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Supertransferred Hyperfine Fields at the Nuclei of Various Diamagnetic Ions in Yttrium Iron Garnet

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The internal fields at the nuclei of Ga^{3+}, Al^{3+}, V^{5+}, Sc^{3+}, and In^{3+} ions present in some iron garnets have been measured by the spin-echo method. Their values at the octahedral 16*a* and tetrahedral 24*d* sites are in agreement with the superexchange process and with the relative Fe^{3+}-ion configurations on the two sites. The transferred hyperfine fields at the *a* sites were composed on an isotropic part and a much smaller anisotropic part. The hyperfine field due to a valence *ns* electron was calculated by using Goudsmit's formula with some appropriate modifications. The fractions f_s of the unpaired *ns* spin of these diamagnetic cations were deduced from these calculated values and the isotropic hyperfine fields. It was shown that this *ns* polarization is much higher for the *a* site than for the *d* site in accord with the covalent character of the Fe^{3+} ion at the tetrahedral site. The nuclear-quadrupole splittings at two magnetically inequivalent *a* sites were measured. The electric field gradients without the antishielding effect were then shown to be approximately the same for *S*-state cations at the *a* sites

I. INTRODUCTION

Transferred hyperfine fields are of importance because in certain cases they allow a better understanding of the hyperfine interactions. In ferrimagnetic insulators where the magnetic order is due to the superexchange interaction, the internal field at the nucleus of a diamagnetic cation arises from the supertransferred hyperfine field and to some less extent the dipolar field. The NMR of Ga nuclei on the tetrahedral sites in substituted yttrium iron garnet (YIG) was first reported by Streever *et al.*[1] We have investigated, by the spin-echo technique, the supertransferred hyperfine fields at the nuclei of several diamagnetic ions with atomic numbers *Z* varying between wide limits and which were present in a ferrimagnetic garnet lattice. We report here our results on ^{27}Al, ^{45}Sc, ^{51}V, ^{69}Ga, ^{71}Ga, and ^{115}In nuclei in YIG.

The cubic crystal structure of the yttrium garnet[2,3] belongs to the space group O_h^{10}-*Ia*3*d*. The oxygen ions define three kinds of sites in which are placed the cations: The Fe^{3+} ions occupy the 16*a* octahedral sites and the 24*d* tetrahedral sites, while the Y^{3+} ions occupy the 24*c* dodecahedral sites. The site preference of the diamagnetic cations in substituted YIG then depends on their size. The chemical formulas of the garnet compositions can be represented as $Y_3Fe_{5-x}M_xO_{12}$, where *M* is Al^{3+}, Ga^{3+}, In^{3+}, or Sc^{3+}, and $Y_{2.8}\,Ca_{0.2}\,Fe_{4.9}\,V_{0.1}\,O_{12}$ The *x* values for Ga^{3+} were 0.15 and 0.5; for Al^{3+}, 0.03, 0.30, and 0.60; for In^{3+}, 0.006 and 0.04; and for Sc^{3+}, 0.03 and 0.15, respectively. The distribution of these ions are known, from the magnetization values,[4,5] to be as follows: Al^{3+} and Ga^{3+} enter predominantly the 24*d* tetrahedral sites for small values of *x* though a small fraction of them also can enter the 16*a* octahedral sites. The V^{5+} ions enter only in 24*d* sites whereas Sc^{3+} and In^{3+} ions only in 16*a* sites at least for *x* value studied here. In conformance with the above prevision we could detect the nuclear magnetic resonance of Al^{3+} and Ga^{3+} nuclei present at *a* sites as well. Streever *et al.* interpreted the hyperfine field at the Ga *d* site as due to the polarization of 4*s* electron of Ga by the Fe^{3+} spins through a superexchange mechanism.[6] Let us consider a Ga^{3+} ion and a Fe^{3+} ion separated by an O^{2-} ion (Fig. 1). In the ground state the two *p* electrons of O^{2-} remain in the 2*p* shell of oxygen and there is no net spin on Ga^{3+}. In fact, the state of the oxygen ion with the lowest energy is a superposition of the ground state O^{2-} and of a small fraction of excited states such as O^- and O. The excited state O^- may be realized by the jump of one 2*p* electron to the 4*s* orbit of gallium. The other *p* electron, according to Anderson,[7] interacts with one of the 3*d*-ion electrons as in the covalent bond in which they exchange their antiparallel spins. The

