Lecture 12
Magnetic impurities in metals. Kondo effect. Spin Glasses

We consider in this lecture the new properties a normal metal (say, Cu) acquires when it is doped by a small concentration of a transition metal (Fe, Ni, Mn). An atom of a transition element has a partially filled d-shell and, due to Hund's rule, this atom has a non-compensated spin $\mathbf{S}$. In what follows, we will answer several simple questions:

- What happens to an impurity atom in the metallic host? Does it remain magnetic ? What is the condition for that?
- How do the electrons of the metal interact with an isolated magnetic impurity and what happens to it as a result of this interaction ?
- What happens at a finite concentration of magnetic impurities ?

Anderson model

Consider a single atom of a transition element in a normal metal, whose conduction electrons have the energy spectrum $\epsilon(\mathbf{p})$ and chemical potential μ[1]. The occupation number in the quantum state $|\mathbf{p}, \sigma >$ is equal to the product $c^+(\mathbf{p}, \sigma)c(\mathbf{p}, \sigma)$, where c^+ and c are the creation and annihilation operators respectively. The atom of a transition element has extra energy states. Consider for simplicity the case when there is only one such state with the energy ϵ_d, which may be occupied by the electrons with two possible projections $\sigma = \pm$ of their spins[2]. The creation and annihilation operators in these states are denoted as d_σ^+ and d_σ^+ respectively. Obviously, the states in the conductance band and at the impurity site are not orthogonal. They overlap, which leads to their hybridization. Finally, we take into account a strong Coulomb repulsion between electrons, while they are on impurity cite. The Hamiltonian, which takes into account all these interactions, has the form:

$$\begin{aligned}
\mathcal{H} = &\sum_{\mathbf{p},\sigma} \epsilon(\mathbf{p})\ c^+(\mathbf{p},\sigma)\ c(\mathbf{p},\sigma) + \ \epsilon_d \sum_{\sigma} \ d_\sigma^+\ d_\sigma + \\
&+ \sum_{\mathbf{p},\sigma} \left\{ \ V(\mathbf{p})\ c^+(\mathbf{p},\sigma)\ d_\sigma + V^*(\mathbf{p})\ d_\sigma^+\ c(\mathbf{p},\sigma) \right\} + \\
&+ U\ n_+\ n_-, \qquad\qquad n_\pm = d_\pm^+ d_\pm. \qquad (1)
\end{aligned}$$

The energies in Eq (1) differ in their order of magnitude:

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[1]In what follows, level of the chemical potential will be taken equal to zero

[2]In general case, the number of states in the inner shell of the atom of a transition element may be larger and its spin S may be larger than $S = 1/2$

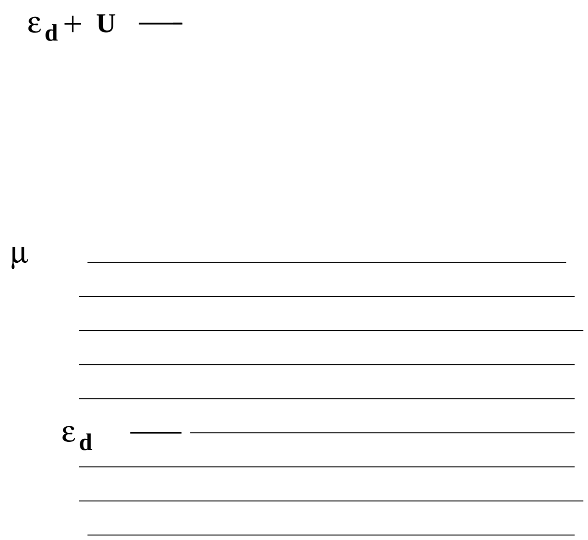

Figure 1: Energies for an extra electron in the Anderson model

the range of variation of the band spectrum $\epsilon(\mathbf{p})$ and the Coulomb repulsion U are both of the order of atomic energies $\approx 10\ eV$; the position of the energy ϵ_d of the impurity level may vary in approximately the same limits, while the hybridization V is smaller and vary from .5 eV for transition elements of the iron group to a much smaller value for Rare Earthes and Actinides. This inequality $V \ll U$ allows to consider hybridization V as a small perturbation.

