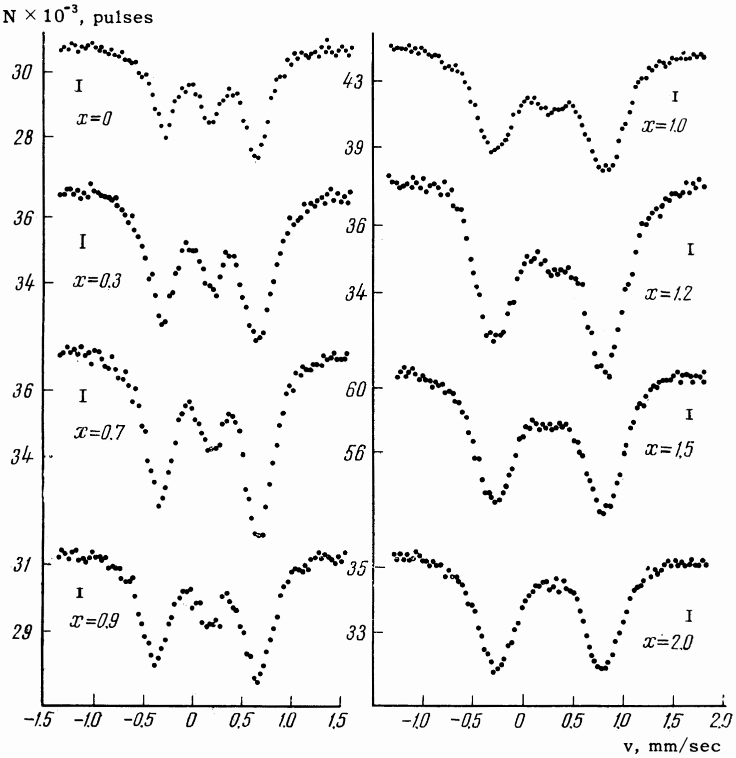

FIG. 5. Mössbauer spectra for Fe^{3+} ions in the two sublattices of iron garnets, in the paramagnetic temperature region.

Data	Δ, mm/sec		Data	δ*, mm/sec	
	a-sublattice sites	d-sublattice sites		a-sublattice sites	d-sublattice sites
From[17], $T = 300$°K	0,94±0,19	0.78±0.16	From [16]	0,57±0.05	0.26±0,05
From[20], $T = 610$°K	0.52±0,04	0,92±0.04	From [20]	0,49±0.04	0,32±0.04
				0,36±0,07**	0,19±0,07**
Our data, $T = 575$°K	0.47±0,02	0.93±0.02	Our data	0,46±0.05	0,23±0,05

*For stainless steel.

**Values corrected by us, as explained in the text.

ions responsible for the dipole field has been decreased one-half, we may conclude that dipole fields have little influence on the magnitude of H_{eff}.

2) The isomer shifts for Fe^{3+} ions in the octahedral and tetrahedral sublattices of $Y_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$ ferrites and the anomalously large quadrupole bond constant (see the table in Sec. 3) show that the chemical bond between Fe^{3+} ions in tetrahedral sites and oxygen ions is partly covalent.[16] Thus s electrons can be mixed with the 3d^5 state of Fe^{3+} ions in d sites. The contribution to H_{eff} that comes from the contact interaction between s electrons and the nucleus appears as a positive term, and therefore diminishes the negative contribution coming from the polarized ion core. This admixture of a covalent bond is probably the principal cause of the difference between H_{eff} in the octahedral and tetrahedral sublattices of the ferrites.

As x is increased in $Y_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$ the isomer shifts and quadrupole bond constants for a- and d-sublattices remain approximately constant (Fig. 7). This result also evidently accounts for the constant difference between the fields H_{eff} in the two sublattices.

3. HYPERFINE ELECTRIC INTERACTIONS OF Fe^{57m}

A. The quadrupole interaction in a single crystal of yttrium iron garnet was first observed, using the Mössbauer effect, by Alff and Wertheim,[17] who applied a 0.5-kOe magnetic field along the [111] and [100] axes. They obtained measurements at 300°K, which is below the Curie point Θ = 550°K. However, Bauminger et al.[5] did not detect a quadrupole interaction in polycrystalline samples at 300° and 80°K, and therefore concluded that $e^2qQ = 0$. Our measurements at T < Θ also fail to reveal a quadrupole interaction.

