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## 3d–5d band magnetism in rare earth transition metal intermetallics: LuFe<sub>2</sub>

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**Abstract.** Self-consistent energy band calculations for LuFe<sub>2</sub> are reported. LuFe<sub>2</sub> is found to order magnetically according to the Stoner criterion and the calculated moment is 2.85  $\mu_B$ /formula unit in agreement with experiment. Spin–orbit coupling was included in the calculation and the spin and induced orbital contributions to the moment at the Fe site also found to be in agreement with experiment. The total moment is calculated to include a contribution of  $-0.41 \mu_B$  at the Lu site, which as yet has not been observed. The mechanism responsible for the ferrimagnetic alignment of the 3d and 5d spin densities is investigated in detail, and the Lu–5d moment related to 3d–5d hybridisation.

### 1. Introduction

The useful technical properties of rare earth(R) transition metal(M) intermetallics have encouraged much basic research into their electronic structure (for reviews see Buschow 1977, 1979 and Hilscher 1982). Apart from their capacity for hydrogen storage, one of the most interesting characteristics of these intermetallics is the combination of itinerant transition metal magnetism with the localised and anisotropic magnetism of the rare earth ions. This has naturally led to investigations of the coupling between the transition metal and rare earth magnetic moments, and the C15 Laves phase compounds have been studied intensively. It is now clear that the spins on the transition metal and rare earth sites are coupled antiparallel (Buschow 1977, 1979). The total moments on the atoms will be parallel if the orbital moment of the rare earth is opposite to, and greater than, the spin. Wallace (1968) proposed that polarisation of the conduction electrons with sp-character was parallel to the more local spin with d-character at the transition metal sites, but antiparallel to the local spin at the rare earth sites, thus coupling the rare earth and transition metal spins anti-parallel. On the other hand, Campbell (1972) suggested that it was the R-5d M-3d coupling that was important, and that the local exchange interactions were parallel. It is the latter explanation that is correct, as we shall show rigorously in this paper.

The individual (or site-resolved) moments can be studied in neutron diffraction experiments (for a review, see Boucherle *et al* 1982). Belorizky *et al* (1987) divided the interactions between the magnetic moments in RM<sub>2</sub> compounds into R–R, M–M, and

R–M exchange interactions. It is easier to study the R–M interactions for a magnetic system with a filled 4f shell and such a system is LuFe<sub>2</sub>. Furthermore Givord *et al* (1980) have published neutron diffraction data for this compound and attempted to resolve the partial moments. However, Givord *et al* (1980) were unable to resolve a moment on the Lu site. We find, in agreement with earlier work by Yamada and Shimizu (1986), that there is a moment of  $-0.41 \mu_B$  at the Lu site of which  $-0.27 \mu_B$  is of partial 5d character. We calculate the form factor and suggest that the 5d contribution (the s-p conduction electron contribution is not observable) may have been missed because the form factor was too small at the scattering vectors used.

The organisation of this paper is as follows: we describe calculations of the charge and spin densities of LuFe<sub>2</sub>, we calculate the partial and total moments, and we relate the Lu-5d moment to the hybridisation between 3d and 5d bands in § 2. This hybridisation, and its effect upon the sign of the 5d polarisation has already been investigated by Yamada and Shimizu (1986). The present work differs in several ways: it is fully self-consistent with all states included; we do not adjust the local exchange interactions, the calculation being from the first principles in the local spin density approximation; spin-orbit effects are included self-consistently and we calculate the orbital moments. We also analyse the band structure and show how the Lu-5d moment may be estimated if the Fe-3d moment is known in § 3. Finally, we demonstrate in § 4 how the model used in § 3 may be used to help understand rare earth intermetallics in general.

## 2. Method and numerical results

In the local density approximation (LDA) the total electronic potential,  $V$ , is the sum of the external, coulomb, and exchange-correlation potentials (Kohn and Sham 1965). The functional form of the exchange-correlation energy used in the present work was the free electron gas parametrisation of von Barth and Hedin (1972).

The linear muffin tin orbital (LMTO) method in the atomic sphere approximation (ASA), detailed expositions of which have been given by Andersen (1975) and Skriver (1983), were used for the self-consistent band structure calculations. For the measured lattice constant

$$a = 7.22 \text{ \AA}$$

at which the calculations were also made, the Wigner–Seitz radii  $S_{Lu} = 1.7551 \text{ \AA}$ ,  $S_{Fe} = 1.4267 \text{ \AA}$  were chosen. The Fe sphere radius was more or less unchanged from its metallic radius, whereas the Lu sphere radius was adjusted so that the correct lattice constant was obtained. This is according to the suggestion of Watson *et al* (1984). These three parameters, together with the C15 Laves structure, were the only input to the calculations.

The scalar relativistic wave equation (Andersen 1975, Koelling and Harmon 1977) was solved and spin-orbit coupling added at the band structure stage of the calculations. The atom core charge densities were kept frozen, and the valence charge density was converged to better than 1 part in  $10^3$  at each point of the radial mesh and the total spin to 1%. The irreducible wedge of the Brillouin zone was sampled at 89 points, and the charge density was spherically averaged after each iteration. The change of total energy with volume, or electronic pressure (Pettifor 1976, Nieminen and Hodges 1976, Mackintosh and Andersen 1979), was also calculated.

**Table 1.** Lattice constant,  $a$ , and calculated electronic pressure,  $P$  ( $V$  is the primitive cell volume), from self-consistent band calculations. The main results—the state density at the Fermi level, Stoner parameter, partial occupation numbers and potential parameters (see text) are listed.

