Comment on contact contributions to the magnetic hyperfine interaction of rare-earth impurities in iron

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The influence of the Fe conduction band's strong d character on the hyperfine interaction of dilute rare-earth impurities is emphasized, and the contact contributions are estimated. Apparent inconsistencies between hyperfine field measurements for Eu and Gd in Fe are noted.

Shortly after the pioneering recoil-implantation (IMPAC) experiments of Grodzins and Boehm *et al.*,[1] the main features of the magnetism of dilute rare-earth (RE) impurities in Fe—a RE localized moment[2,3] and crystalline-field effects[4]—were reported and analyzed. Recently, two groups have extended this work.[5,6] Their results provide information on the orbital component of the hyperfine interaction, although in the absence of independent data on the crystal-field potential an accurate analysis is difficult unless the reduced matrix elements multiplying the Stevens operators are small (i.e., for the heavy rare earths[5]). On the other hand, some confusion remains concerning the origin and sign of the coupling between the $4f$ and conduction electrons. The discussion presented by Kugel *et al.*,[6] and their experimental result for *Fe*Gd, has suggested the following presentation of the problem. My rather empirical discussion is based on a previous idea,[7] and closely resembles the analysis of RE solid solutions by Gomès and Guimaraẽs.[8] It leads to the suggestion that the amplitude of the hyperfine field for *Fe*Gd and its sign for *Fe*Eu be reexamined.

Consider a RE localized spin $\vec{S}_0$ interacting with the conduction band of Fe, i.e., with both s- and d-character electrons. The interaction may be expressed as

$$\mathcal{H} = -\sum_{i=s,d} J_{if}\,\delta(r-R_0)\vec{S}_0\vec{s}^{(i)}(r), \qquad (1)$$

where $\vec{s}^{(i)}(r)$ are the spins of the conduction electrons and J_{if} is an effective exchange coupling integral, which is the sum of a Heisenberg overlap integral $J_{if}^{(H)}$ (by definition a positive quantity) and of an inteband mixing integral $J_{if}^{(I)}$, which is negative for s electrons and zero for d electrons.[9]

We shall take the total hyperfine field at a RE impurity in Fe as an incoherent sum of fields due to (a) the polarized d and s conduction electrons of Fe; (b) the field due to the RE core polarization by its own $4d$ states; (c) the conduction-band polarization at the RE site by the $4f$ moment; (d) the orbital and spin magnetism of the RE ion. In terms (a) and (c), the polarization of the s-like conduction electrons acts directly via the contact interaction, while the d-like conduction electrons act indirectly via core polarization. The total field is

$$H_0 = A(Z)m_s + \alpha_d m_d + H_{sf} + H_{df} + H_{FI}. \qquad (2)$$

The first contribution is the direct contact part of term (a), proportional to the (positive) s-electron hyperfine coupling parameter $A(Z)$ (Ref. 10) and to the Fe conduction-electron moment m_s at the RE site [$m_s = -0.2\mu_B$ in Fe (Ref. 11)]. The second contribution is the core polarization by d electrons in terms (a) and (b): α_d is constant in each transition series and approximately equal to -400 kOe μ_B^{-1} for the $4d$ series.[10] The RE d moment may be deduced[7] from the results for d-series impurities in Fe (Ref. 12); for large negative charge differences (here $\Delta Z \sim -4$), screening in the d band produces $m_d \sim -1\mu_B$. Terms (a) and (b) alone account for the hyperfine field of RE impurities with empty (La) or closed (Lu) $4f$ shells (Table I). The negative sign is due to the dominating direct contact term.

For the other RE ions, the next two contributions are due to term (c): H_{sf} is the direct contact field due to the coupling integral J_{sf}, while H_{df} is the core polarization field due to the overlap integral J_{df}. Since $|J_{sf}| < J_{df}$, the RE spin couples ferromagnetically to the RE d moment, i.e., antiparallel to the host magnetization, and spin-orbit coupling determines the orientation of the orbital moment.[7] This is not in contradiction with the results of Ref. 9. These fields may be calculated in the same manner as above, with moments $m_i = J_{if}N_i(E_F)\langle s\rangle$, where $N_i(E_F)$ is the d or s density of states at the Fermi level and $\langle s\rangle$, the thermal average of the host spin. Taking typical values of $N_d(E_F)$ and $N_s(E_F)$—respectively, 1 and 0.3 eV^{-1}—and[9] of J_{df} and J_{sf} (respectively, +0.10 and −0.04 eV), the field due to term (c) is about −50 kOe. It is interesting to note that although the exchange coupling has a drastic effect on the *sign* of the orbital field,

its total contribution to the amplitude of the contact term is quite small and practically constant throughout the RE series.

The last contribution to the total field is due to the free ion (we do not discuss crystal-field effects). In the case of the half-filled $4f^7$ shell (Gd^{3+} or Eu^{2+}), term (d) reduces to the familiar core polarization value [−340 kOe (Ref. 9)]. From this value, the $4f$ spin contribution to the hyperfine field is deduced for other RE ions by the approximate expression[9] $\vec{H}_{core} \approx -90\vec{S}$ (kOe).

Adding all the terms in Eq. (2), with the appropriate interpolated[10] values of $A(Z)$, we obtain the estimates of Table I for the nonorbital components of the RE hyperfine fields. Comparison of these estimates with experimental results is possible in a few cases, albeit not always significant because of the uncertainties. The field on La is found[4] to be ±200 (100) kOe and the field on Lu (Ref. 13) is −575 (40) kOe. A lower limit of H_0 is obtained when the experimentally measured hyperfine field exceeds the free-ion value. This is the case for[6] *Fe*Sm: −210 (350) kOe, for[5] *Fe*Tb: ~500 kOe, and for[3,5] *Fe*Dy: −500 (170) kOe. These values are in overall agreement with the estimates of Table I. The field at Ce in Fe is found[4] to be ~−800 kOe (far larger than the calculated value of H_0 and the experimental value for La), indicating that Ce is not in the diamagnetic 4+ state in Fe.

Comparison with experiment for Eu and Gd is of special interest. Our result for Gd in Fe is very far from the value obtained[1,6] by IMPAC techniques: −182 (18) kOe. However, from a Mössbauer experiment on Eu^{3+} implanted in Fe, Cohen *et al.*[14] deduced $H_0 = -800$ kOe, in quite good agreement with the value calculated taking into account the $^7F_0$ ground state of Eu^{3+} ($H_{core} = -270$ kOe) (Table I). Now because of this configuration, the Gd and Eu values should not differ by more than their differences in H_{core}. The discrepancy between the two results seems to warrant a critical reexamination of the experiments. Among other difficulties which may affect the *Fe*Gd result,[6] we note that although IMPAC experiments produce alloys far more dilute than those obtained by isotope-separator implantation, they generally do *not* produce much lower radiation damage because of the high elastic-to-Coulomb excitation cross-section ratio. On the other hand, in Ref. 1 the sign of the Eu field in Fe was found to be positive, in contradiction to the result of Ref. 14. If the positive sign is correct, both the analysis of Ref. 14 and the present discussion are in serious difficulty.

TABLE I. Contact contribution to rare-earth ion hyperfine fields in Fe calculated from Eq. (2). Expected uncertainties in the calculated values are ≲ 20%.

Ion[a]	H_0	Ion[a]	H_0
La	−220	Tb	−740
Ce	−260	Dy	−720
Pr	−250	Ho	−690
Nd	−230	Er	−680
Sm	−210	Tm	−660
Eu	−720	Yb	−640
Gd	−790	Lu	−560

[a]Only (3+) ions are considered.

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