Journal of Alloys and Compounds 408–412 (2006) 2–8

Journal of
ALLOYS
AND COMPOUNDS

www.elsevier.com/locate/jallcom

Rare earth elements and magnetism in metallic systems

Junjiro Kanamori

International Institute for Advanced Studies, Kizugawadai 9-3, Kizu, Soraku-gun, Kyoto 619-0225, Japan

Abstract

A theoretical review of roles of rare earth elements in determining magnetic properties of metallic materials is presented. Starting with the problem of the formation of a magnetic moment in the 4f state in a solid, the discussion covers the interaction between magnetic moments, the Kondo effect and related problems. Subsequently the interaction between rare earth and transition elements and the role of interstitial typical elements in ferromagnetic intermetallic compounds are discussed on the basis of electronic structure calculations.

Keywords: Metals; Intermetallics; Kondo effects; Electronic band structure; Exchange and superexchange

1. Introduction

I would like to present a theoretical survey of roles of rare earth elements in metallic magnetic substances. A partially filled f shell which gives rise to an atomic magnetic moment characterizes a rare earth element atom. The magnetic moment is usually maintained in a solid where a given rare earth element atom interacts and shares electrons with neighboring atoms. The moment can be quenched, however, through the Kondo effect [1] when embedded as impurity in a nonmagnetic metal. The effect can persist even when rare earth atoms are more densely distributed. In particular, Ce compounds where the rare earth element atoms occupy lattice sites periodically may acquire at low temperatures either a magnetic order or the heavy electron (fermion) behavior or both. The topic has been one of the central themes in the field of magnetism as basic science. On the other hand, intermetallic compounds of rare earth-transition elements have drawn attention as important permanent magnet materials since the latter half of the 20th century in both applied and basic magnetism. Particularly innovation of the Nd–B–Fe magnet [2] has presented several interesting theoretical problems.

I intend to give an introductory review on the above-mentioned topics. Starting with the atomic state, I discuss the formation of a magnetic moment in a metallic solid in the next section (Section 2). In Section 3, I discuss the interaction between magnetic moments, the Kondo effect and related problems. Section 4 deals with intermetallic compounds such as Nd–B–Fe. The final section (Section 5) is devoted to concluding remarks.

2. f-Levels and magnetic moment

The 4f states of rare earth elements are characterized by the fact that the wave function is mostly confined to a region inside the valence shells of smaller orbital angular momenta. The 3d states of transition elements have the same tendency to a less extent. The confinement is explained by the fact that the effective potential determining the radial part of the 4f atomic orbital has a sharp minimum inside the valence shells; the minimum is produced by the centrifugal force term $\hbar^2\ell(\ell+1)/2mr^2$ in combination with the atomic potential arising from nucleus and other electrons, where $\ell = 3$ for f levels and r denotes the distance from nucleus. Thus, a state of high orbital angular momentum retains its atomic character more or less when the atom is embedded in a solid.

We discuss the atomic state in a metallic system. We assume first that the 4f level is orbitally nondegenerate and lies in the energy range of a given conduction band. The conduction band is occupied by electrons up to the Fermi energy $E_{F.}$. Suppose an electron occupies the f level at the position denoted by ε_f ($<E_F$). If another electron with opposite spin is

---

E-mail address: kanamori@iias.or.jp.

0925-8388/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2005.04.103

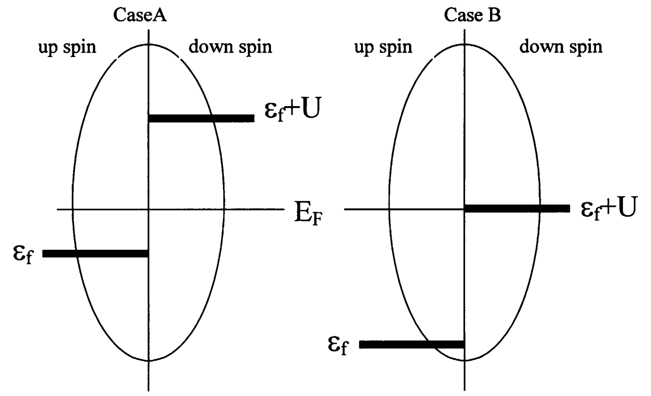

Fig. 1. Effective f levels and conduction band in the case where the f level is occupied by an up spin electron.

added, the total energy will be given by $2\varepsilon_\mathrm{f} + U$ with U denoting the coulomb interaction energy between two electrons in the same atomic orbital. Thus, we may suppose that an effective energy level for the second electron is situated at $\varepsilon_\mathrm{f} + U$. Depending on the relative magnitude of $E_\mathrm{F} - \varepsilon_\mathrm{f}$ to U we can distinguish several cases. If $U \gg E_\mathrm{F} - \varepsilon_\mathrm{f}$, the 4f level will be occupied by an electron only, since the effective level for the second electron is above the Fermi energy. It is illustrated as the case A in Fig. 1. In the case B, where $U \cong E_\mathrm{F} - \varepsilon_\mathrm{f}$ we may find the case of valence fluctuation; the f electron number may change depending upon the condition. We omit in Fig. 1, the cases where the f level is doubly occupied fully with $U < E_\mathrm{F} - \varepsilon_\mathrm{f}$ or empty with $E_\mathrm{F} < \varepsilon_\mathrm{f}$, since they are rather irrelevant to the following discussion.

