LETTER TO THE EDITOR

Origin and *ab initio* evaluation of magnetic interactions in rare earth intermetallics

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Abstract. The interaction, K_{RM}, between the rare earth 4f moment and the transition metal 3d moments in the series RFe2 (R = Gd–Yb) is shown to depend upon the R-5d moment, which is due to 3d–5d hybridization and local 4f–5d exchange integrals. K_{RM} is calculated *ab initio* from density functional theory and is in excellent agreement with values extracted from inelastic neutron scattering experiments.

Intrinsic magnetic anisotropy, rather than shape anisotropy, is responsible for the large coercive fields in modern permanent magnets [1], which are compounds of rare earths (R) and 3d transition metals (M). The magnetic anisotropy is thought to originate at the R sites from the influence of the crystalline electric field upon the localized 4f shell. In contrast, the magnetism at the M sites is of almost pure spin character and cannot itself be very anisotropic. The key to the large magnetic anisotropy of the entire magnet must therefore be the interaction that couples the directions of the R-4f and M-3d magnetic moments. The simplest approximation to this interaction, irrespective of its origin, is of the Heisenberg form $-2 \Sigma K_{RM} J_R \cdot J_M$, where J_R and J_M are the total angular momenta at the R and M sites, respectively. It is clearly desirable to be able to identify the nature and origin of K_{RM} and, if possible, to calculate it. Although this may superficially appear to be a very complex problem we show here that not only is the solution both physically and mathematically simple but that, in comparison with K_{RM} extracted from neutron inelastic scattering experiments [2, 3], the values calculated *ab initio* from density functional theory [4] are accurate.

We have computed the spin densities of the RFe_2 (R = Gd–Yb) series self-consistently using the LMTO method [5] by fixing the 4f occupation numbers and moments at their Russel–Saunders values and treating the 4f wavefunctions as spin polarized outer-core wavefunctions [6]. The calculated total magnetic moments are in agreement, to within a few per cent, with the measurements of Clark [7] on single crystals. The numerical test verifies the theory but more important than the actual calculations that will be reported in detail elsewhere [6], is what may be obtained from an analysis of them. The calculated total conduction electron, R-5d and M-3d moments for the series are shown in figure 1. Both R-5d and M-3d moments increase as the 4f spin, given by $S_{4f} = (g_j - 1)J_{4f}$ with g_j the Lande factor, in Russel–Saunders coupling, increases.

However, they are antiparallel and the changes nearly cancel leaving a total conduction-band moment which is almost constant across the series.

That this is no coincidence is easily understood in terms of 3d–5d hybridization. Before hybridization the R-5d bands are essentially empty and moments, μ'_{3d}, form in the 3d bands. Hybridization results in transfer of charge from M-3d character to R-5d character (spin up and down separately since spin–orbit coupling is small) such that, after hybridization, $n_{3d\pm} + n_{5d\pm} = n'_{3d\pm}$. Hence the site-resolved moments before and after hybridization obey the sum-rule $\mu'_{3d} = \mu_{3d} = \mu_{5d}$ and the total moment remains unchanged [8]. Since the gap between the unhybridized spin-down bands is smaller than between the unhybridized spin-up bands, hybridization and spin transfer are greater for the spin-down bands and the interaction between the M-3d and R-5d moments is ferrimagnetic [9].

It is therefore 3d–5d hybridization which produces significant conduction-electron charge and spin density at the R sites, even when the 4f moments are zero; it is also responsible for the crucial coupling between the 4f and 3d spin directions. The essential point to realize is that in the local spin density approximation (LSDA) to density functional theory [4] the R-4f and R-5d spins are coupled by *local* exchange interactions (which are always ferromagnetic) and that the interaction between R-4f and M-3d spins is mediated *entirely* by the R-5d spin. The exchange interaction energy between the R-4f and R-5d states is, to be a very good approximation [10], of the quadratic form

$$E_{4f5d} = -2K_{4f5d}\bar{S}_{4f}\bar{S}_{5d} \tag{1}$$

where $\bar{S}$ denotes the average spin and the LSDA exchange integral K_{4f5d} is

$$K_{4f5d} = \int g(n(r))\phi_{4f}(r)^2\phi_{5d}(r)^2 \, \mathrm{d}r \tag{2}$$

and therefore depends upon 4f–5d overlap densities. $g(n)$ is a well known function of the density [10]. We calculate K_{4f5d} to be given by

$$K_{4f5d} = 94 - 3.4(x - 1) \, \mathrm{meV} \tag{3}$$

where $x = 1$ for Gd, 2 for Tb etc.

It remains to make contact with experiment. K_{RM} must influence the spin dynamics and be extractable from the spin-wave spectra of these compounds. Inelastic neutron scattering experiments have been carried out by Nicklow *et al* [2] and by Koon and Rhyne [3] for $TbFe_2$, $HoFe_2$ and $ErFe_2$. The generic form of the observed spectra is shown in figure 2. C15 laves phase compounds have two R atoms and four M atoms per primitive cell and, although there must be six spin-wave modes, it is evident that the three modes involving a de-phasing of the M spins at the zone centre must be too high in energy to be observed, as M–M spin interactions are large. Of the three observed modes at the zone centre, one is the uniform mode and one the exchange resonance mode. The third, which is a de-phasing of the R spins, is dispersionless indicating that R–R interactions are negligible. Nicklow *et al* [2] were therefore able to successfully fit the spectra with the simplest possible spin Hamiltonian, restricted to nearest-neighbour interactions, of the form

$$\mathcal{H} = -2 \sum_{(\alpha l, \alpha l')} K_{\alpha l, \alpha l'} J_{\alpha l} \cdot J_{\alpha l'} - 2 \sum_{(\alpha l, \beta l')} K_{\alpha l, \beta l'} J_{\alpha l} \cdot J_{\beta l'} \tag{4}$$

where α refers to the M sublattices, β to the R sublattices, l, l' to the Bravais lattice, and the prime denotes a sum over pairs. Since each R atom has twelve M nearest neighbours

