FIP10604 – Text 14 – Impurities and alloys

So far, in our study of magnetic properties of solids we have seen that

- **insulating solids** exhibit localized magnetic moments, and are described by *spin Hamiltonians*;

- **metallic solids** exhibit itinerant magnetic moments, characterizing what is usually termed *band magnetism.*

However, there is a wide range of compounds in which both types of magnetic moment coexist. We will see some typical cases.

Magnetic impurities in non-magnetic metals

This is the simplest occurrence of such a coexistence. Typical examples of non-magnetic metal are Al, Cu, Ag, or Au. Besides the closed atomic shells, these elements have s and p valence electrons, as in Al, or just s, as in Cu, Ag and Au, being paramagnetic or diamagnetic. Any of these metals can be a *host* material into which *magnetic impurities* are introduced. The latter are usually transition-metal atoms, such as V, Cr, Mn, Fe, Co, or Ni, which have the 3d shell partially filled. These atoms, when isolated, present permanent magnetic moments. A key question is whether these moments remain or not when the atoms are placed in the metallic host.

Let us consider the dilute limit, where one can suppose that each impurity interacts with the host but there is no interaction between impurities. From a theoretical point of view, one can treat the problem of a single impurity, with measurable physical effects including the impurity concentration as a multiplicative factor.

Anderson Model

The simplest model assumes a conduction band without interaction between the electrons, and does not take into account the orbital degeneracy of the impurity d levels (which could be physically realized by the presence of a strong low-symmetry crystal field). This is the Anderson model, or s-d model, for which we can write the Hamiltonian

$$\mathcal{H} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} n_{\mathbf{k}\sigma} + \varepsilon_d \sum_{\sigma} n_{d\sigma} + U n_{d\uparrow} n_{d\downarrow} + \frac{1}{\sqrt{N}} \sum_{\mathbf{k}\sigma} (V_{dk}\, c^{\dagger}_{\mathbf{k}\sigma} d_{\sigma} + V_{kd}\, d^{\dagger}_{\sigma} c_{\mathbf{k}\sigma}) \ . \qquad (1)$$

Note that there is Coulomb repulsion in the impurity d level and hybridization of that level with the conduction band. The impurity is located at an arbitrary site of the lattice, here chosen to be the origin of the coordinate system. The condition $V_{kd} = V^*_{dk}$ ensures that the Hamiltonian is Hermitian.

In the absence of hybridization, band and impurity are decoupled. The situation of interest is when the d level lies below the band's Fermi level ($\varepsilon_d < \varepsilon_F$) but the addition of one extra electron would cost an energy $\varepsilon_d + U > \varepsilon_F$. This makes double occupancy of the d orbital energetically unfavorable. The impurity behaves, then, as a localized spin 1/2.

To determine what happens to the local magnetic moment when there is hybridization (which is the realistic situation), we may evaluate the average number of d electrons (with any spin orientation) in model (1).

At $T = 0$, we have

$$\langle n_{d\sigma} \rangle = \int_{-\infty}^{\varepsilon_F} d\varepsilon D_{d\sigma}(\varepsilon) \ . \tag{2}$$

If we had just an isolated d level ($V_{d\mathbf{k}} = 0$) and no interaction ($U = 0$), the density of d states would be simply

$$D_{d\sigma}^0(\varepsilon) = \delta(\varepsilon - \varepsilon_d) \ , \tag{3}$$

independent of spin. This density of states (DOS) can be obtained from the Green's function (GF)

$$G_{d\sigma}^0(\omega) = \frac{1}{\omega - \varepsilon_d + \mu + i\eta} \ , \qquad \eta \to 0^+ \ , \tag{4}$$

using the relationship

$$D_{d\sigma}^0(\omega) = -\frac{1}{\pi} \mathrm{Im}\, G_{d\sigma}^0(\omega) \ . \tag{5}$$

The presence of Coulomb interaction and hybridization with the band makes the problem substantially more complex, so that we will have to resort to some approximation scheme.