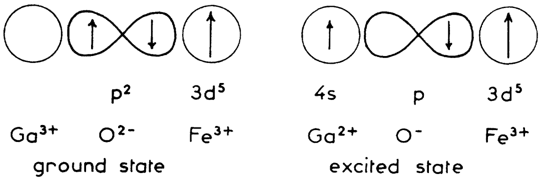

FIG. 1. Schematic superexchange process giving rise to a field at a diamagnetic cation.

amount of unpaired spin of 4*s* electron on gallium is expected to depend strongly on the polarization of the 2*p* electron by the 3*d* spins. As the hyperfine field due to the Fermi-contact term is antiparallel to the *s* spin density at the nucleus this transferred hyperfine field is antiparallel to Fe^{3+} spin. In other words, the supertransferred hyperfine field is parallel to the polarizing magnetic moment. This simple picture shows that this field depends mainly on the neighboring magnetic ions.

In substituted YIG the polarizing sources are the Fe^{3+} spins at the *a* and *d* sites constituting two antiparallel magnetic sublattices. The transferred hyperfine field at the *a* site should be different from that at the *d* site in two respects: First, the valence electrons of O^{2-} are more polarized by the *d*-site Fe^{3+} spin (Fe_d^{3+}) than by the *a* site Fe^{3+} spin (Fe_a^{3+}) because of the covalent bonding[8] of the tetrahedral site; second, the *a*-site ion is surrounded by six Fe_d^{3+} at 3.46 Å, whereas the *d*-site ion "sees" only four Fe_a^{3+} at the same distance. Moreover, unlike the *d* site having a negative contribution to the transferred field from the four Fe_d^{3+} at 3.79 Å, the eight-nearest Fe_a^{3+} farther away (5.36 Å) would contribute very little to the transferred field at the *a* site.

II. EXPERIMENTAL

The spin-echo apparatus for the study of nuclear-magnetic resonance in ferromagnetic materials was described in an earlier paper.[9] The oscillating circuit is utilized for both excitation and reception. A set of coils having the same section are used in this frequency range such that the number of turns in the coil is approximately inversely proportional to the tuned frequency of the oscillating circuit. In these conditions the nuclear signal is roughly proportional to the square of the resonance frequency. The maximum exciting rf-pulse amplitude was about 400 V with widths up to 5 μsec. The maximum rf field in the coil was then about 8 Oe. The two rf pulses were adjusted carefully at each frequency for a maximum echo in order to obtain a reproducible spectrum. At 4.2 °K the nuclear transverse relaxation time T_2 of all nuclei studied here is much longer than the interval between the two rf pulses so that the variations of T_2 have practically no effect on the echo amplitude. Moreover, the repetition frequency was low enough in order not to deteriorate the nuclear signal. The samples used for our present investigations were ground single crystals of the above-mentioned compositions. Some single crystals were also used in order to excite selectively the nuclei within the domains for the measurement of the quadrupole couplings.

