Nuclear magnetic resonance in $Gd_xY_{1-x}Fe_3$ compounds

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The spin-echo method was used to measure the hyperfine fields at the Gd, Y, and Fe nuclei in $Gd_xY_{1-x}Fe_3$. The hyperfine fields were different for atoms of the same kind at inequivalent positions. This difference was attributed to oscillations of the collective-state electrons.

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One of the special features of intermetallic compounds of rare earths and iron is the depression of the Curie temperature with increasing molar content of iron, which is sometimes attributed to a change in the degree of delocalization of the 3d electrons of Fe atoms.[1] The same electrons are responsible for the induced hyperfine fields at the nuclei of rare-earth metals in RFe_2 compounds[2] so that it is natural to assume a correlation between the hyperfine fields at the rare-earth metal nuclei and the exchange interaction in all RFe_2 compounds.

This assumption was checked by investigating the nuclear magnetic resonance (NMR) spectra of all types of nuclei in the $Gd_xY_{1-x}Fe_3$ system, which had the crystal structure of the $PuNi_3$ type and in which gadolinium and yttrium were located at two inequivalent positions in the lattice, whereas iron occupied three such positions.[3] Figure 1 shows the nearest neighbors of GdI and GdII atoms (Fig. 1a) and of FeI, FeII, and FeIII atoms (Fig. 1b); it is clear that, in the case of GdI, the point symmetry is 6/mmm, whereas, in the case of GdII, it is 3/m and, in the case of iron, it is $\bar{3}$m, 3m, and m, respectively. The compounds of this system are ferrimagnetic with gadolinium and iron atoms forming two sublattices with antiparallel directions of the magnetization. Neutron-diffraction investigations of $HoFe_3$ demonstrated[4] that the magnetic moments of iron varied quite considerably with the crystallographic position.

The NMR spectra of Gd^{155}, Gd^{157}, Y^{89}, and Fe^{57} were recorded by the spin-echo spectrometer method. The duration of the first and second pulses τ_1 and τ_2 ($\tau_1 = \tau_2$), the delay between them, and the repetition frequency were varied within a wide range so as to maximize the spin echo signal. The NMR signal was recorded in the temperature range from 4.2 to 300°K. The samples were prepared by a method described earlier.[5] Metallographic and x-ray diffraction analyses and the NMR spectra themselves showed that some samples contained a small amount of a second phase of RFe_2 or R_6Fe_{23} composition. Repeated measurements on several samples of the same composition, subjected to various heat treatments, enabled us to identify the RFe_3 structure lines.

The compound $GdFe_3$ exhibited four resonance lines of the gadolinium sublattice at frequencies of 54.6, 64.9, 70.3, and 81.8 MHz. Bearing in mind the ratio of the nuclear magnetic moments of the gadolinium isotopes, we attributed the 54.6 and 64.9 MHz lines to the two inequivalent positions of Gd^{155} and the 70.3 and 81.8 MHz lines to the inequivalent positions of Gd^{157}. An analysis of the composition dependences of each of these lines enabled us to attribute the 54.6 and 70.3 MHz frequencies to the crystallographic sites which were analogous (in respect of asymmetry) to the Gd atomic sites in $GdFe_2$ (in four nearest neighbors of Gd), whereas the frequencies 64.9 and 81.8 MHz were attributed to crystallographic sites with the hexagonal local symmetry (two nearest neighbors of Gd).

Thus, in the case of one gadolinium isotope (Gd^{157}) the hyperfine fields were 495 ± 5 and 425 ± 5 kOe, respectively, with the higher value of the field corresponding to the hexagonal symmetry of the local environment (site of type I) and the lower to the cubic environment, similar to a Laves phase (site of type II).

