photons was found to be $\sim 5\times 10^{17}$ cm^{-3} sec^{-1}. The efficiency of the three-photon process is therefore $\sim 10^{-10}$. The half-life of the fluorescence was obtained from a semilogarithmic plot of fluorescent intensity against time, and it was found to be 83 nsec,[6] which is in very good agreement with the previously measured lifetime of naphthalene fluorescence.[6,7]

Within the limits of the sensitivity of the experimental arrangement used, no phosphorescence or delayed fluorescence was detected.

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NUCLEAR MAGNETIC RESONANCES OF ^{69}Ga AND ^{71}Ga IN GALLIUM-SUBSTITUTED YTTRIUM IRON GARNET*

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We have observed the nuclear magnetic resonances of ^{69}Ga and ^{71}Ga in the mixed garnet system $3Y_2O_3\cdot(5-x)Fe_2O_3\cdot xGa_2O_3$. At 77°K the resonances have been observed over a concentration range from $x=0.25$ to $x=2.6$ and at room temperature over a smaller concentration range. At 77°K the resonance frequency for ^{71}Ga extrapolated to $x=0$ is about 25 Mc/sec in zero applied field. The frequency increases with increasing x and reaches a maximum of 30.0 Mc/sec at about $x=1.5$. This corresponds to a hyperfine field of about 2.3 tesla (23 kilogauss). The resonance is believed to be from nuclei of ions on the tetrahedral (d) sites. The hyperfine field is believed to arise from an unpaired spin density at the gallium site which is coupled strongly to neighboring iron ions. Gallium ions on d sites can have neighboring iron ions on both octahedral (a) and tetrahedral (d) sites. The resonance is particularly interesting because the concentration dependence allows us to separate out the sign and magnitude of the contribution to the field from iron ions on these sites. At 77°K we have also estimated that the sample is no longer ferromagnetic at a concentration of about $x=2.8$.

The samples used in this work consisted of about 10 grams of the polycrystalline powders prepared by the usual ceramic method. The sintering and grinding process was repeated several times to insure good homogeneity. The resonances were studied using the spin-echo method and the line shapes were obtained by measuring the spin-echo amplitude as a function of frequency across the inhomogeneously broadened lines. The exciting rf pulses were left at their minimum width of about 1 μsec, while the rf pulse level was adjusted at each frequency to a maximum echo signal. In all cases except when an external field was applied, the echo maximum occurred at a very low rf level (only a few volts), so that the signals were from nuclei in domain walls where the rf levels are enhanced. The line shape obtained for the 5% sample ($x=0.25$) at 77°K is shown in Fig. 1.

The transient signal[1] observed in a spin-echo experiment is proportional to the macroscopic moment M. Since this is proportional to the microscopic moment μ times the polarization $\mu H/kt$, we expect the ratio of the ^{69}Ga and ^{71}Ga amplitudes to go as μ^2 times the relative abundance. Consequently, the intensity of the ^{69}Ga resonance will be 0.95 times that of the ^{71}Ga resonance, which is approximately what we observed.

At low gallium concentration, magnetization measurements[2,3] and also nuclear resonance studies[4] of the ^{57}Fe resonance in these samples indicate that gallium substitutes preferentially onto the d site, and for $x<1$ most of the gallium ions are on d sites. Therefore, the resonances are from gallium nuclei on these sites.

