

1 G. Kotliar: Lecture 2

In the previous lecture, following some motivation to study strongly correlated electron systems, we introduced a general methodology for constructing mean field theories. To apply them to electronic structure, we need to identify an observable, a reference system to calculate the zeroth order approximation to the observable and an approximation to the exchange and correlation functional. We illustrated these ideas with the density functional theory and with the dynamical mean field theory.

Excercise1: Consider the many body Hamiltonian of the solid. Take the electronic charge density as the observable of interest and the kinetic energy part of the Hamiltonian as a reference system. Construct the density functional theory using the method of lecture 1 and the local density approximation (LDA) by using the uniform electron gas to approximate Γ_{xc} .

Excercise2: consider the one band Hubbard model and take the *local* Greens function as the observable of interest. Take the kinetic energy part of the Hamiltonian as a reference system to construct the spectral density functional theory. Construct the Dynamical Mean Field Theory approximation using a collection of atoms to approximate Γ_{xc} .

Excercise3: combine the results of excercises 1 and 2 to arrive at the LDA+DMFT Functional.

For the solution to the excercises attend the lectures or read the relevant sections of the review below.

In this lecture we will review some applications of DMFT to the materials that motivated this lectures, starting with the Vanadium Sesquioxide Problem and the actinide series. A lot more about the methodological aspects of DMFT and many more applications, can be found in **G. Kotliar, S.Savrasov, K. Haule, V.Oudovenko, O. Parcollet, and C.Marianetti, Rev. Mod. Phys. 78, 000865 (2006)**

2 Vanadium Sesquioxide V_2O_3

One of the earliest "strong correlation problems" was posed by the Vanadium Sesquioxide system. It's phase diagram is shown in Fig . The x axis describes Cr substitution which had been shown to act as inverse chemical pressure expanding the lattice. The y axis is the temperature.

Within band theory V_2O_3 should have been a good metal thru all its phase diagram while experimentally it displays a metallic regime which is incoherent over a broad range of temperatures. Furthermore a dramatic metal insulator transition takes place between a paramagnetic metallic phase

and a paramagnetic insulating phase as the resistivity jumps by several orders of magnitude. This dramatic failure of the standard band theory, motivated and advanced the development of many theoretical tools. The Gutzwiller approach was applied to V_2O_3 in a famous paper by Brinkman and Rice. A slave boson approach to the Hubbard model for which the Gutzwiller approximation appears as a saddle point was developed to go beyond this approximation.

Looking at the resistivity curves, it is clear that over a broad temperature range, the Fermi liquid theory which predicts a small resistivities quadratic in temperature does not apply. The regime where the resistivity increases with increasing temperature but it is so large that the mean free path is comparable with the inter-electron spacing is referred to as the bad metal regime. In the insulating or semiconducting regime the resistivity increases with decreasing temperature.

V_2O_3 was also the subject of early applications of DMFT.

An important observation is that the topology of the *high temperature* part of the phase diagram, is common not only to V_2O_3 but to other compounds such as the κ organics and the NiSeS system, it made sense to compare the results of a partially frustrated Hubbard model, against the experiments starting from the qualitative sketch of the phase diagram displayed in figure 2.

Each one of the phases is described by a sketch of the spectral function. In the paramagnetic insulating phase, there is no weight at low energies and the spectra consist of just an upper and lower Hubbard bands. In the correlated Fermi liquid phase, in addition to the Hubbard bands there is a quasiparticle band, crossing the Fermi level. As U and temperature increase, there is a transfer of spectral weight from low energies to high energies.

Density functional theory, misses completely the richness of this diagram, within this approach, the only variable available to characterize each one of the phases is the site density which is identically one at half filling. The spectral function provides a "frequency resolution" of the density, and serves as the "order parameter" characterizing the nature of the phases and how they evolve as a function of the correlation strength. The spectral function, and the Weiss field of DMFT quantify the (frequency dependent) notion, of "degree of localization" of the electron.

