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R–T and R–R exchange interactions in the rare-earth (R)–transition-metal (T) intermetallics: an evaluation from relativistic atomic calculations

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Abstract. Intra-atomic exchange integrals J_{4f-5d} , J_{4f-6s} and J_{4f-6p} for rare-earth trivalent ions were obtained from relativistic self-consistent field atomic calculations, using the local-density approximation for exchange and correlation potential. The effective (molecular-field) exchange coefficients n_{RT} between rare-earth and transition-metal ions and n_{RR} between rare-earth ions were obtained based on a simplified three-sublattice (4f, 3d and conduction electron) mean-field model. Quantitative results show a decrease in magnitude of n_{RT} across the rare-earth series, which agrees well with values observed in many rare-earth–transition-metal intermetallic series. It is shown that the 4f–5d exchange interaction is far more important than the 4f–6s and 4f–6p interactions, as expected from the Campbell model for the exchange interactions occurring in rare-earth–transition-metal intermetallics.

1. Introduction

In the rare-earth (R)–transition-metal (T) intermetallics, three types of exchange interactions may occur: T–T, R–T and R–R. The exchange interactions involving rare earths (R–T and R–R) are usually described using an indirect exchange mechanism originally proposed by Campbell (1972). In this model the 4f electron spin of the rare earth induces a positive local 5d spin moment through the ordinary intra-atomic 4f–5d exchange with subsequent direct 5d–nd interactions with any other neighbouring nd spin moment (including those on other rare-earth sites, as rare earths can be considered as early 5d transition-metal elements). In fact, because of the localized nature of the 4f electronic shell, the interaction between the 4f spin and an itinerant electron spin can occur only through the local exchange interaction on the rare-earth atom, described by the intra-atomic exchange integrals J_{4f-5d} , J_{4f-6s} and J_{4f-6p} . Among these three exchange integrals, the first one, J_{4f-5d} , is dominant, which is the essential point of Campbell's model. On the other hand, in the RKKY model as originally formulated (Ruderman and Kittel 1954, Kasuya 1956, Yoshida 1957) it is assumed that J_{4f-6s} is dominant, but as Campbell pointed out, the RKKY model cannot adequately explain many of the experimental results. The Campbell model and the RKKY model are two extremes: one is short-range, whereas the other is long-range and oscillatory, which is incompatible with the universal antiparallel

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coupling between 4f and 3d spins observed in all rare-earth-3d-transition-metal intermetallics (Wallace and Segal 1973, Buschow 1977). More recent developments of the RKKY mechanism allow for coupling of the 4f shell with all the conduction band electrons (Staunton *et al* 1989), but still show oscillatory behaviour. Self-consistent spin-polarized energy band calculations on Gd metal (Harmon and Freeman 1974) and on RFe₂ (R = Ce and Lu) compounds (Eriksson *et al* 1988, Brooks *et al* 1989) strongly support Campbell's picture of antiparallel coupling of 4f and 3d spins. It was shown that the 4f-5d exchange interaction acts like an internal magnetic field and increases the 5d spin moment with the help of 5d-3d hybridization.

The R-T and R-R exchange paths can thus be denoted as 4f-5d-3d (mixed with some 4f-6s-3d and 4f-6p-3d) and 4f-5d-5d-4f (mixed with some 4f-6s-6s-4f and 4f-6p-6p-4f), respectively. Considering a given series (R varied and T fixed) of rare-earth-transition-metal compounds it is likely that the direct 5d-nd exchange interaction remains roughly constant. Therefore any variation of R-T and R-R interactions across the series will mainly be determined by the intra-atomic exchange integral J_{4f-5d} of the R atom (with lesser contributions from $J_{4f-6s,p}$). From the analysis of the Curie temperatures of a large variety of series (R₂Fe₁₄B, R₂Fe₁₇, R₆Fe₂₃, RFe₃, RFe₂ and RCo₂), it has been estimated that the molecular-field coefficient n_{RT} is not constant across a given series but decreases by a factor of about 2 from compounds with light R to those with heavy R elements (Belorizky *et al* 1987). The magnitudes of n_{RT} are very similar in all these series (see figure 1 later).

Recently, inelastic neutron scattering studies on the R₂Fe₁₄B series have provided direct confirmation that there is a decrease in the molecular field acting on R atoms across the rare-earth series (Loewenhaupt *et al* 1991). Furthermore, nuclear magnetic resonance (NMR) and magnetic order investigations on the RAl₂, RZn and RNi₅ series (Berthier *et al* 1978, Waind *et al* 1983, Belorizky *et al* 1988a) have shown that the molecular-field coefficient n_{RR} , which describes the exchange interaction between the 4f spin moments of R atoms, decreases as n_{RT}^2 , where n_{RT} is obtained in isomorphous series with iron. These variations imply that the dominant intra-atomic 4f-5d exchange interaction at R sites decreases from the beginning (Ce or Pr) to the end (Tm or Yb) of the rare-earth series. It is concluded that the observed variations in exchange are essentially determined by the atomic nature of the rare-earth elements.

