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Enhancement of exchange interactions in Bi- and La-substituted $Y_3Fe_5O_{12}$

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The NMR of ^{57}Fe in Bi:YIG and La-YIG (where YIG is yttrium iron garnet) polycrystalline samples was measured between liquid-helium and room temperatures. In spectra of both tetrahedral and octahedral Fe^{3+} ions, satellite lines appear, corresponding to Fe^{3+} ions with Bi^{3+} or La^{3+} ions in their vicinity. The resonance frequency f_{res} of the satellites decreases with increasing temperature more slowly than f_{res} of the main lines. The different temperature dependences reflect the enhancement of the Fe^{3+}-Fe^{3+} superexchange interaction in the vicinity of the diamagnetic substitution. In the simplest model, the presence of Bi^{3+} or La^{3+} leads to two modified exchange integrals. Corresponding changes obtained by the molecular-field analysis are 4.5 and 1.6% for Bi:YIG, while they are 1.3 and 0.5% in the La-doped system. The smaller effect of the La^{3+} ion indicates that local deformation around the substitution plays only a minor role in the enhancement of the superexchange.

For the past twenty years the behavior of ferrimagnetic garnets substituted by bismuth has represented a puzzling problem to those concerned with magnetic insulators. In the Bi:YIG system, (YIG is yttrium iron garnet) Bi^{3+} substitutes for Y^{3+} in the dodecahedral (c) sublattice and is nominally diamagnetic. Despite its closed shells, Bi^{3+} significantly influences the magnetic properties of YIG (see Hansen and Krumme[1] for review). In particular, the magneto-optic activity is strongly enhanced, in liquid-phase-epitaxy thin films a large noncubic anisotropy appears, and the Curie temperature increases.

In the present paper we report a study of the temperature dependence of ^{57}Fe NMR in $Bi_{0.3}Y_{2.7}Fe_5O_{12}$ and $La_{0.3}Y_{2.7}Fe_5O_{12}$ garnets with the goal of understanding in more detail the increase of T_C caused by Bi substitution. The first question we would like to answer is whether this increase is connected with a change of electronic structure or with a local deformation around the substituted ion. Geller and Colville[2] studied the geometry of Bi-substituted YIG. They came to the conclusion that for a tetrahedrally coordinated Fe^{3+} ion the $Fe^{3+}-O^{2-}$ bond is somewhat shorter than in pure YIG (by $\simeq 0.15$ Å), while for octahedral Fe^{3+} ions this bond is lengthened by $\simeq 0.63$ Å and the angle (tetrahedral Fe^{3+})-O^{2-}-(octahedral Fe^{3+}) remains essentially unchanged. As far as the exchange is concerned the point of view of Geller and Colville is purely geometrical, i.e., they suggest that the small shortening of the (tetrahedral Fe^{3+})$-O^{2-}$ bond is decisive in enhancing the exchange. We believe that the Bi^{3+} ion may play a more active role by changing the electronic structure of the affected ions. To get relevant information we compare the NMR in Bi:YIG with that in La:YIG. In the highly symmetrical garnet structure the ionic radius of Bi^{3+} is expected to be slightly smaller[3] (by $\simeq 1.3\%$) than that of La^{3+}. As Y^{3+} is smaller than Bi^{3+} we expect larger exchange enhancement in La:YIG if local deformation is responsible for it. The second problem we consider is whether the enhancement of the exchange interaction is localized to the vicinity of Bi^{3+}. Naturally, we would also like to estimate the amount by which individual exchange interactions are increased.

The way in which these problems are addressed is closely related to our previous studies of substituted garnets by the NMR method.[4-6] The nuclei of Fe^{3+} ions which are near Bi^{3+} or La^{3+} substitution are subjected to a hyperfine field which differs from that of Fe^{3+} in an ideal environment. Microscopically, this difference is connected with different electron transfer,[6] but it is not the purpose of this paper to study the mechanism responsible. Rather, we use the fact that the resolution of our NMR spectrometer is high enough to observe—besides the main lines—also the satellites corresponding to those Fe^{3+} ions in the vicinity of which the substitution is situated.

The resonance frequency f_{res} of the ^{57}Fe nucleus is to a good approximation proportional to the electronic magnetic moment on a given Fe^{3+} site. If the exchange is increased locally, then with rising temperature the moments of Fe^{3+} ions influenced by Bi^{3+} will decrease more slowly compared with Fe^{3+} in an ideal environment. An analysis of corresponding differences of $f_{res}(T)$ dependences then yields the information required.