The qualitative understanding of how the electronic spectra evolves as a function of temperature and correlation strength led to one of the first important experimental predictions of the Dynamical Mean Field Theory. Namely, that small changes in temperature in the metallic phase of pure V_2O_3 should result in dramatic redistributions of optical spectral weight in a broad frequency region. Non local transfers of spectral weight in photoemission and

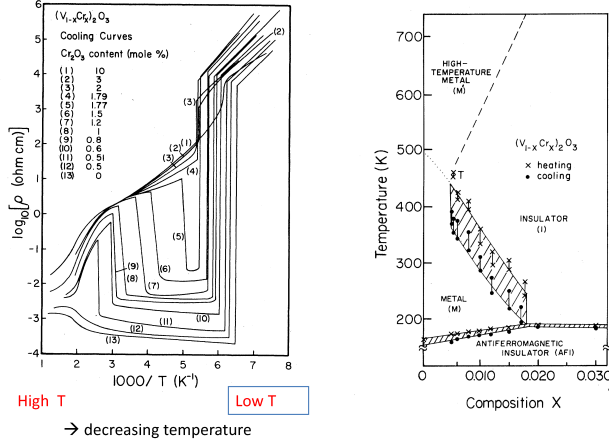


Figure 1: Right: Experimental Phase Diagram of V_2O_3 . Left resistivity curves used to identify the different regimes of the phase diagram (Fermi Liquid, Bad Metal, Semiconductor and Mott insulator) . From Kuwamoto et. al.

optical spectra is a genuine strong correlation effect, a spin density wave gap, removes spectral weight from below the spin density wave gap to the immediate vicinity of the optical gap. The schematic illustration of the connection of one electron spectral changes and optics is shown in fig 4

The results of DMFT were initially treated with skepticism. On one side, the key prediction of DMFT, i.e. the existence of quasiparticle features and Hubbard bands in the correlated metal had not been unambiguously determined. On the other hand, it was clear that the one band Hubbard model was too simple to model the complexity of the oxides, and it was not clear if it could capture on a qualitative level the physics of strongly correlated oxides. Furthermore, the quasiparticle features which are the essential elements of the theory and that should have been visible in photoemission experiments were missing in the early photoemission data. This change thanks to the advent of high energy photon photoemission, and an international collaboration lead by J. Allen's group succeeded in detecting the quasiparticle resonance in V_2O_3 . The comparison of the old photoemission data and the high photon energy photoemission data is shown in fig 6. The dominant configuration in Vanadium oxide is d^2 with two electrons in a t_{2g} manifold split by the corundum crystal field. Fig 4 shows a computation of the spectral function

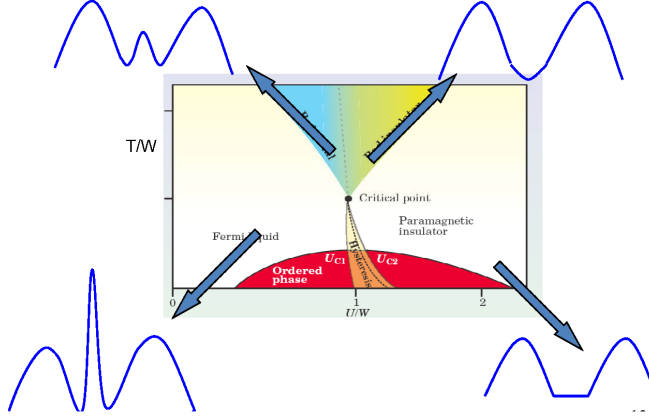


Figure 2: Qualitative Dynamical Mean Field Phase Diagram of the partially frustrated Hubbard model. The spectral function characteristic of each one of the regimes is sketched.

for a multiorbital model of V_2O_3 by K. Held. It has been very satisfying that as more realistic details were incorporated in the modelling of materials, the agreement between theory and experiment improves.