Hence we decided to evaluate systematically the exchange integrals J_{4f-5d} , J_{4f-6s} and J_{4f-6p} from relativistic atomic calculations for most of the rare-earth elements, and to investigate the variation of these exchange interactions with the R element. A molecular-field model was established based on Campbell's picture, and the expressions that relate the phenomenological parameters n_{RT} and n_{RR} and the exchange integrals J_{4f-5d} , J_{4f-6s} and J_{4f-6p} , are obtained. In section 2, the method is described and the numerical results for intra-atomic exchange integrals are given. In section 3 n_{RT} and n_{RR} are evaluated, and it was assumed that they can be used to describe universally the R-T exchange interactions occurring in R-T intermetallics, and are independent of the specific crystallographic structure due to its atomic nature. We show rigorously that J_{4f-5d} , is indeed far more important than J_{4f-6s} and J_{4f-6p} , and explain the observed variations of R-T and R-R interactions across the rare-earth series.

2. Exchange integrals: method and numerical results

The exchange interactions within configurations of type 4f^{*n*}nl may be divided into two parts: (i) the exchange interactions within the 4f^{*w*} core and (ii) the exchange interactions

of the nl electron with the $4f^m$ core. Here we are interested only in the latter. By using Dirac's vector model (Dirac 1929), in the SL -coupling scheme the effective $4f^m$ - nl exchange Hamiltonian can be expressed as (Racah 1942, Wybourne 1965):

$$\mathcal{H} = -\frac{1}{2} \sum_k \langle f \| C^{(k)} \| l \rangle^2 \sum_x (-1)^x (2x + 1) \left\{ \begin{matrix} 3 & 3 & x \\ l & l & k \end{matrix} \right\} [U_f^{(x)} \cdot u_l^{(x)} + 4V_f^{(1x)} \cdot v_l^{(1x)}] G^k(4f, nl) \tag{1}$$

where $U^{(x)}$ and $u^{(x)}$ are the Racah unit tensors for $4f$ and nl electrons respectively, and $V^{(1x)}$ and $v^{(1x)}$ are the double tensors defined as $V^{(1x)} = S^{(1)}U^{(x)}$, $C^{(k)}$ is the normalized spherical tensor and $G^k(4f, nl)$ is Slater's radial integral. As was pointed out by Liu (1961), the spin-only exchange coupling contribution will dominate, even for non-S-state ions. Therefore, only the term containing spin is needed, which, after interchanging the order of the summations, can be expressed as

$$\mathcal{H} = -2 \sum_x (-1)^x (2x + 1) \left(\sum_k \langle f \| C^{(k)} \| l \rangle^2 \left\{ \begin{matrix} 3 & 3 & x \\ l & l & k \end{matrix} \right\} G^k(4f, nl) \right) V_f^{(1x)} \cdot v_l^{(1x)}. \tag{2}$$

This can be further separated into isotropic (orbit-independent) and anisotropic parts. The magnitude of the isotropic exchange is far greater than that of the anisotropic exchange. It has been shown that the multipole-type Coulomb interactions and the anisotropic exchange interactions between $4f$ and $5d$ electrons almost cancel each other out, leaving nearly isotropic exchange interactions (Yanase and Kasuya 1970). Assuming that this is also true in the $4f$ - $6s$ and $4f$ - $6p$ cases, we consider further only the isotropic exchange. Therefore the Hamiltonian in equation (2) is reduced to the terms with $x = 0$:

$$\mathcal{H} = -2 \left(\sum_k \langle f \| C^{(k)} \| l \rangle^2 \left\{ \begin{matrix} 3 & 3 & 0 \\ l & l & k \end{matrix} \right\} G^k(4f, nl) \right) V_f^{(10)} \cdot v_l^{(10)}. \tag{3}$$

Using the relations $V_f^{(10)} = (1/\sqrt{7})S_f^{(1)}$, $v_l^{(10)} = [1/\sqrt{(2+1)}]s_l^{(1)}$ and $S_f^{(1)} \cdot s_l^{(1)} = S_f \cdot s_l$, equation (3) can be transformed as:

$$\mathcal{H}_{ex, 4f-nl} = -2J_{4f-nl} S_f \cdot s_l \tag{4}$$

where

$$J_{4f-nl} = \frac{1}{\sqrt{7}(2l+1)} \left(\sum_k \langle f \| C^{(k)} \| l \rangle^2 \left\{ \begin{matrix} 3 & 3 & 0 \\ l & l & k \end{matrix} \right\} D_k G_k(4f, nl) \right) \tag{5}$$

gives the isotropic exchange integral which we want to evaluate by self-consistent atomic calculations. (The relation $G_k = G^k/D_k$ has been used, where D_k is the common denominator of Condon and Shortley (1935).) Equation (4) is the familiar dipolar form of Dirac's spin exchange Hamiltonian. The values of the reduced spherical tensor matrix elements and the $6j$ -symbol are easily found in the literature (e.g. Cowan 1981). Finally we have:

$$J_{4f-5d} = 3G_1(4f, 5d) + 12G_3(4f, 5d) + 66G_5(4f, 5d) \tag{6a}$$

$$J_{4f-6s} = G_3(4f, 6s) \tag{6b}$$

$$J_{4f-6p} = 15G_2(4f, 6p) + 12G_4(4f, 6p). \tag{6c}$$

In order to evaluate the values of $\{G_k\}$, a self-consistent-field Dirac-Slater program,

originally written by Liberman *et al* (1965) and modified by Koelling (1977), was employed. The Latter correction (Latter 1955) for the large-radius region was adopted in the program. In the modified version of the program, the local Slater exchange potential is replaced by a more sophisticated local spin-density approximation for exchange and correlation due to Gunnarsson and Lundqvist (1976). It has been shown that this approximation gives excellent results in the atomic calculations (Koelling and Harmon 1977). It should be noted that, in the present work, we are limited to the paramagnetic case. It was assumed that the wavefunction of an atom can be represented by a single determinant of one-electron wavefunction $|nlj\rangle$. Calculations are performed each time for a given jj subconfiguration. The radial domain extended from 1.056×10^{-4} Bohr units to 60 Bohr units. The practical infinity was determined by the condition (in atomic units)

$$[V(r) - E]r^2 \approx 75. \quad (7)$$

Iteration continued until

$$|\rho_{\text{new}}(r_i) - \rho_{\text{old}}(r_i)| < 10^{-4}. \quad (8)$$

The radial wavefunctions obtained are then used to generate the Slater radial integrals G_k , by using a routine written by the present authors.

The relativistic Dirac approach is restricted to a jj -coupling scheme and requires prohibitively expensive multiconfiguration calculations to get back to the LS -like coupling ground state. However, it has been demonstrated that a proper averaging of configurations does give good results (Desclaux *et al* 1971, Freeman and Desclaux 1972).

In a metal, one 4f electron of the rare-earth atom is usually promoted to the conduction band resulting in a trivalent configuration $4f^w(5d6s6p)^3$ with $w = Z - 57$ (Freeman 1972, Min *et al* 1986). In order to make atomic calculations for rare-earth atoms as close as possible to the situation in the metal, we choose the configuration as $4f^w5d^16s^16p^1$. In general, for a given configuration nl^N in the non-relativistic case will correspond to several possible jj subconfigurations in the relativistic case: $(nlj_-)^{N_-}(nlj_+)^{N_+}$ with $N_+ + N_- = N$ and $j_{\pm} = l \pm \frac{1}{2}$, where $N_+ \leq 2l + 2$ and $N_- \leq 2l$. We are then dealing with four open electronic shells, namely 4f, 5d, 6s and 6p. Except for 6s, each shell will split into two subshells: nl_- and nl_+ (here nl_{\pm} denotes nlj_{\pm}). For each configuration $4f^w5d^16s^16p^1$ will therefore have many corresponding jj subconfigurations: $4f_-^{w_-}4f_+^{w_+}5d_-^{N_{d-}}5d_+^{N_{d+}}6s^16p_-^{N_{p-}}6p_+^{N_{p+}}$ (herein denoted as $[w_-w_+N_{d-}N_{d+}N_{p-}N_{p+}]$) with $w_+ + w_- = w$ (where $w_- < 6$ and $w_+ < 8$) and $N_{l\pm} = 0$ or 1 and $N_{l+} + N_{l-} = 1$. For example, the configuration of Ce, $4f^15d^16s^16p^1$ has eight jj subconfigurations: [101010], [101001], [100101], [100110], [011010], [011001], [010101], [010110]. The numbers of the jj subconfigurations for each rare-earth element, N_s , are listed in table 1.

The Slater radial integrals for a given subconfiguration $[i] (= [w_{-(i)}w_{+(i)}N_{d-(i)}N_{d+(i)}N_{p-(i)}N_{p+(i)}])$ are then defined as

$$G_k(4f, nl)_{(i)} = (w_{-(i)}/w)G_k(4f_-, nl)_{(i)} + (w_{+(i)}/w)G_k(4f_+, nl)_{(i)} \quad (9a)$$

where

$$G_k(4f_{\pm}, nl)_{(i)} = N_{l-(i)}G_k(4f_{\pm}, nl_-)_{(i)} + N_{l+(i)}G_k(4f_{\pm}, nl_+)_{(i)}. \quad (9b)$$

Following the suggestion by Desclaux *et al* (1971), the average configurations for the Slater radial integrals (which are equivalent to the energy) are defined as

$$G_k(4f, nl) = \sum_i (2J_i + 1)G_k(4f, nl)_{(i)} / \sum_i (2J_i + 1) \quad (10)$$

where the i summation extends over the total number of states, $(jj)_i$, in the configuration.

Table 1. The number of 4f electrons, w , and jj subconfigurations, N_s , for each rare-earth ion considered, and the values of Slater radial integrals $G_k(4f, nl)$ obtained from the relativistic self-consistent-field atomic calculation by using the appropriate configuration average (see equation (11)).

