Anomalous strengthening of the hyperfine field at gadolinium nuclei as the gadolinium sublattice is diluted with nonmagnetic lutetium in $Gd_{1-x}Lu_xFe_2$ compounds

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An anomalous strengthening of the hyperfine field at gadolinium nuclei in $Gd_{1-x}Lu_xFe_2$ compounds has been observed by an NMR method as the rare-earth sublattice is diluted with nonmagnetic lutetium. The observed strengthening may be due to an interband mixing.

In an NMR study of the distribution of the spin density in $Gd_{1-x}Lu_xFe_2$ compounds we have found an anomalous strengthening of the hyperfine field at the gadolinium nuclei as the gadolinium sublattice is diluted with nonmagnetic lutetium atoms.

Samples of alloys with $0 \leqslant x \leqslant 0.5$ were smelted in an electric arc furnace by the standard procedure and then subjected to a phase analysis. The results of this analysis support the assertion that the composition obtained had the C15 structure. Some NMR spectra of ^{155}Gd and ^{157}Gd were measured on an incoherent-spin-echo spectrometer at 77 K.

Table I shows the frequencies corresponding to the position of the center of gravity of the NMR spectra found for Gd. We see that the frequency of ^{155}Gd increases monotonically as the Gd lattice is diluted with lutetium, from 56.6 for $GdFe_2$ to 58.3 MHz in $Gd_{0.5}Lu_{0.5}Fe_2$. For the isotope ^{157}Gd, the frequency increases from 74.3 to 76.5 MHz. This increase is especially surprising because the opposite tendency has been observed previously in some similar compounds, $Gd_{1-x}Y_xFe_2$. Specifically, in those other experiments the hyperfine field at the gadolinium decreased with increasing yttrium concentration, as the result of a weakening of the exchange interaction in the Gd sublattice.[1]

To determine why nonmagnetic lutetium and yttrium ions have opposite effects on the hyperfine field H_{cm}^{Gd} we need to look at a decomposition of this field into its components. One component stems from a decompensation of the *s* shells of the Gd atom by its intrinsic magnetic moment, while two others, which are in the same direction, are due to the polarization of conduction electrons by neighboring atoms from the Gd and Fe sublattices. The last component is predominant, so the resultant hyperfine field at the Gd nuclei is collinear with the magnetic moment. When gadolinium is replaced by nonmagnetic atoms, both of the latter components can obviously change. A decrease in the contribution of the Fe sublattice results from a decrease in the iron magnetic moment μ_{Fe} as we go from $GdFe_2$ to $LuFe_2$ or YFe_2, but this decrease in μ_{Fe} is larger for compositions with yttrium and cannot explain the ob-

TABLE I. Resonant frequencies corresponding to the centers of gravity of the NMR spectra for two gadolinium isotopes in $Gd_{1-x}Lu_xFe_2$ compounds.

Compound	Frequency, MHz	
	^{155}Gd	^{157}Gd
$GdFe_2$	56.6	74.3
$Gd_{0.9}Lu_{0.1}Fe_2$	57.2	75.0
$Gd_{0.8}Lu_{0.2}Fe_2$	57.4	75.4
$Gd_{0.7}Lu_{0.3}Fe_2$	57.8	75.8
$Gd_{0.6}Lu_{0.4}Fe_2$	58.1	76.3
$Gd_{0.5}Lu_{0.5}Fe_2$	58.3	76.5

served increase in H_{cm}^{Gd}. The introduction of nonmagnetic atoms in the Gd sublattice should promote some decrease in the hyperfine field. Quantitatively, induced hyperfine fields are usually described on the basis of the RKKY approximation of indirect-exchange theory. The results of our measurements demonstrate first and foremost that this approximation is not sufficient here, and d electrons must be taken into account.[2,3]

Comparing the electronic structures of the Y and Lu atoms, we easily see that the former has $5s^2$ and $4d^1$ electrons, while Lu has $6s^2$ and $5d^1$ electrons, in precise correspondence with the structure of the valence electrons of gadolinium. The opposite effects of yttrium and lutetium on the hyperfine fields at the Gd nuclei can thus be linked with the energy difference between the d electrons of the nonmagnetic atoms which mix with the $5d$ density of gadolinium atoms.

In general, the appearance of an additional d spin density near the Gd atom may lead to different effects: The hyperfield may either increase or decrease, depending on the direction of the polarization which arises. If the d polarization is parallel to the magnetic moment of the Gd atom, the contribution of this polarization to the hyperfine field is negative. If the field is to undergo a net increase with increasing lutetium content, we must thus assume that there is a decrease in this contribution. If the polarization of the d electrons is instead negative with respect to the magnetic moment, we would need an increase in the d polarization in order to reach the observed increase in H_{cm}^{Gd}.

Measurements of the hyperfine fields under hydrostatic compression[4] show that the latter assumption is correct. The appearance of a negative $5d$ polarization in this case is linked with a $4f$–$5d$ mixing as the result of virtual transitions between $4f$ and $5d$ levels of gadolinium. By analogy with calculations by Kondo,[5] we can show that the probability density for virtual transitions is given by an expression of the form

$$w^{\pm}=\frac{1}{|E_{5d}-E_{\pm}|}\langle\psi'_{4f}V_{fd}\psi_{5d}\rangle\langle\psi_{5d}V_{fd}\psi_{4f}\rangle, \tag{1}$$

where ψ_{4f} and ψ'_{4f} are the wave functions of the $4f$ electrons in the ground and perturbed states, ψ_{5d} is the wave function of the $5d$ electrons, E_{5d} and $E_{\pm}$ are the energies of the $5d$ and $4f$ electrons with different spin directions, respectively, and V_{fd} is the matrix element of the f–d interaction.

Since the nuclear charge of gadolinium is lower than that of lutetium, the $5d$ levels of the latter are closer to the levels of the $4f$ electrons. A dilution of the gadolinium sublattice with lutetium results in the formation of an "extrinsic" $5d$ level, closer to the $4f$ states. As a result, there is a decrease in the denominator in expression (1), i.e., an increase in the $5d$ density near the gadolinium atoms. For yttrium, on the other hand, the opposite situation holds: Its charge is lower than that of gadolinium, and its extrinsic level lies higher in the structure of bands, leading to a decrease in the d component.

An alternative explanation for the increase in the hyperfine field might come from a decrease in the $5d$ spin density parallel to the magnetic moment of the gadolinium atom. The appearance of a density in this direction follows from band-structure calculations on Laves phases.[6] In this case there is a decrease in the $5d$ moment because of a decrease in the $3d$–$5d$ covalent mixing. The extent of mixing in this case is inversely proportional to the difference between the energies of the centers of the $3d$ and $5(4)d$ bands.[7] For compounds with yttrium, the $4d$ band is closer than the lutetium $5d$ band to the $3d$ band.[6,7] Consequently, if the mechanism of an induction of a $5d$ density did in fact operate, it would be more apparent in $Gd_{1-x}Y_xFe_2$ compounds, in contradiction of experimental results.[1] It thus seems more likely that the observed increase in the hyperfine field at the Gd nuclei in $Gd_{1-x}Lu_xFe_2$ compounds is due to a change in the extent of the $4d$–$5d$ interband mixing.

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