If the impurity site is empty, it does not contribute to total energy. In the case it is occupied by one electron, its energy is ϵ_d. If two electrons with opposite spins sit at the impurity, their total energy is $2\epsilon_d + U$ (ϵ_d the first electron and $\epsilon_d + U > \epsilon_d$ for the second).

Thus, neglecting hybridization, we may conclude that if $\epsilon_d > 0$, then $\epsilon_d + U > 0$ and the lowest energy corresponds

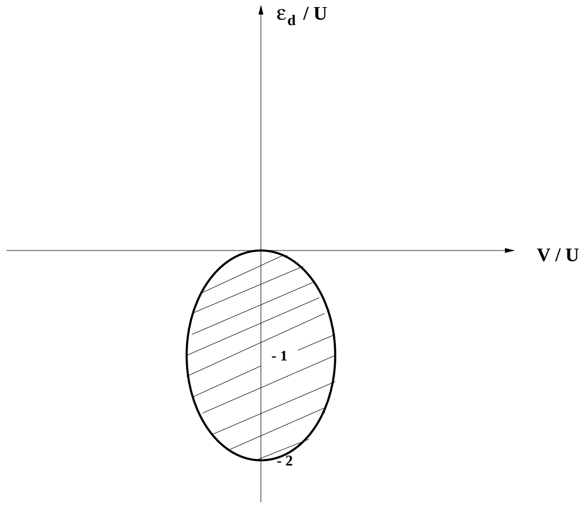

Figure 2: Parameter space for Anderson model and domain of parametrov at which the impurity is magnetic

to the empty impurity site. Under this condition the impurity is **not magnetic**.
If $\epsilon_d < 0$ but $\epsilon_d + U > 0$, the lowest energy corresponds to the impurity occupied by a single electron irrespective of its spin state. The ground state has degeneracy, associated with the impurity spin. Under this condition, the impurity is **magnetic**. The energy levels diagram for this case is presented in Fig 1.

Finally, if $\epsilon_d < 0$ and $\epsilon_d + U < 0$, the lowest energy corresponds to the double occupancy of the impurity site. Then the impurity is **not magnetic**.
Finite strength of hybridization gives rise to deviation of the occupation number of the impurity states from the prescribed integer values. This is especially important if, by an accident, either ϵ_d, or $\epsilon_d + U$ is close to the chemical

potential (This case is called "mixed valence"). Schematically, the domain of the magnetic state of impurity in the $\epsilon_d - V$ plane is shown in Fig 2.

Exchange scattering

Thus, for $\epsilon_d < 0$, $\epsilon_d + U > 0$ and $V \ll |\epsilon_d|, \epsilon_d + U$, the ground state is two-fold degenerate: the spin of impurity $\mathbf{S}$ may have either the z-projection $+1/2$ or $-1/2$. A conduction electron interact with the impurity. Such an interaction leads to a scattering from the state $\mid \mathbf{p}, \sigma >$ into the state $\mid \mathbf{p}', \sigma' >$. If relativistic interactions (spin-orbit, magnetic dipole-dipole, etc) are neglected, the effective scattering amplitude $f_{\sigma\sigma'}(\mathbf{p}, \mathbf{p}')$ may be presented in the form:

$$f_{\sigma\sigma'}(\mathbf{p}, \mathbf{p}') = a(\mathbf{p}, \mathbf{p}')\delta_{\sigma\sigma'} + b(\mathbf{p}, \mathbf{p}')S^i\sigma^i_{\sigma\sigma'}, \qquad (2)$$

which means that the interaction of the magnetic impurity with conduction electrons may be described by a potential and an exchange Hamiltonian. The latter has the following form:

$$\mathcal{H}_{ex} = \int \; J(\mathbf{r} - \mathbf{r}_i) \; \psi^+_\sigma(\mathbf{r})\sigma^i_{\sigma\sigma'}\psi_{\sigma'}(\mathbf{r})S^i \; d\mathbf{r} \qquad (3)$$