$a = 7.22 \text{ \AA}$	
$3 PV = -0.31 \text{ Ryd}$	
$I$ (Stoner)	14.6 mRyd
$D(E_F)$	157.6 states/Ryd/f.u.
$ID(E_F)/2$	1.15
$n_{\text{Fe-3d}}/\text{atom}$	6.6
$n_{\text{Lu-5d}}/\text{atom}$	1.51
$C_{\text{Fe-3d}}$	-151 mRyd
$C_{\text{Lu-5d}}$	202 mRyd
$\Delta_{\text{Fe-3d}}$	11 mRyd
$\Delta_{\text{Lu-5d}}$	80 mRyd

The results of the calculations for the paramagnetic ground state are summarised in table 1. The calculated total electronic pressure is small, and the theoretical lattice constant at zero pressure is within about 1% of experiment for a bulk modulus of about 2 Mbar, typical for rare earth transition metal intermetallics. The Stoner product is greater than one, and we expect ferromagnetism in agreement with experiment.

When the state densities are dominated by single partial state densities for each atom type (as is the case here where the partial 3d and 5d state densities dominate their respective atoms) the atom type Stoner parameters,  $I_t$ , are given by (see e.g. Janak 1977, Vosko and Perdew 1975, Brooks *et al* 1988)

$$I_t = \Sigma R_t^2 J_{tt} \quad (2.1)$$

where the exchange integrals,  $J_{tt}$ , are obtained from LDA and

$$R_t = D_{tt}(E_F)/D(E_F) \quad (2.2)$$

in terms of the atom type partial state density per primitive cell at the Fermi energy,  $D_{tt}(E_F)$ , and the total state density at the Fermi energy,  $D(E_F)$ . Finally, the cellular Stoner parameter shown in table 1, is given by

$$I = \Sigma_t I_t/n_t \quad (2.3)$$

where  $n_t$  is the number of atoms of type  $t$  in the primitive cell (2 Lu and 4 Fe). The total state density at the Fermi level,  $D(E_F)$ , is 158 states/Ryd and its character is almost entirely Fe-3d—144 states/Ryd—with a small amount of Lu-5d—6 states/Ryd. Then, from (2.1)–(2.3),  $I$  is dominated by the Fe-3d contribution as all other partial state densities are negligible. The Stoner parameter is then just one quarter of the Fe-3d LDA exchange integral since there are four Fe atoms per primitive cell. We calculate the exchange integrals,  $J_{tt}$ , in LDA (Vosko and Perdew 1975, Janak 1977, Gunnarsson 1976) to be

$$J_{\text{Fe-3d}} = 65 \text{ mRyd}; J_{\text{Lu-5d}} = 47 \text{ mRyd}.$$

Yamada and Shimizu (1986) used intra-atomic exchange integrals,  $U$ , fitted to the measured total moment, keeping their ratio to that obtained by Janak (1977) for the Stoner parameters of the metals. Although these exchange integrals are defined in a

**Table 2.** Lattice constant,  $a$ , and calculated electronic pressure,  $P$  ( $V$  is the primitive cell volume), from self-consistent spin polarised band calculations. The main results—the magnetic moment, its resolution by site and angular momentum and potential parameters (see text) are listed. For comparison: 1. Yamada and Shimizu (1986).

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$a = 7.22 \text{ \AA}$		
$3PV = 0.22 \text{ Ryd}$		
$\mu/\text{LuFe}_2$	2.67	2.95 <sup>1</sup>
$\mu_{\text{Fe}}/\text{Fe}$	1.55	1.64 <sup>1</sup>
$\mu_{\text{Fe-3d}}/\text{Fe}$	1.62	
$\mu_{\text{Lu}}/\text{Lu}$	-0.44	-0.33 <sup>1</sup>
$\mu_{\text{Lu-5d}}/\text{Lu}$	-0.29	
$C_{\text{Fe}}$ (spin-up)	-199 mRyd	
$C_{\text{Fe-3d}}$ (spin-down)	-93 mRyd	
$C_{\text{Lu-3d}}$ (spin-up)	220 mRyd	
$C_{\text{Lu-5d}}$ (spin-down)	200 mRyd	
$\Delta_{\text{Fe-3d}}$ (spin-up)	5 mRyd	
$\Delta_{\text{Fe-3d}}$ (spin-down)	6 mRyd	
$\Delta_{\text{Lu-3d}}$ (spin-up)	115 mRyd	
$\Delta_{\text{Lu-5d}}$ (spin-down)	115 mRyd	

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manner similar to the Hubbard (1963) integrals they are used by Yamada and Shimizu (1986) in such a manner that they correspond to  $J_{\text{Fe-3d}}$  and  $J_{\text{Lu-5d}}$ , above, if the total state density is dominated by the partial Fe-3d and Lu-5d partial state densities, as is the case here. They found that values for the exchange integrals of

$$U_{\text{Fe}} = 55 \text{ mRyd} \quad U_{\text{Lu}} = 38 \text{ mRyd}$$

fitted the data quite well. These values for  $U$  are quite similar to those of the corresponding exchange integrals calculated in the present work. Actually, as we have just shown,  $U_{\text{Lu}}$  is of minor importance as both the onset and magnitude of the magnetism is driven by the  $U_{\text{Fe}}$ . It will become clear later that the Lu moment is almost entirely due to hybridisation between the 3d and 5d states.