Hartree-Fock approximation

As a first approach, we will treat the Coulomb interaction within the Hartree-Fock approximation. In contrast to what we did in Text 12, here the HF decoupling is made directly on the product of local number operators, so that the HF Hamiltonian is

$$\mathcal{H}^{\mathrm{HF}} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} n_{\mathbf{k}\sigma} + \sum_{\sigma} \varepsilon_{d\sigma} n_{d\sigma} + \frac{1}{\sqrt{N}} \sum_{\mathbf{k}\sigma} (V_{dk}\, c_{\mathbf{k}\sigma}^{\dagger} d_{\sigma} + V_{kd}\, d_{\sigma}^{\dagger} c_{\mathbf{k}\sigma}) \ , \tag{6}$$

with

$$\varepsilon_{d\sigma} \equiv \varepsilon_d + U\langle n_{d\bar{\sigma}} \rangle \ . \tag{7}$$

Due to the hybridization term, we have four relevant GF's: G_{dd}^{σ}, $G_{\mathbf{k}\mathbf{k}'}^{\sigma}$, $G_{d\mathbf{k}}^{\sigma}$ and $G_{\mathbf{k}d}^{\sigma}$. We will use equations of motion to evaluate these GF's. The (retarded) GF involving two generic fermionic operators A and B is defined as

$$G_{AB}(t) \equiv \langle\langle A; B \rangle\rangle_t = -i\theta(t)\langle\{A(t), B(0)\}\rangle \ . \tag{8}$$

Evaluating the time derivative $\dot{G}_{AB}(t)$, and taking the Fourier transform, we obtain

$$(\omega + \mathrm{i}\eta)\langle\langle A; B\rangle\rangle = \langle\{A, B\}\rangle + \langle\langle[\mathcal{H}, A]; B\rangle\rangle \ . \tag{9}$$

The limit $\eta \to 0+$ is implicitly assumed, this parameter being included to ensure the condition imposed by the step function $\theta(t)$ when taking the inverse Fourier transform.

For the GF's defined here, and taking into account the explicit form of Eq. (6), one obtains the following set of equations (with ω replaced by ε):

$$(\varepsilon - \varepsilon_{d\sigma} + \mathrm{i}\eta)\, G_{dd}^{\sigma}(\varepsilon) - \frac{1}{\sqrt{N}}\sum_{\mathbf{k}} V_{d\mathbf{k}} G_{\mathbf{k}d}^{\sigma}(\varepsilon) = 1 \ ,$$

$$(\varepsilon - \varepsilon_{\mathbf{k}} + \mathrm{i}\eta)\, G_{\mathbf{k}\mathbf{k}'}^{\sigma}(\varepsilon) - \frac{1}{\sqrt{N}} V_{\mathbf{k}d}\, G_{d\mathbf{k}'}^{\sigma}(\varepsilon) = \delta_{\mathbf{k}\mathbf{k}'} \ ,$$

$$(\varepsilon - \varepsilon_{\mathbf{k}} + \mathrm{i}\eta)\, G_{\mathbf{k}d}^{\sigma}(\varepsilon) - \frac{1}{\sqrt{N}} V_{\mathbf{k}d}\, G_{dd}^{\sigma}(\varepsilon) = 0 \ ,$$

$$(\varepsilon - \varepsilon_{d\sigma} + \mathrm{i}\eta)\, G_{d\mathbf{k}}^{\sigma}(\varepsilon) - \frac{1}{\sqrt{N}}\sum_{\mathbf{k}'} V_{d\mathbf{k}'} G_{\mathbf{k}'\mathbf{k}}^{\sigma}(\varepsilon) = 0 \ . \tag{10}$$

Since we are dealing with an effective single-particle Hamiltonian, this system of equations is closed, allowing to obtain the four GF's. In particular, isolating $G_{\mathbf{k}d}^{\sigma}(\varepsilon)$ in the third equation and substituting into the first, we find the impurity GF

$$G_{dd}^{\sigma}(\varepsilon) = \frac{1}{\varepsilon - \varepsilon_{d\sigma} - \dfrac{1}{N}\sum_{\mathbf{k}} \dfrac{|V_{\mathbf{k}d}|^2}{\varepsilon - \varepsilon_{\mathbf{k}} + \mathrm{i}\eta}} \ . \tag{11}$$

Separating real and imaginary parts in the last term of the denominator, the real part can be absorbed as a renormalization of $\varepsilon_{d\sigma}$, but there is a finite imaginary part

$$\Delta = \pi \frac{1}{N}\sum_{\mathbf{k}} |V_{d\mathbf{k}}|^2 \delta(\varepsilon - \varepsilon_{\mathbf{k}}) \ . \tag{12}$$

Using the equivalent of Eq. (5) yields

$$D_{d\sigma}(\omega) = \frac{\Delta/\pi}{(\varepsilon - \varepsilon_{d\sigma})^2 + \Delta^2} \ . \tag{13}$$