Though we assumed an orbitally nondegenerate level so far, we can generalize the discussion easily to multiple degenerate cases. The case A corresponds to the case, where the f levels behave like atomic levels accommodating integral number of electrons even in metallic systems. In the following, we assume this case unless otherwise mentioned. The atomic states of a rare earth element are classified in the Russel–Saunders scheme; the intraatomic electron–electron coulomb interaction that is of primary importance produces the *LS* multiplet with *L* and *S* representing the total orbital angular momentum quantum number and the total spin one, respectively. We can confine ourselves safely to the ground *LS* multiplet in the discussion of magnetism at temperatures of ordinary interest. The *LS* multiplet is split by the spin-orbit coupling into the *J* multiplets with *J* representing the total angular momentum quantum number. Following Van Vleck's monumental work [3] on the paramagnetism of rare earth ions, we may need to take into account the presence of *J* multiplets of higher energy than that of lowest energy in the cases of Sm and Eu in quantitative discussions. Otherwise we can confine ourselves to the *J* multiplet of lowest energy in the ground *LS* multiplet at and below room temperatures. With this picture of the rare earth atomic states we proceed to the discussion of interactions of a rare earth magnetic moment with metallic environment in the next section (Section 3).

3. The interaction with environment

Historically the crystalline or ligand field model was the first attempt to take into account the effect of environment on the atomic d and f states in a solid. In the case of rare earth elements, the crystalline field is generally small compared with the spin orbit coupling. Thus, its effect is to split the *J* multiplet of lowest energy into sublevels. It is an important origin of the magnetic anisotropy energy in the case of permanent magnet materials which will be discussed in the next section (Section 4). Though the crystalline field effect should be taken into account in discussions of individual substances, I continue the general discussion of the preceding section under the assumption that it can be neglected. Then one may have the impression that a rare earth element atom in a metal will keep the magnetic moment associated with the ground *J* level. Actually metals of Gd and heavier rare earth elements become either ferromagnetic or helimagnetic at low temperatures, where these magnetic moments make a magnetic order, keeping essentially its original magnitude [4]. The ordering is ascribed to the interaction between the magnetic moments mediated by conduction electrons called the RKKY interaction usually. The name is taken from Ruderman and Kittel's theory of the interaction between nuclear moments in a metal, Kasuya's discussion on the ferromagnetism of rare metals and Yosida's detailed investigation of the interaction [5], though Zener [6] was the first to propose the interaction of the 3d moments with the s band as a principal mechanism underlying the ferromagnetism of transition metals. In the case of transition metals, however, the direct interaction between 3d states of neighboring atoms caused by electron transfer has been concluded to be mainly responsible for magnetic ordering [7]. The electron transfer is also responsible for the d band formation. It suppresses the spin orbit coupling and causes spin to be a main origin of the magnetic moment. In the case of rare earth elements, it is generally agreed that the corresponding f band effect is irrelevant except for some heavy electron systems.

We derive an order estimation of the magnitude of the RKKY interaction which is needed to discuss the competition with the Kondo effect. We introduce a local spin operator $\boldsymbol{s_i}$ of conduction electron states defined by:

$$s_{iz} = (1/2)({c_{i\uparrow}}^{*}c_{i\uparrow} - {c_{i\downarrow}}^{*}c_{i\downarrow}), \quad s_{ix} + is_{iy} = {c_{i\uparrow}}^{*}c_{i\downarrow} \text{ and } s_{ix} - is_{iy} = {c_{i\downarrow}}^{*}c_{i\uparrow}, \tag{1}$$

where $c^{*}_{i\sigma}$ and $c_{i\sigma}$ are the creation and annihilation operator of the Wannier state at the site i with spin $\sigma(\sigma = \uparrow$ or $\downarrow)$. Then we express the exchange interaction between $\boldsymbol{s_i}$ and a given rare earth atom spin at the site i, $\boldsymbol{S_i}$ as:

$$E_\mathrm{ex} = -J_\mathrm{cf}\boldsymbol{S_i} \cdot \boldsymbol{s_i}, \tag{2}$$