TABLE I. Statistical weights P_n of *a* sites with different cationic neighboring. *c* is the concentration of substituted ion at the *d* site.

x	c	P_0	P_1	P_2
0.03	0.01	0.94	0.05	
0.15	0.05	0.73	0.23	0.03
0.30	0.10	0.53	0.35	0.10
0.50	0.16	0.35	0.40	0.19
0.60	0.20	0.26	0.39	0.25

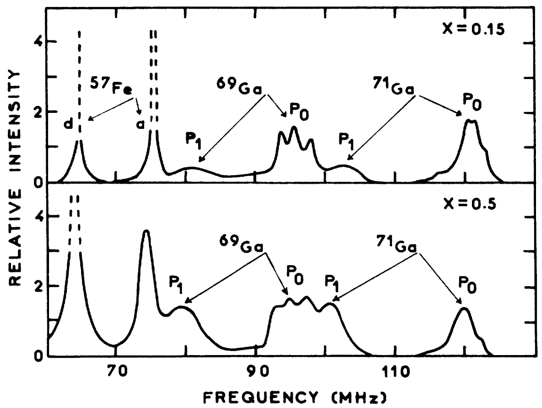

FIG. 2. Nuclear-spin-echo amplitude in two gallium-substituted iron garnets at 4.2 °K, plotted as a function of frequency.

III. RESULTS AND DISCUSSION

A. Octahedral *a* Site

The resonance spectrum of ^{69}Ga and ^{71}Ga at the *a* sites is shown in Fig. 2. The resonance frequencies for these sites are much greater than those found previously for the Ga nuclei at the *d* sites,[1] in agreement with the views expressed in Sec. I. The observed P_0 and P_1 lines correspond to different environments of the Ga^{3+} *a* sites due to the presence of Ga^{3+} at the *d* sites. In the garnets studied with $x = 0.15$ and 0.50, the gallium concentrations *c* are about 0.05 and 0.16 at the *d* sites. For a given concentration the probability P_n that one *a* site might have *n* Ga^{3+} ions among its six-nearest cationic neighbors is

$$P_n = \binom{n}{6} c^n (1-c)^{6-n} , \qquad (1)$$

where $\binom{n}{6}$ is the binomial coefficient. Calculated values of P_n are given in Table I.

It is seen that the spectrum at 95 and 121 MHz corresponds to Ga^{3+} having six Fe_d^{3+} as neighbors and that at 81 and 103 MHz mainly to P_1. Further, the ratio of the frequencies of the P_0 and P_1 lines is observed to be about $\frac{5}{6}$ as one could expect it from the configuration described above. The P_2 lines that would occur towards 65 and 82 MHz are masked by the signal from Fe_d^{3+} and that from ^{69}Ga of P_1. The agreement between the intensities observed and calculated is satisfactory taking into account the F^2 correction. The intensity of the lines from a sites shows that for the garnet with $x = 0.5$ the Ga occupation in a sites is of the order of 1%.

The situation is similar for ^{27}Al in the garnets with $x = 0.30$ and 0.60 (Fig. 3). The perturbed P_1 and P_2 lines are included in the broad line. From the intensities of the Al_a and Al_d lines corrected for F^2, it was deduced that the Al^{3+} ions are distributed on the a and d sites roughly in the 1 : 7 ratio, as against about 1 : 24 for the Ga^{3+} ions. This greater preference of Ga^{3+} ions for the tetrahedral site was already reflected in the magnetization studies.[4]

Since the a site has its trigonal c axis oriented along one [111] easy direction of magnetization there are two magnetically inequivalent a sites named a_1 and a_2 in the 1 : 3 ratio. The hyperfine field at the a_1 site is parallel to the c axis giving the maximum quadrupole splitting. That at the a_2 site makes an angle $\theta = \arccos \frac{1}{3}$ with the c axis giving then, to the first order, a quadrupole splitting three times smaller. The dipolar field at the a site along the c axis in YIG has been calculated by Boutron and Robert[10] to be 4088 Oe relative to the total magnetization. The transferred hyperfine field at the a site is parallel to the polarizing Fe_d^{3+} moment as shown in Figs. 4 and 5, in accordance with the superexchange process. The internal fields resulting from the isotropic H_0 and anisotropic H_{an} parts of the transferred hyperfine fields and the dipolar field H_d for the a_1 and a_2 sites in the approximation $H_0 \gg H_{\text{an}} + H_d$ are