V_2O_3 was the first material in which the spinodal lines for the metal insulator transition were carefully mapped out, and the criticality of the Mott endpoint was studied. The results are shown in fig 6. While, in reality the metal to insulator transition is strongly coupled to the lattice and the volume continuously changes optimizing the distance to the given electronic structure, it is significant that a purely electronic model, the Hubbard model, in a simple but reliable approximation, DMFT can produce the observed MIT. While in an experimental situation the electronic and the structural degrees of freedom are inextricably linked, the theoretical approach can separate neatly between the two. Thus the debate of whether the MIT in V_2O_3 was structurally driven or electronically driven, which lasted several decades was finally settled by DMFT studies.

3 Actinides and Plutonium

The actinide series, illustrates the important interplay between crystal structure electronic structure. As in the Vanadium Oxide case, its problems have

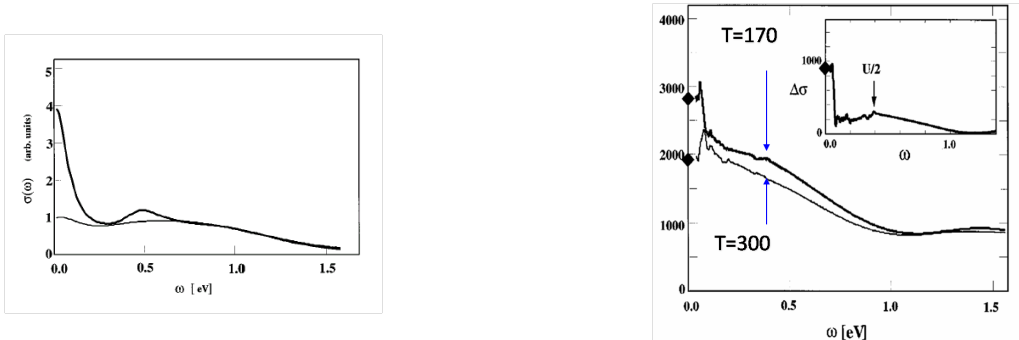


Figure 3: Left, sketch of the evolution of the optical conductivity as a function of temperature. Notice the disappearance of spectral weight in the Drude peak as well as in the mid infrared region. Experimental confirmation of the DMFT predictions in V2O3. From Rozenberg et. al.

challenged scientist since the early fifties, where it became clear, that while the nuclear physics of the actinides was well understood, the solid state physics of these material was not. These materials, and plutonium in particular, bring to the fore the physics of the localization delocalization in an element. It motivated several advances in Dynamical Mean Field Theory.

Figure 7 describes how the volume changes across the actinide series as f electrons are added to the $5f$ shell. In the early actinides, (up to Pu), the f electron is itinerant, and participates in the bonding. Starting from Am onwards, the f electron is localized, which becomes evident in the fact that the volume of Am, Bk, Cm etc, is approximately the same independent of the f electron content. In the early 60's Johanssen proposed to view this situation as a result of a Mott transition in the f series taking place around Pu. At that time, a localized electron was treated as a core electron and a delocalized electron was treated as band-like in density functional calculations.

Plutonium, and in particular its fcc δ phase, is poised near a localization delocalization instability, and has very unusual properties which could not be accounted by the standard model of solid state physics. For example: a) density functional theory predicts it to be magnetic with a large spin moment, while experimentally no moment is observed and the susceptibility is Pauli like. b) If a paramagnetic LDA solution is imposed its volume is underestimated by more than 20 percent. c) Many of its transport properties and photomission spectra is reminiscent of other correlated heavy fermions.