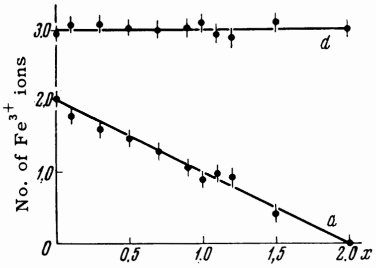

FIG. 6. Number of Fe^{3+} ions per formula unit in the a- and d-sublattices of $Y_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$ versus the concentration x of tin ions.

We attribute the foregoing disagreement to the fact that when electric quadrupole and magnetic dipole interactions occur simultaneously with $e^2qQ \ll \mu H$ and $I = 3/2$ we have

$$(e^2qQ)_{\text{meas}} \approx e^2qQ(3\cos^2\vartheta - 1)/2,$$

where ϑ is the angle between the direction of the effective magnetic field (which in the absence of an external magnetic field coincides with the easiest direction of magnetization) and the axis of symmetry of the electric field gradient.[18] For $\vartheta = 54°44'$ we obviously have $3\cos^2\vartheta - 1 = 0$, and therefore $(e^2qQ)_{\text{meas}} = 0$.

The foregoing case is realized in polycrystalline samples of our compound at temperatures below Θ. Indeed, the easiest direction of magnetization is here along [111],[19] although the axis of symmetry of the electric field gradient in the d-sublattice is then along [100], while in the a sublattice it is along [111]. We easily see that for all Fe^{3+} ions in the d-sublattice with no external field we have $\vartheta = 54°44'$, while for 75% of the Fe^{3+} ions in the a-sublattice $\vartheta = 70°32'$ $[(e^2qQ)_{\text{meas}} = (1/3)e^2qQ]$, with $\vartheta = 0$ and thus $(e^2qQ)_{\text{meas}} = e^2qQ$ for only 25% of the Fe^{3+} ions.

It is worth mentioning that in polyatomic cubic crystals, where the neighborhood of a Mössbauer atom possesses less than cubic symmetry, the situation in which $\vartheta = 54°44'$ is not exceptional. This fact must be taken into account when analyzing the hyperfine structure of polycrystal and single-crystal spectra in the absence of an external magnetic field.

It is practically impossible, therefore, to observe quadrupole interactions of Fe^{57m} in polycrystalline yttrium iron garnet below Θ. In this

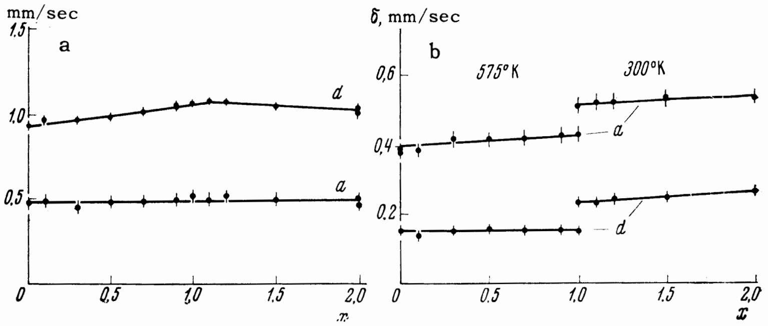

FIG. 7. (a) Quadrupole splitting and (b) isomer shifts for Fe^{57} nuclei vs. degree of substitution in the a-sublattice and d-sublattice of tin-substituted iron garnets.

case the precise values of e^2qQ for both types of Fe^{3+} sites can be obtained in the paramagnetic region; such measurements are given in[20] for a number of rare-earth iron garnets.

B. Figure 5 shows the Mössbauer spectra for different iron garnets at temperatures above Θ. Each spectrum, except the last, consists of three lines whose intensities are not all equal. The widths of the two outer lines are always equal: 0.3 mm/sec in pure yttrium iron garnet and 0.4—0.45 mm/sec in the substituted garnets.