$$H_{a_1} = H_0 + H_{\text{an}} + H_d \,, \tag{2}$$

$$H_{a_2} = H_0 - \tfrac{1}{3}(H_{\text{an}} + H_d) \,. \tag{3}$$

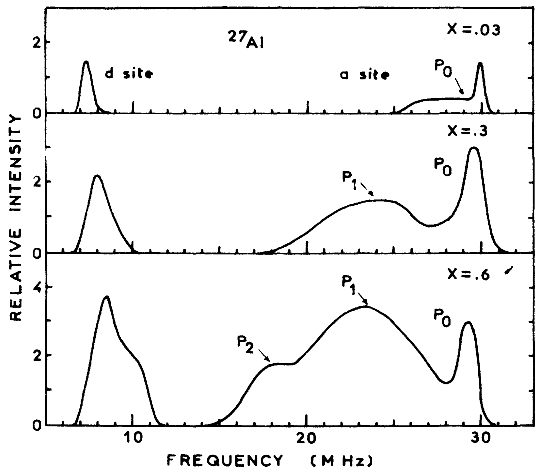

FIG. 3. Nuclear-spin-echo amplitude in aluminium-substituted iron garnets with $x = 0.6$ and 0.3 at 4.2 °K and $x = 0.03$ at 1.8 °K, plotted as a function of frequency.

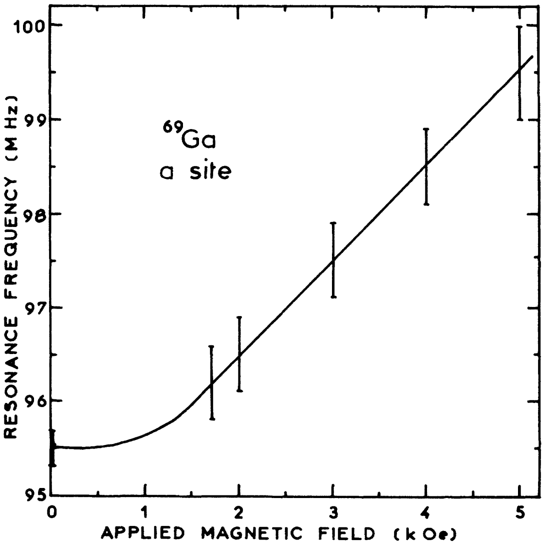

FIG. 4. External magnetic field dependence of ^{69}Ga NMR frequency at a site in single crystals at 4.2 °K.

The resonance spectra of the a_1 and a_2 sites in single crystals in zero external field are shown in Fig. 6. For the spectra with higher values of x (0.04 and 0.15 for ^{115}In and ^{45}Sc, respectively), each line was broadened but its resonance frequency was practically unchanged. As we had mentioned before, unlike the previous cases, all the Sc^{3+} and In^{3+} ions are in the a sites. The new feature of the resonance spectrum is that the number of the perturbed a sites due to the presence of diamagnetic ions at the neighboring a sites is high while the perturbation itself is expected to be un-

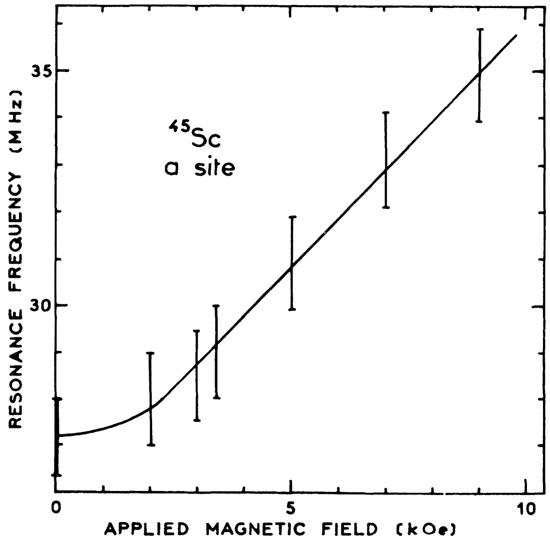

FIG. 5. External magnetic field dependence of ^{45}Sc NMR frequency at a site in ground single crystals at 77 °K.