In the simplest case the impurity has a point-like shape and the exchange integral $J(\mathbf{r}) = J\delta(\mathbf{r})$. The Anderson model (1) allows to estimate the order of magnitude of the exchange integral J. For this purpose, consider the spin-flip scattering processes in a second order in the hybridization

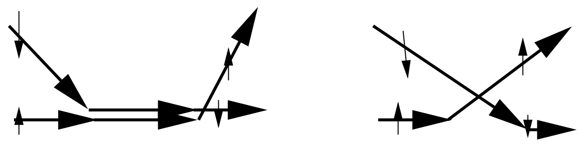

Figure 3: Exchange precesses which lead to the mutual spin flips of the impurity spin and the spin of a conduction electron

amplitude V. These two virtual processes, shown in Fig 3 diagrammatically, correspond either to an empty impurity as an intermediate state or to two-fold occupied. This gives the estimate

$$J \simeq \frac{|V|^2}{|\epsilon_d|} + \frac{|V|^2}{U + \epsilon_d}. \tag{4}$$

For $V \simeq .5\ eV$ and $|\epsilon_d| \sim U + \epsilon_d \simeq 5\ eV$, the exchange integral $J \simeq .05\ eV \approx 500K$.

Spin-flip scattering of electrons by the impurity leads to the relaxation of impurity spin polarization (*Korringa relaxation*, see problems). If the concentration of magnetic impurities is finite, the spin of a conduction electron flips at these impurities, which gives rise to the finite relaxation rate $1/\tau_s$ of the spin of a conduction electron.

Kondo Effect

The exchange interaction of conduction electrons at the magnetic impurity has an interesting quality: since the impurity's internal degree of freedom (the spin) varies in time,

the magnetic impurity behaves not like a static potential for scattering an electron, but rather like another electron in a very narrow band, collisions with which may cause virtually inelastic processes. As a result, the effect of higher orders in the exchange interaction (3) differs from that of an interaction with a potential.
A first order in the potential interaction of conduction electron with the magnetic impurity together with the exchange interaction (3) leads to the scattering amplitude (2). A second order in the potential interaction gives rise to a small correction to the potential amplitude $a(\mathbf{p}, \mathbf{p}')$ in Eq (**??**). Since the potential scattering is an elastic scattering, all electrons of the Fermi sea don't influence the re-scattering and a second order correction to the potential amplitude behaves like the correction to the scattering of an electron by an impurity in vacuum.
A second order correction to the exchange scattering amplitude $b(\mathbf{p}, \mathbf{p}')$ in the strength J of the exchange interaction (3) is small, but brings about to a singular dependence of the scattering amplitude on the energy ϵ of the scattered electrons. This correction is presented in Fig 4 a, b by the Feynman diagrams, where the dashed lines correspond to the spin propagation in time, while the solid lines denote the Green functions of the conduction electrons. If the initial electron is scattered from the state $\mid \mathbf{p}, \sigma >$ into an intermediate state $\mid \mathbf{p}_1, \sigma_1 >$ and then to the final state $\mid \mathbf{p}', \sigma' >$, the amplitude of this process (diagram of Fig 4 a) is proportional to the probability $[1 - n(\mathbf{p}_1)]$ of the state $\mid \mathbf{p}_1 >$ being not occupied and the total correction to the

