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Aspects of strongly correlated insulators

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It is pointed out that Kondo-effect rare-earth compounds with insulating ground states must, except for a small probability, be mixed valent. The lack of low-energy magnetic correlations and the optical properties are discussed in a mixed-valent model. The curious properties of FeSi are also discussed.

INTRODUCTION

A recent revival in the interest in rare-earth compounds has uncovered several new features, especially in those that have insulating ground states. Some of the newly discovered properties of the insulators that I will discuss here are (i) the lack of any magnetic correlations[1,2] among the rare-earth (or the transition-metal) ions at low energy; (ii) the distribution of the spectral weight as a function of energy in optical experiments;[3] (iii) a model of FeSi, which has a long history of curious experimental results[4] and on which optical[3] and inelastic-neutron-scattering experiments[2] have been recently performed.

But first I will discuss the minimum necessary model for these compounds. They have recently been discussed on the basis of the Kondo-lattice model.[5] Very extensive analytical and numerical studies have been performed. I shall argue that while the Kondo-lattice model is a model with interesting properties, it is inappropriate for the insulators under discussion. For earlier discussions of the materials, see Refs. 6 and 7.

MINIMUM NECESSARY MODEL

A model for rare-earth compounds, the Anderson lattice model, was proposed in Ref. 8. The model Hamiltonian is

$$\mathcal{H}=\sum_i \epsilon_f n_{fi}+\sum_{i,k\sigma} t_k f_{i\sigma}^\dagger c_{k\sigma}+\text{H.c.}+\sum_{i,\sigma} U n_{fi\sigma} n_{fi\bar\sigma}+\sum_{k,\sigma}\epsilon_k n_{k\sigma}\ , \tag{1}$$

with appropriate generalization for orbital degeneracy, etc. For $\epsilon_f-\mu$ and $\epsilon_f+U-\mu \gg \Gamma \equiv t^2\rho$, where ρ in the density of states of the conduction electrons, this model can be transformed to the Kondo-lattice model using the Schreiffer-Wolff transformation:

$$\mathcal{H}=J\sum_{i,k,k'} \mathbf{S}_{fi}\cdot c_k^\dagger \sigma c_k+\sum_{k,\sigma}\epsilon_k n_{k\sigma}\ . \tag{2}$$

The conditions for this derivation require that there be negligible charge fluctuations on the rare-earth ions and that particle-hole asymmetry is unimportant. These conditions appear to be well met in heavy-fermion compounds CeCu_2Si_2, UPt_3, UBe_{13}, etc., which are all metallic. There are empirical reasons to believe that the insulators are all mixed valent, i.e., charge fluctuations of $O(1)$ occur in them. The insulators are all formed from the beginning (Ce), middle (Sm, Eu), or the end (Tm, Yb) of the rare-earth series, which for reasons of atomic physics[6] form insulating compounds with more than one valence and are therefore likely to be mixed valent in the metallic states. I argue below that the Kondo-lattice model, Eq. (2), will, except for a small probability, be a metal. To be an insulator, the rare-earth ion must be in a mixed-valent state $(\epsilon_f-\mu)$ or $(\epsilon_f+U-\mu)\lesssim\Gamma$. The transformation to the Kondo-lattice model, is then not possible.

A basic feature of all interacting lattice problems is Luttinger's theorem, i.e., the conservation of the number of nodes of the wave function below the chemical potential as U is varied from zero upwards provided nothing nonanalytic, such as formation of bound states occurs. Analytic behavior plus conservation of number of particles guarantees Luttinger's theorem.

For $U=0$, the model of Eq. (1) has an insulating ground state provided there is twice an integral number of electrons per band. Whether or not this condition holds depends only on the lattice structure. Provided Luttinger's theorem holds, we need only the same condition for large U to get an insulating ground state. The charge in the f orbitals in this state (for $U\to\infty$) can be anywhere between 0 and 1.