The origin of the partial occupation numbers in table 1 will be discussed in detail in § 3 where the bandwidth parameters,  $\Delta$ , and band centre parameters,  $C$ , which summarise the band structure, will also be required.

The magnetic moments were then obtained from self-consistent spin-polarised calculations. We first omitted spin-orbit coupling. The computed total and partial—pure spin—moments are shown in table 2 where we also compare with the results of Yamada and Shimizu (1986). In contrast to the result for the paramagnetic ground state, the electronic pressure becomes positive although small, yielding a small magnetovolume effect. Finally the magnetic moments computed in the self-consistent spin-polarised calculations—with spin-orbit coupling included—are compared with experiment in table 3. As may be seen, the spin moments are relatively little affected by the spin-orbit coupling.

We have found two values for the total moment measured in magnetisation experiments—from Givord *et al* (1980) and Buschow (1977)—table 3. They are similar and we obtained perfect agreement with the moment measured by Givord *et al*. The partial magnetic moments, resolved according to lattice site, were measured in neutron scattering experiments. In the work of Givord *et al* (1980), the measured moments at the Lu

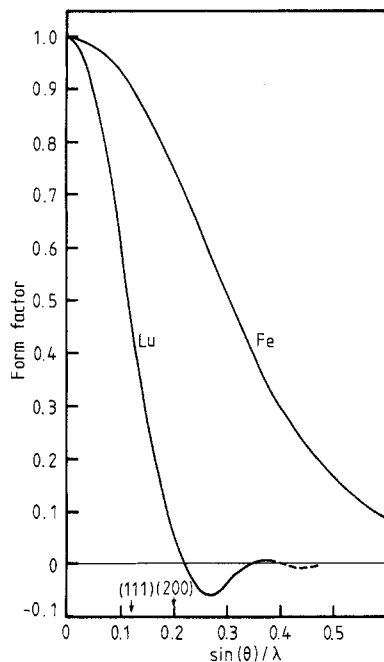
**Table 3.** Complete moment decomposition by site and angular momentum, spin and orbital character. For comparison: 1. Givord *et al* (1980). 2. Buschow (1977, 1979). 3. Yamada and Shimizu (1986).

	Measured	Calculated
$\mu/\text{LuFe}_2$	2.85 <sup>1</sup> 2.93 <sup>2</sup>	2.85
$\mu_{\text{Fe-3d}}/\text{Fe}$	1.74 <sup>1</sup>	1.69
$\mu_{\text{Fe-3d}}^{\text{spin}}/\text{Fe}$	1.67 <sup>1</sup>	1.62
$\mu_{\text{Fe-3d}}^{\text{orb}}/\text{Fe}$	0.07 <sup>1</sup>	0.07
$\mu_{\text{Lu-5d}}^{\text{spin}}/\text{Lu}$		-0.28
$\mu_{\text{Lu}}^{\text{orb}}/\text{Lu}$		0.01
		Calculated
Moment decomposition—Fe		
$\mu_{\text{Fe}}/\text{Fe}$	1.63	
$\mu_{\text{Fe}}^{\text{spin}}/\text{Fe}$	1.56	1.64 <sup>3</sup>
$\mu_{\text{Fe}}^{\text{orb}}/\text{Fe}$	0.07	
Moment decomposition—Lu		
$\mu_{\text{Lu}}/\text{Lu}$	-0.41	
$\mu_{\text{Lu}}^{\text{spin}}/\text{Lu}$	-0.42	-0.33 <sup>3</sup>
$\mu_{\text{Lu-5d}}/\text{Lu}$	-0.27	

and Fe sites correspond to Lu-5d and Fe-3d moments since the form factors of the s-p conduction electrons fall off far too rapidly to make any contribution for the scattering vectors in the experiments. We have therefore denoted these measured partial moments by 3d and 5d in table 3 and compare them with our corresponding calculated moments. Clearly the agreement between experiment and theory is excellent for the Fe site. We also obtained the correct orbital moment at the Fe site, which we could calculate as spin-orbit coupling was included in the self-consistent band calculations.

That no moment was observed at the Lu site by Givord *et al* (1980) whereas the calculated moments by both Yamada and Shimizu (1986) and ourselves might seem large enough to be measurable, deserves comment. We note from the decomposition of the Lu moment in the lower third of table 3 that the Lu orbital moment, which is almost entirely of 5d character, is directed opposite to the spin moment, as one would expect for a less than half-filled shell. Therefore the total partial 5d moment is  $-0.27 \mu_{\text{B}}$  per formula unit and small compared with the total partial 3d Fe moment of  $3.5 \mu_{\text{B}}$  per formula unit.

We have plotted the calculated Fe and Lu normalised magnetic form factors in figure 1. They are dominated by the respective partial-d contributions as the sp-conduction electron form factors fall to zero for  $\sin(\theta)/\lambda > 0.5$ . We note that our calculated Lu form factor falls off more rapidly than the calculated induced form factor of Lu metal (Stassis *et al* 1977). This is probably due to 5d bonding charge caused by 3d-5d hybridisation not present in the elemental metal. Our calculated Fe form factor agrees well with experiment but the Lu form factor is very small for  $\sin(\theta)/\lambda > 0.2$  and this, we believe, is the origin of experimental difficulties. In the Laves phase structure Fe scattering dominates at most Bragg reflections either through the structure factor or due to the fact that for  $\sin(\theta)/\lambda > 0.2$  the Lu form factor is zero (a thorough analysis may be found in recent work on PuFe<sub>2</sub> by Wulff *et al* 1988). This makes it very difficult to extract the small Lu moment. The critical Bragg reflections are at (111) and (200). For the (111)