Assuming that the hybridization is local, we can write $V_{d\mathbf{k}} = V$ (independent of $\mathbf{k}$), so that

$$\Delta = \pi V^2 \frac{1}{N}\sum_{\mathbf{k}} \delta(\varepsilon - \varepsilon_{\mathbf{k}}) = \pi V^2 D_s(\varepsilon) \ , \tag{14}$$

where $D_s(\varepsilon)$ is the conduction-band DOS, which is in general a smoothly varying function of energy. Thus, for small V, when Eq. (13) restricts the relevant energies to the vicinity of

$\varepsilon_{d\sigma}$, we can use $D_s(\varepsilon) \simeq D_s(\varepsilon_{d\sigma})$, and Δ does not depend on energy. Then, the right-hand side of Eq. (13) has a Lorentzian shape, with center at $\varepsilon_{d\sigma}$ and width Δ.

The evaluation of $\langle n_{d\sigma} \rangle$ through Eq. (2) is straightforward, resulting in

$$\langle n_{d\sigma} \rangle = \frac{1}{\pi} \cot^{-1} \left[\frac{\varepsilon_d + U \langle n_{d\bar{\sigma}} \rangle - \varepsilon_F}{\Delta} \right] \equiv \Phi(\varepsilon_d + U \langle n_{d\bar{\sigma}} - \varepsilon_F \rangle) . \tag{15}$$

We may now verify if there exists a non-zero value of the quantity $m_d \equiv \langle n_{d\uparrow} \rangle - \langle n_{d\downarrow} \rangle$, subject to the condition $\langle n_{d\uparrow} \rangle + \langle n_{d\downarrow} \rangle = 1$. Expressing the two average occupation numbers in terms of m_d, we can write

$$m_d = \Phi(\bar{\varepsilon}_d - U m_d - \varepsilon_F) - \Phi(\bar{\varepsilon}_d + U m_d - \varepsilon_F) , \tag{16}$$

where $\bar{\varepsilon}_d \equiv \varepsilon_d + U$. It is clear that $m_d = 0$ is a possible solution. On the other hand, there is a solution with $m_d \neq 0$ if the initial derivative of the right-hand side of Eq. (16) is larger than unity, since the left side, viewed as a function of m_d, is a unit-slope straight line (similarly to what we have seen in other contexts before). From Eqs. (15) and (2), it follows that $\Phi(\varepsilon_d + U \langle n_{d\bar{\sigma}} \rangle - \varepsilon)$ is the primitive function of $D_{d\sigma}(\varepsilon)$. So, at $m_d = 0$ we have that $-\Phi'(\bar{\varepsilon}_d - \varepsilon_F) = D_d(\varepsilon_F)$, independent of spin. Therefore, the condition for existence of a solution with $m_d \neq 0$ is

$$U D_d(\varepsilon_F) > 1 . \tag{17}$$

The above analysis leads to a "local version" of the Stoner criterion. There is a "local magnetization" $m_d \neq 0$ if, for a given U, the density of d states at the Fermi level is sufficiently large. From Eq. (13), it is clear that Δ cannot be large (since the total area is constant). Then, Eq. (14) indicates that a low conduction-band DOS favors the condition (17). If one assumes that $m_d \neq 0$ indicates the existence of an impurity magnetic moment, this characteristic of the conduction band is consistent with experimental observations for the 3d impurities mentioned above: they keep their magnetic moments in Cu, Ag, or Au hosts, but not in Al, for which the DOS at the Fermi level is higher.

Despite this apparent success, the situation described by the HF approximation does **not** correspond to what one would expect. Having a localized magnetic moment should not imply having that moment oriented in a given direction. The physical situation (a single localized spin 1/2) is actually consistent with $m_d = 0$ and $\langle n_{d\uparrow} \rangle + \langle n_{d\downarrow} \rangle = 1$, i.e., $\langle n_{d\uparrow} \rangle = \langle n_{d\downarrow} \rangle = 1/2$, which means that the localized spin fluctuates between its two orientations.