Now let us try to use Luttinger's theorem for the case that the occupation of the f orbitals is very close to 1 per site as in the Kondo-lattice model. It is hard to apply Luttinger's theorem to Eq. (2), since there is no appropriate noninteracting limit for it. So it is best to stick to the original model, Eq. (1). Then, to get an insulator the occupation of the conduction electron states has to be also almost exactly 1. This is achieved only with a very small probability, as further explained below.

The constraint of dividing up two electrons per unit cell equally between the local orbitals and the conduction band is absent at mixed valence, and so no remarkable accident of nature is required. This can be discussed quite generally,[9] as follows.

Consider the electronic configuration f^{n-1} and f^n of isolated ions. There will exist some energy boundary $E_{n-1,n}$ such that if the chemical potential μ is below $E_{n-1,n}$, the ions will be in the f^{n-1} configuration and if above, in the f^n configuration. There is a similar boundary $E_{n,n+1}$ dividing the f^n and the f^{n+1} configuration.

The correct meaning of the parameter U in Eq. (1) is

$$U \equiv E_{n+1,n} - E_{n,n-1} \ . \tag{3}$$

Let these ions be in weak contact with a reservoir of conduction electrons. The reservoir is such that in the absence of the strongly correlated ions, the Fermi energy is E_{Fr} if these are r electrons per atom. Let there be $(n+r)$ electrons per atom for charge neutrality. This situation is illustrated in Fig. 1. Now if $E_{n,n+1}$ lies between $E_{F,r}$ and $E_{F,r-1}$; the mixed-valence situation must occur due to the weak contact provided by the term proportional to t in Eq. (1). The state of the system in which all ions have n f electrons is impossible because $E_{F,r}$ is too high to be consistent with the f^n ionic states; and similarly having all ions in f^{n+1} is impossible because $E_{f,r-1}$ lies below $E_{n,n+1}$. Thus the Fermi level is pinned to $E_{n,n+1}$ within the hybridization width Γ. Some fraction of the ions are on the average in f^{n+1} and the rest in f^n. This consideration also reveals that about $(E_{fr}-E_{fr-1})/U \approx O(\frac{1}{10})$ fraction of rare-earth ions should belong to the intermediate valence category. This is consistent with observations.[6]

Let us now examine the Kondo-lattice case more closely including corrections due to particle-hole asymmetry. The deviation from the particle-hole symmetric case in which Eq. (2) is obtained from Eq. (1) can be discussed by adding a potential scattering term to (2):

$$H_{\text{pot}} = \sum_i V(n_{fi}-1) \sum_{\sigma,k,k'} (c^\dagger_{k\sigma} c_{k'\sigma} - 1) \ . \tag{4}$$

Here V is the same order as J:

$$V \approx 2t^2 \left[\frac{1}{\epsilon_f - \mu} - \frac{1}{\epsilon_f + U - \mu} \right] \ . \tag{5}$$

The average occupation of the localized f orbital departs now from unity, because the Hartree-Fock levels at $(\epsilon_f - \mu)$ and $(\epsilon_f + U - \mu)$ are not symmetrically placed about the chemical potential μ. Then

$$|\langle n_f \rangle - 1| \approx \Gamma A / (U/2)^2 \equiv \delta \ , \tag{6}$$

where

$$A \approx |\epsilon_f - \mu| - |\epsilon_f + U - \mu| \ . \tag{7}$$

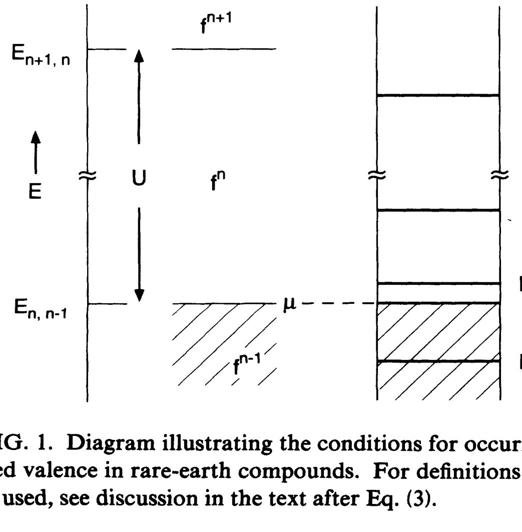

FIG. 1. Diagram illustrating the conditions for occurrence of mixed valence in rare-earth compounds. For definitions of symbols used, see discussion in the text after Eq. (3).

