NMR investigation of $Gd_xY_{1-x}Fe_2$ compounds

V. A. Vasil'kovskiĭ, N. M. Kovtun, A. K. Kuprianov, S. A. Nikitin, and V. F. Ostrovskiĭ

Donets Physico-technical Institute, Ukrainian Academy of Sciences
Moscow State University
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The NMR spectra for gadolinium and yttrium nuclei in $Gd_xY_{1-x}Fe_2$ compounds are measured at 77 °K. The contributions of the nearest neighbors of the gadolinium atom sublattice to the hyperfine fields at the gadolinium and yttrium nuclei are estimated. It is shown that the iron atom sublattice yields the greatest contribution to the hyperfine fields at the yttrium and gadolinium nuclei.

We determined the nuclear magnetic resonance (NMR) spectra of the Gd^{155}, Gd^{157}, and Y^{89} nuclei in $Gd_xY_{1-x}Fe_2$ compounds forming a cubic Laves phase (C15 structure). The magnetic order in $Gd_xY_{1-x}Fe_2$ is ferrimagnetic, i.e., these compounds are uncompensated antiferromagnets in which the gadolinium and iron atoms form two sublattices with opposite directions of the magnetization. The atomic magnetic moment of gadolinium is 7.0 μ_B, whereas the atomic moment of iron atoms ranges from 1.44 μ_B for YFe_2 to 1.68 μ_B for $GdFe_2$.[1-3] Our investigation was carried out using a spin-echo spectrometer at 77°K. The first and second pulses were of 2 μsec duration and the delay between them was ~60 μsec. The repetition frequency was 100 Hz.

Polycrystalline samples were prepared in an arc furnace on a water-cooled copper base in the laboratory of O. P. Elyutin at the Central Scientific-Research Institute of Ferrous Metallurgy in Moscow. These samples were ground to a powder in an agate mortar under a layer of liquid paraffin in order to prevent oxidation by atmospheric oxygen.

In the case of $GdFe_2$ we obtained two NMR lines at 51.1 ± 0.1 and 73.5 ± 0.1 MHz frequencies; the widths of these lines were 0.6 ± 0.2 and 0.9 ± 0.2 MHz, respectively. The ratio of the frequencies was close to the ratio of the nuclear magnetic moments of Gd^{155} and Gd^{157} so that we concluded that the NMR signals were due to the Gd^{155} and Gd^{157} nuclei. The NMR lines of $Gd_{0.95}Y_{0.05}Fe_2$ and $Gd_{0.9}Y_{0.1}Fe_2$ were broader than those of $GdFe_2$ and we also observed a signal separated from the main one by 0.1 ± 0.2 MHz in the case of Gd^{157}. Further replacement of gadolinium with the nonmagnetic yttrium ions resulted in even stronger inhomogeneous broadening of the NMR line of gadolinium but other satellites were not resolved. Moreover, an additional peak appeared on the low-frequency side of this line and the intensity of this peak increased with increasing yttrium content so that we attributed it to the NMR of Y^{89}.

The compound YFe_2 had a narrow line at 45.3 ± 0.1 MHz; its width was 0.6 ± 0.1 MHz. When the amount of gadolinium in the $Gd_xY_{1-x}Fe_2$ system was increased, the yttrium signal broadened but we could still resolve five satellites separated from one another by 2.2 ± 0.2 MHz..

The shifts of the centers of gravity of the Gd^{157} and Y^{89} spectra are plotted in Fig. 1 as a function of the concentration of gadolinium. We can see that in the case of yttrium the shift is directly proportional to the gadolinium content, with the exception of the gadolinium-rich compositions; the corresponding dependence for gadolinium is strongly nonlinear.

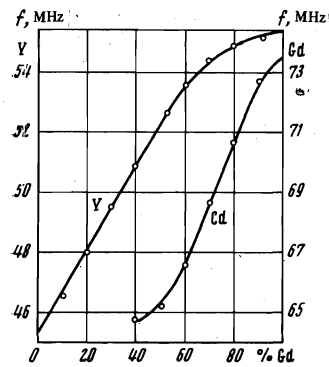

FIG. 1

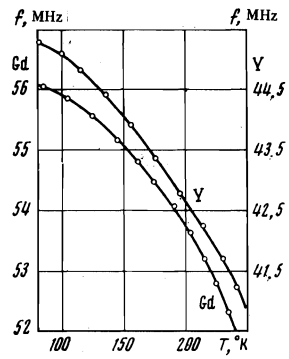

FIG. 2

FIG. 1. Dependence of the position of the centers of gravity of the NMR spectra of gadolinium and yttrium on the concentration of gadolinium (in at.%).

FIG. 2. Temperature dependences of the NMR frequency of Gd^{155} in $GdFe_2$ and of Y^{89} in YFe_2.

Figure 2 shows the temperature dependences of the frequencies of the NMR lines of Y^{89} in YFe_2 and Gd^{155} in $GdFe_2$. The NMR signals disappeared in a background of noise at temperatures of the order of 270°K.