R	w	N_s	$G_1(4f, 5d)$ (K)	$G_3(4f, 5d)$ (K)	$G_5(4f, 5d)$ (K)	$G_3(4f, 6s)$ (K)	$G_2(4f, 6p)$ (K)	$G_4(4f, 6p)$ (K)
Ce	1	8	555.9	46.39	7.138	493.7	8.286	6.852
Pr	2	12	529.3	44.57	6.875	474.6	7.919	6.555
Nd	3	16	507.7	43.03	6.649	461.4	7.651	6.328
Sm	5	24	473.5	40.43	6.259	445.0	7.269	6.005
Gd	7	28	447.6	38.31	5.934	437.3	7.017	5.788
Tb	8	28	436.1	37.33	5.782	435.3	6.926	5.704
Dy	9	24	425.3	36.40	5.635	434.3	6.840	5.635
Ho	10	20	415.1	35.50	5.493	434.1	6.777	5.571
Er	11	16	405.5	34.63	5.355	434.7	6.720	5.519
Tm	12	12	396.2	33.78	5.220	436.1	6.680	5.476
Yb	13	8	387.2	32.94	5.087	438.0	6.640	5.444

Equation (10) is equivalent to the average over subconfigurations taking account of their respective degeneracies

$$G_k(4f, nl) = \frac{\sum_i P(i) G_k(4f, nl)_{(i)}}{\sum_i P(i)} \quad (11a)$$

with

$$P(i) = \binom{6}{w_{-(i)}} \binom{8}{w_{+(i)}} \binom{4}{N_{d-(i)}} \binom{6}{N_{d+(i)}} \binom{2}{N_{p-(i)}} \binom{4}{N_{p+(i)}} \quad (11b)$$

where

$$\binom{n}{m} = \frac{n!}{m!(n-m)!}.$$

We calculate all possible jj subconfigurations and then use equations (9) and (11) to obtain the Slater radial integrals $G_k(4f, nl)$. Results for R from Ce to Yb, except Pm and Eu, are given in table 1. The corresponding exchange integrals J_{4f-nl} thus can be easily calculated using equations (6), and the values obtained are listed in table 2.

As already mentioned, rare-earth ions have a trivalent configuration $4f^w(5d6s6p)^3$ in the metals. By introducing the 5d, 6s and 6p conduction band occupation numbers n_{5d} , n_{6s} and n_{6p} , the configuration can be rewritten more explicitly as $4f^w 5d^{n_{5d}} 6s^{n_{6s}} 6p^{n_{6p}}$ with $n_{5d} + n_{6s} + n_{6p} = 3$. Values of n_{5d} , n_{6s} and n_{6p} for rare-earth metals have been obtained from spin-polarized energy band calculations by Min *et al* (1986) and Skriver (1983), as reproduced in table 2; n_{5d} is in the range of 1.5–2.0, $n_{6s} \sim 1.0$ and $n_{6p} \sim 0.5$. In principle, the exchange interactions between 4f and conduction band electrons may be derived by using the values of J_{4f-nl} and these occupation numbers if the coupling scheme is known. Unfortunately, the coupling scheme for such a complex configuration is a problem. It may be expected that the contributions from 4f–5d, 4f–6s and 4f–6p will be additive and not interfere with each other, as they all experience a strong crystal field. We shall therefore assume that the interactions between conduction electrons is weak and that

Table 2. Effective intra-atomic exchange integrals deduced from the value of $G_k(4f, n_l)$ according to equations (6) and (12). The occupation numbers n_{5d} , n_{6s} and n_{6p} are those found from spin-polarized energy band calculations for the rare-earth metals by Min *et al* (1986).

R	J_{4f-5d} (K)	J_{4f-6s} (K)	J_{4f-6p} (K)	n_{5d}	n_{6s}	n_{6p}	J_{4f-c} (K)
Ce	2695	493.7	206.5	1.95	0.65	0.40	1886
Pr	2576	474.6	197.4	1.90	0.67	0.43	1766
Nd	2478	461.4	190.7	1.86	0.71	0.44	1674
Sm	2319	445.0	181.1	1.76	0.74	0.50	1500
Gd	2194	437.3	174.7	1.69	0.77	0.54	1380
Tb	2138	435.3	172.3	1.65	0.78	0.56	1321
Dy	2085	434.3	170.2	1.62	0.80	0.58	1275
Ho	2034	434.1	168.5	1.57	0.80	0.63	1216
Er	1985	434.7	167.0	1.55	0.82	0.63	1179
Tm	1938	436.1	165.9	1.52	0.85	0.63	1140
Yb	1893	438.0	164.9				

they may be considered independently (Lacueva *et al* 1982). In order to make a quantitative analysis, we introduce an effective exchange integral between the 4f electrons and the conduction band electrons, J_{4f-c} , defined as the weighted average contributions from 5d, 6s and 6p bands,

$$J_{4f-c} = \frac{1}{3}(n_{5d}J_{4f-5d} + n_{6s}J_{4f-6s} + n_{6p}J_{4f-6p}). \quad (12)$$

Using the values of J_{4f-nl} and n_{5d} , n_{6s} and n_{6p} found in table 2, J_{4f-c} deduced according to equation (12) for most of rare-earth ions are listed in table 2.