Anderson model in the atomic limit

The Hartree-Fock approach is expected to give reasonable results when the local Coulomb interaction is small compared to the conduction-band width. Employing it to a localized level, even if somewhat broadened by hybridization to a conduction band, is far less justifiable. We now address the opposite extreme, the so-called *atomic limit* of the Anderson model. It corresponds to writing the conduction-band term in Wannier representation, and

choosing the hopping $t = 0$, so that the impurity is decoupled from the rest of the lattice, and the "band" is replaced by a local level of energy ε_c at the impurity site. This site is described by the Hamiltonian

$$\mathcal{H} = \varepsilon_c \sum_\sigma n_{c\sigma} + \varepsilon_d \sum_\sigma n_{d\sigma} + U n_{d\uparrow} n_{d\downarrow} + V \sum_\sigma (c_\sigma^\dagger d_\sigma + d_\sigma^\dagger c_\sigma) \,. \tag{18}$$

For simplicity, we choose the parameters so as to ensure particle-hole symmetry: $\varepsilon_c = 0$, coinciding with the Fermi level for a half-filled band, and $\varepsilon_d = -U$, which implies $\varepsilon_d + U = U$ and $2\varepsilon_d + U = 0$. The eigenvectors for $V = 0$ are easily written, and provide a basis to build a matrix representation of the Hamiltonian.

We are interest in the case of two electrons at the impurity site. The basis states, with respective eigenvalues of total S_z and energy, are

$$
\begin{aligned}
|d\uparrow, d\downarrow\rangle \,, \ |c\uparrow, c\downarrow\rangle \,; & \quad M_z = 0 \,, & E_{V=0} &= 0 \\
\left.\begin{array}{r}
|c\uparrow, d\uparrow\rangle \,; \quad M_z = 1 \,, \\
|c\uparrow, d\downarrow\rangle \,, |c\downarrow, d\uparrow\rangle \,; \quad M_z = 0 \,, \\
|c\downarrow, d\downarrow\rangle \,; \quad M_z = -1 \,,
\end{array}\right\} & & E_{V=0} &= \varepsilon_d
\end{aligned}
\tag{19}
$$

In this notation of basis vectors, c and d are labels for the two local levels, the spin states being indicated by arrows. The states with $M_z = \pm 1$ do not hybridize since their hybridization would generate states that violate the exclusion principle. Therefore, these states keep their energy ε_d. They are obviously part a spin triplet. The third member of the triplet must be the symmetric combination $(|c\uparrow, d\downarrow\rangle + |c\downarrow, d\uparrow\rangle)/\sqrt{2}$. On the other hand, the anti-symmetric combination, $(|c\uparrow, d\downarrow\rangle - |c\downarrow, d\uparrow\rangle)/\sqrt{2}$, and the two states with a doubly occupied orbital form a basis for a representation in the subspace of zero total spin. The Hamiltonian matrix in this subspace is

$$(\mathcal{H})_{S=0} = \begin{pmatrix} 0 & \sqrt{2}V & 0 \\ \sqrt{2}V & \varepsilon_d & \sqrt{2}V \\ 0 & \sqrt{2}V & 0 \end{pmatrix} \,, \tag{20}$$

whose eigenvalues are

$$E = \begin{cases} 0 \,, \\ \frac{1}{2}(\varepsilon_d \pm \sqrt{\varepsilon_d^2 + 16V^2}) \,. \end{cases} \tag{21}$$

The ground state is thus a singlet with energy $E_0 = \frac{1}{2}(\varepsilon_d - \sqrt{\varepsilon_d^2 + 16V^2})$, which lies below the triplet of energy ε_d, with a difference of the order of $V^2/|\varepsilon_d|$ in the limit of weak hybridization. This ground-state singlet has one electron in each of the two local levels, with opposite spins. The important point is that there is **no net magnetic moment** at the impurity site. Thus, at the atomic level, the energy is minimized when the spins of the "conduction" electron and the localized one are opposite. We may say that the (localized) d-level moment is *screened* due to its hybridization with the conduction "band". Does this effect survive when we turn on the hopping? We will try to answer this in the following.

Kondo model

In the weak-hybridization limit, i.e., when V is small compared with both U and $\varepsilon_F - \varepsilon_d$, we can make a canonical transformation of the Anderson Hamiltonian, Eq. (1), removing the hybridization term in first order and keeping terms of order V^2. It is known as *Schrieffer-Wolff transformation*, and yields a Hamiltonian of the form

$$\mathcal{H} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} \, n_{\mathbf{k}\sigma} + J_K \, \mathbf{S} \cdot \mathbf{s} \, , \tag{22}$$

where $\mathbf{S}$ is the impurity spin, $\mathbf{s}$ is the conduction-electron spin density at the impurity site, and

$$J_K = V^2 \left(\frac{1}{\varepsilon_F - \varepsilon_d} + \frac{1}{\varepsilon_d + U - \varepsilon_F} \right) \, . \tag{23}$$

The Hamiltonian (22) is known as *Kondo Model* because it was used by Kondo to explain experimental results about the electrical resistivity of diluted systems. We see that the *Kondo interaction* J_K reflects virtual processes in which electrons "jump" between the impurity level (singly or doubly occupied) and states of the conduction band (at the Fermi level). Since $J_K > 0$, the Kondo interaction favors **antiparallel** orientation between the spins of conduction electrons and impurity.