The observed inhomogeneous broadening of the NMR lines of Gd^{155}, Gd^{157}, and Y^{89} resulting from the replacement of gadolinium with the nonmagnetic yttrium ions can be explained satisfactorily by changes in the local environment of the ions in the rare-earth sublattice. The influence of iron atoms can be ignored because the iron sublattice is practically unaffected (the magnetic moment per iron ion remains constant for all concentrations of gadolinium or at least in the range $0.2 \leq x \leq 0.8$).

We may thus assume that the changes in the hyperfine fields at the gadolinium and yttrium nuclei, resulting from the replacement of gadolinium with yttrium in the $Gd_xY_{1-x}Fe_2$ system are due to the four nearest gadolinium atoms. If a pseudobinary compound $Gd_xY_{1-x}Fe_2$ does not exhibit a superstructure, the dilution of the rare-earth sublattice with yttrium may result in equiprobable replacement of any one of the four gadolinium atoms. The probabilities of obtaining various configurations of the nearest neighbors on replacement of gadolinium are listed in Table I. A comparison of the results given in Table I with the observed NMR spectra of Y^{89} demonstrates that the calculations are in satisfactory agreement with the experimental

TABLE I. Probability of replacement of nearest Gd atoms with Y atom

Composition	Number of Y atoms				
	0	1	2	3	4
$Gd_{0.95}Y_{0.05}Fe_2$	0.820	0.170	0.011		
$Gd_{0.9}Y_{0.1}Fe_2$	0.660	0.290	0.049	0.002	
$Gd_{0.8}Y_{0.2}Fe_2$	0.410	0.410	0.153	0.025	0.002
$Gd_{0.7}Y_{0.3}Fe_2$	0.240	0.400	0.256	0.077	0.008
$Gd_{0.6}Y_{0.4}Fe_2$	0.129	0.346	0.345	0.153	0.026
$Gd_{0.50}Y_{0.50}Fe_2$	0.063	0.252	0.377	0.252	0.063
$Gd_{0.43}Y_{0.57}Fe_2$	0.035	0.182	0.357	0.318	0.105
$Gd_{0.2}Y_{0.8}Fe_2$	0.002	0.025	0.153	0.410	0.410
$Gd_{0.1}Y_{0.9}Fe_2$		0.003	0.048	0.290	0.660

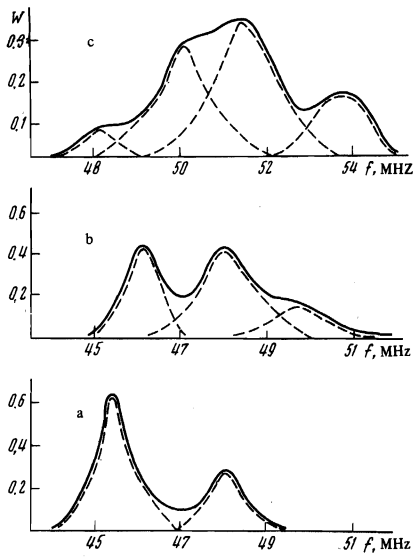

FIG. 3. Comparison of the NMR spectra of Y^{89} of samples of various compositions (a–$Gd_{0.1}Y_{0.9}Fe_2$, b–$Gd_{0.2}Y_{0.8}Fe_2$, c–$Gd_{0.43}Y_{0.57}Fe_2$) with the calculated values of the satellite amplitudes listed in Table I; W is the relative amplitude.

results (Fig. 3), provided we assume that the widths of the lines of the neighboring satellite differ by about 20%. Preliminary measurements of the transverse relaxation times T_2 have demonstrated that this assumption is correct but the difference between the values of T_2 lie within the limits of the experimental error.

Since the neighboring satellites in the NMR spectrum of Y^{89} are separated by 2.2 ± 0.2 MHz, the contribution of one gadolinium ion to the hyperfine field at the Y^{89} nuclei is 11 ± 1 kOe. The total contribution of the gadolinium sublattice to the hyperfine field at the Y^{89} nuclei, deduced from the differences between the frequencies of the outer satellites, is 45 ± 4 kOe. The hyperfine fields at the nuclei of the nonmagnetic ions in gadolinium compounds may be due to different radial variation of the 5p and 5s functions for different directions of spins in the gadolinium ions so that the overlap of these functions with those of the nonmagnetic ion need not be constant. Freeman and Watson[4] used these ideas to estimate the hyperfine field at the iron nuclei in $GdFe_2$ and obtained 7.2 kOe, which is close to the value deduced in the present investigation. However, the metallic nature of the binding between the gadolinium and yttrium ions and a comparison with the results reported in[5] and [6] suggest that in the case of $Gd_xY_{1-x}Fe_2$ the induced hyperfine field at the Y^{89} nuclei includes a contribution associated with the polarization of the conduction electrons. The degree of this polarization can be estimated from a formula which is well known in the theory of indirect exchange:[7]

$$\rho^{\pm} = \frac{N_s}{2V} \mp \frac{9\pi N_s}{2N} \frac{A_{sf}}{E_f} \frac{N_s}{V} \sum_n F(2k_f R_n) S_n^z.$$