Following Johansen, we proposed that Pu properties are a manifestation of strong correlations in the f electrons, and that the insights and from Dynamical Mean Field Theory should be used to understand the experimental observations. For example, the enhancement of the linear term in the speci-

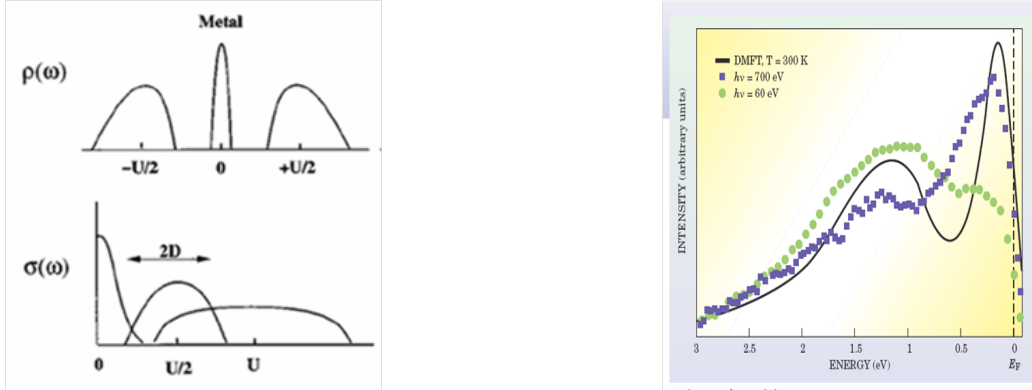


Figure 4: Connection between spectral features and optical conductivity. Right. Photoemission in V2O3 older data (green dots) do not display a quasiparticle peak which only becomes visible with higher energy photons (Moo et. al. PRL).

cic heat of the actnides, increases rapidly near the volume corresponding to δ Pu in line with the modern DMFT understanding of the MIT. (see fig 7).

Actinide puzzles, provided a major motivation for the development of the self consistent implementations of LDA+DMFT. The functional formulation described in the previous lecture, yields the total energy of the material. One can then study how the total energy varies of volume and determine the equilibrium volume of a phase. This is shown in Fig 9. Therefore for realistic values of the interaction U , of around 4.2 ev, a *paramagnetic* DMFT solution has the correct volume of the delta phase.

Having the total energy as a function of atomic positions, also allows the determination of the forces acting away from the equilibrium position. One of the first predictions of the LDA+DMFT method was the phonon dispersions in delta Pu, which are shown in fig 9. The phonon spectra of Pu had not been measured, the cross section for absorption of neutrons is very high, and the single crystal avaialables are too small to perform neutron scattering experiments. Using Hubbard I as the impurity solver, the linear response method was applied to the LDA+DFMT functional. The results of the DMFT calculations are shown in Fig ?? together with the results of subsequent experiments using the inelastic X-Ray scattering techniques at the ESRF in Grenoble.

The physics of tranfer of spectral weight in photoemission spectra, is also apparent in Pu. Figure 10 displays experimental and theoretical DMFT results for both alpha and delta Pu. Alpha Pu is modeled by a volume contraction. The physics of transfer of spectral weight to high energies with



Figure 5: More recent experiments with a more extensive dataset (right) and DMFT calculations in a multiorbital model by Held and coworkers. The qualitative physics of transfer of spectral weight is manifest. Quantitative agreement with experiments has improved.

increasing correlation is clear in both theory and experiments. This lead to a new view of the alpha phase of Pu, as a strongly correlated phase, albeit of its smaller volume. There are also higher energy features, in the spectra indicated by arrows in fig 10. They are the fingerprints of the realistic electronic structure and the sign that Pu is a mixed valent element.

4 Other Sysetms

Due to time constraints we did not review the applications of Dynamical Mean Field Theory to the copper oxides the organic superconductors and Ce115 materials. These and many other remarkable materials can be studied with LDA+DMFT and its cluster extensions and are currently the subject of intensive studies.

