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GAINING CONTROL OVER RARE EARTH VALENCE FLUCTUATIONS

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SOME WORKSHOP-STYLE REMARKS ON THE PROBLEM OF NARROW BAND MATERIALS

The problem addressed in this workshop is in my view a very old one. It came up for the first time in the early thirties with the discovery of the resistivity minimum in dilute alloys of simple metals with magnetic transition metal impurities. If this view is correct, then the existence of this workshop in 1987 proves, that the problem turned out to be a very difficult one, because it is apparently not yet solved to anybody's satisfaction in spite of the vast amount of experimental and theoretical work done so far.

In the course of time many names have been attached to the field: Kondo effect, spin fluctuations, interconfigurational fluctuations, valence fluctuations, mixed valence, narrow band phenomenon, f instability, Anderson lattice, heavy fermion phenomenon, strongly correlated systems, dynamic alloy etc. Curiously, all these names have been applied to the very same physical system at some time or another (e.g. to CeAl_3). If nothing else, all these names then reflect a sequence of hope and despair and finally a great amount of confusion; it is in fact sometimes very difficult, even for an old hand like me, to keep the basic problem in view through this fog of semantics.

The names derive either from a particular theoretical model, which addresses a limited aspect of the problem (Kondo effect, spin fluctuations, Anderson lattice) or from a particularly striking experimental observation like the large electronic specific heat coefficient (narrow band and heavy fermion phenomenon) or from a desire to keep the entire problem in view, at the cost of being unable to lean on a crisp but inherently limited i.e. unrealistic theoretical model (valence fluctuations).

What then is the basic problem? There is no doubt in anybody's mind, that the phenomena of interest arise from an instability of the partially filled d or f shell of certain atoms when they are put into a metallic host. The theoretical models which dominate the scene work with two local d or f states on one hand (they have now actually gone beyond a local s electron!) and a structureless sea of free conduction electrons on the other. In my view this procedure ignores at least half of the essential physics; the other half is kept alive in the term valence fluctuation. Basically, what the prevalent models ignore, is that in all these systems we are actually

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dealing with entire atoms as the source of the anomalies, not just with their f shells. In other words, there is important structure in the sea of conduction electrons.

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If one assumes charge neutrality of the RE unit cell in the metal (a very reasonable first approximation), the creation of a hole in the f shell implies the creation of a new electron on the valence electron shell of the same atom after a time of order $\hbar/\epsilon_F$. This time is very short compared to the lifetime of the f hole in any narrow band material and therefore the existence of the new valence electron has drastic effects for the equilibrium properties; it should not be left out of the Hamiltonian, as it is in the Anderson model. The new valence electron is also a conduction electron, but the conduction electron density is drastically different before and after the creation of the f hole on this particular RE atom. Early attempts to include this electron were made by Falicov and Kimball (1) and by Kaplan and Mahanti (2), but a vigorous follow through along this line has unfortunately not materialized.

The most important consequences of the existence of this new valence electron are:

- (a) A change of the binding energy of the atom to its environment. I do not understand why this energy must be buried in some effective f-f Coulomb repulsion. The total energy of the transition is, at zero mixing matrix element, the sum of a well known f-d-transfer energy (about 2.6 eV in the di- to trivalent transition of RE atoms) and of the difference of the atomic binding energies to the environment which depend on the particular solid and which can be measured by high energy spectroscopies (one of their two foremost tasks, in my view) or can be calculated in Miedema's scheme (3). Why abandon control over this most important energy parameter for some models sake?
- (b) A drastic change of the charge distribution in the RE atom. This means, that a slow f spin fluctuation is necessarily accompanied by an intra-atomic charge fluctuation which is just as slow.
- (c) The scattering crosssection for conduction electrons of an electron in the valence electron shell of a RE atom is nearly two orders of magnitude larger than that of an electron in the f shell. The resistivity anomalies are therefore dominated by the forgotten extra valence electron (4).
- (d) A change of the radius of the RE atom, which will induce displacements of the atoms (nuclei) of the nearest neighbor shell and beyond, if the lifetime τ_h of the f hole is longer than $\hbar/k_B \Theta_D$, where Θ_D is the Debye temperature. In the most interesting narrow band materials we do have $\tau_h > \hbar/k_B \Theta_D$.
- (e) The charge distributions of most states of the open f and d shell are aspherical, and there is usually strong and always at least residual spin orbit coupling in all these shells. Therefore, if this aspherical charge distribution is involved in a slow charge fluctuation ($\tau_h > \hbar/k_B \Theta_D$), the f or d magnetic moment may be demagnetized by the electron-phonon interaction, rather than by interaction with the conduction electrons. I fail to see why this important possibility has been ignored for so long, until recently (5). This example shows, that one may actually solve the wrong problem when trying to demagnetize the local f or d magnetic moment via the Anderson or Kondo lattice models in narrow band materials. In fact, Nozières argues that this cannot be done at all (6).