TABLE II. Isotropic H_0 and anisotropic H_{an} transferred hyperfine fields at the a sites.

	Sc^{3+}	Ga^{3+}	In^{3+}
H_0 [kOe]	26	93	150
H_{an} [kOe]	3	3	6

important. For ^{57}Fe nuclei having no quadrupole moment there are merely two lines in the ratio 1:3, at 74.9 and 75.85 MHz, respectively. For the nuclei of diamagnetic ions the second-order shift of the $-\frac{1}{2}\rightarrow\frac{1}{2}$ transition due to the quadrupole splitting at the a_2 site is quasinull ($9\cos^2\theta \simeq 1$) so that this transition corresponds nearly to the field H_{a_2}. From these spectra we deduced the isotropic H_0 and anisotropic H_{an} parts of the transferred hyperfine fields, taking into account the calculated dipolar field (Table II).

The anisotropic transferred hyperfine fields H_{an} would arise mainly from the unpaired spin of $3p$, $3d$, $4p$, and $5p$ electrons for Al^{3+}, Sc^{3+}, Ga^{3+}, and In^{3+}, respectively. For np valence electrons the field due to the dipolar hyperfine interaction can be written[11]

$$H_{np} = \tfrac{4}{5}\mu_B \langle r^{-3}\rangle_{np}[f_z - \tfrac{1}{2}(f_x + f_y)] , \qquad (4)$$

where f_x, f_y, and f_z are the fractions of unpaired spin on p_x, p_y, and p_z orbitals, respectively. For the axial symmetry with p_z along the c axis, $f_x = f_y$. Using Goudsmit's formula (see, e.g., Ref. 12) the $\langle r^{-3}\rangle_{np}$ were evaluated to be 2.9, 7.3, and 11 in a.u. for Al^{3+}, Ga^{3+} and In^{3+}, respectively. The difference $f_z - f_x$ corresponding to the observed field H_{an} is then 0.8 and 1.1.% for Ga^{3+} and In^{3+}, respectively. Assuming the difference $(f_z - f_x)$ to be the same for Al^{3+} and Ga^{3+}, the anisotropic field H_{an} was calculated to be 1.2 kOe. From the measured value of H_{a_2} of 26.4 kOe, the isotropic field H_0 can then be deduced as 25.6 kOe using the relation (3).

TABLE III. Experimental values of the quadrupole coupling constant eqQ/h and electric field gradient in absolute value without antishielding effect at the a site.

	^{45}Sc	^{69}Ga	^{115}In
I	$\frac{7}{2}$	$\frac{3}{2}$	$\frac{9}{2}$
Q (b)	−0.22	0.19	1.16
(eqQ/h) (MHz)	14.7	12	140
γ_∞	−9.46[a]	−9.50[b]	−24.9[b]
$[q/(1-\gamma_\infty)]$ (10^{14} esu)	0.88	0.83	0.64

[a] Value taken from Ref. 13.

[b] Values taken from Ref. 14.

The estimated electric field gradients (EFG)

