Hyperfine and exchange fields in $Gd_{1-x}Lu_xFe_2$

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The magnetic characteristics and hyperfine fields in $Gd_{1-x}Lu_xFe_2$ have been measured. The results of the magnetic measurements have been analyzed in the molecular-field approximation. The molecular-field coefficients and the partial contributions of each of the types of exchange interactions inherent in these compounds to the total value of the Curie temperature have been determined. It has been theorized that a small magnetic moment is induced at the lutetium atoms, and its presence accounts well for the observed anomalies in the concentration dependence of the hyperfine fields. © *1995 American Institute of Physics.*

1. INTRODUCTION

In the development of structural materials for magnetostrictors based on $TbFe_2$, great importance is attached to the problem of increasing their mechanical strength as much as possible. The solution to this problem often reduces to altering the distance between the magnetically active atoms; however, such alteration can have an appreciable influence on the level of intersublattice $f-d$ exchange, which plays a significant role in the phenomenon of giant magnetostriction.[1] Intersublattice exchange is a new type of exchange.[2,3] For this reason, its phenomenological description is inadequate, and microscopic investigations are required to ascertain its features. One of the ways to perform such investigations is to measure induced hyperfine fields, since both exchange and hyperfine fields are associated to some extent with the transfer of spin density.

The most convenient object for such investigations is the compound $GdFe_2$, none of whose constituent atoms it has an orbital magnetic moment, so that the crystal-field effects can be disregarded. The investigation of such quasibinary compounds has been the subject of numerous studies,[4,5] but the substitutions employed in them generally resulted in appreciable distortion of the band structure, making it difficult to obtain information on the variation of the microscopic parameters of $f-d$ exchange. Therefore, we undertook to study the magnetic properties and hyperfine fields in $Gd_{1-x}Lu_x Fe_2$, where the nonmagnetic dopant metal has outer electronic subshells which are totally equivalent to the $5d$ and $6s^2$ subshells of the gadolinium atom. The identical nature of the subshells allows us to hope for minimal changes in the band structure in the samples studied.

The saturation magnetization, Curie temperature, and lattice constants of samples with values of x in the range $0 < x < 0.5$ were measured. The magnetization was measured on a magnetic balance in the 77–980 K temperature range. The lattice constant of the C15 structure, in which all the compositions obtained crystallize, was determined from x-ray structural data. In addition, the NMR spectra for the ^{155}Gd, ^{157}Gd, and ^{175}Lu nuclei were recorded at 77 K. The NMR spectra of gadolinium were obtained on a spin echo spectrometer, and a generator composed of a series of co-axial cylinders[6] and a separate video amplifier were used to observe the lutetium NMR spectra.

Figure 1 presents the results of the measurements of the lattice parameter in $Gd_{1-x}Lu_xFe_2$ alloys and their magnetic characteristics: the Curie temperature T_C, which was determined by measuring thermodynamic parameters, and the magnetic moment of iron, which was calculated from the results of measurements of the saturation magnetization under the assumption that the magnetic moment of the gadolinium atom remains constant and equal to $7\mu_B$ (μ_B is the Bohr magneton). As is seen from the figure, all the measured parameters decrease linearly as the lutetium content increases, in complete agreement with the theories that have evolved regarding the structure and exchange interactions of intermetallic compounds.[4,5] At the same time, the measured hyperfine fields exhibit the opposite tendency: increases in the fields at both the gadolinium nuclei (Fig. 2) and the lutetium nuclei (Fig. 3) are observed when the gadolinium sublattice is diluted. There is a simultaneous increase in the relaxation time at the gadolinium nuclei (Fig. 3). The complete absence of any satellites in any of the gadolinium NMR spectra recorded is noteworthy and distinguishes them from the analogous NMR spectra of $Gd_{1-x}Y_xFe_2$ alloys,[7] where small replacements of gadolinium by yttrium caused additional signals shifted by about 3 MHz toward lower frequencies. Due to the use of a different technique for recording the lutetium NMR signals, we were unable to obtain records of these spectra; however, visual observations made it possible to detect appreciable broadening of the region where echo signals exist when the Lu content was increased. For example, an echo was observed for a sample of $Gd_{0.8}Lu_{0.2}Fe_2$ in the 235 ± 10 MHz frequency range, while this range was at 250 ± 25 in the case of $Gd_{0.5}Lu_{0.5}Fe_2$. Similar drastic broadening of the line shape of the NMR signals was observed in $Gd(Fe_{1-x}Co_x)_2$ alloys (Ref. 8), in which atomic magnetic moments of different magnitude, which are coupled to one another by direct exchange, appear in the local environment of the atom under consideration, so that the observed broadening of the ^{175}Lu NMR lines can serve as indirect evidence of the existence of exchange coupling between the lutetium atoms.