The replacement of gadolinium with nonmagnetic yttrium ions resulted in the broadening of the GdI and GdII NMR lines and distortion of their profiles; the NMR spectrum of GdII exhibited four resolved satellites separated, on the average, by 3.8 ± 0.2 MHz, whereas the GdI lines remained unresolved and decreased gradually in amplitude. The change in the profile of the GdII NMR line and the appearance of satellites with decreasing x in $Gd_xY_{1-x}Fe_3$ can be explained bearing in mind that yttrium atoms are equally likely to replace any one of the four nearest neighbors of Gd. The relative proportion of a given configuration can easily be calculated from the well-known binomial distribution formula:

$$W(x)=\frac{m!}{n!\,(m-n)!}\,(1-x)^m x^n. \tag{1}$$

If we know the frequency separation between the satellites (3.8 MHz), we can show that each gadolinium atom creates a hyperfine field 25 ± 2 kOe at the nucleus of another gadolinium ion and the total contribution of the whole gadolinium sublattice, found from the frequency separation between the outermost satellites, is 75 ± 8 kOe.

The contribution of iron atoms to the hyperfine field can be determined by representing this field at a gadolinium nucleus in the form

$$H_{\rm hf}=H_{\rm cp}+H^{\rm Gd}_{\rm nn}+H_{\rm ind} \tag{2}$$

where $H_{\rm cp}$ is the field due to the exchange polarization of the atomic core, $H^{\rm Gd}_{\rm nn}$ is the field created by the near-

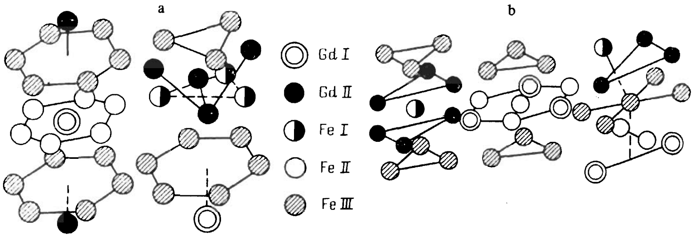

FIG. 1. Nearest-neighbor environments of atoms in $Gd_xY_{1-x}Fe_3$.

est neighbors of gadolinium, and H_{ind} is the field induced at a gadolinium nucleus by the polarization of delocalized electrons produced by the magnetic moment of the iron atoms and by the intrinsic spin of the gadolinium atom. Simple calculations, similar to those in [6], show that, in the $Gd_xY_{1-x}Fe_3$ system, the hyperfine field at the GdII nuclei created by the iron sublattice is 480 kOe, which is approximately 9% smaller than the hyperfine field in $GdFe_2$.

The compound YFe_3 exhibited two resonance lines at 38.4 and 48.2 MHz, corresponding to the NMR of the YI and YII nuclei, i.e., the situation was the reverse of that found for $GdFe_3$: the higher frequency was associated with the yttrium nuclei which had a cubic local symmetry. When the gadolinium content was increased, the 48.2 MHz line became homogeneously broadened and it was possible to distinguish four satellites separated, on the average, by 1.6 ± 0.2 MHz, which was somewhat less than in $Gd_xY_{1-x}Fe_2$.[6] The YI NMR line at 38.4 MHz was not split (like the GdI NMR line) but simply broadened, and its center of gravity shifted slightly in the direction of higher frequencies. The nature of the change in the position of the center of gravity of the NMR spectra with the degree of substitution at both gadolinium sublattice sites is illustrated in Fig. 2, which shows that the NMR spectra of YI and YII exhibit somewhat different but nearly linear composition dependences, whereas, in the case of GdI and GdII, the corresponding dependences are strongly nonlinear.

The use of a stroboscopic integrator made it possible to determine the temperature dependence of the NMR frequency in the range 4.2–300°K (Fig. 3). It is clear from Fig. 3 that the Y and Gd atoms at different crystallographic sites exhibit different temperature dependences of the NMR frequency. The amplitude of the NMR signal decreases with rising T and, at about 300°K, the signal is lost in the background noise.

A detailed investigation of the NMR spectra of Y and Gd reveals that only four satellites are observed for YII and GdII, whereas five would be expected on the basis of the nearest-neighbor environment and the YI and GdI lines are not split at all. This is probably due to the fact that the hyperfine interaction of the Gd atoms with one another is anisotropic so that there is no coupling between the GdI(YI) and GdII atoms along the c axis of the rhombohedral lattice of the $Gd_xY_{1-x}Fe_3$ system. We shall call the nearest neighbors that do not produce any field at the nucleus of the central atom the "0 (null) neighbors." An analysis of the local symmetry of sites of the first and second kinds shows that, in the case of GdI(YI), both nearest neighbors of the rare-earth atom are of the null kind, whereas, in the case of GdII, there is only one null neighbor, i.e., the observed spectra are in good agreement with the proposed model.