Deferring the discussion of the origin of the exchange interaction, we summarize the argument to derive an interaction between rare earth spins from the exchange interaction (2). If we replace the rare earth spin by its average value $\langle \boldsymbol{S_i} \rangle$, the exchange interaction represents a magnetic field $J_{\mathrm{cf}}\langle \boldsymbol{S_i}\rangle/g_{\mathrm{s}}\mu_{\mathrm{B}}$ at the site i for the conduction states which will produce a spin polarization of conduction electrons at a site j given by:

$$\langle \boldsymbol{s_j}\rangle = J_{\mathrm{cf}}\boldsymbol{\chi}(j,i)\cdot\langle \boldsymbol{S_i}\rangle \tag{3}$$

with $\chi(j,i)$ representing the nonlocal spin susceptibility tensor of the conduction band. We obtain then the interaction energy between $\langle \boldsymbol{S_i}\rangle$ and $\langle \boldsymbol{S_j}\rangle$ as

$$E(\mathrm{RKKY}) = -J_{\mathrm{cf}}^2\sum\nolimits_{\langle ij\rangle}\langle \boldsymbol{S_j}\rangle\boldsymbol{\chi}(j,i)\langle \boldsymbol{S_i}\rangle \tag{4}$$

where the sum is taken over pairs of ij. When we introduce the Fourier transforms of $\langle \boldsymbol{S_i}\rangle$'s and the susceptibility as

$$\langle \boldsymbol{S}(\boldsymbol{q})\rangle = 1/N^{1/2}\,\Sigma_i\langle \boldsymbol{S_i}\rangle\ \exp(i\boldsymbol{q}\cdot\boldsymbol{r_i})\quad \text{and}$$
$$\boldsymbol{\chi}(\boldsymbol{q}) = \Sigma_{\langle ij\rangle}\boldsymbol{\chi}(j,i)\exp[i\boldsymbol{q}\cdot(\boldsymbol{r_i}-\boldsymbol{r_j})], \tag{5}$$

we obtain the expression,

$$E(RKKY) = -\ J_{\mathrm{cf}}^2/2\,\Sigma_q\langle \boldsymbol{S}(-\boldsymbol{q})\rangle\cdot\boldsymbol{\chi}(\boldsymbol{q})\cdot\langle \boldsymbol{S}(\boldsymbol{q})\rangle, \tag{6}$$

we take into account the J multiplet formation due to the spin-orbit coupling by replacing $\boldsymbol{S}$ by its projection to $\boldsymbol{J}$ given by $(\mathrm{g}-1)\,\boldsymbol{J}$ with the Lande g factor [8].

The ordering corresponding to $\boldsymbol{q}$ that maximizes χ will be realized. This is the basis of the phenomenological argument of various magnetic orderings observed in the cases of rare earth metals. In order to explain the observed orderings and transitions caused by pressure, magnetic field, etc. we need to take into account the crystalline field, magnetoelastic energy and mixing of J multiplets in addition to the interaction (6). Details are referred to literature [4].

The discovery of the Kondo effect [1] and subsequent developments lead us to the recognition that the validity of the classical picture of the rare earth atomic state in a metal so far discussed has a limitation. First of all we note here that the exchange interaction (2) can be antiferromagnetic, i.e. $J_{\mathrm{cf}} < 0$, if the mixing of the f state with the conduction band state is mainly responsible for it. We summarize the discussion in the following. The mixing is caused by the interaction given by:

$$\Sigma_{k\sigma}V_{\mathrm{fc}}(c_{\mathrm{f}\sigma}{}^{*}c_{k\sigma} + c_{k\sigma}{}^{*}c_{\mathrm{f}\sigma}), \tag{7}$$

with second quantization operators of the f level and conduction band states specified by wave vector k. $c_{k\sigma}$'s correspond to the Fourier transforms of c_i's previously introduced in Eq. (1). The second order perturbation of the mixing term (7) gives rise to an effective exchange interaction given by Eq. (2) with

$$J_{\mathrm{cf}} = -2\langle|V_{\mathrm{fc}}|^2\rangle[1/(U - E_{\mathrm{F}} + \varepsilon_{\mathrm{f}}) + 1/(E_{\mathrm{F}} - \varepsilon_{\mathrm{f}})] \tag{8}$$

which is of antiferromagnetic sign (see the case A in Fig. 1). This discussion applies also to the 3d-states in the case of transition element impurities which was the original target of Kondo's theory; we use the same symbol J_{cf} instead of J_{cd} in the following discussion in spite of this history.