We have observed the resonances in concentra-

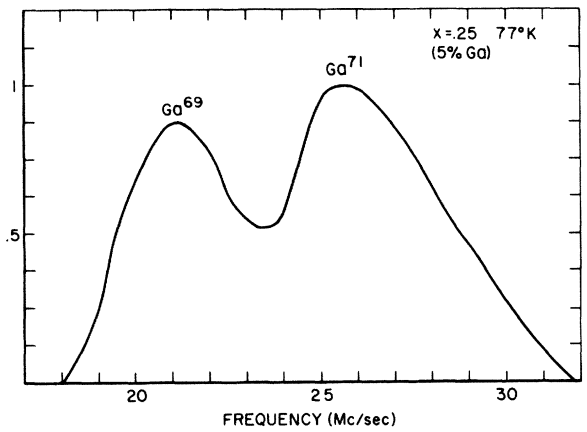

FIG. 1. Spin-echo amplitude uncorrected for the factor $\mu^2 H$ (see text), plotted as a function of frequency.

tions up to 52% substitution at 77°K. The lines broaden with concentration, and at 46% substitution each resonance is about 7 Mc/sec. The line shapes are similar to those shown in Fig. 1 but broader and somewhat asymmetric. Below 46% the ^{69}Ga and ^{71}Ga resonances were well enough resolved that we could separate out contributions from each.

In Fig. 2 we have plotted the ^{71}Ga resonance frequency as a function of concentration at 77°K and room temperature. The frequency was obtained by separating out contributions from ^{69}Ga and ^{71}Ga resonances and then dividing each curve by the frequency to correct for the increased signal due to the higher polarization at higher fields. The latter correction is more important on the wider lines. The center of gravity of the corrected curve is then taken to be the resonance frequency. We have observed the resonances in samples up to 52% substitution. However, above 46% the studies are not complete, as the resonance lines become very broad and thus difficult to resolve. At room temperature, although the linewidths are somewhat narrower, the signals are weaker and studies were made up to only 25% substitution.

We can explain the results at least phenomenologically as follows. The magnetic fields acting on the nuclei may be written

$$H = H_0 + H_D + H_d + H_L + H_n. \quad (1)$$

Here H_0 is the applied field, H_D is the demagnetizing field, H_d is the local dipolar field, H_L is the Lorentz field, and H_n is the hyperfine field. In zero applied fields, H_0 is zero and H_D is essentially zero. The Lorentz field H_L is about 0.08 T (800 gauss) in pure YIG. The local dipolar fields have been calculated by Boutron and

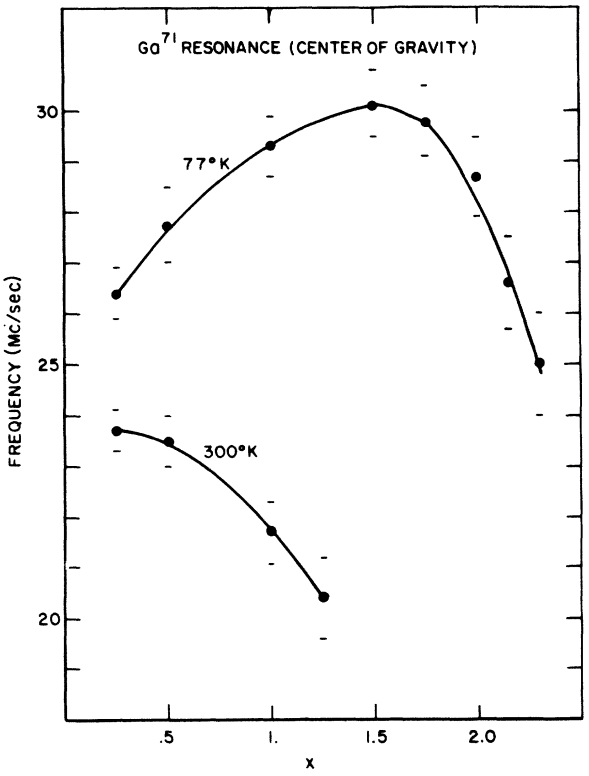

FIG. 2. ^{71}Ga resonance frequency plotted as a function of concentration. ($x = 1$ corresponds to a gallium substitution of 20%.)