3. Molecular-field model: evaluation of n_{RT} and n_{RR}

In order to make a possible comparison between J_{4f-c} and the experimental Curie temperature T_C , we deduced the relations between J_{4f-c} and the molecular-field coefficients n_{RT} and n_{RR} as defined by Belorizky *et al* (1987). Following Campbell's picture, within a simplified molecular-field approximation, the 3d, 4f and conduction electron (5d, 6s and 6p of R atom) magnetization M_{3d} , M_{4f} and M_c in an applied field H at $T > T_C$ may be written as (Shimizu 1961, Morin 1988)

$$M_{3d} = \chi'_{3d}(H + n_{3d-c}M_c) \quad (13a)$$

$$M_c = \chi'_c(H + n_{3d-c}M_{3d} + \gamma n_{4f-c}M_{4f}) \quad (13b)$$

$$M_{4f} = \chi_{4f}(H + \gamma n_{4f-c}M_c) \quad (13c)$$

where

$$\chi'_{3d} = \chi_{3d}/(1 - \chi_{3d}n_{3d-3d}) \quad (14a)$$

and

$$\chi'_c = \chi_c/(1 - \chi_c n_{c-c}) \quad (14b)$$

are the exchange enhanced susceptibilities, and $n_{nl-nl'}$ are molecular-field coefficients

representing the different exchange strengths between spin magnetic moments of nl and nl' type electrons. The rare-earth susceptibility χ_{4f} is expected to obey a Curie-Weiss law $\chi_{4f} = C_{4f}/T$, where the Curie constant $C_{4f} = N_R g_J^2 J(J+1) \mu_B^2 / 3k_B$ (N_R is the number of R atoms per unit volume). The spin projection factor $\gamma = 2(g_J - 1)/g_J$ is included in equations (13) because the exchange interactions act on the spin magnetic moments only. The temperature dependence of χ_{3d} is less obvious due to the itinerant nature of the 3d magnetism. It was argued that a Curie-Weiss law observed over limited or extended temperature ranges is compatible with the itinerant model (Shimizu 1977, Wohlfarth 1974). However, it has recently been shown that the temperature dependence of inverse susceptibility of Fe, Co, Ni and their alloys follows very well and reproducibly a linear Curie-Weiss law in the paramagnetic region (Renz and Methfessel 1988). So, as proposed by Rhodes and Wohlfarth 1961 (see also Wohlfarth 1978), χ_{3d} may conveniently be analysed by assuming $\chi_{3d} = C_{3d}/T$ (where C_{3d} is an effective Curie constant), if the 3d moment is well established. Values of C_{3d} have been determined from the high-temperature susceptibility measurement for many R-T series (Burzo 1973, Kirchmayr and Poldy 1979, Burzo *et al* 1985). The Curie-Weiss law temperature dependence for χ_{3d} is acceptable based on the fact that the amplitude of longitudinal spin fluctuations does not vary with temperature at high temperatures (Moriya 1985). The conduction electron susceptibility χ'_c will be discussed later.

From equations (13) the Curie temperature T_C is determined by the condition of non-vanishing solution for M_{3d} , M_{4f} and M_c in the absence of an applied field, which gives

$$1 - \chi'_{3d} \chi'_c n_{3d-c}^2 - \chi_{4f} \chi'_c \gamma^2 n_{4f-c}^2 = 0. \quad (15)$$

Considering the reciprocal temperature dependence of χ_{4f} and χ_{3d} , equation (15) can be rewritten as

$$T_C = \frac{1}{2} \{ T_{3d} + T_{4f} + [(T_{3d} - T_{4f})^2 + 4T_{fd}^2]^{1/2} \} \quad (16)$$

where

$$T_{3d} = (n_{3d-3d} + \chi'_c n_{3d-c}^2) C_{3d} \quad (17a)$$

$$T_{4f} = \gamma^2 C_{4f} \chi'_c n_{4f-c}^2 \quad (17b)$$

$$T_{fd} = |\gamma| (C_{3d} C_{4f})^{1/2} \chi'_c n_{3d-c} n_{4f-c}. \quad (17c)$$

Comparing equations (17) with equations (5), (6) and (7) given by Belorizky *et al* (1987), we find that

$$n_{RT} = \chi'_c n_{3d-c} n_{4f-c} \quad (18a)$$

$$n_{RR} = \chi'_c n_{4f-c}^2. \quad (18b)$$

Equation (18b) has been derived by Belorizky *et al* (1988b) to describe rare-earth intermetallics in which only rare-earth ions are magnetic, and is similar to that obtained by Takahashi and Shimizu (1965) in the 3d itinerant systems. It should be noted that an extra term, $\chi'_c n_{3d-c}^2 C_{3d}$, appears in the 3d Curie temperature, T_{3d} , in the present model (equation (17a)), mainly due to the indirect 3d-5d-3d exchange interaction. This extra term implies that the difference of Curie temperatures observed between Y-T and La, Lu-T isomorphous compounds (Buschow 1977, 1988) can now be understood as due to the difference of 4d-3d and 5d-3d exchange interactions.