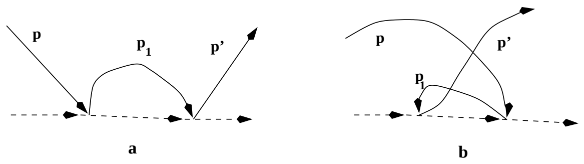

Figure 4: A second order correction to exchange scattering amplitude

scattering amplitude is proportional to

$$J^2 \sum_{\sigma_1} \int \frac{\sigma^j_{\sigma'\sigma_1}\ S^j\ \sigma^i_{\sigma_1\sigma}\ S^i\ [1-n(\mathbf{p}_1)]}{\epsilon(\mathbf{p})-\epsilon(\mathbf{p}_1)}\ (d\mathbf{p}_1)$$

For the process of Fig 4 b, when the electron from the occupied state $\mid \mathbf{p}_1, \sigma_1 >$ is first transfers into the state $\mid \mathbf{p}', \sigma' >$ and only after that the hole in the state $\mid \mathbf{p}_1, \sigma_1 >$ is filled by the electron from the state $\mid \mathbf{p}, \sigma >$, the amplitude of the process is proportional to the probability $n(\mathbf{p}_1)$ the state $\mid \mathbf{p}_1 >$ being occupied and the total correction to the scattering amplitude is proportional to

$$-J^2 \sum_{\sigma_1} \int \frac{\sigma^j_{\sigma_1\sigma}\ S^j\ \sigma^i_{\sigma'\sigma_1}\ S^i\ n(\mathbf{p}_1)}{\epsilon(\mathbf{p}_1)-\epsilon(\mathbf{p}')}\ (d\mathbf{p}_1).$$

Since

$$\hat{\sigma}^i\hat{\sigma}^j = \hat{1}\delta^{ij} + i\,\hat{\sigma}^k e^{ijk}, \quad \mathbf{S}^2 = S(S+1),\ S^iS^j - S^jS^i = iS^k e^{ijk},$$

the total scattering amplitude gets the following correction:

$$\frac{\nu J^2}{2}\int_{-\infty}^{+\infty} \left\{ \frac{S(S+1)}{\xi-\xi_1}\ \delta_{\sigma\sigma'} + \frac{2n(\xi_1)-1}{\xi-\xi_1}\ S^i\ \sigma_{\sigma'\sigma} \right\} d\xi_1. \quad (5)$$

It is clear from Eq (5) that the correction to the exchange scattering amplitude originates in non-commutativeness of the Cartesian components of the spin operator $\mathbf{S}$. Since

$$2n(\xi) - 1 = -\tanh\frac{\xi}{2T},$$

the logarithmically divergent second term in the integrand in Eq (5) is determined by the maximum of the initial energy ξ of the electron and the temperature T. Finally, the effective exchange integral J_{eff} is equal to

$$J_{\text{eff}} = J\left(1 + \nu J \ln\frac{E_F}{\max[\xi, T]}\right). \tag{6}$$

As it has been anticipated, the quantum character of the internal degree of freedom (spin non-commutativeness) gives rise to a singular correction in the second order in exchange interaction between the impurity spin and the spin of a conduction electron. The effective coupling constant $\lambda = \nu J$ is of the order of $|V|^2/UE_F$ and, therefore, is small. Nevertheless, the correction (6) gives an extra dependence of the scattering rate on temperature, which explains the temperature dependence of conductivity in dilute alloys of transition elements and the normal metals (Kondo effect). This correction leads to the coupling constant decreasing with decreasing the temperature for the ferromagnetic coupling of the impurity spin with the spin of conduction electrons ($J < 0$). In the case of anti-ferromagnetic coupling ($J > 0$), the re-scattering leads to the effective coupling increasing with decreasing the temperature.