These δ electrons per rare-earth ion must go to the s-p-d electrons of the metal, which changes the Fermi energy by $O(\delta W) \approx \Gamma$. The Kondo resonance must of course be self-consistently located at the chemical potential. Because of the periodicity of the lattice, it splits into hybrid bands with gaps of $O(T_K)$. To obtain an insulator the (self-consistent) chemical potential must lie in the gap; if it lies at the band edges, the material is a metal or a semimetal. The f-electron weight in the bands near the chemical potential is only $O(T_K/\Gamma) \ll 1$; the rest of the weight is in the (incoherent) Hartree-Fock resonances at ϵ_f and $\epsilon_f + U$. This weight is quite insufficient to provide a pinning mechanism of the chemical potential uniquely in the gap, based on minimization of the energy when the Fermi energy of the s-p-d electrons changes on the scale of Γ. The chemical potential in general will therefore be in the hybrid bands, as there is neither symmetry reason or energetic reason for it to lie in the middle of the gap. The gap will then fill up due to particle-hole scattering. The insulating state, may, however, be obtained by tuning some continuous parameter such as pressure.

The situation is quite different for the mixed-valence case where the resonance at the chemical potential has a weight of order unity. In that case $T_K \approx \Gamma$. Consistent with the above argument is the fact that when T_K/Γ is non-negligible, so are charge fluctuations on the local orbital, which violate the conditions for reducing the model of Eq. (1) to Eq. (2) with or without inclusion of the potential scattering term, Eq. (4). It should also be clear that Kondo insulators (with very small deviations of charge from unity in the localized orbital) are not impossible; they are only unlikely in the rare earths.

These arguments do not follow from the Gutzwiller wave-function method[12] or the slave-boson approximation,[13] which ignore the incoherent Hartree-Fock resonances and can be wrongly interpreted to imply that the one-particle spectral weight of the f resonances near the chemical potential is unity, even in the Kondo-lattice case. The discussion of the mixed-valence lattice can, however, be made with such methods. One-electron spectra follow as in band-structure calculations, but with renormalized parameters. As insulating band structure is shown in Fig. 2(a). With a magnetic field such that $g\mu_B H \gg \Delta$, but much less that the conduction electron bandwidth only the rare-earth ions get polarized. The wrong species of spins of the conduction electrons (for negligible spin-orbit scattering) then do not hybridize, as illustrated in Fig. 2(b). One then has an insulator to metal transition as a function of field. This is discussed in more detail in Ref. 7.

From this picture, there is no reason to expect differences in the spin and charge gaps in these insulators. It should be understood that while all strongly correlated insulators must be mixed valent, mixed-valent metals can exist. The difference arises purely from the lattice structure, consistent with Luttinger's theorem.

It should be stressed at this point that the Anderson model away from particle-hole symmetry cannot satisfy the Friedel screening sum rule for both the charge states of the mixed-valence problem.[10] To do so longer-range interactions have to be included. Such interactions can change the metallic state to a non-Fermi-liquid state.[11] The presently known experimental properties of mixed-valence metals are not conclusive about whether or not they are Fermi liquids. One concludes from Fig. 2(b) that mixed-valence insulators in a magnetic field could be a good source for polarized electrons.

MAGNETIC CORRELATIONS

The argument that strongly correlated insulators must be mixed valent and therefore not describable by the Kondo-lattice model raises a distinction which has important consequences. In heavy-fermion metals, which have negligible charge fluctuations, low-energy magnetic correlations due to Ruderman-Kittel-Kasuya-Yosila (RKKY) interactions among the magnetic ions are clearly seen in neutron-scattering experiments. In the insulators they are absent. In this section, we show that this is so because of mixed-valent nature of the insulators.