Robert.[5] At the d sites the dipolar fields along the direction of the magnetization have contributions from iron moments on a and d lattices, and these very nearly cancel out in pure YIG at the d site. As the gallium concentration increases, dipolar fields result at the d site, but we estimate that the dipolar broadening is never more than about 0.1 T (1000 gauss). Pseudodipolar fields associated with an anisotropy in H_n may be larger. These dipolar fields will broaden the line for polycrystalline samples, and in cases of strong magnetic anisotropy lead to asymmetric line shapes, but should not greatly affect the center of gravity of the line. Consequently, the main contribution to H must be the hyperfine field, H_n. In addition, we have the quadrupole interaction, but this also is a broadening mechanism. The electric field gradient at the d site in pure YIG has been calculated by Nicholson and Burns.[6] Assuming that the quadrupole field at the d site for low gallium concentration is the same as in pure YIG, the ^{69}Ga first-order quadrupole splitting would be about 3.6 Mc/sec and somewhat less for ^{71}Ga.

We will assume that the hyperfine field at the gallium site is due mainly to an overlap of a p electron on the oxygen ion into an s state on the

gallium. We expect this electron to be polarized by exchange interactions with neighboring iron ions. Consequently, we have tried to fit the experimental data to an expression of the form

$$H = A(\sigma_a f_a + \gamma \sigma_d f_d). \quad (2)$$

Here σ_a is the average moment per iron atom for irons on a sites, and similarly for σ_d (σ_a and σ_d are always positive quantities), f_a is the fractional number of iron atoms on a sites relative to pure YIG and similarly for f_d. A and γ are constants. σ_a and σ_d are functions of concentration as well as temperature. Using the ^{57}Fe nuclear resonance data together with net magnetization results, we have been able to obtain values of the σ and f at low concentrations (for less than $x = 1$) and reasonably good estimates at higher concentrations. Using these values, we can fit the Ga hyperfine field data quite well, at least at 77°K, if we take γ to be about -0.5.

Qualitatively, what is happening is that both contributions decrease with increasing gallium substitution, but σ_a and σ_d at low temperatures and low concentrations do not change too rapidly, and the more rapid decrease in f_d causes the rise in H_n. At higher concentrations an appreciable number of gallium ions enter on a sites as well as d sites, and σ_a begins to decrease quite rapidly. H reaches a maximum and then begins to decrease as the two contributions to H approach zero quite rapidly. From an extrapolation of the 77°K curve in Fig. 2, we estimate that at around $x = 2.8$ the sample is no longer ferromagnetic. At higher temperatures σ_a and σ_d decrease more rapidly with concentration. Since the decrease in σ_a is faster, the initial rise in H is suppressed.

We have applied an external magnetic field using the 35% sample at 77°K. A sufficiently high rf level was used so that nuclei in domains were being observed. We found that the resonance frequency of ^{71}Ga increases with a slope corresponding to about 1.3 Mc/sec for a 0.1-T field, as would be expected if there were no shielding. Since for concentrations above about 25% (at low temperatures) the net magnetization is along the a sublattice magnetization,[4] the constant A in Eq. (2) is positive; that is, the direction of the hyperfine field is in the same direction as the a sublattice magnetization. In the 20% sample, the frequency decreased with approximately the same slope, since at this concentration the net magnetization is along the d sublattice magnetization.

The assumption that the hyperfine field is due to admixture of an electron into an s state on the gallium is consistent with the usual picture of superexchange.[7] Consider the a-d interaction which is the dominant one. Using the usual superexchange argument, this electron would be expected to be aligned along the direction of the iron spin on the a site and would consequently give a hyperfine field along this direction. Iron spins on d sites being oppositely aligned would give an opposite contribution.

Details of the ^{57}Fe resonance studies in these samples, as well as more details of the gallium resonance, will be given at a later time.

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[1]The actual emf induced in the receiving coil is proportional to ωM; however, we calibrate the equipment by means of a standard signal generator inductively coupled to the receiving coil, and this signal is also proportional to ω. Hence, the additional factor of ω cancels.

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