The physical origin of the Kondo correction to the strength of the exchange interaction is in the long-time correlations of the spin in the Fermi gas, which, by itself, roots in existence of the electrons and the holes, with very close energies. After being scattered by the spin, the electron may, for a little while, transform into a hole. In the case of the anti-ferromagnetic coupling, this leads to partial screening of the impurity spin, which is reflected in a negative correction to the spin susceptibility. Since the correction (6) is singular, the effective interaction tends to grow in the strong coupling limit if the temperature T is of the order of the, so called, Kondo temperature

$$T_K = E_F \exp\left[-\frac{1}{\nu J}\right].$$

At $T \ll T_K$, the scattering cross-section σ saturates at a so called unitary limit $\sigma \approx \pi\lambda_F^2 = 4\pi^3/p_F^2$, and the temperature dependence of the resistivity $\rho(T)$ saturates as well.

$$\rho(T) = \rho(0)\left[1 - A\,\left(\frac{T}{T_K}\right)^2\,\right]; \qquad T \ll T_K. \tag{7}$$

The mentioned strong coupling regime corresponds to a nearly complete screening of the spin of the magnetic impurity by the spins of conduction electrons. As a result, the Curie law for the spin susceptibility χ of the impurity spins saturates as $T \to 0$ at the value

$$\chi_{\text{imp}}(T=0) \approx \frac{\mu_B^2 S(S+1)}{3T_K}.$$

We may say that with the screening of the impurity spin by those of conduction electrons, the Curie spin susceptibility becomes to the Pauli susceptibility. This makes a perfect sense, because as a result of the screening the $(2S+1)$-fold degeneracy of the ground state disappears, and the normal metal plus the magnetic impurity reaches its single Fermi-liquid-like ground state. This Fermi liquid has several temperatures of degeneracy, the Kondo temperature T_K being the lowest one. In the spirit of Fermi-liquid, we may expect that the extra specific heat C_{imp} associated with the impurity is linear in temperature T:

$$C_{\text{imp}} \simeq \frac{T}{T_K}. \tag{8}$$

Indirect exchange Interaction of Impurity Spins and Spin Glasses

The Kondo effect is associated with a single magnetic impurity in a normal metal. If the concentration of magnetic impurities c is finite, their mutual interaction may become more important at the temperature well above the Kondo temperature T_K.

The interaction between two spins $\mathbf{S}_1$ and $\mathbf{S}_2$ of two magnetic impurities at coordinates $\mathbf{r}_1$ and $\mathbf{r}_2$ respectively is the exchange interaction (3). The spin $\mathbf{S}_1$ generates a spin polarization around itself. This spin polarization, as we have already seen on the example of the density variation, decays slowly. This generates an exchange field acting on spin $\mathbf{S}_2$. As a result, an indirect (electron mediated) exchange interaction occurs (*Ruderman, Kittel, Kasuya, Yosida*; RKKY

) :

$$\mathcal{H}_{\text{indir}} = \sum_{ij} \mathcal{V}_{ij} \mathbf{S}_i \mathbf{S}_j, \quad \mathcal{V}_{ij} = \mathcal{V}\,\frac{\cos 2p_F r_{ij}}{r_{ij}^3}, \quad \mathcal{V} = \nu\, J^2 \quad (9)$$

For an alloy of concentration c, the RKKY interaction of two impurity spins at an averaged distance is $\mathcal{V}\langle r^{-3}\rangle \approx \mathcal{V}c$. If this energy is larger than the Kondo temperature T_K, then the mutual interaction dominates the properties of this alloy, while in the opposite case, these properties are dominated by the Kondo effect. In the former case, most of the spins precess independently, if $T \gg T_{SG} = c\mathcal{V}$. If $T \ll T_{SG}$, then most of the spins feel a very strong exchange field due to other spins, and the whole spin system gets frozen. A peculiar quality of the RKKY interaction is that the sign of the exchange interaction between any two spins depends on the distance between them and varies strongly when this distance varies very slightly. This leads to a very strong fluctuations of the local molecular field both in value and direction. The frozen state, which emerges at $T \approx T_{SG}$, is, therefore, called a *spin glass* for a very random local arrangement of spins in such a phase.