**Figure 1.** Calculated form factor, resolved by site, of  $\text{LuFe}_2$ . The critical Bragg reflections are indicated by arrows.

reflection  $\sin(\theta)/\lambda = 0.12$  and the Lu form factor is quite large (figure 1). However, at this reflection, the scattering is from both Fe and Lu with an Lu contribution of about 10%. One would have to be very confident of the Fe form factor to extract an Lu moment. The scattering at (200) is entirely due, through the structure factor, to Lu. Unfortunately  $\sin(\theta)/\lambda = 0.20$  for this reflection and the Lu form factor is about zero (figure 1). It is therefore not surprising that the Lu moment was not detected. Our conclusion is, however, that there is a significant moment on the Lu site.

Givord *et al* (1980) comment upon the fact that the total moment deduced from neutron scattering ( $3.48 \mu_{\text{B}}/\text{FU}$ ) is much larger than the total moment from magnetisation measurements ( $2.85 \mu_{\text{B}}/\text{FU}$ ). They attribute the difference to an anomalously large (and unobservable by neutron scattering) antiparallel sp-conduction electron contribution of  $0.31 \mu_{\text{B}}/\text{Fe}$  at the Fe sites. We suggest, however, that the discrepancy is due primarily to the moment on the Lu site. We calculate an antiparallel conduction electron polarisation of  $0.12 \mu_{\text{B}}/\text{Fe}$  at the Fe sites, which is not at all anomalous.

### 3. 3d–5d hybridisation and induced moment in the 5d bands

In order to disentangle the various factors that influence the 3d–5d energy band structure and, through it, the bonding and magnetism we wish to outline a more approximate, but analytic, approach. To do so we draw heavily upon publications by Andersen *et al* (1978, 1979) and a similar application to actinide compounds by Brooks and Glötzel (1980). Our objective is to analyse the manner in which 3d–5d hybridisation affects the band structure, and the relative magnitude and sign of the spin polarisation at the Lu and Fe sites. We are using  $\text{LuFe}_2$  as a prototype for rare earth transition metal intermetallics because, paradoxically, its 4f shell is filled. This we can do because the *sign* of the 4f

polarisation in these rare earth compounds is parasitic, the interaction between the different types of atom in the unit cell being via 3d-5d hybridisation.

The complete separation of structural and potential information inherent in ASA makes it possible to analyse the electronic structure in an approximate but accessible manner. The condition that the Bloch sum of linear atomic sphere orbitals be a solution to the wave equation leads to the set of homogeneous linear equations

$$\sum_{Q'} [S_{QQ'}(k) - P_T(E)\delta_{TT'}] C_{Q'}^k = 0 \quad (3.1)$$

where  $Q = tlm$  labels the atom type ( $t$ ) and orbital quantum numbers ( $l, m$ ) simultaneously, and  $T = (t, l)$ . The structural information is contained in the *scale and potential independent* structure constant matrix,  $S$ . An approximate form for the potential function  $P_T(E)$  is (Andersen *et al* 1978)

$$P_T(E) = (E - C_T)/\Delta_T \quad (3.2)$$

where  $C_T$  is the centre of the unhybridised  $T$ -band and  $\Delta_T$  is its bandwidth parameter, proportional to the square of the radial amplitude of the atomic sphere orbital at a distance characteristic of the lattice (Andersen *et al* 1979, 1980)

$$\Delta_T = [\mu_T S_t^2 (1/N_c v_t)^{(2l+1)/3}]^{-1} \quad (3.3)$$

where  $v_t$  is the fractional volume,  $V_t/V$ , of the unit cell occupied by an atom of type  $t$  and  $N_c$  is the number of atoms in the unit cell. Here  $S_t$  is the Wigner Seitz (or atomic sphere) radius of a type  $t$  atom and  $\mu_T$  is the band mass of a type  $T$  atomic sphere orbital, equal to  $[S_t^3 \varphi^2]^{-1}$ , where  $\varphi$  is the radial wave function at  $r = S_t$ .

In this approximation equation (3.1) reduces to an eigenvalue problem with Hamiltonian matrix

$$H_{QQ'}(k) = C_T \delta_{QQ'} + \Delta_T^{1/2} S_{QQ'} \Delta_T^{1/2} \quad (3.4)$$

Here  $\Delta^{1/2} S \Delta^{1/2}$  is the transfer matrix corresponding to a particularly simple form of the Slater-Koster (Slater and Koster 1954) two-centre LCAO integrals. Thus the bands are scaled by the bandwidth parameters,  $\Delta$ , and positioned on the energy scale by the energy band centres  $C$ . Bandwidth and band centre parameters for the 3d and 5d bands in LuFe<sub>2</sub> are listed in table 2. The eigenvalues of the  $T$  diagonal blocks (i.e. for a given atom and angular momentum) of the structure constants are the canonical unhybridised  $T$  bands from which may be derived canonical state densities. Since they are functions of energy the canonical state densities,  $D_T(E)$ , may be expanded in a set of diagonal energy moments