$Y_3Fe_5O_{12}$ is a classical example of a collinear ferrimagnet, the dominating exchange interaction being between octahedral (a) and tetrahedral (d) Fe^{3+} ions. The equations for the reduced sublattice magnetizations of YIG as functions of temperature in the molecular-field approximation, may be written as[7]

$$\sigma_a = B_{5/2}(x_a),\ x_a = (c/T)(-N_{aa}\sigma_a + \tfrac{3}{2} N_{ad}\sigma_d) ,$$
$$\sigma_d = B_{5/2}(x_d),\ x_d = (c/T)(N_{ad}\sigma_a - \tfrac{3}{2} N_{dd}\sigma_d) , \qquad (1)$$

where $B_{5/2}(x)$ is the Brillouin function, $c = 2(g\mu_B S)^2 N_A/k$, $g = 2$ and $S = \frac{5}{2}$ are the g factor and spin of the Fe^{3+} ion, N_A is the Avogadro number, T is the temperature, and σ_a, σ_d are reduced magnetizations of a and d sublattices, respectively. The best fit[8] to the experimental results in pure YIG is obtained with the following values of the molecular-field coefficients (in mol cm^{-3}):

$$N_{aa} = 65,\ N_{ad} = 97,\ N_{dd} = 30.4 . \qquad (2)$$

Expanding the Brillouin functions in powers of x_a, x_d, we find that the Curie temperature which corresponds to (1) is given by

$$T_c = \frac{7c}{30}\{-(N_{aa} + \tfrac{3}{2} N_{dd}) + [(N_{aa} + \tfrac{3}{2} N_{dd})^2 + 6(N_{ad} - N_{aa}N_{dd})]^{1/2}\} . \qquad (3)$$

The environment of the c site, on which Bi^{3+} or La^{3+} is located, is schematically shown in Fig. 1. It has two nearest (NN) and four slightly more distant second-nearest (NNN) d neighbors and there are four NN a sites. In accord with the superexchange theory we suppose that the presence of Bi will affect those $Fe^{3+}(a)$–O^{2-}–$Fe^{3+}(d)$ exchange paths for which O^{2-} is one of the eight Bi^{3+} ligands. Two modified exchange integrals J'_{ad} and J''_{ad} are then to be distinguished. They correspond to exchange between $Fe^{3+}(a)$ and those $Fe^{3+}(d)$ which are nearest (in what follows denoted d') and second-nearest neighbors of Bi^{3+} will be denoted a'.

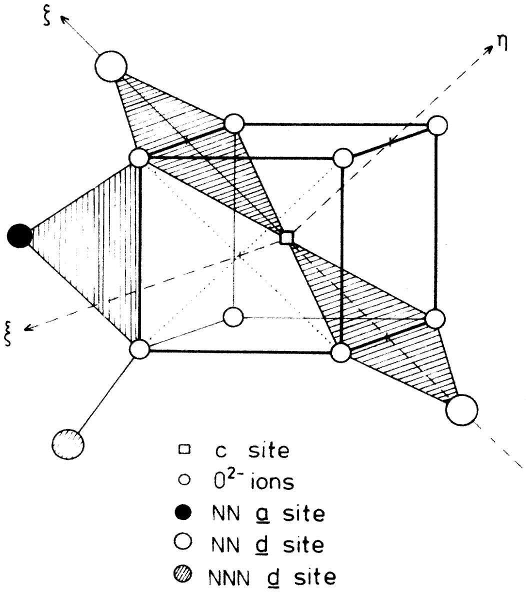

FIG. 1. Environment of the dodecahedral site in garnet. Only one NN a site and the NNN d site are shown. The remaining three may be obtained by C_2 rotations around axes ξ, η, ζ.

If we take into account that an a' site has four d neighbors, one d' neighbor and one d'' neighbor, a d' site has two a and two a' neighbors and a d'' site has three a and one a' neighbor, we may write the equations for reduced magnetizations of Fe^{3+} ions influenced by Bi^{3+}:

$$\begin{aligned}
&\sigma(a') \equiv \sigma'_a = B_{5/2}(x'_a) ,\\
&x'_a = \frac{c}{T}(-N_{aa}\sigma_a + N_{ad}\sigma_d + N'_{ad}\sigma'_d/4 + N''_{ad}\sigma''_d/4) ,\\
&\sigma(d') \equiv \sigma'_d = B_{5/2}(x'_d) ,\\
&x'_d = \frac{c}{T}(-N_{dd}\sigma_d + N_{ad}\sigma_a/2 + N'_{ad}\sigma'_a/2) ,\\
&\sigma(d'') \equiv \sigma''_d = B_{5/2}(x''_d) ,\\
&x''_d = \frac{c}{T}(-N_{dd}\sigma_d + 3N_{ad}\sigma_a/4 + N'_{ad}\sigma'_a/4) ,
\end{aligned} \qquad (4)$$

where N'_{ad}, N''_{ad} are the molecular field coefficients which correspond to J'_{ad} and J''_{ad} introduced above.