We interpret each recorded spectrum as consisting of two quadrupole doublets where the lines corresponding to the higher velocities coincide to comprise the third and strongest line of the given spectrum. The stronger doublet with larger splitting and smaller isomer shift is assigned to Fe^{3+} ions in the d-sublattice, which contains most of these ions. The accompanying table compares our results for pure yttrium iron garnet with those obtained by other investigators.[16,17,20] Here $\Delta = \frac{1}{2}e^2qQ$ represents the quadrupole splittings and δ represents isomer shifts at 300°K.

We note that the anomalously large quadrupole splitting Δ for compounds of Fe^{3+} in the d-sublattice is evidently associated with a considerable degree of covalence; this is confirmed by calculations in[20] of the electric-field (q) gradient on the point-charge model. The calculated values of e^2qQ somewhat exceed the experimental results for the a-sublattice but are considerably smaller than the experimental values for the d-sublattice.

The data of Nicholson and Burns on isomer shifts[20] require correction, because to their values for the shifts measured at 610°K they added the thermal shift of metallic iron obtained from[21]; the latter is 0.22 mm/sec at 300°. Our measurements on substituted garnets (Fig. 7b) showed that with a temperature drop from 575° to 300°K the thermal shift is 0.08 ± 0.03 mm/sec for both sublattices. Assuming linear temperature dependence for the thermal shift when $T > 300°K$, we obtain the corrected values of the isomer shifts in the table.

Thus the thermal shifts for Fe^{57} in metallic iron and in yttrium iron garnet differ by a factor of 2.5 in the range 300—575°K, indicating a great difference between the respective phonon spectra.

It is interesting to compare the isomer shift ratio $\delta_a/\delta_d = 2$ with the ratio of the respective volumes occupied by an Fe^{3+} ion in the two sublattices. We know from x-ray data on yttrium iron garnet[22] that the $Fe^{3+}—O^{2-}$ separation is 1.88 Å for tetrahedral sites and 2.00 Å for octahedral sites. Taking 1.36 Å as the O^{2-} ionic radius, we obtain the volume ratio $(2.00—1.36)^3/(1.88—1.36)^3 = 1.9$. This result is consistent with the linear variation of isomer shifts for Fe^{57} nuclei in metallic iron[23] under external hydrostatic pressure, and also with the linear variations of the shift in Laves phases as the atomic volume is varied.[24] The latter observation indicates that the electronic density of Fe^{57} nuclei increases as the atomic volume decreases. A similar effect has been observed for Sn^{119}.[25]

C. We note in the spectra of the substituted garnets (Fig. 5) that the second and third lines of each spectrum are attenuated as the tin content diminishes. The second (i.e., central) line vanishes completely when $x = 2.0$; this suggests that the two remaining lines represent Fe^{3+} ions located only in the d-sublattice. The two lines have equal areas.

The a-sublattice doublet is asymmetric with the area ratio 1 : 0.75. This symmetry is obviously associated with anisotropy of the Debye-Waller factor for Fe^{3+} in the a-sublattice.[26] Combining the two component areas in the case of each doublet of pure yttrium iron garnet and taking into account the Fe^{3+} content ratio of the two sublattices, we compute the Mössbauer effect probability ratio $f_d/f_a \approx 1.1$, which also does not depend on the degree of substitution.

The total number of Fe^{3+} ions per formula unit of $Y_{3-x}Ca_xFe_{5-x}Sn_xO_{12}$ varies from 5 at $x = 0$ to 3 at $x = 2.0$. In view of the foregoing discussion we see that the experimental spectra yield the different values of x for the Fe^{3+} ions in the two sublattices (Fig. 6).

Our results show that Sn^{4+} ions replace Fe^{3+} ions only in the octahedral sublattice; this confirms earlier x-ray data for $x = 1.0$ and 2.0.[10] For $x = 1.0$ Geller et al.[10] found that 100% of the Sn^{4+} ions are located in the a-sublattice, and 90% when $x = 2.0$. Our data for $x = 2.0$ show with 5% accuracy that the Fe^{3+} ions are completely replaced in the a-sublattice of iron garnets.