The Kondo model has been studied by many theoretical methods, from perturbative approaches to rigorous solutions based on the Bethe *ansatz*. Without going into details, we present a summary of key findings.

- There is a characteristic temperature, called *Kondo temperature*, given by

$$T_K = W \, e^{-1/[2D(\varepsilon_F)J_K]} \, , \tag{24}$$

  which depends on the Kondo interaction and the characteristics of the conduction band (DOS at the Fermi level and bandwidth W). This temperature defines a *crossover* between the high-temperature regime, where impurities behave as free spins, and the low-temperature regime, where a *Kondo effect* is observed, whose features are discussed below.

- For $T \sim T_K$, there is a **minimum of the electric resistivity**, which is one of the manifestations of the Kondo effect. Above T_K, the Kondo interaction is not effective and the resistivity is typical of a normal metal, dominated by phonon scattering: it decreases when T is reduced. As the temperature is lowered, the Kondo interaction becomes effective, and we have a new (spin-dependent) scattering mechanism that causes an increase in resistivity, resulting in a minimum for a temperature near T_K. Immediately below this minimum, the resistivity has a logarithmic dependence with temperature. This was first obtained by Kondo evaluating the relaxation time in perturbation theory to second order in J_K. The minimum resistivity had already been experimentally observed in dilute alloys. For $T \ll T_K$, the resistivity ceases to grow, and tends to a finite value, indicating that the mechanism of spin-dependent scattering disappears. This can be understood by examining the magnetic behavior.

- At high temperatures, the magnetic susceptibility (χ) presents a Curie-Weiss term, because the impurities are essentially decoupled from the band and behave as localized moments. Below T_K, the susceptibility quickly attains a constant limit. This indicates the suppression of local moments, since the Kondo interaction, favoring opposite orientation of conduction-electron and impurity spins, causes **screening of the localized magnetic moments**, which is another manifestation of the Kondo effect. Now the relationship between height of conduction-band DOS at the Fermi level and existence of localized moments may be reinterpreted through Eq. (24). This equation shows that a low conduction-band DOS at ε_F yields a low T_K, the temperature above which local moments can be observed.

- The *screening cloud* of conduction electrons around the impurity gives rise to an enhanced DOS (almost localized electrons) at the Fermi level, producing a sharp structure known as *Kondo peak*, in addition to broader peaks around ε_d and $\varepsilon_d + U$. The latter have widths defined by the hybridization V (similar to what was obtained in HF), while the Kondo peak has a width of the order of T_K.

Friedel oscillations

Complementary to the screening of an impurity spin by conduction electrons in the Kondo regime, we may ask ourselves how the density of conduction-electron spins is affected in the process. Using a mean-field-like approach, we define an effective magnetic field

$$\mathbf{H}^{\text{eff}}(\mathbf{r}) = -J_K \, \mathbf{S} \, \delta(\mathbf{r}) \,, \tag{25}$$

which acts on the density of conduction-electron spins and is due to an impurity spin $\mathbf{S}$ (at the origin). In wave-vector space, we have

$$\mathbf{H}^{\text{eff}}(\mathbf{q}) = -J_K \mathbf{S} \,. \tag{26}$$

The conduction-band response to this field is measured by an average spin density

$$\langle \mathbf{s}(\mathbf{q}) \rangle = \chi_0(\mathbf{q}) \mathbf{H}^{\text{eff}}(\mathbf{q}) \,, \tag{27}$$

using the independent-electron susceptibility

$$\chi_0(\mathbf{q}) = \frac{2}{N} \sum_{\mathbf{k}} \frac{f(\varepsilon_{\mathbf{k}}) - f(\varepsilon_{\mathbf{k+q}})}{\varepsilon_{\mathbf{k+q}} - \varepsilon_{\mathbf{k}}} \tag{28}$$