The linear decrease in the values of the measured magnetic characteristics with increasing lutetium content makes
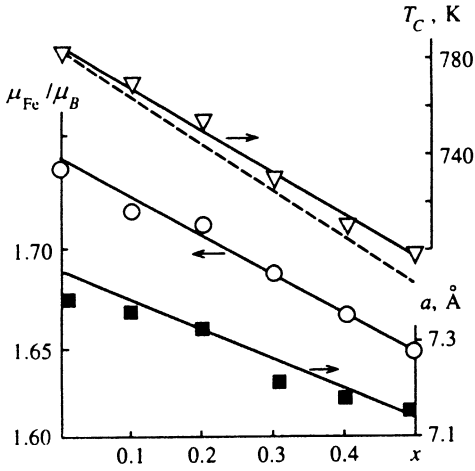
FIG. 1. Concentration dependence of the lattice constant a (■), the Curie temperature T_C (▽), and the magnetic moment of iron (O) for $Gd_{1-x}Lu_xFe_2$.

it possible to analyze the data obtained in the molecular-field approximation,[9] within which the fields acting on the magnetic atoms can be represented in the form

$$H_m^{Gd} = \alpha_{11}\mu_{Gd}(T) + 2\alpha_{12}\mu_{Fe}(T), \tag{1}$$

$$H_m^{Fe} = \alpha_{21}\mu_{Gd}(T) + 2\alpha_{22}\mu_{Fe}(T), \tag{2}$$

where the α_{ik} are the molecular-field coefficients (here $\alpha_{12} = \alpha_{21}$), T is the temperature, and the values of $\mu_{Gd}(T)$ and $\mu_{Fe}(T)$ can be approximated by the corresponding Brillouin functions:

$$\mu_{Gd}(T) = \mu_{Gd}(0)B_{7/2}(x_{Gd}), \tag{3}$$

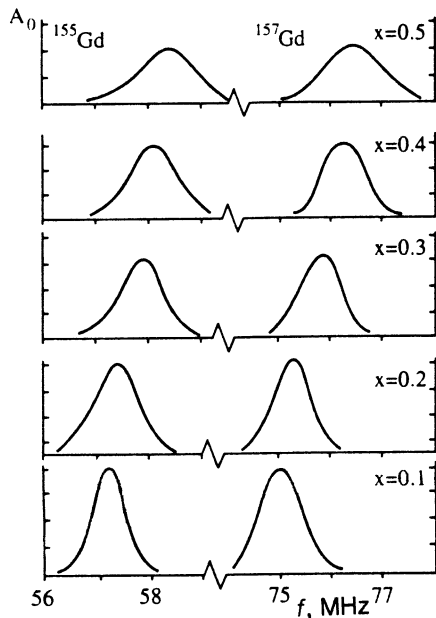$$\mu_{Fe}(T) = \mu_{Fe}(0)B_{3/2}(x_{Fe}). \tag{4}$$

FIG. 2. Displacement of the ^{155}Gd and ^{157}Gd NMR spectra as a function of the lutetium content.
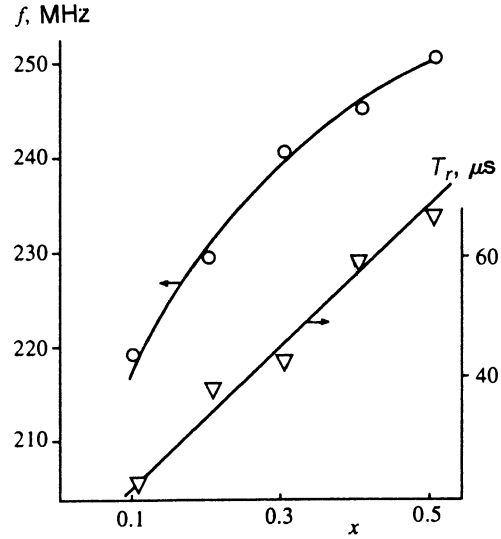

FIG. 3. Variation of the ^{175}Lu NMR frequency (O) and the magnetic relaxation time T_r of the gadolinium nuclei (▽) in $Gd_{1-x}Lu_xFe_2$.