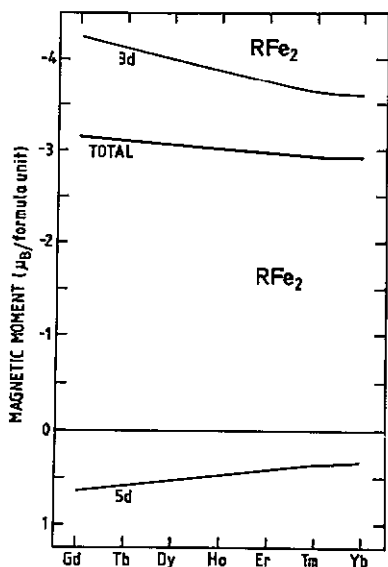**Figure 1.** The calculated total conduction electron, R-5d and Fe-3d moments per formula unit in the RFe_2 series. The total moments are obtained by adding the R-4f moment calculated in Russel–Saunders coupling, and this gives agreement with the moments measured by Clark [7].
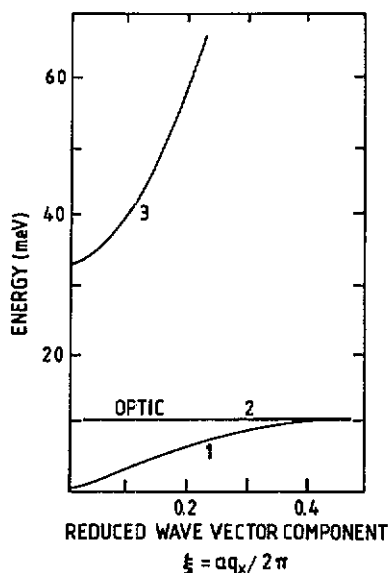

Figure 2. Typical spin-wave spectra at low energies for the RFe_2 series after Nicklow *et al* [2] and Koon and Rhyne [3].

and each M atom has six R nearest neighbours it is quite easy to show that the dispersionless R–R mode has energy equal to $24\,K_{RM}\bar{J}_M$ (where again the bar denotes the average value), which is just the energy of an excitation corresponding to $\Delta J_R = \pm 1$ in the molecular field at the R site. The overall consistency of the spin Hamiltonian is verified by the fact that the energy of the exchange resonance mode, equal to $12\,K_{RM}(\bar{J}_R - 2\bar{J}_M)$, is also given correctly by the same parameter K_{RM}.

The relationship between the LSDA exchange inegral, K_{4f5d}, and the RM interaction, K_{RM}, in the spin Hamiltonian is established through the spin-wave gap for the R–R mode, which is a quantity determined by the molecular field at the R site. Firstly we recognise that E_{4f5d}, (1) may be rewritten as

$$E_{4f5d} = -2(g_j - 1)\kappa_{4f5d}\bar{J}_{4f}\bar{S}_{5d}. \tag{5}$$

Therefore the energy of a 4f spin-wave excitation, $\Delta J = -1$, is $2(g_j - 1)\kappa_{4f5d}\bar{S}_{5d}$, which we identify with the spin-wave gap. From figure 1 for $\bar{S}_{5d}$, (3) for κ, and with $g_j = 1.25$, we obtain a gap of 9.4 meV for $HoFe_2$, that is in excellent agreement with the experimental values of about 8.4 meV [3] for $HoFe_2$ and 10.1 meV [2] for $Ho_{0.88}Tb_{0.12}Fe_2$. K_{RM} is easily obtained by identifying the LSDA and spin Hamiltonian expressions for the spin-wave gap. Then

$$K_{RM} = (1/12)(g_j - 1)\kappa_{4f5d}(\bar{S}_{5d}/\bar{S}_M) \tag{6}$$

since g_j for the conduction-electron states is two. We plot the calculated values of K_{RM}
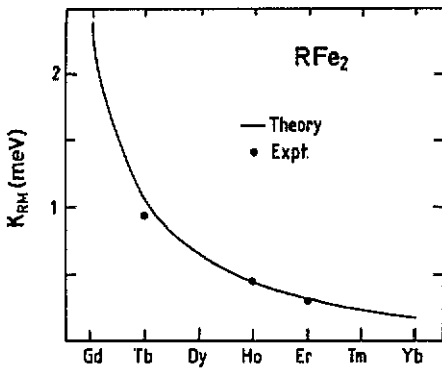
Figure 3. The calculated R–M moment interaction, K_{RM}, for the RFe$_2$ series, compared with the values extracted from the spin-wave spectra by Koon and Rhyne [3].

for the series in figure 3, where they are compared with the values deduced [2, 3] by fitting to the measurements.

In conclusion, the interaction between the rare-earth local moment and the transition metal itinerant moments can be derived both concisely and precisely, providing a rigorous quantum mechanical solution to what is an important technological problem. The magnitude of the interaction depends above all on the R-5d spin, induced by hybridization with the M-3d bands, and local exchange integrals which are less dependent upon the environment in which the rare earth finds itself.

References

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