One may state categorically, that the rich phenomenology of the systems in question as function of temperature, pressure, and composition will never come under quantitative control, if one keeps ignoring what is going on in the RE valence electron shell and in the phononic system of narrow band materials. It is hard for me to understand why progress in addressing

the entire problem has been so slow. We are constantly promised by the theoreticians, that once they have solved their limited problem of the Anderson model, they will include the rest of the physics into the Hamiltonian. But the extra valence electron cannot be treated as a perturbation on the Anderson Hamiltonian. Therefore, what will be the use of all those beautiful solutions of the Anderson model in the groundstate vis a vis reality? (The success of the Anderson model in explaining the high energy excitations in photoemission and in BIS (7) seems to say merely, that one can forget the extra valence electron in these fast measurements).

One wonders what would happen, if somebody would start again from scratch, for instance with an atomic configurational model similar to that of Hirst (8), but including the valence electron configuration together with the f shell configuration. Should the theoretical chemists not get into the game here, finally?

THE GIBBS FREE ENERGY OF VALENCE FLUCTUATORS

Some of us experimentalists who have been sitting on a vast amount of groundstate data for a very long time and are tired of churning out more of the same, are beginning to look for ways out of the dilemma of being unable to process these data sensibly on the basis of existing theoretical results. One way out is to anticipate the results of the more comprehensive theory, necessary to really solve the problem by constructing phenomenologically an expression for the free energy of these systems as function of temperature and pressure with states whose energies and degeneracies are measurable. In the following I shall describe the main results of our work in Cologne in this direction done over the last few years. By trial and error fits to the data we have constructed a free energy expression which describes by now very well the susceptibility, the volume, the neutron quasielastic linewidth, the L_{III} valence, and the resistivity as function of temperature and pressure for elemental Ce and for $RE Cu_2Si_2$ with $RE = Ce, Eu$ and Yb . Basically, what we were able to achieve, is to calculate the properties of these narrow band materials from the measurable properties of the two metals with adjacent integral valence.

We use an expression for the Gibbs free energy of the unit cell of the system with six terms (9) (10) (11) (12)

$$G = F_C + F_S + F_E + F_M + F_P + pV$$

All these terms depend on volume V and/or on the valence, i.e. the ratio $v/(1-v)$ in which two adjacent integral valent atomic configurations are present. We minimize G with respect to V and v at fixed temperature T and pressure p .

F_C , the chemical term, contains the basic f-d transfer energy and the basic difference in chemical binding energies of the two valence states in their respective compounds at some fixed T and at $p = 0$. It is a linear function of v .

F_S , the solution term, takes account of the energy of solution of a very dilute atom with minority valence in a matrix with majority valence. It is important at nearly integral valence; without it, all γ type Ce systems would e.g. be strictly trivalent, i.e. would show no f instability whatsoever.

F_E , the elastic term (also called the alloy segregational term), takes into account the alloy strain energy which follows from the difference of the charge densities on the valence electron shell in the two valence states.

This term is zero at integral valence and large and positive at fractional valence. At fixed fractional valence, it is large when the f hole lifetime is short ($\tau_h < \hbar/k_B \Theta_D$, up to 0.4 eV in α Ce), i.e. when the nuclei in the environment cannot follow the charge fluctuation, but becomes very small at long f hole lifetime (in γ Ce and in very narrow band or heavy fermion situations at small T), when the neighborhood can relax elastically. This term and its drastically different behavior at long and short τ_h is crucial in the $\gamma - \alpha$ transition of all Ce systems which we have tested so far.

F_M is the mixing term. At high temperature and long hole lifetime (weak mixing) it corresponds exactly to the entropic term $-TS$ of the free energy of a mixture of two species of noninteracting RE atoms with their respective crystal field and spin orbit splittings and degeneracies. At low temperature this term also includes the energy gain by quantum mixing between these states, which we calculate by a scheme described repeatedly elsewhere (9) (10) (11) (13). We have found that the difference between heavy and bantam fermion systems (e.g. between CeCu_6 and CeFe_{13}) does not come from a difference in fractional valence, as we all expected naively in the past, but from a difference in mixing: At low temperature (thermal energy small compared to crystal field splitting) in bantam fermion systems the groundstates of the two valence states mix as strongly as at elevated temperature, while in heavy fermion systems the mixing almost ceases when $k_B T$ drops far below the CF splitting. This means, that in general the mixing matrix element depends on the pair of configurational substates which it connects, that there are weakly and strongly mixing pairs, and that the special feature of heavy fermion systems (and probably also of RE impurities with small "Kondo" temperatures) is that in these the groundstates are very weakly mixing. We also mention that all matrix elements depend on volume (14) (9) (15).

F_P is the phonon term. The frequency of the local Einstein oscillator represented by the RE atom depends on its valence state (on the local valence electron charge density and on the binding energy to the environment). This term causes e.g. the different thermal expansion coefficients of RE compounds with different valence. Without this term it turns out to be impossible to track by calculation the temperature dependence of the valence as observed by L_{III} X-ray absorption or by temperature dependent X-ray diffraction.

Obviously the number of energy terms necessary to describe the temperature and pressure dependence is large, much larger than anticipated in the prevalent theoretical models. However, everyone of these terms makes physical sense and nearly all energies necessary for the calculations can be obtained by independent measurements on integral valent reference compounds or by inelastic neutron scattering on the system in question. There is no doubt that the problem is very complicated and that a lot of data are necessary on each individual system to gain quantitative control. There is, however, also no doubt in my mind that the problem can be and has been solved in practice without waiting for higher theory to come down to reality.

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