The arguments of the Brillouin functions are defined by the expressions

$$x_{Gd} = \frac{\mu_{Gd}(0)}{kT} H_m^{Gd}, \tag{5}$$

$$x_{Fe} = \frac{\mu_{Fe}(0)}{kT} H_m^{Fe}. \tag{6}$$

At temperatures close to T_C the Brillouin functions can be replaced by their approximate values

$$B_S(x) = \frac{3S}{S+1} x \tag{7}$$

(S is the spin of the atom), so that the characteristic equation relating the molecular-field coefficients to the Curie temperature has the form

$$\left[\alpha_{11} - \frac{7kT_C}{3\mu_{Gd}^2(0)}\right]\left[\alpha_{22} - \frac{9kT_C}{10\mu_{Fe}^2(0)}\right] - \alpha_{12}^2 = 0. \tag{8}$$

This equation makes it possible to calculate only one parameter (α_{22} in our case) from experimental values of T_C, and other relations must be used to determine the remaining two parameters (α_{11} and α_{12}).

The values of α_{11} were determined independently using the following relation known from molecular-field theory:[10]

$$T_C\mu_i - C_i\Sigma\alpha_{ik}\mu_k = 0, \tag{9}$$

where

$$C_i = \frac{2}{k} \mu_B(S+1)\mu_i(0).$$

Hence the partial contribution of each of the types of exchange interactions is defined as a consequence of the linearity of Eq. (9):

TABLE I. Molecular-field coefficients and partial contributions to the Curie temperature for GdFe$_2$.

Interacting pairs	Values of the molecular-field coefficients, k/μ_B^2	Contributions to the total Curie temperture, K
Gd–Gd	$\alpha_{11} = 9.0$	$\alpha_{11}\dfrac{\partial T_C}{\partial \alpha_{11}} = 75$
Gd–Fe	$\alpha_{12} = 36$	$\alpha_{12}\dfrac{\partial T_C}{\partial \alpha_{12}} = 190$
Fe–Fe	$\alpha_{22} = 190$	$\alpha_{22}\dfrac{\partial T_C}{\partial \alpha_{22}} = 520$

$$T_C^i = \alpha_{ik}\frac{\partial T_C}{\partial \alpha_{ik}}. \tag{10}$$

The partial contribution of the Gd sublattice was evaluated in our work from the results of various studies[11-13] and was found to be equal to 75 K for the compound GdFe$_2$.

Assuming that the value of the derivative in (10) remains constant for all gadolinium compounds with $3d$ metals in the C 15 structure, we can easily find the value of α_{11}, which is equal to 9 in units of k/μ_B^2.

To determine the values of α_{12} we used expressions (1)–(6), whence we can obtain a relation of the form

$$kT = \frac{3S_{Gd}}{(S+1)\mu_{Gd}^2}\left[\alpha_{11} - \frac{2\alpha_{12}}{Z}\right], \tag{11}$$

where

$$Z = \mu_{Gd}(T)/\mu_{Fe}(T).$$

The numerical values of Z for a sample of GdFe$_2$ are found by a self-consistent procedure:[11] an approximate value of Z equal to the ratio between the reduced magnetic moments $\bar{\mu}_{Gd}$ and $\bar{\mu}_{Fe}$, which are defined by the relation

$$\bar{\mu}(T) = \frac{\mu(T)}{\mu(0)} = B_S\left(\frac{3ST\mu(0)\bar{\mu}}{(S+1)T}\right), \tag{12}$$

is assigned in the range of temperatures close to T_C, and a certain temperature T', which corresponds to the value of Z selected, is found. This temperature, in turn, specifies new values of $\bar{\mu}_{Gd}$ and $\bar{\mu}_{Fe}$ and a new value Z', which gives a new value T'', and so forth and so on.

To minimize the number of iterations, it is convenient to use tabulated values of the corresponding Brillouin functions, which describe the behavior of the reduced magnetic moments in both sublattices as a function of the reduced temperature T/T_C.

For GdFe$_2$ we found $T/T_C = 0.93$ and $\mu_{Gd}(T)/\mu_{Fe}(T) = 3.3$.

The known values of Z and T make it possible to determine α_{12} from expression (11) and α_{22} from Eq. (8). The values found are equal to 36 (in units of k/μ_B^2) and 190, respectively.

By differentiating Eq. (8) and using the known values of α_{ik} we can find the values of the corresponding derivatives $\partial T_C/\partial \alpha_{ik}$ and, consequently, the partial contributions to the total value of the Curie temperature, which are presented in Table I.

The values of α_{ik} and $\partial T_C/\partial \alpha_{ik}$ found should remain unchanged in the quasibinary compounds, while the characteristic equation takes on a somewhat different form:

$$\left[\alpha_{11}(1-x) - \frac{7kT_C}{3\mu_{Gd}^2(0)}\right]\left[\alpha_{22} - \frac{9kT_C}{10\mu_{Fe}^2(0)}\right]$$
$$= (1-x)\alpha_{12}^2. \tag{13}$$

Now the Curie temperatures can be calculated on the basis of Eq. (13) for all x (the dashed line in Fig. 1). As is seen from the figure, the calculated values of T_C are somewhat lower than the measured values, and the difference increases with increasing x.