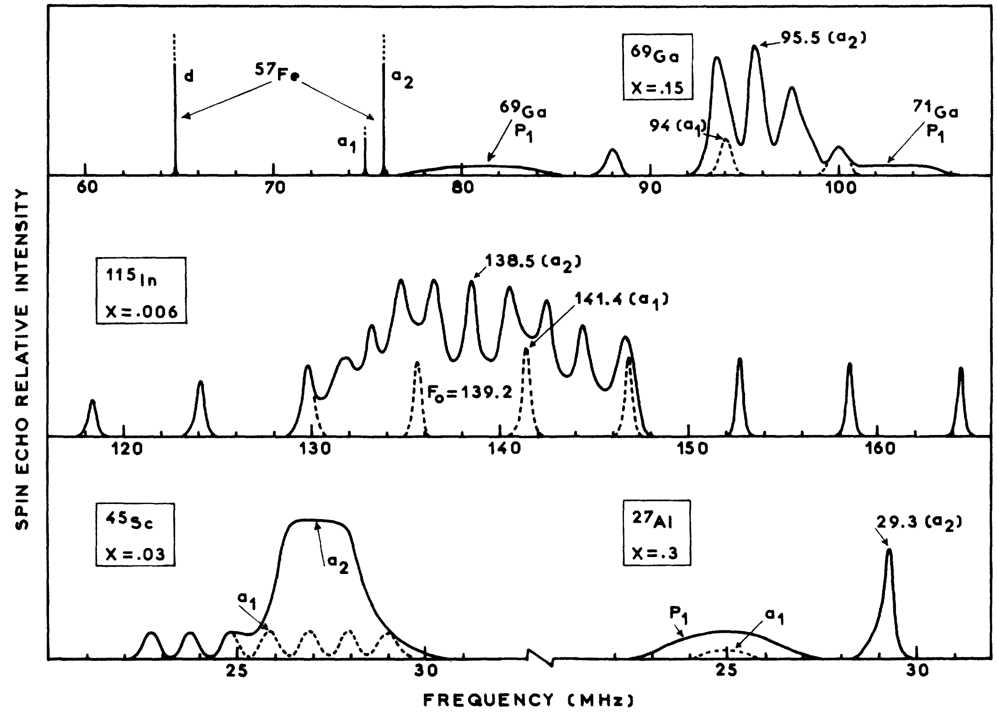

FIG. 6. Resonance spectra of the magnetically inequivalent a_1 and a_2 sites in single crystals in zero external field at 4.2 °K.

without the antishielding effect for Sc^{3+}, Ga^{3+}, and In^{3+} at the *a* site are shown in Table III.

The quadrupole coupling constant eqQ/h of Fe^{3+} has been measured by Nicholson and Burns[15] using the Mössbauer techniques as 12.1 ± 0.9 MHz at the *a* site in YIG. Taking (as in Ref. 15) the value of $\gamma_\infty = 9.14$ and $Q = 0.2$ b for the ^{57}Fe first excited state, we calculated the EFG without the antishielding effect to be $(0.82 \pm 0.06) \times 10^{14}$ esu in absolute value. However, the comparison can only be qualitative due to the uncertainties in the theoretical estimates of shielding factors.

B. Tetrahedral *d* Site

The ^{27}Al spectrum is shown in Fig. 3. The Ga nuclei spectrum is similar to that observed by Streever *et al.*[1] In V^{5+}-doped YIG, the ^{51}V echo signal observed extend from 8 to 14 MHz. This broadening is due to the fact that Ca^{2+} ions which partially replace Y^{3+} introduce fluctuations in the charge distribution. The nuclear-resonance frequencies and the internal field at the *d* sites measured for ^{27}Al, ^{51}V, and ^{69}Ga nuclei at 4.2 °K are given in Table IV.

For the *d* site the oxygen tetrahedron has the D_{2d} symmetry with the *c* axis oriented along one [100] direction. The dipolar field at the *d* site in pure YIG is very small because the contributions from *a* and *d* sublattices nearly cancel out.[10] If the anisotropic part of the transferred hyperfine field is small as compared to the isotropic one then the quadrupole interaction is null to the first order when the magnetization is oriented along one [111] direction. The nuclear spin-lattice relaxation time T_1 at 4.2 °K for the Ga nuclei at the *d* site was very long (several sec) in single crystals so that it was practically impossible to obtain a correct resonance spectrum. For ^{27}Al and ^{51}V nuclei the resonance frequencies being still lower the echo signals were not observed in single crystals probably again due to the increase in T_1. The resonance spectrum of ^{27}Al nuclei at the *d* sites in ground single crystals is similar to that of Ga nuclei[6]: for the low concentrations studied here, the shift of the center of gravity of the line is proportional to Al^{3+} concentration *c* on the *d* sites (Fig. 7). This shift is equal to $4c\Delta F$, where ΔF is the contribution of one Fe_d^{3+} ion to the resonance frequency at the Al_d^{3+} ion. It is thus seen that each Fe_d^{3+} ion contributes a field of about 1.6 kOe to the total transferred hyperfine field at the *d* site. By referring to the relative configurations of the *a* and *d* sites the contribution of each Fe^{3+} spin to the transferred hyperfine field at the *a* and *d* sites can be summarized as in Table V.