No magnetically ordered mixed-valence compound has ever been discovered except TmSe. Neglecting the small crystal-field splitting, which is small compared to Γ, both charge states Tm^{2+} and Tm^{3+} have magnetic moments. All other mixed-valent ions studied have one or the other charge states with zero ground-state moment. The consequences of this difference and the difference from the Kondo-lattice case, with no charge fluctuations, were pointed out some time ago,[6,9] but seem worth reiterating.

The magnetic interactions among mixed-valence ions are of two kinds: (1) Spin interaction between the two sites without any *real* charge exchange. This is the only interaction which is present between two Kondo ions. The process is schematically illustrated in Fig. 3(a). It leads to the familiar RKKY interaction

$$H_{\mathrm{RKKY}} = K f(R_{ij}) \mathbf{S}_i \cdot \mathbf{S}_j \ , \tag{8}$$

where the magnitude

$$K \approx t^4 \rho^3 = \Gamma^2 \rho \ . \tag{9}$$

(2) Spin interactions with real charge exchange: These are not available to Kondo ions. The process, (mis)named double exchange proposed by Zener[14] and investigated further,[15] is illustrated in Fig. 3(b). It leads to an interaction between nearest-neighbor ions i and j of the form

$$H_{\mathrm{DE}} \approx -D |\mathbf{S}_{i,n} + \mathbf{S}_{j,n+1}| \ , \tag{10}$$

which tends to align the moments antiferromagnetically. Here $D \approx \Gamma \gg K$. $\mathbf{S}_{i,n}$ in the ground-state spin of the ion at i when it is in the f^n configuration. Now if either $\mathbf{S}_n$ or $\mathbf{S}_{n+1} = 0$, as in all known mixed-valence ions except Tm, this interaction is absent. This interaction is also absent if there are no carriers, i.e., in the insulating state. In fact the metallic state and the magnetic state are closely related. From these considerations TmSe was predicted to have an antiferromagnetic ground state in the insulating phase and to transform to a metallic ferromagnetic state on variation of the mixed-valence ratio by alloying with Tm-Te.[16] Both phenomena are observed.[17]

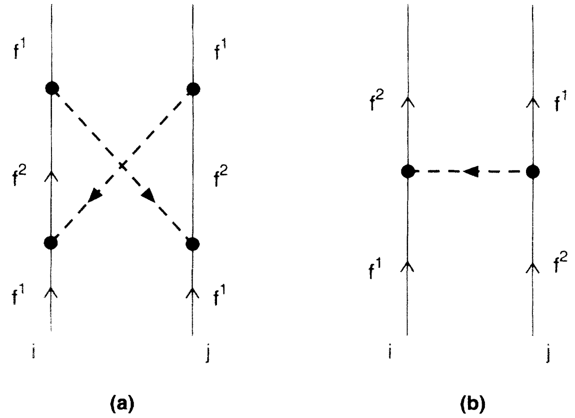

FIG. 3. (a) Process for RKKY and (b) double-exchange interactions.

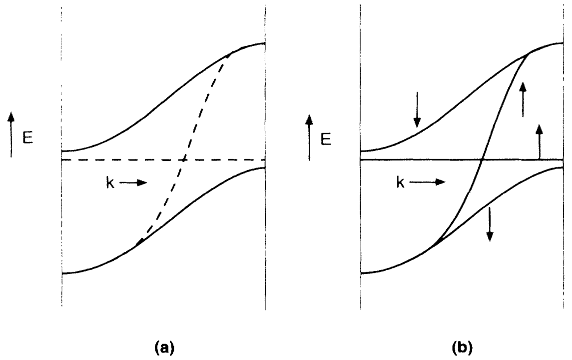

FIG. 2. One-electron states (band structure) for mixed-valence insulators; (b) illustrates the passage to a polarized metallic phase in a magnetic field with $g\mu_B H$ larger than the insulating gap.

Further experiments[18] on $\mathrm{TmSe}_x\mathrm{Te}_{1-x}$ under pressure have revealed a semiconductor to semiconductor transition followed by a metallic magnetic phase. The semiconductor to semiconductor transition resembles an excitonic transition. The magnetic correlations in their phase should be most interesting to study.