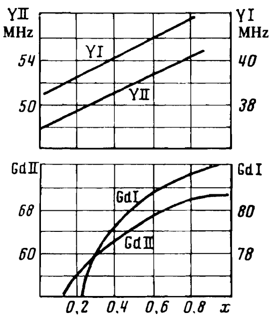

FIG. 2

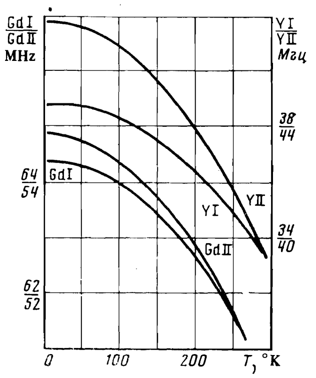

FIG. 3

FIG. 2. Dependences of the positions of the center of gravity of gravity of the Y^{89} and Gd^{157} NMR lines on the Gd concentration.

FIG. 3. Temperature dependences of the NMR frequencies of Gd^{155} and Y^{89} in $GdFe_3$ and YFe_3.

However, such partial "exclusion" of the gadolinium sublattice atoms from the participation in the hyperfine field at the Gd nuclei cannot be explained by a reduction in the influence of the rare-earth sublattice on transition from RFe_2 to RFe_3. For example, the contribution of this sublattice to the hyperfine field at the YII nuclei in $Gd_xY_{1-x}Fe_3$ is only 23 ± 5 kOe, which is about half the corresponding contribution in the case of $Gd_xY_{1-x}Fe_2$. If we bear in mind that the exchange interaction inside the Gd sublattice is due to the RKKY interaction,[7] the observed reduction in the contribution to the hyperfine field at the Y nuclei due to the gadolinium sublattice should be attributed to the change in the period of the RKKY oscillations because of a change in the carrier density and the Fermi wave vector k_F.

The nonlinear composition dependence of the NMR of Gd (Fig. 2) is due to a reduction in the mean free path of electrons because of the scattering by nonmagnetic yttrium ions. Clearly, the same factor is responsible for the difference between the temperature dependences of the hyperfine fields at the Gd and Y nuclei at inequivalent crystallographic sites, but an analysis of $H_{hf}(T)$ requires the application of a concrete interaction model.

In addition to the NMR spectra of Y and Gd in the $Gd_xY_{1-x}Fe_3$ system, we also recorded the NMR lines of Fe^{57} throughout the substitution range. The shape of the signals obtained from some samples is shown in Fig. 4. It is clear from this figure that, in the case of $GdFe_3$, there are three signals at 31.5, 35.3, and 38.0 MHz, and, when gadolinium is replaced with nonmagnetic yttrium ions, the first two signals approach each other. In the case of $Gd_{0.5}Y_{0.5}Fe_3$, these signals merge, forming a single line at 32.6 ± 0.2 MHz, which decreases in width and, in the case of YFe_3, becomes a narrow line at 31.7 MHz (the width of this line is 0.6 ± 0.1 MHz). The transition from $GdFe_3$ to YFe_3 shifts the 38.0 MHz signal toward lower frequencies to 34.7 MHz. However, according to measurements on several samples of YFe_3, the relative amplitude of this signal does not remain constant from one sample to another, which suggests the presence of an impurity. A comparison of the corresponding hyperfine field (258 ± 5 kOe) with the Mössbauer data for Y_6Fe_{23} and Y_2Fe_{17} [8] shows that this field is of the same order as the hyperfine field at the FeIII site in the Y_6Fe_{23} structure. The 34.7 MHz signal is exhibited by all the YFe_3 samples prepared from different melts. A comparison of the average magnetic moment in YFe_3 with the average hyperfine field of this compound shows that, if the ratio H_{hf}/μ_{at} is constant, this compound should exhibit a second NMR signal at ~35 MHz.