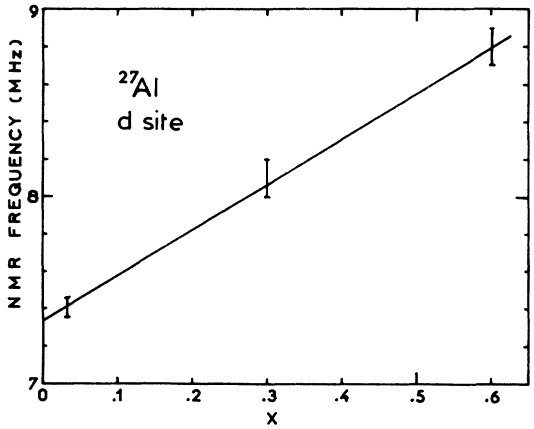

FIG. 7. Shift of the center of gravity of the ^{27}Al line at the *d* site, plotted as a function of Al^{3+} concentration in aluminium-substituted iron garnets.

TABLE IV. Nuclear-resonance frequencies *F* and internal fields H_n at the *d* site.

	^{27}Al	^{51}V	^{69}Ga
F [MHz]	7.3	~11	20
H_n [kOe]	6.6	~10	20

It should be pointed out that the field due to the superexchange mechanism between *a* and *d* sites is greater when the polarizing moment is at the *d* site.

C. Evaluation of the Unpaired *ns* Spin at the *a* and *d* Sites

The isotropic transferred hyperfine field arises from the density of unpaired spin of the valence *ns* electrons at the nucleus of the diamagnetic ion. The field H_{ns} due to one peripheral *ns* electron at the nucleus can be evaluated by using Goudsmit's formula with appropriate modifications as discussed by Kopfermann.[12] Using atomic-spectroscopy data we calculated this contact term for the diamagnetic cations studied here and also for Sn^{4+} and Sb^{5+} whose hyperfine fields have been already measured in YIG[16,17] by the Mössbauer technique. The fraction $f_s = H_0/H_{ns}$ of the unpaired *ns* spin for the *a* and *d* sites are shown in Table VI.

It is noted that the f_s values apparently do not depend on the quantum number *n* of the valence elec-

TABLE V. Contribution in kOe of each Fe^{3+} ion to the transferred hyperfine field (THF) at the *a* and *d* sites in Al- and Ga-substituted YIG.

	THF in kOe from one Fe^{3+}			
	YIG : Al^{3+}		YIG : Ga^{3+}	
	a site	*d* site	*a* site	*d* site
Fe^{3+} at *a* site	negligible	+3.2	negligible	11.6[a]
Fe^{3+} at *d* site	4.2	−1.6	15.5	-4.4^{+}

[a] Values deduced from Ref. 6.

TABLE VI. The fields H_{ns} due to one *ns* peripheral electron of various diamagnetic cations. The fractions f_s of unpaired spin are estimated for these ions at *a* and *d* sites in YIG.