Here, N_S is the number of conduction electrons; E_f is the Fermi energy; A_{sf} is the exchange integral; V is the volume of the metal under investigation; $F(2k_fR_n)$ is the Ruderman-Kittel function. Since the hyperfine field produced by the polarization of the conduction electrons is $H_{hf} = (1/2)Ag_n\mu_n\Delta\rho$ and $\Sigma_n F(2k_fR_n)$ is negative, we may conclude that the exchange integral A_{sf} is positive for yttrium and gadolinium.

The iron sublattice produces a hyperfine field of 220 ± 5 kOe at the yttrium nuclei and this field is due to the direct overlap of the wave functions of the 3d electrons with the wave functions of the yttrium ion. If we take account only of the nearest neighbors, the contribution of each of the iron atoms is ~19 kOe, i.e., it is almost twice as large as the contribution of a gadolinium ion. In view of the fact that an increase in the concentration of gadolinium reveals yttrium satellites at higher frequencies, we may conclude that the hyperfine fields produced at the yttrium nuclei by the iron and gadolinium sublattices have the same direction.

A comparison of the experimental results with those given in Table I demonstrates that the agreement for gadolinium ions is not very satisfactory. The interpretation of the spectra of these ions is extremely difficult because even a 20% dilution with yttrium superimposes a high-frequency NMR satellite of Y^{89} on the signal of Gd^{155} and this satellite is comparable with the gadolinium signal. The spectra of Gd^{157} differ considerably in amplitude from the calculated values in Table I. It is probable that this is due to the different gains of the individual NMR satellites.[8]

As mentioned earlier, the allowed Gd^{157} satellites are separated by 3.0 ± 0.2 MHz, i.e., each gadolinium ion produces a hyperfine field of 20 ± 2 kOe at the nucleus of another gadolinium ion. Assuming that, as in the case of yttrium, gadolinium can occupy five different types of site, we can determine the contribution of the nearest Gd neighbors (80 ± 10 kOe) to the hyperfine field at the gadolinium nuclei and the total field (460 ± 6 kOe) at the Gd^{157} nuclei. According to Freeman and Frankel,[9] the hyperfine field at the gadolinium nuclei in $GdFe_2$ has the same direction as the magnetic moment of the atoms because the polarization of the valence electrons makes a contribution H_{hf}^{val} = 800 kOe. The hyperfine field at the gadolinium nuclei can be represented in the form

$$H_{hf} = H_{core} + H_n^{Gd} + H_i,$$

where H_n^{Gd} is the field generated by the nearest neighbors of gadolinium; H_i is the field induced at the gadolinium nuclei as a result of the polarization of the conduction electrons by the magnetic moment of the iron atoms and the intrinsic spin of the gadolinium atoms. It follows from the above expression for the hyperfine field that H_i = 720 kOe. The hyperfine field induced by the intrinsic magnetic moment of the atom should not exceed 200 kOe, as estimated by Dintelmann, Dormann, and Buschow.[6] This means that the iron atoms make a considerable contribution to the hyperfine field.

It follows from our investigation that the dependences of the NMR signals of Gd^{155}, Gd^{157}, and Y^{89} on the composition and temperature are governed by the iron and gadolinium sublattices.

[1]K. H. J. Buschow and R. P. van Stapele, J. Appl. Phys. 41, 4066 (1970).
[2]E. Burzo, Z. Angew. Phys. 32, 127 (1971).
[3]K. P. Belov, S. A. Nikitin, A. M. Bisliev, E. M. Savitskiĭ, V. F. Terekhova, and V. E. Kolesnichenko, Zh. Eksp. Teor. Fiz. 64, 2154 (1973) [Sov. Phys.-JETP 37, No. 6 (1973)].
[4]A. J. Freeman and R. E. Watson, in: Sverkhtonkie vzaimodeĭstviya v tverdykh telakh (Hyperfine Interactions in Solids), Mir, M., 1970, p. 97.
[5]R. E. Gegenwarth, J. I. Budnick, S. Skalski, and J. H. Wernick, Phys. Rev. Lett. 18, 9 (1967).
[6]F. Dintelmann, D. Dormann, and K. H. J. Buschow, Solid State Commun. 8, 1911 (1970).
[7]S. V. Vonsovskiĭ, Magnetizm (Magnetism), Nauka, M., 1971.
[8]M. B. Stearns and J. F. Ullrich, Phys. Rev. B, 4, 3825 (1971).
[9]A. J. Freeman and R. B. Frankel, Hyperfine Interactions, Academic Press, New York, 1967, p. 725.

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