Before going into discussion of negative J_{cf} effects, we note that J_{cf} seems to be positive, i.e. ferromagnetic in the case of rare earth metals to result in a polarization of conduction electron spins parallel to spins of rare earth atoms. This is experimentally evidenced by the saturation magnetization per atom of Gd metal which exceeds the atomic moment of Gd [4]; since Gd magnetic moment arises only from spins with $L=0$, the additional part of the magnetization should be ascribed to the conduction electron spin polarization. We expect the positive sign of J_{cf} in this case, since the conduction band states of rare earth metals are of 5d character to a large extent. A large overlap of wave functions makes the contribution of the 5d–4f direct atomic exchange interaction dominant.

The Kondo effect refers to a quantum phenomena caused by the exchange interaction (2) between a localized spin and spins of conduction electrons. Electrical resistivity of normal and noble metals show often a minimum at low temperatures as a function of temperature. It took time to reach the conclusion that the minimum was caused by magnetic impurities, since the temperature of minimum resistivity depended only slightly on the impurity concentration. Kondo [1] elucidated the underlying mechanism by taking into account the contribution of the exchange interaction (2) to the third order in perturbation calculation of electrical resistance. The noncommutability of local spin operator components S_x and S_y gives rise to a third order term proportional to $J_{\mathrm{cf}}^3\ \log(k_{\mathrm{B}}T/D)$ with T denoting temperature and D the band width, which increases with decreasing temperature if $J_{\mathrm{cf}} < 0$. The total resistivity ρ is obtained by adding the result of the perturbation calculation to the resistivity of pure system arising from the scattering due to lattice vibration. The latter is proportional to T^5 at low temperature. Thus we obtain

$$\rho = AT^5 + \rho_{\mathrm{B}}[1 + 2J_{\mathrm{cf}}\eta_{\mathrm{c}}(E_{\mathrm{F}})\log(k_{\mathrm{B}}T/D)]\quad \text{with}$$
$$\rho_{\mathrm{B}} = ch(\pi J_{\mathrm{cf}}\eta_{\mathrm{c}})^2 S(S+1)/(2e^2k_{\mathrm{F}}), \tag{9}$$

where ρ_{B} is the residual resistivity independent of temperature obtained in the second order perturbation calculation (the Born approximation) with c representing the concentration of the impurity, η_{c} the density of conduction states at the Fermi level, and k_{F} the Fermi wave vector. We can see easily that ρ takes a minimum value at a temperature proportional to $c^{1/5}$, which explains the weak dependence of its position on the impurity concentration.

The enigma that ρ given by Eq. (9) diverged when $T\to 0$ started subsequent theoretical developments. Deferring details to literature [9,10], I sketch here a rough physical picture of the negative J_{cf} effect. In the calculation of the resistivity, we compute the probability of processes in which an electron is scattered from an initial state of a given wave vector into a final state having a different wave vector. In the third order process whose importance was pointed out by Kondo, a scattering of another electron can be involved in intermediate states. In the case of the scattering due to the exchange interaction (2), the local spin S may change its direction in such intermediate processes. Actually the noncommutability of S_x and S_y that cause a change of local spin direction in the processes gives rise to the Kondo term in Eq. (9). In higher order terms of the perturbation calculation, the local spin will change its direction over and over. Eq. (9) indicates that if J_{cf} $\eta_{\mathrm{c}}(E_{\mathrm{F}}) \log(k_{\mathrm{B}}T/D)$ becomes of the order of 1, the higher order terms will become important. The Kondo temperature T_{k} is usually defined by the condition $J_{\mathrm{cf}}\ \eta_{\mathrm{c}}(E_{\mathrm{F}}) \log(k_{\mathrm{B}}T_{\mathrm{k}}/D) = 1$ which yields:

$$k_B T_k = D\exp[-1/|J_{cf}|\eta_c(E_F)], \tag{10}$$

When temperature is lowered to $T \approx T_{\mathrm{k}}$, conduction electrons in the energy range $|\varepsilon - E_{\mathrm{F}}| \approx k_{\mathrm{B}}T_{\mathrm{k}}$ that contribute to electrical conduction will see the local spin changing its direction frequently; we may say that the spin is practically quenched for $|\varepsilon - E_{\mathrm{F}}| \ll k_{\mathrm{B}}T_{\mathrm{k}}$ to fall into a singlet state. This physical picture which was proposed first by Yosida [11] was justified later by Wilson's rigorous treatment [12].