When deducing (4) we have neglected any modification of the intrasublattice exchange which might be connected with the Bi^{3+} presence. Equations (1) and (4) represent now a set of five coupled nonlinear equations from which the reduced magnetizations of sites a, d, a', d', and d'' may be obtained for any given temperature and molecular field coefficients. In this approximation, however, T_C is not influenced by Bi^{3+} presence. To obtain the change of T_C we insert into (3) an averaged molecular-field coefficient

$$\langle N_{ad}\rangle = N_{ad} + c_{\text{sub}}(N'_{ad} + N''_{ad} - 2N_{ad}) , \qquad (5)$$

where c_{sub} is the concentration of the substitution.

The samples used in our NMR experiments were compact polycrystalline garnets prepared by conventional ceramic technology and sintered at 1450 °C. The phase purity and homogeneity were checked by x rays.

NMR spectra were measured by the spin-echo technique using a phase-coherent spectrometer with averaging and complex Fourier transformation.[9] The final spectra were drawn by the envelope of the local spectra taken at various frequencies with a typical step of 50 kHz.

In pure YIG the NMR lines of ^{57}Fe are narrow with linewidth $\simeq 40$ kHz. To maintain good resolution also in substituted systems, it is necessary to keep the concentration of Bi or La low and excite the domain signal only. The nonobservance of the latter condition is the probable source of the loss of resolution in NMR spectra of the Bi:YIG system reported by Hosoe, Takanashi, Yasuoka, and Suzuki.[10]

In Fig. 2 the NMR spectra of $Y_{2.7}Bi_{0.3}Fe_5O_{12}$ and $Y_{2.7}La_{0.3}Fe_5O_{12}$ polycrystalline samples measured at 4.2 K are shown. The magnetization is parallel to the ⟨111⟩ direction and there is thus a single main line corresponding to Fe^{3+} ions in the d sublattice ($f_{\text{res}} \simeq 65$ MHz) and two main lines a_1 and a_2 of Fe^{3+} ions in the octahedral sublattice ($f_{\text{res}} \simeq 75$ and 76 MHz).

Symmetry predicts and our previous works[5,6] confirm

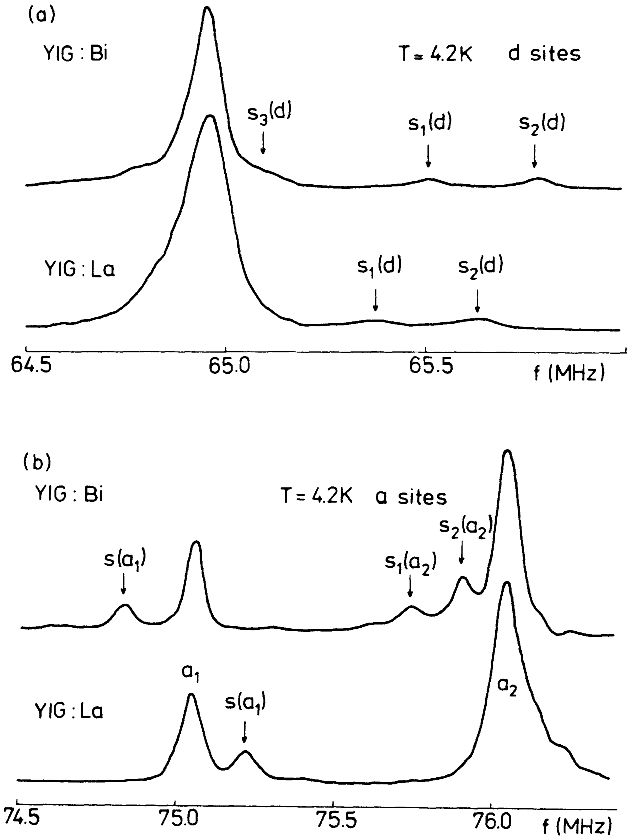

FIG. 2. NMR spectra of ^{57}Fe in $Y_{2.7}Bi_{0.3}Fe_5O_{12}$ and $Y_{2.7}La_{0.3}Fe_5O_{12}$ garnets at 4.2 K.