The double-exchange interaction is absent in the recently investigated[1] mixed-valence insulators, CeNiSn (Ce fluctuating between f^0 with zero moment and f^1), so we examine the role of the RKKY interactions for the magnetic correlations. These RKKY interactions can of course act between two sites only if both of them have the charge state with the magnetic moment (f^1 in the case of Ce), and provide an energy lowering of $O(K)$. On the other hand, Γ is the rate of charge fluctuations whereby charge leaves a given site and returns to the same site with arbitrary spin direction. If we keep the charge at a given site fixed in the state with spin and ask for the magnetic correlation energy with its neighbor, it is only of $O(K^2/\Gamma)$. The observed dimensionless magnetic correlations then are of $O(K^2/\Gamma^2) \approx (\Gamma\rho)^2$ which for a typical rare-earth ion is less than a percent. This argument assumes roughly equal ratio of the two valences.

One can ask for the valence ratio x at which RKKY interactions will become important by focusing spin memory in the charge fluctuations. The f-electron delocalization energy is $\Gamma x(1-x)$. The gain in energy by ordering magnetically is again K. A simple application of Stoner criteria $K\chi \approx 1$, where χ is the itinerant electron susceptibility $\approx[\Gamma x(1-x)^{-1}]$ gives $x \approx K/\Gamma \approx \Gamma\rho < 0.1$ for a typical rare-earth ion. This illustrates that the RKKY interactions will lead to magnetic correlations only in the Kondo-lattice limit of negligible charge fluctuations.

These arguments of course pertain to the ground-state and low-energy fluctuations. Excitations with energy of $O(\Gamma)$ or higher with eigenvectors displaying magnetic correlations are to be expected and experimentally seen.[1]

OPTICAL SUM RULE

In connection with some recent experiments,[3] it is useful to discuss the contributions of different energy regions to the optical sum rule

$$\int_0^{\omega_c} \mathrm{Re}\sigma(\omega)d\omega = \frac{4\pi e^2}{m} N(\omega_c) , \tag{11}$$

where $N(\omega_c) = \int_{\mu-\omega_c}^{\mu} A(\omega)d\omega$, where $A(\omega)$ is the single-particle spectral function

$$A(\omega) = \sum_{\epsilon,\sigma} |a(\epsilon)|^2 \delta(\omega-\epsilon) , \tag{12}$$

where ϵ labels the quantum numbers, and $a(\epsilon)$ are the residues in the single-particle Green's function.

Let us consider a single mixed-valent impurity in a metal first. The spectral function can then be calculated approximately from the variational wave function

$$\psi = \left[\alpha_0 + \sum_{\epsilon,\sigma} \alpha(\epsilon) f_\sigma^\dagger c_{\epsilon\sigma}\right] |FS\rangle , \tag{13}$$

where $|FS\rangle$ is the unperturbed Fermi sea. It can be shown that

$$\alpha(\epsilon) \approx \epsilon_B/(\epsilon+\epsilon_B) , \tag{14}$$

over most of ϵ with a sharper cutoff near the bandwidth W. ϵ_B is the binding energy, which in the mixed-valence regime is[8]

$$\epsilon_B \approx \Gamma \ln W/\Gamma . \tag{15}$$

The spectral function then is

$$A(\omega) \approx (1-\alpha_0^2)\epsilon_B/(\omega+\epsilon_B)^2 . \tag{16}$$

Here $(1-\alpha_0^2)$ measures the fractional mixed-valence character. The rest of the integrated weight α_0^2 is in the Hartree-Fock resonance.

Imagine embedding an array of mixed-valence ions in the lattice. Assume interimpurity interactions do not change the spectral function; this is an especially good approximation of $\omega \gg \epsilon_G$, where ϵ_G is the gap in the insulator. The renormalizations at any energy scale depend on energy scales above it but not those below it. So if the ground state is an insulator with a gap ϵ_G (of order ϵ_B), the spectral function at $\omega \gg \epsilon_G$ may still be calculated from (10) while it is zero for $\omega < \epsilon_G$.