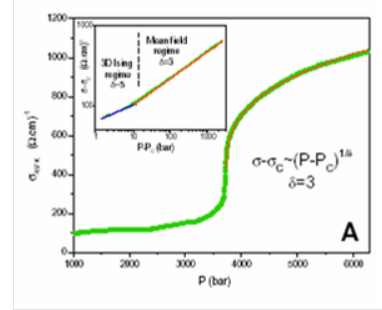
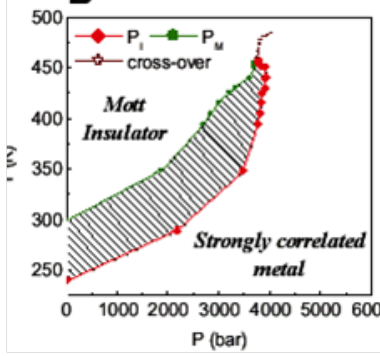


Figure 6: Observation of the Uc1 and Uc2 lines of the mean field theory in V2O3 by the group of D. Jerome. From Limelette et. al. a) Observation of the Ising criticality at the end point of the metal to insulator transition in V2O3 by the group of D. Jerome. From Limelette et. al.

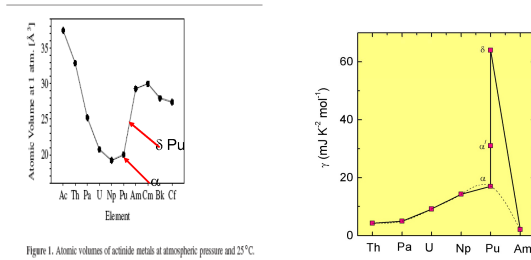


Figure 7: Atomic volumes of actinide metals at atmospheric pressure and 25°C.

Figure 7: Localization Delocalization Transition Across the Actinide Series: (right) volume vs element (left) specific heat coefficient of the elemental actinides. The DMFT program, approaches the computation and the understanding of the phase diagrams of materials, as a result of adding realistic electronic structure (realistic bands, crystal fields, etc.) and the coupling to the crystal structure to the physics of the pure localization delocalization phase diagram of the simplified Model Hamiltonian.

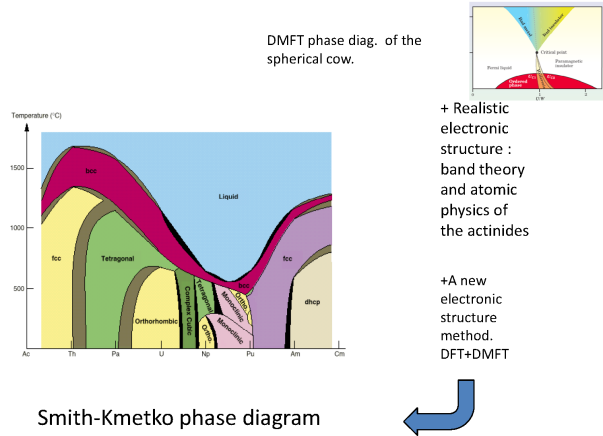


Figure 8: Phase diagram of the actinides. The interpolation between elements is carried out by alloying. After Smith and Kmetko



Figure 9: b) Phonon dispersions in δ Pu. DMFT theoretical *prediction* black dots, and its subsequent experimental determination via inelastic X ray scattering open dots. a) Energy vs volume for fcc (δ) Pu

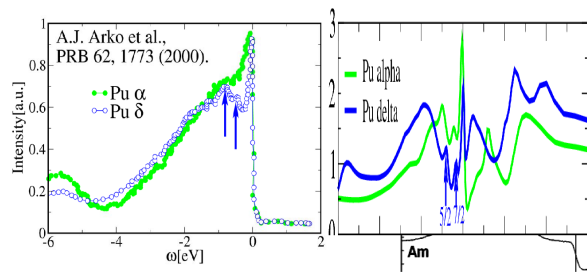


Figure 10: Experimental (left) and theoretical (right) determination of the spectra of alpha and delta Pu.