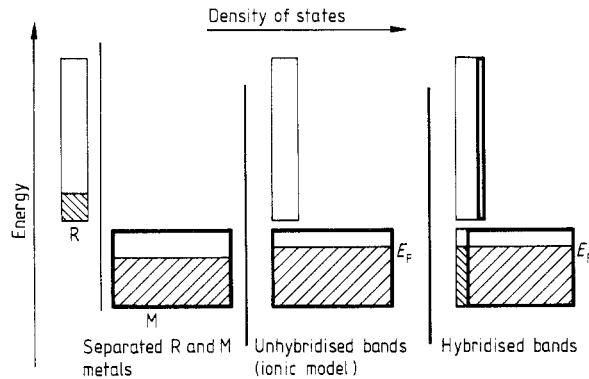
$$M_{TT}^n = \int (E - C_T)^n D_T(E) dE \quad (3.5)$$

The zeroth moment is the total number of type  $T$  states,  $N_T$ , and a truncation of the moment expansion at the second moment—which is the approximation that we make here—is equivalent to approximating the unhybridised canonical state densities by rectangular state densities with zeroth first moment (Andersen 1975) and width

$$W_T^c = (12N_T^{-1} M_{TT}^2)^{1/2} \quad (3.6)$$

Here  $N_T = (2l + 1)N_t$  is the number of type  $t$  atoms per unit cell and  $l$  is the angular momentum.





**Figure 2.** Model state densities (d bands only), drawn to scale, for  $\text{LuFe}_2$ .  $R$  and  $M$  denotes the rare-earth and late 3d transition metal density of states, respectively. To the left is shown the case of separated metals. In the middle the unhybridised (ionic) density of states is shown and the occupied 3d density of states is hatched. To the right the model density of states for the hybridised bands is drawn with the associated 3d and 5d electron occupations hatched from left to right and right to left, respectively. In all figures the 3d density of states is drawn with thick lines.

We have compiled the relevant canonical second moments,  $M_{TT}^2$ , for the C15 Laves phase lattice:

$$M_{3d-3d}^2 = 1178; M_{5d-5d}^2 = 53$$

The unhybridised bandwidths,  $W_T$ , are easily calculated by scaling the canonical bandwidths,  $W_T^c$  from equation (3.6), by the bandwidth parameters,  $\Delta$  (table 2). Inserting the numbers for  $\text{LuFe}_2$ , we find the following bandwidths

$$W_{\text{Fe-3d}} = 0.287 \text{ Ryd}; W_{\text{Lu-5d}} = 0.633 \text{ Ryd}$$

A model rectangular unhybridised state density for paramagnetic  $\text{LuFe}_2$  is sketched in figure 2. The bands have been positioned by the band centres (table 1) and are drawn approximately to scale. The calculated state densities are plotted in figure 3 for comparison so that the reader might acquire an idea of the approximation being made.

In LDA the rectangular state densities must be populated by the available valence electrons according to Fermi statistics. There are 38 valence electrons in the primitive cell of  $\text{LuFe}_2$  which contains two formula units. We know from our self-consistent energy band calculations that about 8 of these valence electrons lie in the sp-conduction bands. Therefore, in the middle part of figure 2, the 3d bands contain nearly all the other 30 electrons if 3d–5d hybridisation is neglected. We take this ionic model, with loss of electrons from Lu, as our starting point for an analysis of the d-bands.

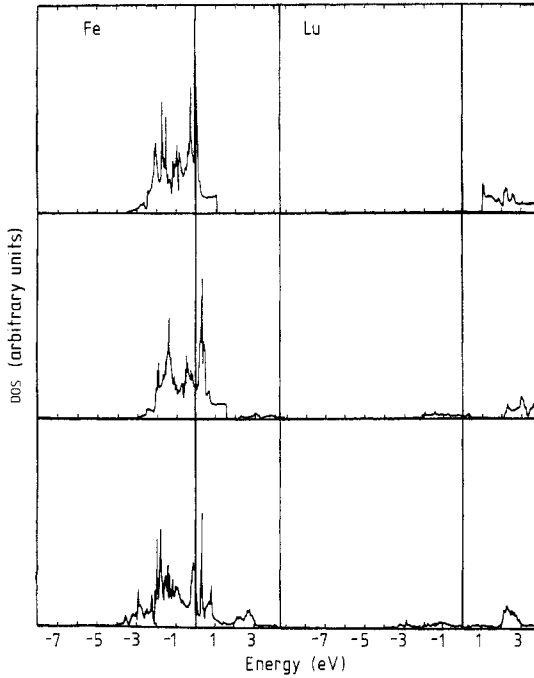
Hybridisation between the bands arises from the off-diagonal blocks of structure constants and enters the theory through the off-diagonal canonical second moments:

$$M_{3d-5d}^2 = 241$$

The repulsion between two bands, in the limit of weak hybridisation, can be estimated in first order perturbation theory whence the change,  $\delta_T$ , in the average  $T$ -band position due to hybridisation with the  $T'$ -bands is

$$\delta_T = N_T^{-1} M_{TT'}^2 \Delta_T \Delta_{T'} / (C_T - C_{T'}) \text{ mRyd} \quad (3.7)$$

We calculate, using (3.7) and table 1, that  $\delta_{\text{Lu-5d}} = 59 \text{ mRyd}$ . The shift in the Fe-3d states of which there are twice as many is, of course, half as much in the opposite direction.



**Figure 3.** Calculated state densities for LuFe<sub>2</sub>. In the upper panel the Fe3d and Lu5d density of states are shown for the case of totally unhybridised bands. The middle panel shows the same but where hybridisation between 3d and 5d states is included. The lower panel shows the same but for a fully hybridised calculation. Energies are in eV and the Fermi level is at zero energy. All calculations are for a paramagnetic state.