The Kondo effect was observed first in the cases of transition element impurities. If the impurity concentration is increased, a phase transition into a magnetically ordered state wipes out the effect at low temperatures. In 1976 Andres, Graebner and Ott [13] discovered that $\mathrm{CeAl_3}$, which showed the $1/T$ dependence of magnetic susceptibility at high temperatures gradually fell into a state of nearly constant magnetic susceptibility at low temperatures, where the electronic specific heat capacity $C_{\mathrm{V}} = \gamma T$ yielded an effective mass 1000 times larger than the value of a bare electron. They suggested that the Kondo effect might be operating even in the case where Ce atoms made a lattice. Following this discovery Doniach [14] pointed out that the Kondo effect might be able to overcome the RKKY interaction to quench the magnetic moment. Roughly speaking the RKKY interaction given by Eq. (6) is of the order of $J_{\mathrm{cf}}^2\eta_{\mathrm{c}}(E_F)$, while the Kondo effect is characterized by $D\exp[-1/|J_{\mathrm{cf}}|\eta_{\mathrm{c}}(E_{\mathrm{F}})]$ with $D \approx 1/\eta_{\mathrm{c}}(E_{\mathrm{F}})$. If $|J_{\mathrm{cf}}|\eta_{\mathrm{c}}(E_{\mathrm{F}}) \approx 1$, they can be comparable. Since$|J_{\mathrm{cf}}|$is expected to be smaller than $1/\eta_{\mathrm{c}}(E_{\mathrm{F}})$, the Kondo effect seems to have hardly a chance to dominate from this estimate. Yamada, Yosida and Hanzawa [15] have shown, however, that the Kondo temperature for the $2J+1$ fold degenerate level is given by:

$$k_{\mathrm{B}}T_{\mathrm{k}} = D\exp[-2/\{(2J+1)|J_{\mathrm{cf}}|\eta_{\mathrm{c}}(E_{\mathrm{F}})\}], \tag{11}$$

while Eq. (10) assumes a doubly degenerate level for localized electrons, or in other words, a s orbital state with spin degeneracy [16]. We can expect an enhancement of T_{k} from the value given by Eq. (10), since J of Ce is equal to 5/2. Even when we take into account the crystalline field splitting, we can still expect an enhancement of T_{k} [15].

I shall not go into further discussion of the heavy electron (fermion) systems. A variety of experimental facts have been obtained for rare earth and actinide compounds; in some cases a magnetic order with considerably reduced magnetic moments appears at low temperatures than T_{k} and also the superconductivity can appear to present a subject of great interest. In order to cover these subjects, we may need to extend the Kondo model (the expression (2)) so far discussed in this paper. The mixing term (7) leads us to the virtual bound state concept of the f level originally proposed by Friedel for transition metal alloys [17]. An electron can stay at the f level only for a finite time τ because of the mixing, which gives rise to a broadening of the level given by $\Delta = \hbar/\tau = \pi\eta_{\mathrm{c}}\langle|V_{\mathrm{fc}}|^2\rangle\cdot$ In the absence of the intraatomic coulomb interaction the local density of states of the f level is given by:

$$\eta_{\mathrm{f}}(\varepsilon) = (\Delta/\pi)/[(\varepsilon - \varepsilon_{\mathrm{f}})^2 + \Delta^2], \tag{12}$$

Anderson [18] proposed the Anderson model whose Hamiltonian is given by:

$$\begin{aligned} H = {} & \Sigma_{k\sigma}\varepsilon_k c_{k\sigma}{}^* c_{k\sigma} + \Sigma_\sigma \varepsilon_{\mathrm{f}} c_{\mathrm{f}\sigma}{}^* c_{\mathrm{f}\sigma} \\ & + \Sigma_{k\sigma} V_{\mathrm{fc}}(c_{f\sigma}{}^* c_{k\sigma} + c_{k\sigma}{}^* c_{\mathrm{f}\sigma}) \\ & + U c_{\mathrm{f}\sigma}{}^* + c_{\mathrm{f}-\sigma}{}^* c_{\mathrm{f}-\sigma}, \end{aligned} \tag{13}$$

where the first term represents the band energy of conduction electrons, the second term the energy of the f level and the last term the intra atomic coulomb energy. If $U = 0$, we obtain Eq. (12) for the local density of states for the f states from Eq. (13). The relation between the Kondo model and the Anderson model is not very clear, though the former corresponds to a limit of the parameters in the latter including $\mathrm{U} \to \infty$ in many respects. A rigorous treatment of the Anderson model elucidated the Kondo effect and .its dependence on ε_{f}, U and V_{fc} [19]. For the case where the f level atoms occupy sites of a periodic lattice, we need the (periodic) Anderson model particularly when f states seem to participate in the states of itinerant electrons. I am not in the position to present any summary of the present status of research in this direction, since it is still being intensively studied.