Z	Ions	*ns* electron	H_{ns} in MOe	f_s% of *a* site	f_s% of *d* site
13	Al^{3+}	3*s*	2.29	1.12	0.29
21	Sc^{3+}	4*s*	2.57	1.01	···
23	V^{5+}	4*s*	5.44	···	~0.18
31	Ga^{3+}	4*s*	6.93	1.34	0.29
49	In^{3+}	5*s*	11.4	1.32	···
50	Sn^{4+}	5*s*	15.3	1.31	···
51	Sb^{5+}	5*s*	18.9	1.53	···

trons. For the *a* sites where the *ns* polarization practically arises from only the nearest Fe_d^{3+} spins, the average f_s value is about 1.35%. For the *d* sites where the next-nearest Fe_d^{3+} spins could reduce significantly the principal polarization due to the nearest Fe_a^{3+} spins the f_s value is only 0.29%. The rather small values for V^{5+} (0.18%) at the *d* site and Sc^{3+} (1%) at the *a* site could be due to the mixing of 3*d* and 4*s* valence electrons.[18] From the isomer-shift measurements in YIG by Walker[8] and the isomer-shift calibrations by Trautwein *et al.*[19] the fraction of 4*s* electron for Fe^{3+} ions is estimated as 0.08 ± 0.03 and 0.20 ± 0.03 in the *a* and *d* sites, respectively, using the Fermi-Segré-Goudsmit formula. If we assume the same fractions for the diamagnetic cations, then the polarization of the valence *ns* electron at the *a* site with $f_s = 1.35\%$ would be in the range 12–27%; that is indeed much greater than the value of about 1.5% for the *d* site.

IV. CONCLUSION

We have measured by the spin-echo technique, the supertransferred hyperfine fields at the ^{27}Al, ^{45}Sc, ^{51}V, ^{69}Ga, ^{71}Ga, and ^{115}In nuclei present in a garnet structure. The anisotropic part of these fields is found to be much smaller than the isotropic one. The quantity $f_z - f_x$ of the unpaired spin of *p* valence electrons deduced from the anisotropic tranferred hyperfine field was about 1%. The calculation of the hyperfine fields due to one *ns* valence electron based on the Goudsmit formula have enabled us to evaluate the fraction f_s of unpaired *s* spin for the *a* and *d* sites to be about 1.3 and 0.29%, respectively. As they arise from a superexchange process it is instructive to report here the molecular fields at these two sites in YIG. Using the exchange parameters $J_{aa} = 0.5\ \text{cm}^{-1}$, $J_{dd} = 2\ \text{cm}^{-1}$, and $J_{ad} = 22.5\ \text{cm}^{-1}$,[20] we deduced a molecular field of 7 MOe at the *a* site that is indeed higher than 4.4 MOe at the *d* site. However, these molecular fields should not be proportional to the transferred hyperfine fields because the exchange interaction between two iron ions is symmetrical while the exchange mechanism between one iron ion and one diamagnetic cation is not so. For the *a* site the transferred hyperfine field practically arises from the nearest Fe_d^{3+} spins while for the *d* site the next-nearest Fe_d^{3+} spins also contribute significantly to the transferred field. This is coherent with the fact that J_{aa} is much smaller than J_{dd}.

The quadrupole splittings were measured for two magnetically inequivalent *a* sites when the magnetization is oriented along one [111] easy direction. The electric field gradients without antishielding effect estimated for Sc^{3+}, Ga^{3+}, and In^{3+} were shown to be of the same order of magnitude.

Further this study gives the distribution of Ga^{3+} and Al^{3+} ions among the *a* and *d* sites and shows the greater preference of Ga^{3+} for the *d* site. While as a principle the distribution of diamagnetic ions among these sites could also be deduced from the magnetization measurements at 4.2 °K, this technique is limited by its precision for low concentration and by the well-known canting effects in such cases of diamagnetic cations especially at high concentration. While the cation distribution deduced by us are in general agreement with that from magnetization measurements[4] the detection of a very small concentration such as Ga_a^{3+} ($c = 0.3$ at.%) is evidently beyond the possibility of the magnetization or magnetic anisotropy measurements.

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