(see Text 13). For a parabolic band ($\varepsilon_{\mathbf{k}} = k^2/2m^*$), transforming the sum over $\mathbf{k}$ into an integral, one obtains (in the limit $T \to 0$)

$$\chi_0(\mathbf{q}) = \chi_P F(q/2k_F) \,, \tag{29}$$

χ_P being the Pauli susceptibility, and

$$F(x) = \frac{1}{2} - \frac{1}{4x}(1 - x^2) \ln \left| \frac{1-x}{1+x} \right| \; . \tag{30}$$

From Eqs. (27)–(30), we can obtain the spin density in position space,

$$\langle \mathbf{s}(\mathbf{r}) \rangle \sim \frac{\sin(2k_F r) - 2k_F r \cos(2k_F r)}{(k_F r)^4} \xrightarrow[r \to \infty]{} -\frac{\cos(2k_F r)}{r^3} \; . \tag{31}$$

Hence, there is a long-range polarization of the conduction-electron spins, whose density oscillates with a wavelength $1/2k_F$ and decays as $1/r^3$. The region of most intense polarization can be viewed as a *screening cloud* around the impurity. The oscillating behavior, known as *Friedel oscillations*, is an effect of the existence of a Fermi surface (abrupt change in the occupation of states in $\mathbf{k}$-space). Similar oscillations occur in the electron charge density when screening an impurity charge.

Interacting impurities

Departing from the dilute limit, we can visualize the following physical situation: a magnetic impurity (at the origin) polarizes the conduction-electron spins, generating an oscillating spin density $\langle \mathbf{s}(\mathbf{r}) \rangle$; another magnetic impurity, at a position $\mathbf{R}$, "feels" an effective magnetic field $\mathbf{H}_{\text{imp}}^{\text{eff}}(\mathbf{R}) = -J_K \langle \mathbf{s}(\mathbf{R}) \rangle$. The result is an effective interaction between impurities, known as RKKY (Ruderman-Kittel-Kasuya-Yosida) interaction. It is described by the Hamiltonian

$$\mathcal{H}_{\text{RKKY}} = -J_{\text{RKKY}} \, \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{R}) \; , \tag{32}$$

with

$$J_{\text{RKKY}} = J_K^2 \chi_P \mathcal{F}(R) \; , \tag{33}$$

where $\mathcal{F}(R)$ is the Fourier transform of the function $F(q/k_F)$ [see Eqs. (29) and (30)] evaluated for $r = R$. Thus, the RKKY interaction oscillates with position as does the electron-spin density, according to Eq. (31).

Comparing with our previous study of localized spins, the RKKY interaction can be viewed as a kind of *superexchange* mediated by conduction electrons. An important feature of this interaction is its sign changes due to Friedel oscillations. In a system with randomly distributed impurities, each impurity will be subjected to competitive interactions with the others, varying in sign and intensity. This is a basic ingredient for establishment of a *spin-glass* state, in which long-range magnetic order is **not** observed, but each local spin has a nonzero average value.

Kondo lattice

Turning now to the so-called concentrated limit, we find systems with "one impurity per site". They are actually translation-invariant systems, in which localized magnetic moments and conduction electrons coexist. Typical examples are some rare-earth (or actinide)

compounds, in which the 4f (or 5f) incomplete shell generates a localized moment, while the *s* electrons form the conduction band (together with electrons from other elements possibly present in the compound).

As far as magnetic properties are concerned, some pure elements that we mentioned at the beginning of Text 12 (Gd, Tb, Dy, . . .) can be seen as localized-spin systems with exchange interactions mediated by conduction electrons (RKKY), thus being described by the Heisenberg model. Other compounds, however, show a more complex physics, dominated by a competition between RKKY interaction and Kondo effect. We mention, for example, compounds containing cerium ($CeAl_2$, $CeCu_6$, $CeCu_2Si_2$, $CeRh_2Si_2$, etc.) or uranium (UPt_3, UBe_{13}, etc.). They are known as *Kondo lattices*, for which a generalization of Eq. (22) yields the Hamiltonian

$$\mathcal{H} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} n_{\mathbf{k}\sigma} + J_K \sum_i \mathbf{S}_i \cdot \mathbf{s}(\mathbf{R}_i) \ . \tag{34}$$

It is also usual to employ the Periodic Anderson Model (PAM), whose Hamiltonian is

$$\mathcal{H} = \sum_{\mathbf{k}\sigma} \varepsilon_{\mathbf{k}} n_{\mathbf{k}\sigma} + \varepsilon_f \sum_{i\sigma} n_{i\sigma}^f + U \sum_i n_{i\uparrow}^f n_{i\downarrow}^f + \sum_{\mathbf{k},i} \left(V_{\mathbf{k}} e^{i\mathbf{k}\cdot\mathbf{R}_i} c_{\mathbf{k}\sigma}^\dagger f_{i\sigma} + \text{H.c} \right) \ . \tag{35}$$

It differs from Eq. (1) in that there is one localized state per lattice site, and one usually refers to f (instead of d) atomic levels.