Hybridisation between the bands leads to charge transfer between them. Quantitatively, again in first order perturbation theory, the admixture of local  $T'$  character in what was a pure  $T$  band before hybridisation is

$$N_{T'T} = 2M_{TT}^2 \Delta_T \Delta_{T'} / (C_T - C_{T'})^2 \quad (3.8)$$

where the factor of 2 is due to spin degeneracy. With the numbers inserted from table 1, (3.8) yields  $N_{3d-5d} = 3.3$  and is symmetric under interchange of 3d and 5d. The actual electron transfer from a partially filled  $T$  band is obtained by multiplying  $N_{T'T}$  by the fractional occupation,  $f_T$ , of the  $T$  band. We calculate, using (3.8) and the fact that before hybridisation practically all 30 available electrons were in the 3d bands ( $f_{3d} = 30/40$ )—that 2.5 electrons are transferred to the 5d bands

$$\delta n_{5d} = 1.25/\text{Lu}$$

which is also the number of Lu-5d electrons in this approximation. The charge transfer is out of the unhybridised 3d-band because charge transfer is proportional to the original fractional occupation. Similarly the entire content of the 5d band is due to hybridisation and  $\delta n_{5d}$  compares well with the Lu<sub>5d</sub> occupation number  $n_{\text{Lu-5d}} = 1.51/\text{Lu}$  obtained in the self-consistent energy band calculations and shown in table 1. To the right in figure 2 this model hybridised 3d–5d state density has been sketched.

When the system is magnetic, the Fe spin-up and spin-down bands are split by approximately  $J_{\text{Fe-3d}}\mu_{\text{Fe-3d}}$  and the Lu-5d bands are split by  $J_{\text{Lu-5d}}\mu_{\text{Lu-5d}}$  which changes the denominator in (3.7) to  $(C_{3d} - \delta G/2 - C_{5d})$  for spin-up bands and to  $(C_{3d} + \delta G/2 - C_{5d})$  for spin-down bands, where  $\delta G$  is

$$\delta G = J_{\text{Fe-3d}}\mu_{\text{Fe-3d}} - J_{\text{Lu-5d}}\mu_{\text{Lu-5d}} \quad (3.9)$$

For anti-parallel 3d–5d moments, the two contributions in (3.9) add. Since  $C_{5d} > C_{3d}$ ,

the hybridisation is reduced for spin-up bands and increased for spin-down bands as long as  $\delta G$  is positive. This is always so if the 3d and 5d moments are anti-parallel, and also so if the 3d splitting is greater than the 5d splitting, which it normally is. As already noted by Yamada and Shimizu (1986), this is the origin of the anti-parallel polarisation of the local 3d and 5d moments. The same effect appeared in calculations for  $\text{YCo}_5$  and  $\text{Y}_2\text{Co}_{17}$  by Szpunar (1985). We can quantify the effect better by using (3.8) and, when  $\delta G$  is small compared to  $C_{5d} - C_{3d}$ , expanding the denominator to first order in  $\delta G/(C_{5d} - C_{3d})$  for spin-up and spin-down bands separately. The transfer of spin up or down character from the entire Fe-3d bands is then given by

$$N_{5d-3d}^{\pm} = N_{5d-3d}[1 \pm \delta G/(C_{3d} - C_{5d})] \quad (3.10)$$

Where  $\pm$  denotes spin up or down. The actual transfer depends upon the fractional occupation of the 3d bands,  $f^{\pm}$ . In terms of the fractional 3d moment,  $g_{\text{Fe-3d}}$ ,  $f^{\pm} = f \pm g$  we obtain an expression for the Lu-5d moment due to 3d–5d hybridisation

$$\mu_{5d} = N_{5d-3d}[g_{3d} + f_{3d}I_{3d}\mu_{3d}/\Delta C]/[1 + n_{5d}I_{5d}/\Delta C] \quad (3.11)$$

where  $\Delta C = C_{3d} - C_{5d}$ . This is the mechanism of 5d moment formation through hybridisation between the 3d and 5d bands. Normally  $g$ , the fractional 3d moment, is small for rare earth transition metal intermetallics—for  $\text{LuFe}_2$  it is  $4 \times 1.6/40$ —and the second term in (3.11) dominates. Since  $(C_{3d} - C_{5d})$  is negative the 3d and 5d moments are then anti-parallel. The 3d and 5d moments could only be parallel if  $g$  were large, which could happen if, near a half-filled 3d band the 3d moment saturated. However, we do not know of any such case for rare earth transition metal intermetallics. For  $\text{LuFe}_2$ , inserting the numbers into (3.11) one estimates

$$\mu_{\text{Lu-5d}}/\text{Lu} = -0.20\mu_{\text{B}}$$

compared with  $-0.29\mu_{\text{B}}$  (table 2)) from self-consistent spin polarised energy band calculations.