Table 3. N_R is the rare-earth atomic density (Elliott 1972), J_{c-c} and J_{3d-c} are the exchange integrals, and n_{c-c} , n_{3d-c} and n_{4f-c} are the molecular-field coefficients. χ_c is the Pauli paramagnetic susceptibility defined by equation (24) and χ'_c is the exchange enhanced susceptibility given by equation (14b). The important parameters n_{RT} and n_{RR} are obtained following equations (18).

R	N_R (10^{28} m^{-3})	J_{c-c} (K)	J_{3d-c} (K)	n_{c-c} (μ_0)	n_{3d-c} (μ_0)	n_{4f-c} (μ_0)	χ_c ($10^{-5} \mu_0^{-1}$)	χ'_c ($10^{-5} \mu_0^{-1}$)	n_{RT} (μ_0)	n_{RR} (μ_0)
Pr	2.895	4700	6946	5185	4476	1948	2.464	2.825	246	107
Nd	2.926	4601	6872	5022	4405	1827	2.490	2.846	229	95
Sm	3.011	4354	6685	4618	4224	1591	2.496	2.821	190	71
Gd	3.026	4180	6551	4411	4129	1456	2.501	2.811	169	60
Tb	3.119	4082	6473	4179	4019	1353	2.526	2.824	154	52
Dy	3.169	4057	6453	4088	3975	1285	2.540	2.834	145	47
Ho	3.211	3884	6314	3863	3864	1209	2.551	2.830	132	41
Er	3.264	3834	6274	3751	3808	1154	2.565	2.838	125	38
Tm	3.322	3760	6212	3615	3737	1096	2.580	2.845	117	34

Equations (18) give the basis for relating the theoretical value of J_{4f-c} , obtained in the previous section (see table 2), to the phenomenological parameters n_{RT} and n_{RR} which are known from experimental T_C data for most R-T series (Belorizky *et al* 1987). There are three parameters, n_{3d-c} , n_{4f-c} and χ'_c , in equations (18) to be determined. The molecular-field coefficient n is, in general, related to the exchange integral J by

$$n = J/4N\mu_B^2. \quad (19)$$

It follows that

$$n_{4f-c} = J_{4f-c}/4N_R\mu_B^2 \quad (20a)$$

$$n_{3d-c} = J_{3d-c}/4N_T\mu_B^2. \quad (20b)$$

The values of J_{4f-c} can be read from table 2, so we immediately have the values of n_{4f-c} by using equation (20a), which are listed in table 3, where N_R is deduced from the R atomic volume given by Elliott (1972). For n_{3d-c} , it is not so straightforward due to a lack of knowledge of J_{3d-c} . There are no reports of its value in the literature up to now. Assuming that the 3d-c interaction occurs mainly within the atomic spheres of T atoms, and that the 4f-c and c-c interactions occur within those of the R atoms, we define

$$J_{3d-c} \approx (J_{3d-3d}J_{c-c})^{1/2} \quad (21)$$

where J_{c-c} is the exchange integral between 5d(6s, 6p) conduction band electrons, and can be written as

$$J_{c-c} = \frac{1}{3}(n_{5d}J_{5d-5d} + n_{6s}J_{6s-6s} + n_{6p}J_{6p-6p}). \quad (22)$$

As the main contribution is largely from 5d electrons we take the approximate values given by

$$J_{3d-c} \approx (n_{5d}/3)J_{5d-5d} \quad (23)$$

which neglects the contributions from 6s and 6p electrons. The value of J_{3d-3d} for Fe metal was taken as that given by Brooks *et al* (1989) (see also Gunnarson 1977, Andersen 1977), $J_{3d-3d} = 10263 \text{ K}$ (65 mRyd), and that of J_{5d-5d} in LuFe_2 is given by Brooks *et al*

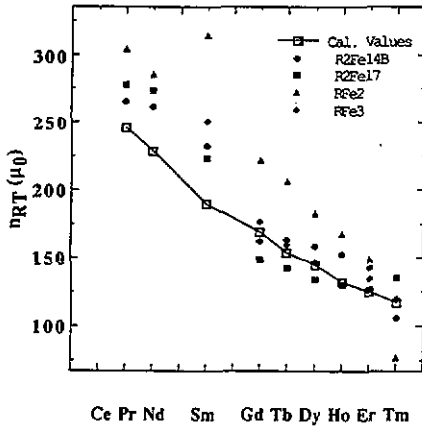


Figure 1. Comparison of calculated values of n_{RT} with those observed in several rare-earth inter-metallic series.

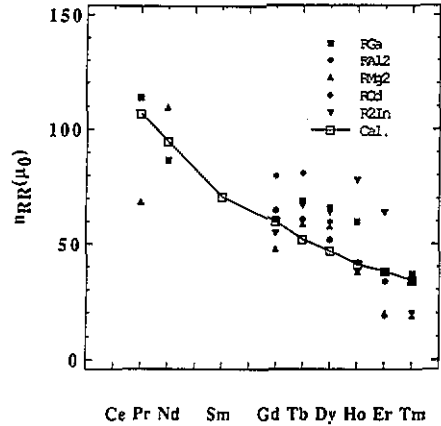


Figure 2. Comparison of calculated values of n_{RR} with those observed in several rare-earth inter-metallic series.