The important point is that the integrated spectral weight to an energy ϵ decreases slowly, only as $1/(\epsilon+\epsilon_B)$. At a temperature T of $O(\epsilon_B/2)$, the insulating gap disappears. (The order of the transition as a function of temperature or magnetic field is not addressed here.) The spectral weight then is expected to be of the form

$$A(\omega) \sim (1-\bar{\alpha}_0^2)\epsilon_B/[(\omega+\epsilon_B)^2+\epsilon_B^2] \quad \text{for } T > 0\left[\frac{\epsilon_B}{2}\right] \tag{17}$$

with some small renormalization of the average mixed valence $\alpha_0 \rightarrow \bar{\alpha}_0$. To recover the weight lost in the low-frequency region in going to low temperatures, one must then integrate all the way to the order of the bandwidth. These conclusions are consistent with the experimental results.[3]

THE CASE OF FeSi

FeSi is a small gap insulator, which has the remarkable property that the magnetic susceptibility tends to zero exponentially (after subtracting a Curie tail) as temperature decreases;[4] the characteristic temperature is similar to the conductivity gap. The clue to understanding FeSi are ancient Mössbauer experiments[4] which show an isomer shift also exponentially activated with a similar characteristic temperature.

This isomer shift is similar to that observed for Eu in some compounds[19] and a similar model is called for. The local correlation energy on Fe in FeSi must be much larger than the Fe-Si hybridization, so that the problem can be spoken in terms of distinct valence configurations on Fe. The ground state is $\mathrm{Fe}^{2+}(d^6)$ hybridized with Si. The local symmetry is threefold so that angular momen-

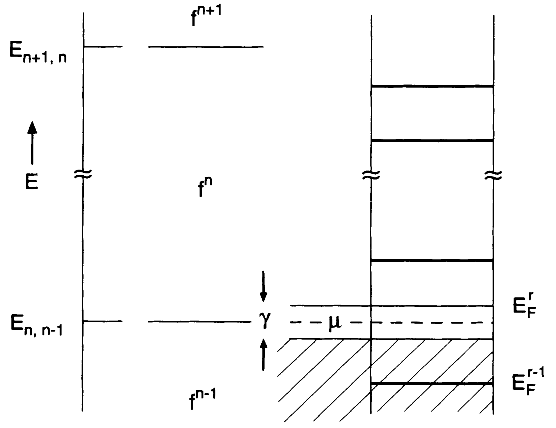

FIG. 4. Version of diagram of Fig. 1 for FeSi. γ is the hybridization gap.

tum is quenched. The ground-state spin is zero. The lowest-energy excitation is a multiparticle-hole excitation to an $\mathrm{Fe}^{1+}(d^7)$ state ($S=\frac{3}{2}$) (with a corresponding local screening by the *s-p* electrons), which is hybridized to Si bands. In terms of our general picture, Fig. 1, of the occurrence of mixed valence, FeSi would lie as shown in Fig. 4. The Fe^{2+}, Fe^{1+} boundary lies very close to the Fermi level for an integral filling of the reservoir. The hybridization with the reservoir puts the self-consistent chemical potential in a gap so that a finite energy must be paid now to go from an Fe^{2+} to an Fe^{1+} configuration. This situation is more likely in a transition-metal compound than a rare-earth compound, since the hybridization energies are much larger. But this kind of accidental situation appears to occur also for some carefully chosen Eu compounds.[19] As for the other mixed-valence insulators, and for the same reasons band-structure calculations on FeSi,[20] yield the insulating state without obtaining the correct correlations or excitations.

The model say, in effect, that mixed valence in Fe-Si is thermally induced. The absence of any low-energy spin correlations necessarily follows, as does their growth at higher energies and/or temperatures as observed experimentally by inelastic neutron scattering.[1]

The discussion of optical experiments requires the additional consideration that the mixed-valence ratio depends on temperature as $\exp(-E_G/2T)$. Otherwise the problem is the same as discussed in the last section.

Magnetic impurities, externally introduced, or those due to imperfect coordination of Fe, such that the chemical potential is pinned by them to lie in the gap of the pure insulator, should in this situation have very interesting renormalizations. Hints of this are found in tunneling experiments.[21]

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