4. Intermetallic compounds of rare earth and transition elements

Intermetallic ferromagnetic compounds of rare earth element R and transition element T have drawn attention as useful permanent magnet materials since 1960s. $\mathrm{RCo_5}$ and $\mathrm{R_2Co_{17}}$ and their modifications were intensively investigated in 1960s and 1970s [20]. In 1984 Sagawa and his collaborators [21] and also other research groups [2] discovered $\mathrm{Nd_2Fe_{14}B}$ as a better permanent magnet material. In 1990 Coey and Sun [22] discovered $\mathrm{Sm_2Fe_{17}N_{3-\delta}}$ as another hopeful material. In these cases the typical element B and N seem to play a very important role to achieve an enhancement of ferromagnetism. Such a possibility was discussed theoretically by myself within the scope of research on the alloying effect on ferromagnetism of transition metals in 1980s without anticipating this epoch-making development [23]. In 1990s the electronic structure of these compounds was investigated by several groups. I refer in this paper to Asano, Ishida, and Fujii [24], Steinbeck, Richter, Nitzsche, and Eschrig [25] and Asano and Yamaguchi [26] as representative calculations.

In the following I shall present first a general picture of alloying effect on the electronic structure of ferromagnetic transition metals. In R–T systems spins of R couple antiferromagnetically with those of T = Fe and Co. In the case of light rare earth elements with less-than-half filled f shell, this exchange interaction aligns the R magnetic moments parallel to those of T because their direction is determined by the contribution of the total orbital angular momentum ***L***; note that the spin orbit coupling favors the antiparallel configuration of ***L*** and the total spin ***S*** in light rare earth elements. After elucidating the nature of the R–T exchange interaction, we proceed to the discussion of the role of typical elements denoted by X in enhancing ferromagnetism in Fe–R. Subsequently I discuss the discovery of a conspicuous difference between the cases of X = B and C and X = N in $R_2Fe_{17}X_\alpha$ and $RFe_{12}X$ made by the band structure calculations [24–26], which seems to explain the observed enhancement of magnetic anisotropy by *N* in Sm_2Fe_{17}.

We note that the electronic structure of the intermetallic compounds around the Fermi level is dominated by the d band states of transition elements. We start with a pure transition metal. The band structure can be understood as the result of hybridization among a nearly free electron branch and the d states which overlap one another between neighboring atoms [27]. We emphasize the fact that the RKKY picture discussed in the preceding section is not applicable to the present case, because the so-called s band states corresponding to the free electron branch are either pushed up above the d band or pushed down below the d band by s–d hybridization (see Fig. 2). One might question the relation of this band structure discussion to the virtual bound state concept that was widely used for transition metals. I mention here that the virtual bound state concept was proved to be compatible with the above-mentioned band structure; in particular the effective interatomic interaction discussed by Alexander and Anderson [28] and Moriya [29] on the basis of the Anderson model is equivalent to the band calculation semi-quantitatively if the width of the virtual state is appropriately interpreted in terms of the interatomic transfer of the d band instead of the sd mixing [30]. The theory [30] shows that not only the confinement due to the centrifugal force potential but also the angular distribution of orbitals characteristic to d states guarantee the compatibility of the virtual level concept with the band structure.

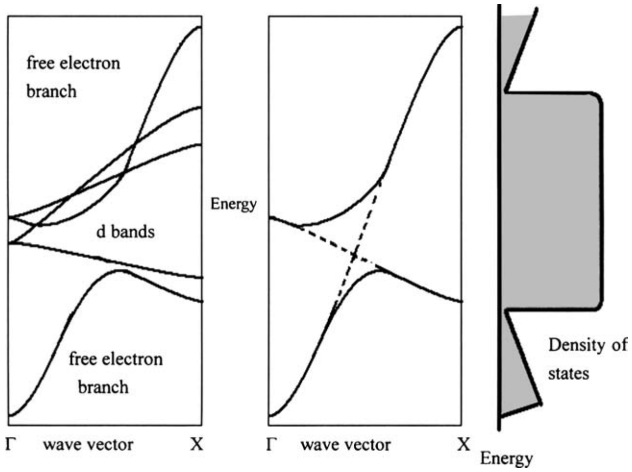

Fig. 2. Sketches of the band structure of a transition metal. The left figure shows energy dispersion of d bands and a free electron branch in the [1 0 0] direction of a fcc transition metal. The middle one explains the effect of the s–d mixing. The right one is a sketch of the density of states vs. energy relation.

When an impurity atom is introduced in a pure transition metal, its valence states hybridize, therefore, primarily with the d band states. In the case of typical elements with a small valence number in a given period their s,p valence levels are situated above the Fermi level as is illustrated in Fig. 3. In the hybridization, the d band states correspond to bonding states and impurity valence ones to antibonding states. The mixing of impurity valence states in the bonding states will supply enough electrons to secure an approximate electrical neutrality of the impurity atom in spite of vacant antibonding states. In the ferromagnetic state the d band of minority spin is shifted towards higher energy relative to that of majority spin to result in a more mixing of impurity valence states than the case of majority spin. Also we note that the d band wave function of minority spin is more extended into the outside of the transition element atomic sphere, because the effective potential for minority spin electrons is shallower than that for majority spin ones because of the intraatomic coulomb interaction. Thus more minority spin electrons are accumulated at the impurity atom than majority spin ones; defining the majority spin direction as positive, we say that the impurity atom is negatively spin polarized. When we go to higher atomic number, the impurity level approaches the Fermi energy and the antibonding states of majority spin start to accommodate electrons, which will decrease the negative polarization at impurity site and finally reverse the polarization. This general discussion is well supported by the hyperfine field data of impurity nuclei in ferromagnetic transition metals [31]. Turning to the intermetallic compounds, we note first that the above discussion applies also to 5d states of R which lie above the d bands of transition elements. Thus we expect