(1989) (see also Yamada and Shimizu 1986), $J_{5d-5d} = 7421$ K (47 mRyd). By using the value of $N_T = 8.48 \times 10^{28} \text{ m}^{-3}$ for BCC Fe metal, the values of n_{3d-c} deduced according to equations (20b), (21) and (23) (values of n_{5d} can be found in table 2) are listed in table 3. There remains the exchange enhanced susceptibility χ'_c of conduction band electrons to be determined. As already mentioned, the $5d(6s,6p)$ spin magnetic moment is largely induced by localized $4f$ moments with some help from $3d-5d(6s,6p)$ hybridization (Brooks *et al* 1989). The non-interacting susceptibility χ_c is just the temperature-independent Pauli paramagnetic susceptibility, within the free-electron approximation, which is given by

$$\chi_c = 2\mu_B^2 N(\epsilon_F) \tag{24}$$

where

$$N(\epsilon_F) = 3\rho/2\epsilon_F \tag{25}$$

and

$$\epsilon_F = (\hbar^2/2m)(3\pi^2\rho)^{1/3} \tag{26}$$

where ρ is the conduction electron density within the R atomic sphere; for R atoms in metal $\rho = 3N_R$ (noting that $n_{5d} + n_{6s} + n_{6p} = 3$). Values of χ_c obtained in this way are listed in table 3. To calculate χ'_c we need the molecular-field coefficient n_{c-c} (see equation (14b)). Employing equation (19) and using the values of J_{c-c} (table 3), it is easy to evaluate χ'_c . Values obtained are also given in table 3. According to equations (18), the values of n_{RT} and n_{RR} are finally deduced. Results are listed in the last two columns of table 3, and are plotted in figures 1 and 2 for comparison with the experimental values.

4. Discussion

In order to check Slater's radial integrals $G_k(4f, nl)$ as well as J_{4f-nl} obtained in the present work, table 4 lists the values of $G_k(4f, nl)$ and corresponding J_{4f-nl} deduced from atomic

Table 4. Experimental values of $G_x(4f, nI)$ obtained from atomic spectroscopy measurements, and the corresponding effective exchange integrals deduced according to equations (6).

R	Configuration	$G_1(4f, 5d)$ (K)	$G_3(4f, 5d)$ (K)	$G_5(4f, 5d)$ (K)	$G_3(4f, 6s)$ (K)	$G_2(4f, 6p)$ (K)	$G_4(4f, 6p)$ (K)	J_{4f-5d} (K)	J_{4f-6s} (K)	J_{4f-6p} (K)	Ref.
Ce	4f ¹ 5d	425.9	57.6	7.20				2444			a
Pr	4f ² 5d	406.5 ± 2.6	47.3 ± 1.0	5.80 ± 0.20				2170 ± 13			b
Pr	4f ⁶ 6s				440 ± 45				440 ± 45		b
Pr	4f ² 6p					11.7 ± 2.3	19.0 ± 3.0			404 ± 36	b
Pr	4f ² 5d6s	405.8 ± 2.2	47.5 ± 0.9	5.80 ± 0.20	447 ± 30			2170 ± 13	447 ± 30		b
Tm	4f ¹² 5d	311.5 ± 2.9	45.3 ± 1.4	7.58 ± 0.52				1978 ± 34			c
Tm	4f ¹² 6s				394 ± 43				394 ± 43		c
Tm	4f ¹² 6p					14.7 ± 0.5	14.7 ± 1.0			397 ± 15	c
Yb	4f ¹³ 5d	303.6 ± 3.3	43.2 ± 1.9	7.18 ± 0.60				1903 ± 40			d

* McClure and Kiss (1963).

b Feneuille and Pelletier-Allard (1968).

c Sugar (1970a).

d Sugar (1970b).

Table 5. Values of the effective 4f-conduction electron exchange for Gd obtained in the present work compared to the experimental values observed in diverse systems.

Compound	J_{4f-c} (K)	Ref.
Gd	1380*	Present work
Gd	1263	a
GdZn	1270	a
GdCd	1505	a
GdIn _{1/3}	1144	a
GdAl ₂	1511	a
Ag:R	1168	b
Ag:R	967	b

* Theoretical value.

a Belorizky *et al* (1988b).b Lacueva *et al* (1982).

spectroscopy measurements for Ce, Pr, Tm and Yb. It can be seen, from comparison of tables 1 and 2 and table 4, that the overall agreement is good for 4f-5d and 4f-6s interactions, whereas for 4f-6p the calculations somewhat underestimate the magnitude. It is expected that the presence of the outer 6s and 6p shells has little effect on calculations of the 4f-5d exchange interactions. $G_1(4f, 5d)$ agrees within 30%, where the calculated values are larger than the experimental ones, which indicates that some screening corrections for $G_k(4f, nl)$ might need to be considered. Nevertheless the resulting J_{4f-nl} agree within 10%, so as a first approximation we neglect the screening effects for $G_k(4f, nl)$. It should be mentioned that the exchange integrals J_{4f-5d} for most of the rare earths have been calculated from an atomic calculation by Brooks *et al* (1989). The values given by these authors vary from $J_{4f-5d} = 1421$ K for Ce to $J_{4f-5d} = 947$ K for Yb, which are much smaller than the values obtained in the present work, as well as those deduced from atomic spectroscopy measurements (see tables 2 and 4). In fact the value of J_{4f-5d} depends very much on the atomic configuration (Feneuille and Pelletier-Allard 1968, Sugar 1970a, b). As the configurations in their calculations were not explicitly given, it is difficult to make a direct comparison.