The theoretical treatments of this problem are quite complex. We are dealing with strongly correlated electronic systems, for which the usual methods of perturbation theory do not give good results. Without going into details, which are outside the scope of this course, we present some qualitative comments in comparison to the single-impurity problem.

- The basic features of the single-impurity Kondo effect are still observed: minimum of the electrical resistivity, screening of the local moment, Kondo peak in the DOS.

- A *coherent regime* appears at very low temperatures, due to the lattice-translation invariance. In this regime the electrical resistivity decreases again, and (for systems that do not develop magnetic order) high values are reached by the PM susceptibility and the specific-heat coefficient γ. These features (consistent with the presence of a Kondo peak) gave rise to the denomination *heavy-fermion systems*, since those quantities are directly related to the Fermi-level DOS, for which a high value reflects a large effective mass. Within the heavy-fermion regime, the system can become superconductor, although it happens at very low temperatures (of the order of 1 K).

- The RKKY interaction (not random in this case) tends to induce **ordering** of the localized moments. In general, the order is AF (since $k_F \sim 1/a$) but FM systems also exist. On the other hand, the same (Kondo) coupling that gives rise to the RKKY interaction also tends the screen the local moments. This leads to a **competition** between Kondo effect and magnetic order which is one of most interesting features of this type of systems (and most difficult to deal with).

Other interesting systems

In addition to alloys (diluted or not) and Kondo lattices, there is a variety of systems that show coexistence of localized and itinerant magnetic moments. Let's quickly refer to some features of two classes of systems.

High-T_c superconductors

The so-called high-temperature superconductors where discovered in 1986, starting with the compound La_2CuO_4. This is an AF insulator that upon doping (substitution of Ba or Ca for La in appropriate proportions) becomes superconducting, with $T_C \sim 40$ K. Other families of compounds, with T_C's near or above 100 K, were subsequently synthesized. Examples are $YBa_2Cu_3O_{6+x}$, $Bi_2Sr_2CaCu_2O_{8+x}$, $Tl_2Ba_2CuO_{6+x}$, $Nd_{2-x}Ce_xCuO_4$, etc. Their common characteristic is the presence of CuO_2 planes where, in the absence of doping, the Cu^{2+} magnetic moments ($S = 1/2$) interact via AF superexchange through O^{2-} ions. Figure 1 shows two structures and the CuO_2 planes.

The usual theoretical model is in *hole representation*, because the stoichiometric system has closed ion shells except for one hole per unit cell (nominal configuration $3d^9$ of copper). The simplest model is described by the Hamiltonian

$$\mathcal{H} = \varepsilon_d \sum_{i\sigma} n_{i\sigma}^d + U \sum_i n_{i\uparrow} n_{i\downarrow} + \varepsilon_p \sum_{j\sigma} n_{j\sigma}^p - t \sum_{ij\sigma} (d_{i\sigma}^\dagger p_{j\sigma} + \text{H.c.}) . \tag{36}$$

It is known as *Emmery model*, or the *three-band Hubbard model*, as there are three atoms per unit cell. In fact, one of the linear combinations of p_x and p_y orbitals of oxygen does not hybridize with copper's $d_{x^2-y^2}$ orbital, forming a decoupled (purely p) "zero-width band". The other combination does hybridize, allowing connection between copper ions at different sites. So, the model has effectively two bands.
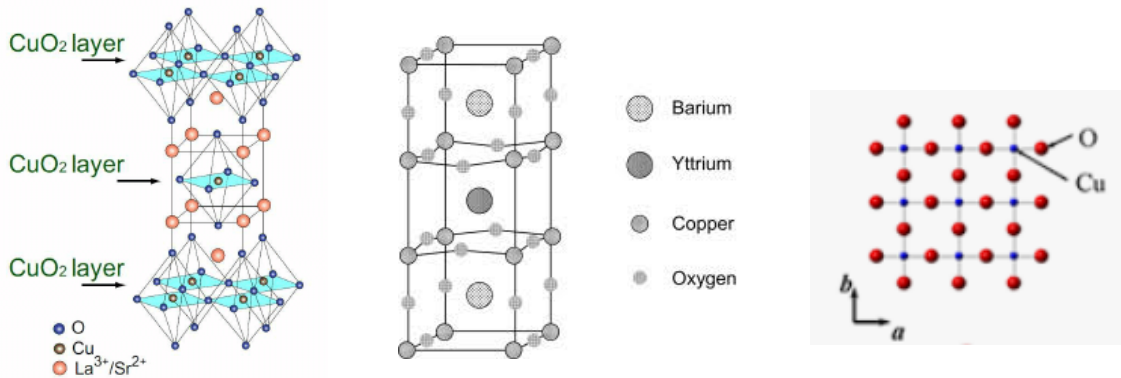
Figure 1: Schemmatic representations of the LaCaO and YBaCuO structures, and of the CuO2 planes common to both.