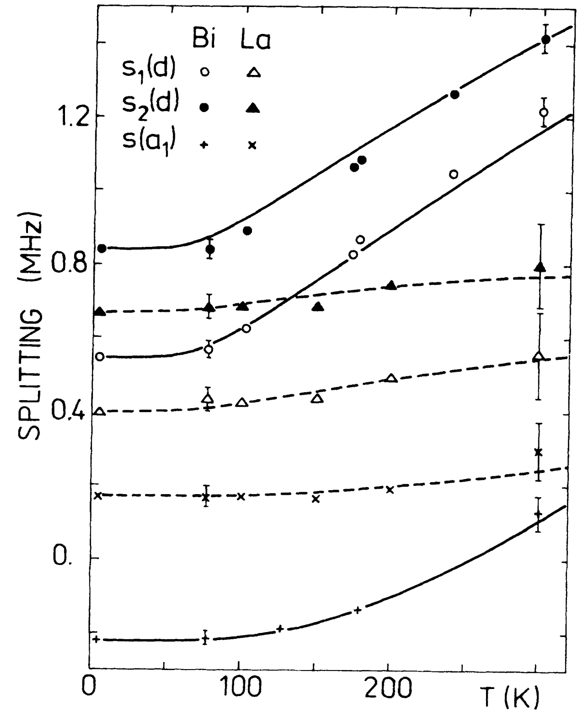

FIG. 3. Temperature dependence of the splittings between satellites and corresponding main lines. The lines (full for the Bi-, dashed for La-doped system) were calculated using (1) and (4) with the molecular-field coefficients given by (2) and (6).

that the *d* line has two satellites, corresponding to Fe^{3+} ions on d' sites. These satellites are resolved at all temperatures for both Bi- and La-substituted systems and we denote them $s_1(d)$ and $s_2(d)$ (Fig. 2). There should be four other satellites of the *d* line which arise from Fe^{3+} ions on d'' sites. These satellites are either unresolved or only partially resolved, however. Their splitting seems to be larger in the Bi system. In accord with symmetry the a_1 line has a single satellite $s(a_1)$ connected with Fe^{3+} ions on a' sites. $s(a_1)$ is clearly resolved in both systems studied. There should be three satellites of the a_2 line —these again are not well resolved, however.

Two remarks concerning evaluation of the NMR spectra are to be made. First, because the spectra are relatively narrow no frequency corrections are necessary. Second, in the systems studied we have found that the spin-spin relaxation time is different in different parts of the spectra, which influences the relative magnitudes of the spin-echo signal. In particular, the intensity of a satellite line is not given by the concentration of the substitution only, but it depends also on the corresponding relaxation time. For this reason we used only well-resolved satellites $s_1(d)$, $s_2(d)$, and $s(a_1)$ when studying the temperature dependence of f_{res}.

From the NMR spectra observed at several temperatures we have first calculated for each line the ratio $f_{\text{res}}(T)/f_{\text{res}}(4.2)$ which corresponds to the reduced magnetization of the Fe^{3+} ion on the site in question. Within our experimental accuracy the main lines exhibit the same temperature dependence as in pure YIG.[11] On the other hand, the temperature dependences of the satellite lines are slightly different. This is demonstrated in Fig. 3 where the temperature dependence of the splittings for $s_1(d)$, $s_2(d)$, and $s(a_1)$ satellites are shown.

From Fig. 3 several conclusions may be deduced immediately. The character of Bi and La influence is similar—in both systems all the splittings are increasing functions of temperature i.e., the reduced magnetizations for the affected Fe^{3+} ions decrease more slowly with increasing temperature. The effect is, however, much more pronounced for the Bi^{3+} substitution. Taking the relative magnitudes of the Bi^{3+} and La^{3+} ionic radii into account, we may conclude therefore that it is the change of electronic structure and not the local deformation which enhances the exchange interaction. In Fig. 3 the temperature dependences of the splittings calculated from (1) and (4) are also shown. A good fit to our experimental data is obtained with

$$N'_{ad} = 1.045(5)N_{ad}, \quad N''_{ad} = 1.016(7)N_{ad} \,, \tag{6a}$$

for Bi:YIG and

$$N'_{ad} = 1.013(7)N_{ad}, \quad N''_{ad} = 1.005(3)N_{ad} \,, \tag{6b}$$

for the La:YIG system. The value of N_{ad} is given by (2).

With such an enhancement of the exchange interactions we may now calculate the change of T_C using (3) and (5).

The result for the Bi:YIG system is $\Delta T_C = 7.7(10)$ K, which is somewhat less than $\Delta T_C \simeq 10$ K obtained from direct measurements of the $M(T)$ dependence.[1] The agreement is nevertheless satisfactory if the roughness of our theoretical model is taken into account.

The temperature dependence of not fully resolved satellite lines is also in qualitative agreement with the above outlined theory. In particular, the resonance frequency of the satellite $s_3(d)$ (Fig. 2) in the Bi:YIG system is found to decrease with temperature more slowly than that of the main line, indicating thus directly that $\mathrm{Fe}^{3+}(d'')$-$\mathrm{Fe}^{3+}(a')$ exchange interaction is also enhanced.

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