In deriving (3.10) we assumed that the band width parameters,  $\Delta$ , do not change when the system spin polarises. This approximation ignores one variational degree of freedom available to self-consistent spin polarised calculations (which are essentially spin unrestricted Hartree Fock). It is well known (see e.g. Andersen *et al* 1977) that the spin-up bands are normally narrower than the spin-down bands. This effect is weak in  $\text{LuFe}_2$ , as confirmed by a glance at the bandwidth parameters for spin-up and spin-down bands in table 2. We also assumed that the Fe-3d splitting was small compared to the difference in band centres, which allowed us to use parameters from unpolarised calculations. One can remove these two approximations by using the results of the spin-polarised calculations. Thus, from (3.8) and table 2 applied to spin-up and spin-down bands separately,

$$N_{\text{Lu-5d}}^+ = 0.82; N_{\text{Lu-5d}}^- = 2.05.$$

Finally, since  $f^+ = (30/40 + \mu_{\text{Fe-3d}}/40) = 0.91$  and  $f^- = (30/40 - \mu_{\text{Fe-3d}}/40) = 0.59$  we find

$$\mu_{\text{Lu-5d}} = -0.23\mu_{\text{B}}/\text{Lu}.$$

which slightly improves the agreement with table 2.

#### 4. Rare earth transition metal intermetallics

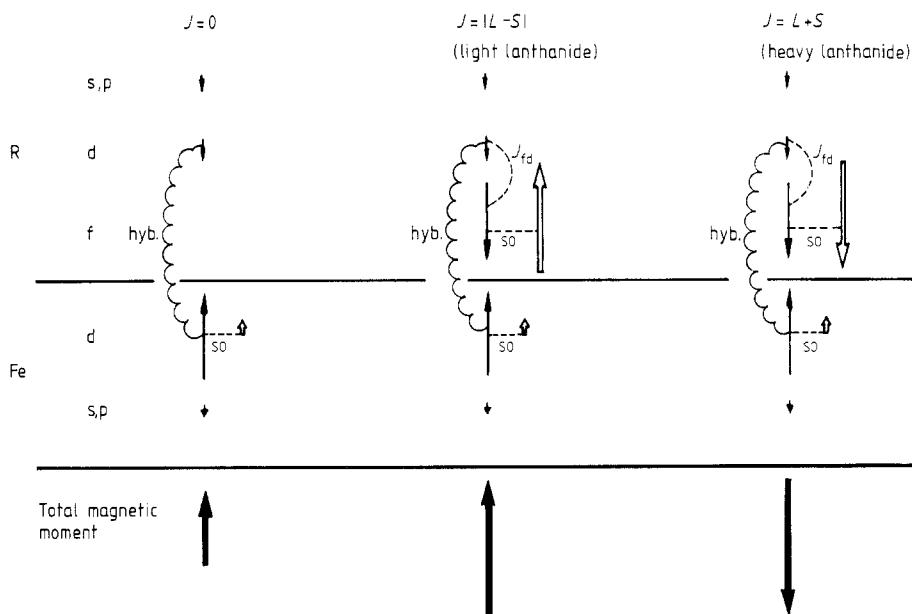
In LuFe<sub>2</sub> there is no Lu 4f moment but in rare earth intermetallic systems,  $RM_2$ , in general, since the 4f states are localised, the interaction between the 4f moment and band magnetism can occur only through the local exchange interaction on the rare earth atom,  $J_{4f-5d}$ , between the 4f and 5d moments.  $J_{4f-5d}$  is always positive and it can be calculated in the energy band calculations or, as shown by Brooks and Johansson (1983), estimated quite adequately from atomic calculations. The exchange integrals for rare earths were not given explicitly by Brooks and Johansson therefore we list some of them here:

$$\begin{aligned}
 \text{Ce: } & J_{4f-4f} = 44 \text{ mRyd}; J_{4f-5d} = 9 \text{ mRyd}; J_{5d-5d} = 29 \text{ mRyd} \\
 \text{Pr: } & J_{4f-4f} = 46 \text{ mRyd}; J_{4f-5d} = 9 \text{ mRyd}; J_{5d-5d} = 29 \text{ mRyd} \\
 \text{Eu: } & J_{4f-4f} = 50 \text{ mRyd}; J_{4f-5d} = 8 \text{ mRyd}; J_{5d-5d} = 30 \text{ mRyd} \\
 \text{Gd: } & J_{4f-4f} = 51 \text{ mRyd}; J_{4f-5d} = 7 \text{ mRyd}; J_{5d-5d} = 30 \text{ mRyd} \\
 \text{Tb: } & J_{4f-4f} = 51 \text{ mRyd}; J_{4f-5d} = 7 \text{ mRyd}; J_{5d-5d} = 30 \text{ mRyd} \\
 \text{Dy: } & J_{4f-4f} = 52 \text{ mRyd}; J_{4f-5d} = 7 \text{ mRyd}; J_{5d-5d} = 30 \text{ mRyd} \\
 \text{Er: } & J_{4f-4f} = 53 \text{ mRyd}; J_{4f-5d} = 6 \text{ mRyd}; J_{5d-5d} = 30 \text{ mRyd} \\
 \text{Yb: } & J_{4f-4f} = 54 \text{ mRyd}; J_{4f-5d} = 6 \text{ mRyd}; J_{5d-5d} = 30 \text{ mRyd}
 \end{aligned}$$

Clearly, there is a monotonic trend across the series and the exchange integrals for other rare earths may be obtained by interpolation. We note that in recent work (Belorizky *et al* 1988) the critical temperatures and susceptibilities of GdM<sub>2</sub> compounds have been used to estimate  $J_{4f-5d}$  and a value of 1300 K = 8.2 mRyd obtained for Gd in Gd compounds. The estimate for this interaction from atomic calculations is therefore good. However the 5d-5d interaction differs more between atom and solid due to greater d-state renormalisation. Thus  $J_{5d-5d}$  computed from the band calculations for Lu is 47 mRyd.