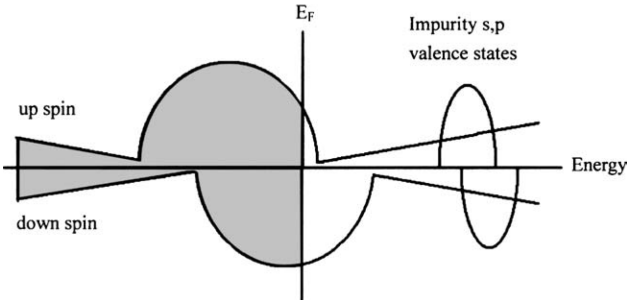

Fig. 3. A rough sketch of the electronic structure of a ferromagnetic transition metal containing a typical element impurity. Through hybridization, wave functions of occupied states contain impurity valence wave functions and correspondingly a portion of d band wave functions are taken away by unoccupied states.

that 5d states of R are negatively spin polarized. Since the intra-atomic d–f exchange interactions favors parallel spin configurations of 4f and 5d states, spins of R will couple antiferromagnetically with those of transition elements.

The increase of the Curie temperature in systems containing interstitial typical elements is often ascribed to volume expansion. As was demonstrated by band structure calculations on $R_2T_{17}X_n$ with T representing transition metals and X typical elements such as C and N at interstitial sites, we need to take into account the change of electronic structure due to the presence of X to understand the enhancement of ferromagnetism fully [24,25]. Moreover, the case of $Nd_2Fe_{14}B$, where the lattice expands if B is absent [26] is hardly understood without paying attention to electronic structure. In the presence of X=B or C the occupation of the d band states has to increase to accommodate the valence electrons of typical elements, since the antibonding states lie above the Fermi energy. This causes an effective increase of atomic number of transition element neighboring directly a typical element atom. In particular the effect will shift the effective atomic number of bonding Fe atoms towards Co [32]. This *cobaltization* has been confirmed by the band calculations of R–T–X systems [24–26] which concluded the fully occupied majority spin d band in R–T–X systems in contrast with the cases R–T. It is well known that the Curie temperature and magnetization increase in Fe–Co alloys with increasing Co concentration when Co concentration is not very large; the magnetization increases because Fe atoms neighboring Co atom increase their magnetic moments (or in other words, the majority spin d states becomes fully occupied). The underlying mechanism in the case of Fe–Co alloys was elucidated by detailed calculations [33]; some portion of the minority spin states of Fe atoms are pushed up across the Fermi energy by alloying with Co which has a relatively lower effective potential for minority spin electrons, while the effective potential of majority spin electrons of Fe is lowered by this loss of minority spin electrons to accommodate more majority spin electrons to keep the electrical neutrality. In the case of T–X, the magnetic moment of Fe atoms directly neighboring X decreases because of the *cobaltization*, while these pseudo Co atoms will increase the magnetic moments of neighboring Fe atoms more distant from X. This prediction was well confirmed by the band calculations [24–26].

In the case of X = N, some portion of the majority spin antibonding states seems to come down below the Fermi energy [22–24]. The picture of *cobaltization* seems to be still valid in this case, since a sizable amount of d states are taken away through hybridization by vacant antibonding states. Apart from the magnetization, to enhance the coercive force is very important for permanent magnet materials. In this connection the band calculations [24–26] revealed a very interesting feature of the electronic structure change due to N. In the case of $R_2Fe_{17}X$ and $RFe_{12}X$, X enters at a site surrounded by four Fe atoms and two R atoms octahedrally. The calculations show that the p orbital of N pointing to R (denoted by p_R) is positively spin polarized, while other p states are negatively spin polarized. Furthermore they calculated the crystalline field parameter of R contributing to the anisotropy energy to conclude an enhancement by N. Asano and Yamaguchi [26] argue that N2p–R5d bonding produces a resonance peak in the local density of states of p_R which comes down below the Fermi energy in the case of majority spin and remains above in the case of minority spin, through 5d–p_R bonding [26].