It must be noted that the reliability of x-ray investigations of substituted garnets depends primarily on the difference between the scattering powers of Fe^{3+} and the substituent ion. For this reason the Sn^{4+} ions are very suitable for x-ray investigations. However, it is also interesting to investigate many other substitute ions, in rare-earth iron garnets as well as in yttrium iron garnet.[11] Our investigations have shown that the Mössbauer method is simpler and more suitable than the other method, since the real ratio of spectral lines in substituted garnets depends principally on the relative numbers of Fe^{3+} ions in the sublattices and probably does not depend on the properties of the substitute ion. It has been shown in[20] that for several rare-earth iron garnets the Mössbauer spectra consist of three lines, as in yttrium iron garnet, and that the quadrupole splittings and isomer shifts in the two sublattices are of the same order as for yttrium iron garnet. The study of the Mössbauer spectra of substituted rare-earth iron garnets is facilitated by the fact that the quadrupole splittings and isomer shifts for Fe^{57} in the sublattices differ by a factor of about two; this permits a reliable separation of the lines in accordance with the different sublattice sites of Fe^{3+}. From the variation of the line intensities we then determine in which sublattice substitution has occurred.

D. We shall now consider how the quadrupole interactions Δ (Fig. 7a) and the isomer shifts δ (Fig. 7b) vary in both sublattices as functions of Sn^{4+} substitution. Figure 7a shows that increased tin content is not accompanied by change of the quadrupole splitting for the octahedral sublattice, despite the fact that Sn^{4+} ions are located only in this sublattice. However, when we consider only the Fe^{3+} and Sn^{4+} ions we find that in the garnet structure each Fe^{3+} ion in the a-sublattice will have in its first coordination sphere only other Fe^{3+} ions located in tetrahedral sites, while the second coordination sphere will contain Sn^{4+} ions and still unsubstituted Fe^{3+} ions in octahedral sites. Therefore the substitutions should affect primarily the magnitude of Δ for Fe^{3+} ions in tetrahedral sites. Indeed, the value of Δ for the d-sublattice at first increases up to $x = 1.0$, after which it decreases slowly. The highest value of Δ corresponds to $x = 1.0$, when half of the Fe^{3+} ions in the a-sublattice are replaced and the greatest distortions of the entire garnet lattice are present.

The isomer shifts do not depend on the value of x in the two sublattices. We are therefore justified in using the temperature dependence of the shift that was obtained for pure yttrium iron garnet at $x = 1.0$; this was done in item B of Sec. 3. Moreover, the absence of concentration dependence for the isomer shift confirms the absence of any direct relationship between Sn^{4+} and Fe^{3+} such as was suggested at one time in studies of the effective-magnetic-field generation mechanism as applied to Sn^{119} in this system.[1-3] The small enhancement of the isomer shift for $x > 1.0$ is obviously associated with the fact that the introduction of tin ions causes an enhanced lattice parameter for yttrium iron garnet. It has been shown in[27] that when $x = 2.0$ the lattice parameter is 2% larger than that of pure yttrium iron garnet.

D. The Mössbauer spectra of Sn^{119} nuclei in the described system of substituted ferrites exhibit a single line broadened by about 0.5 mm/sec in the paramagnetic region.[3] Similar results have been obtained in the present work. If we assume that the electric field gradient in the a-sublattice is generated only by the charges of the surrounding ions, then the value of q for Sn^{119} nuclei will be the same as for Fe^{57} in the a-sublattice. However, when we take into account the fact that the quadrupole moment of Sn^{119} is only one-third of the Fe^{57} quadrupole moment, we expect that the quadrupole splitting for Sn^{119} will be ≈ 0.16 mm/sec if the Sternheimer factor $\gamma_\infty \approx -10$ for Sn^{4+}, as for Fe^{3+}. Using the experimental value $\Delta \approx 0.5$ mm/sec we obtain the upper limit $\gamma_\infty \approx -30$ for Sn^{119}. These estimates of γ_∞ for Sn^{4+} agree with the result $\gamma_\infty = -15.33$ calculated in[28] for the In^{3+} ion, which is a neighbor of tin in the periodic table. Quadrupole interactions $\Delta < 0.5$ mm/sec cannot induce splitting of the Sn^{119} absorption line even when we work with Mg_2Sn or PdSn sources, but result instead in a broadened line. It is clear from the discussion in item A of Sec. 3 that there is an even smaller possibility of observing quadrupole interactions of Sn^{119} when $T < \Theta$.

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