The observed disparity is easily attributed to increases in the molecular-field coefficients, but it is unlikely that the coefficients involved are α_{11} and α_{22}, since the former coefficient has only a weak influence on the Curie temperature and considerable reorganization of the band structure is required to increase the latter coefficient. An increase in α_{12} seems most likely. This is indicated by the observed increase in the induced hyperfine field at the gadolinium nuclei (Fig. 2), whose total value can be represented in the form of a sum of terms:

$$H_{hf}(Gd) = H_{ep} + H_{4f} + H_{3d}, \tag{14}$$

in which H_{ep} is associated with the so-called exchange polarization of the electronic core with the intrinsic magnetic moment of the atom and H_{4f} and H_{3d} are the fields induced by neighboring atoms from the $4f$ and $3d$ sublattices, respectively. The last contribution dominates and determines the direction of the resultant field.[14] The increase in this contribution is the only cause of the increase in the total field $H_{hf}(Gd)$.

The increase in H_{3d} is due to the appearance of an induced magnetic moment in the lutetium $5d$ subshell. These magnetic moments together with the gadolinium $5d$ electrons play an important role in the intersublattice exchange interaction.[15] The $5d$ band formed is found to be exchange-split. This results in a change in its occupancy: an increase in the density of states near the bottom of the band and a decrease near the Fermi level. This decrease in the density of states is indicated by the results of the measurements of the nuclear relaxation in gadolinium (Fig. 3).

It follows from the theory of magnetic relaxation developed for d metals[16] that the relaxation time T_r is given by the expression

$$\frac{1}{T_r} = 2\gamma_n^2 hkT\nu^2(E_F)qH_d^2,\qquad(15)$$

where γ_n is the nuclear gyromagnetic ratio, $\nu(E_F)$ is the density of states at the Fermi level, q is a nuclear coefficient, which varies in the 0.2–0.4 range, and H_d is the field created by the magnetic moment of a single d electron. It follows from expression (15) that the equation for the relaxation time can be associated only with a decrease in the density of states.

The change in the occupancy of the $5d$ band is most clearly manifested by the increase in the hyperfine field on the lutetium nuclei as their content increases.

If the value of the field at the ^{175}Lu nuclei were determined only by the contributions of the $4f$ and $3d$ magnetic moments, as is the case for the field at the ^{89}Y nuclei in $Gd_{1-x}Y_xFe_2$ alloys according to the observations in Ref. 7, this field would not exceed 170 kOe, but it is actually greater than 430 kOe. The value of 170 kOe is obtained from the proportionality between the s electron density $\psi^2(0)$ and the nuclear charge,[17] using the fact that the field at an yttrium nucleus is equal to 220 kOe:

$$\frac{H_{sf}(Y)}{H_{sf}(Lu)} = \frac{\psi_Y^2(0)\,\gamma_n^{Lu}}{\psi_{Lu}^2(0)\,\gamma_n^Y} = \frac{Z_Y\gamma_n^{Lu}}{Z_{Lu}\gamma_n^Y} = 1.3.\qquad(16)$$

The difference between the calculated and experimental results is eliminated if we postulate the presence of a small $5d$ magnetic moment in the lutetium $5d$ band, which creates a hyperfine field in the Lu atom and simultaneously promotes an increase in the field at the gadolinium nuclei. When an intrinsic atomic magnetic moment is present, the hyperfine field at the lutetium nuclei is described by Eq. (14), whence it should be concluded that the field caused by exchange polarization, which is approximately equal to 260 kOe, must be parallel to the contributions from the $4f$ and $3d$ sublattices. The direction of the latter was found to be positive[7] with respect to the macroscopic magnetization. This means that the lutetium magnetic moment must be directed oppositely to the gadolinium magnetic moment, since exchange polarization always creates a field whose direction is opposite to the magnetic moment producing it.

The magnetic moment of lutetium is equal to $0.3\mu_B$, since it is known that one $5d$ electron creates a hyperfine field equal to 750 kOe (Ref. 18). As for the reasons for the

increase in the field at the gadolinium nuclei, they reduce to the phenomenon of $4f-5d$ mixing and were thoroughly studied elsewhere.[19] Thus, the behavior of the hyperfine fields under consideration supports the validity of the hypothesis of an increase in α_{12}.

As a whole, this research demonstrates the correctness of using the hybrid-exchange model[2] to describe the intersublattice exchange interaction in compounds of rare-earth metals and iron.

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