Assumed values of the system parameters are $t \sim 1$ eV, $\Delta \equiv \varepsilon_p - \varepsilon_d \sim 3$ eV, $U \sim 8$ eV. With respect to the d-band, we have a Mott insulator. But the effective *gap* is a charge-transfer one, with a bare value Δ. In hole-doped systems (e.g., substitution of Ca^{2+} for La^{3+}), the additional holes occupy states immediately below the (renormalized) charge-transfer gap, in a band of dominantly p character. We begin, then, to have coexistence of the itinerant moments of this band with the more localized moments of the d-band. But the hopping involves d levels, so that both bands have hybrid character. Further increase of doping gradually reduces the stability of the AF phase. This phase disappears at a certain critical doping, above which there is a doping range where superconductivity is observed.

Colossal-magnetoresistance manganites

Another interesting class of compounds are manganites that exhibit large magnetoresistance (variation of electrical resistance as an effect of applied magnetic field), here called "colossal" due to the intensity of the effect.

The typical compound is $La_{1-x}Ca_xMnO_3$. For zero doping ($LaMnO_3$), we have La^{3+} and O^{2-} with closed shells, and Mn^{3+} with configuration $[Ar]3d^4$.

The crystal has cubic symmetry, so that crystal-field *splitting* of the Mn d orbitals leaves three lower-energy t_{2g} levels and two higher-energy e_g levels. Hund's rule is strong, which means that there is a localized spin $S = 3/2$ (three electrons with parallel spins) in the t_{2g} levels, the remaining electron occupying one of the e_g levels, also with spin parallel to the other three. Even though the e_g levels form a band, the system is a Mott insulator due to Coulomb interaction, and shows AF order. Doping with Ca (Ca^{2+} in place of La^{3+}) reduces the number of e_g electrons, leaving nominally Mn^{4+} sites. The existence of Mn^{3+} and Mn^{4+} "neighbors" (separated by an oxygen) allows the e_g electron to pass from one to the other through a mechanism called *double exchange*. This can be viewed as a process in which an electron of the intermediate oxygen jumps to an orbital e_g of the Mn^{4+} and the e_g electron of the Mn^{3+} jumps to the hole left in the oxygen, as depicted in Fig. 2. Due to Hund's rule, this process is possible when the total spins of the two Mn ions are parallel.
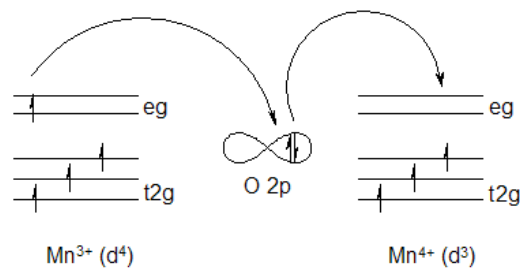
Figure 2: Schematic representation of the double-exchange mechanism in manganites, with the d-level occupation of two Mn ions, and the highest orbital of an intermediate O^{2-} ion.

Therefore, the doped system has low-temperature FM order and is metallic. At high temperatures, thermally induced spin disorder inhibits the double exchange mechanism, suppressing FM order and leading to an essentially insulating PM state. Near the Curie temperature, even a weak magnetic field polarizes the spins, thus switching on double exchange and causing a large increase in conductivity, which characterizes a *colossal* (negative) magnetoresistance. The maximum intensity of this effect occurs for $x \sim 0.33$. For $x > 0.5$ the number of e_g electrons becomes small and their FM effect is overridden by the AF superexchange between t_{2g} spins. The system is then an antiferromagnetic insulator.

Closing this text, it is important to remark once more that we presented here only a few examples of the rich variety of behavior observed in a wide range of compounds in which localized magnetic moments and conduction electrons coexist.