If we return to (3.8)–(3.11) it is possible to estimate the effect of the 4f moment upon the conduction electron polarisation. The 4f-5d exchange interaction splits the 5d bands by  $J_{4f-5d}\mu_{4f}$  which for Gd is 56 mRyd or for Tb is 42 mRyd. Before hybridisation with the 3d bands, the 5d bands are polarised but almost unoccupied; they cannot therefore carry a moment. However, the 5d occupation becomes finite after hybridisation with the 3d states and  $\delta G$ , (3.9), is increased by the splitting due to the exchange interaction between the 4f and 5d states. The 5d moment will, according to (3.11), be increased accordingly. Since the Fe-3d splitting is about 100 mRyd, the increase in  $\delta G$  is about 40% for Tb and the percentage increase of the 5d moment should be similar.

Hence the 4f-5d exchange interaction acts like an internal field and increases the 5d moment. But it could have little effect without 5d-3d hybridisation, as there would then be practically no 5d electrons to polarise. This leads us to consider the case where the transition metal is non-magnetic but there is a local 4f spin-moment which we take to be down, lowering the 5d spin-down bands. Then, since the two 3d spin bands have the same energy the pure (unoccupied) spin-down 5d bands hybridise more strongly with the 3d bands than do the 5d spin-up bands. The result is an excess spin-down 5d population and a spin-down 5d moment. Thus the 4f moment induces a 5d moment with the help of 3d-5d hybridisation. However the spin density with local 5d character was



**Figure 4.** Composition of, and interactions between magnetic moments in  $R\text{Fe}_2$  compounds. In the upper panel the rare earth moment is decomposed into s, p and d conduction (thin arrows) electron contributions and f electron contributions for  $J = 0$ , light and heavy lanthanides. For the  $J \neq 0$  rare earths the f moment is also decomposed into spin (thin arrow) and orbital (thick unfilled arrow) parts. Similarly, in the middle panel the iron moment is decomposed into s, p and d conduction electron contributions (thin arrows). The spin-orbit induced Fe3d orbital moment is denoted by a thick unfilled arrow. In the lower panel the total magnetic moment of the system is shown by thick filled arrows. The antiferromagnetic coupling between the Fe3d and R5d moments derives from hybridisation (denoted by wavy lines). The local exchange coupling between the R5d and the 4f spin moments is denoted by  $J_{fd}$ . The horizontal dashed line (s.o.) represents the spin-orbit coupling.

obtained from the originally pure 3d bands by hybridisation. Since just this spin density is missing from the 3d bands after hybridisation, the sum of the local 3d moments must be anti-parallel to and equal to the sum of the 5d moments. The conduction electron system is antiferromagnetic.

In practice the exchange integral,  $J_{3d-3d}$ , is greater than  $J_{5d-5d}$  and local exchange enhancement will therefore increase the 3d moments further, turning the conduction electron antiferromagnetism into ferrimagnetism. Nevertheless the tendency to antiferromagnetism when the transition metal is non-magnetic exists and should be strong when the transition metal bands have small Stoner enhancement factors.

We note here that remarks in the literature suggesting a polarisation of the transition metal electrons by the 'exchange field' of the rare earth 4f electrons is misleading as it obscures the true mechanism. The true exchange interactions are local and always positive and the transition metal polarisation is mediated by 3d-5d hybridisation. We have drawn three possible different cases—zero 4f moment, heavy rare earth and light rare earth with finite 4f moments—schematically in figure 4. There we show the directions of the partial moments, how they add to the total moments, and the interactions responsible for their size and direction. Thus, if we take  $\text{TbFe}_2$  as the best known example, the Tb-5d electrons polarise anti-parallel to the 3d electrons and, through the

local ferromagnetic interaction,  $J_{4f-5d}$ , the spin of the 4f electrons aligns parallel with that of the 5d electrons. In Tb this effect is reinforced by an orbital 4f contribution parallel to the spin, since the 4f shell is more than half-filled. In light rare earths where localised 4f electrons have a larger orbital component of the moment anti-parallel to the spin component the resulting total 4f moment is parallel to the 3d moment.

We have elsewhere proposed (Eriksson *et al* 1988) that CeFe<sub>2</sub> is anomalous, since the calculated *itinerant* 4f moment is anti-parallel to the 3d moment. The anomaly is due to the almost complete quenching of the orbital 4f moment by band formation.

## 5. Conclusions

The main features of the band structure of  $RM_2$  systems in general are based upon pure d-bands from the two metal sites. Before hybridisation between the two sets of d-bands, the pure 3d-bands are almost filled and the pure 5d bands almost empty. The pure  $M$ -3d and  $R$ -5d bands hybridise to form bonding and antibonding bands. When a moment develops at the  $M$  sites the energy of spin-up 3d states is lowered, reducing the 3d–5d hybridisation for the spin-up states. This lowers the occupation of the 5d spin-up states. The opposite effect occurs for the spin-down states and the induced 5d moment is therefore anti-parallel to the 3d moment and simply related to the 5d occupation which is induced by hybridisation.

The 4f moment interacts with the itinerant electron system through local exchange interactions which may be calculated from first principles in the local density approximation. In this paper we have used free atom calculations to estimate  $J_{4f-5d}$ . However, it should be possible to treat the 4f magnetism efficiently as part of a spin polarised core in the band calculations to obtain results more accurate because they allow for 5d renormalisation in the solid. In this way the mixture of localised and itinerant magnetism which is such an interesting feature of these systems can be handled in energy band calculations.

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