From table 2, one can see that the magnitude of J_{4f-5d} , in the range 1900-2700 K, is far more important than that of J_{4f-6s} , 450 K, or of J_{4f-6p} , 180 K, as was originally assumed by Campbell (1972). The variation of J_{4f-5d} across the rare-earth series is remarkable, decreasing continuously from Ce to Yb by about 42%. J_{4f-6s} decreases from Ce to Gd by about 13% and then remains roughly constant for heavy rare earths.

We turn now to discuss the effective exchange integral J_{4f-c} defined by equation (12). In recent work (Belorizky *et al* 1988b), the ferromagnetic Curie temperature and susceptibilities have been used to deduce the value of J_{4f-c} for Gd metal and Gd compounds. (It should be noted that in their original paper, Belorizky *et al* assign the f-d type exchange for J_0 as defined by them which certainly contain the contributions from 4f-6s and 4f-6p interactions, hence is equivalent J_{4f-c} here.) Yet the values of J_{4f-c} have been deduced from the best fit for the magneto-transport measurements of rare earths diluted in noble metals Ag:R and Au:R (Lacueva *et al* 1982). The values obtained as mentioned above are reproduced in table 5 with the present theoretical values. The calculated value 1380 K falls within the experimental range 967 to 1511 K. This justifies

the definition of J_{4f-c} , which is the overall effective exchange interaction between 4f and 5d(6s,6p) conduction band electrons and can be used to describe the 4f-c-nd exchange mechanism. J_{4f-c} decreases about 65% from Ce to Yb (table 2). It is worth noting that such a general tendency has also been observed from results for J_{4f-c} in RAI_2 compounds from extensive studies of nuclear magnetic resonance (NMR), Knight shift (Jaccarino *et al* 1960, Jones and Budnick 1966), electron paramagnetic resonance (EPR) (Peter 1961), magnetic susceptibility (Williams *et al* 1962), electrical resistivity (van Daal and Buschow 1969) and depression of superconducting transition temperature (Maple 1970). These earlier results together with the recent data mentioned in the introduction draw a conclusive picture: J_{4f-c} decreases about 100% from Ce to Yb, for which the explanation is given from a theoretical view in the present work. It can be concluded that the relativistic atomic calculation gives very satisfactory results in spite of the simple average configuration approach used.

As can be seen from figure 1, the agreement between theoretical and experimental values of n_{RT} is surprisingly good, in view of the simple molecular-field model employed and the approximations made; n_{RT} decreases from Pr to Tm by a factor of 2.1:1, as observed. The decrease is mainly determined by the 80% decrease of n_{4f-c} , while n_{3d-c} decreases only 20%. The value of χ'_c is roughly constant across the R series. The decrease of n_{RT} by a factor of 2.1 is not entirely due to the variation of n_{4f-5d} (78% from Pr to Tm), but there is also a contribution from the decrease of the 5d electron number n_{5d} (25%). From equations (18), we have

$$n_{RT}^2/n_{RR} = \chi'_c n_{3d-c}^2 \quad (27)$$

which decreases slightly, 28%, compared to n_{RT} , 52%, or n_{RR} , 68%. The variation of n_{RR} is thus expected to be approximately proportional to that of n_{RT}^2 as observed by Belorizky *et al* (1988a).

5. Conclusions

Using self-consistent relativistic atomic calculations, values are obtained for the intra-atomic rare-earth exchange integrals J_{4f-5d} , J_{4f-6s} and J_{4f-6p} and their weighted average J_{4f-c} . Easily the largest of these integrals is J_{4f-5d} , as proposed by Campbell (1972). All three exchange integrals decrease across the rare-earth series due to the lanthanide contraction. Agreement between calculated values and those determined spectroscopically is good.

For the first time, a three-sublattice molecular-field model was successfully established to relate the intra-atomic parameters J_{4f-nl} to the phenomenological parameters n_{RT} and n_{RR} . The resulting expressions of equations (16)–(18) reveal different contributions to the exchange interaction occurring in R–T intermetallic compounds. An extra term, mainly from 3d–5d(4d)–3d contributions, was found, which gives the theoretical explanation for the different Curie temperatures observed for many Y–T and Lu–T isomorphous compounds.

Our calculations explain the substantial decrease of the molecular-field coefficients n_{RT} and n_{RR} found experimentally in rare-earth intermetallic compounds. They also explain why the Curie temperatures of rare-earth intermetallic series scale approximately as the de Gennes factor for the heavy rare earths, and why the light rare earths appear to have Curie temperatures that are systematically too high. Most of the decrease

of the exchange integrals occurs at the beginning of the rare-earth series, and the values of J and n_{RT} vary relatively little from Gd to Yb.

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