As pointed out in [9], the occurrence of several Fe^{57} NMR signals is evidence of the inequivalence of the positions of iron atoms in the crystal lattice of $Gd_xY_{1-x}Fe_3$. In contrast to RFe_2, this inequivalence is not due to the differences between the dipole and quadrupole contributions to the hyperfine field but it is due to the fact that the magnetic moments of the iron atoms vary with the crystallographic site. Neutron-diffraction investigations of $HoFe_3$ [4] show that the magnetic moments of iron at

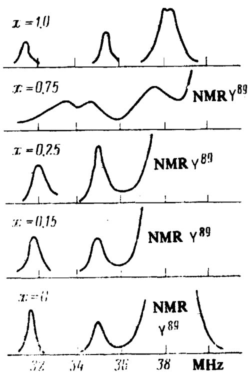

FIG. 4. NMR spectra of Fe^{57} in $Gd_xY_{1-x}Fe_3$. In the $x \leqslant 0.75$ range, the NMR spectra of Fe^{57} are limited on the high-frequency side by the NMR of Y^{89}.

TABLE I. Values of hyperfine fields and magnetic moments at different crystallographic sites of iron

Compound	Type of site	Hyperfine field, kOe	Calculated value of μ_B	Average value of μ_B	Value of μ_B from mag. meas.
$GdFe_3$	Fe II	230±5	1.55	(1.81)	1.83
	Fe I	255±5	1.72		
	Fe III	280±5	1.88		
YFe_3	Fe I	230±5	1.55	1.64	1.65
	Fe III	250±5	1.67		

78°K amount to 1.88 μ_B, 1.43 μ_B, and 1.61 μ_B, respectively, for the first, second, and third kinds of site, i.e., the highest moment is exhibited by the FeI atoms. However, the application of this reasoning to other RFe_3 compounds is justified only if the magnetic moments of the iron atoms are almost completely localized. The hyperfine fields at the Fe^{57} nuclei in $Gd_xY_{1-x}Fe_3$ vary fairly slowly when gadolinium is replaced with yttrium, which is difficult to explain on the basis of the localized state theory.[10] However, the changes in the Fe^{57} NMR lines with increasing Gd content can be understood by assuming that at least some of the 3d electrons are itinerant, i.e., they are in a collective state. The dilution of the gadolinium sublattice reduces the energy of the intersublattice exchange interaction, i.e., it alters the splitting of the 3d band and changes the wave vector k_F.

The magnetic moments of the iron atoms in materials intermediate between $GdFe_3$ and YFe_3 can be found on the assumption of a constant ratio of the hyperfine field H_{hf} to the magnetic moment of at atom μ_{at}. The results of calculations based on the assumption that $H_{hf}/\mu_{at} \approx 150$ kOe/μ_B are listed in Table I. A better agreement between the calculated values of $\bar{\mu}$ and the results of the magnetization measurements can be obtained by assuming that the highest magnetic moment is exhibited by the atoms at the third type of site, as suggested for $ThFe_3$ in [11].

An analysis of the local symmetry of the immediate environment of the iron atoms shows that, at sites of the first and second kinds, the symmetry is approximately the same so that, when the splitting of the d band decreases, the magnetic moments of FeI and FeII and the hyperfine fields may become equal, which explains the disappearance of one of the Fe^{57} NMR lines in the range $x < 0.5$. In the case of the FeIII atoms, the symmetry is much lower and the degree of magnetic symmetry decreases even further on transition from $GdFe_3$ to YFe_3, which alters the ratio of the intensities of the signals due to each of these sites.

Thus, our investigation yielded for the first time information on the NMR spectra of all types of the nuclei of the elements forming intermetallic compounds of the $Gd_xY_{1-x}Fe_3$ type and we established that

1) the contribution of the gadolinium sublattice to the hyperfine fields at the YII and GdII nuclei was 26 and 75 kOe, respectively;

2) the hyperfine interaction of the gadolinium nuclei with the nearest neighbors in the gadolinium sublattice was anisotropic;

3) the magnetic moments of the iron atoms varied with the crystallographic site and depended on the exchange interaction between the rare-earth and iron sublattices.

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