5. Concluding remarks

I presented a very rough sketch of the present status of theoretical investigations on condensed matter containing rare earth elements, confining myself to a few topics in magnetism. The heavy electron (fermion) and valence fluctuation problems were not discussed in detail. We expect the existence of a quantum critical point in the phase diagram of a dense Kondo system at which the nature of the quantum state makes a transition. Except for certain one dimensional models we do not have yet a clear-cut picture of the whole aspect of the problem. I conclude that rare earth elements and actinide elements will continue presenting new topics of condensed matter physics. On application side, rare earth elements will continue to be keys to new materials not only for permanent magnet but also for other devices. Thereby typical elements can play important roles. The band calculations [24–26] have reached the stage that they can estimate the magnetic anisotropy semi-quantitatively in permanent magnet materials. However, a theoretical prediction of enhancing the coercive force seems to be still a future problem.

Acknowledgement

I would like to express my sincere thanks to Professor A. Okiji for illuminating discussion on the Kondo effect and Professor H. Akai for information about electronic structure calculations.

References

[1] J. Kondo, Prog. Theoret. Phys. 32 (1964) 37.

[2] J.F. Herbst, Rev. Mod. Phys. 63 (1991) 819.

[3] J.H. Van Vleck, The Theory of Electric and Magnetic Susceptibilities, Clarendon Press, Oxford, 1932.

[4] J. Jensen, A.R. Mackintosh, Rare Earth Magnetism, Clarendon Press, Oxford, 1991.

[5] M.A. Ruderman, C. Kittel, Phys. Rev. 96 (1954) 99;
T. Kasuya, Prog. Theoret. Phys. 16 (1956) 45;
K. Yosida, Phys. Rev. 106 (1957) 893.

[6] C. Zener, Phys. Rev. 81 (1951) 440.

[7] J. Kanamori, Trans. Magnet. Soc. Jpn. 1 (2001) 1–10 (reviews various mechanisms).

[8] Note that the projection of the magnetic moment $(2S + L)$ in the unit of μB is given by gJ and $S = 2S + L - J$.

[9] P. Coleman, in: F. Mancini (Ed.), Lectures on the Physics of Highly Correlated Electron Systems VI, American Institute of Physics, New York, 2002, pp. 79–160.

[10] A.C. Hewson, The Kondo Problem to Heavy Fermions, Cambrdge University Press, Cambrdge, 1993.
[11] K. Yosida, Phys. Rev. 147 (1966) 223.
[12] K.G. Wilson, Rev. Mod. Phys. 47 (1976) 773.
[13] K. Andres, J. Graebner, H.R. Ott, Phys. Rev. Lett. 35 (1975) 1779.
[14] S. Doniach, Physica 91B (1977) 231.
[15] K. Yamada, K. Yosida, K. Hanzawa, Prog. Theoret. Phys. 71 (1984) 450.
[16] If the localized orbital be of f symmetry, the mixing conduction band states should be partial waves of the same symmetry.
[17] J. Friedel, Nuovo Cimento 2 (Suppl.) (1958) 287.
[18] P.W. Anderson, Phys. Rev. 124 (1961) 41.
[19] A. Okiji, Fermi Surface effects, in: J. Kondo, A. Yoshimori (Eds.), Springer Series in Solid-State Sciences 77, Berlin, 1988, p. 63.
[20] S.R. Trout, Proceedings of the International Symposium on Magnetics, The Korean Magnetics Society, Seoul, 1990, p. 79.
[21] M. Sagawa, S. Fujimura, N. Togawa, H. Yamamoto, Y. Matsuura, J. Appl. Phys., Part II 55 (1984) 2084.
[22] J.M.D. Coey, H. Sun, J. Magn. Magn. Mater. 87 (1990) 251.
[23] J. Kanamori, Hyperfine Interact. 21 (1985) 159.
[24] S. Asano, S. Ishida, S. Fujii, Physica B 190 (1993) 155.
[25] L. Steinbeck, M. Richter, U. Nitzsche, H. Eschrig, Phys. Rev. B53 (1996) 7111.
[26] S. Asano, M. Yamaguchi, Physica B 237–238 (1997) 541.
[27] V. Heine, Phys. Rev. 153 (1967) 673.
[28] S. Alexander, P.W. Anderson, Phys. Rev. 133 (1964) 1594.
[29] T. Moriya, Prog. Theoret. Phys. 33 (1965) 57.
[30] K. Hirai, J. Kanamori, J. Phys. Soc. Jpn. 50 (1981) 2265.
[31] H. Akai, M. Akai, S. Blügel, B. Drittler, H. Ebert, K. Terakura, R. Zeller, P. Dederichs, Prog. Theoret. Phys. Suppl. 101 (1990) 11.
[32] J. Kanamori, Prog. Theoret. Phys. Suppl. 101 (1990) 1.
[33] J. Kanamori, H. Akai, N. Hamada, H. Miwa, Physica 91B (1977) 153.