Abstract

We discuss some aspects of the pressure (or interaction) driven Mott transition, in three dimensional transition metal oxides by means of dynamical mean field theory. We isolate the universal properties of the transition from the aspects which depend more on the detailed chemistry of the compounds. In this light we can understand the main differences and the remarkable similarities between the NiSe$_x$S$_{2-x}$ and the V$_2$O$_3$ system. Both theory and experiment converge on the transfer of spectral weight from low energies to high energies as the universal mechanism underlying the Mott transition, and we comment on the possible relevance of these ideas to other metal to non metal transitions.

Introduction

The Mott transition problem has fascinated a generation of theorists, and is believed to be realized in materials straddling the localization delocalization boundary such as V$_2$O$_3$ and NiSe$_x$S$_{2-x}$[1]. Recently great theoretical progress on this problem has been achieved using dynamical mean field methods[2]. In this paper we will discuss how this approach gives insights into the physics of these two materials. Recent detailed experimental studies show that in spite of the many similarities between these two materials, some physical quantities behave quite different as the metal to non metal boundary is approached [3] [4]. Our goal is to indicate which aspects of the problem can be qualitatively understood from simple models that ignore the detailed solid state chemistry of the compound (i.e. band structure and orbital degeneracy), and which aspects require a more realistic description which takes into account those effects. We will then summarize the differences and similarities between the two systems and how they can be understood in a dynamical mean field framework. We conclude with a brief discussion of the applicability of these concepts to other systems.
Dynamical Mean Field Theory in the Continuum

The dynamical mean field approach (DMFT), in the continuum, can be most easily explained by analogy with the well established Density Functional Theory DFT. In this approach, \( \rho(r) \), i.e. the density is the basic quantity of the theory. Then one defines an exact functional \( \Gamma_{\text{DFT}}(\rho) \), of the density such that its minimization \( \frac{\delta \Gamma_{\text{DFT}}}{\delta \rho}(\rho_{\text{phys}}) = 0 \) yields the physical density of the problem. The reason why the DFT approach, sometimes fails in describing Mott transitions, is that when these transitions involve very small volume changes, as in the \( NiS_2 \) system, the density near the transition does not change that much. An approximate density functional, such as \( \Gamma_{\text{LDA}} \) then fails to detect these changes.

Another way of rationalizing the failures of DFT in describing Mott transitions, and other problems in strongly correlated electron systems, given its extraordinary success for weakly correlated materials, is to notice that while DFT is in principle a theory of ground properties, the excitation spectra of weakly correlated materials, bears a great deal of similarity to the spectra of the Kohn Sham equations, (band theory). On the other hand, the excitation spectra of correlated electrons, as measured in photoemission spectroscopy, has in addition to quasiparticle-like, dispersing features, broader, atomic like, broader and less dispersive features called Hubbard bands. There is no trace of the Hubbard bands in the Kohn Sham spectra. A formalism suitable for correlated electron systems, should treat both the quasiparticle features, and the Hubbard bands, \emph{on the same footing}. Formulating the problem in terms of the local spectral function accomplishes precisely this goal.

The basic object in the DMFT approach is the local Greens function, i.e. the density of states for adding or removing one particle which is measurable in photo-emission and inverse photo-emission spectroscopy. One formulates the theory in terms of the local Greens Function \( G^L \), with \( r \) and \( r' \) are vectors in a Wigner Seitz cell.

\[
G^L(\tau, r, \tau', r') = -\langle T(\psi(r, \tau)\psi^\dagger(r', \tau') \rangle
\]

Intuitively, we can think of DMFT as an attempt to ”frequency resolve the density” since \( \rho(r) = -\frac{1}{\pi} \int f(\omega) \text{Im} G^L_{\text{R}}(r, r, \omega) \). In problems which are driven by transfer of spectral weight from one frequency range to another, without appreciable changes in the total density, the dynamical mean field method is likely to provide a more adequate framework.

The construction of the dynamical mean field theory in the continuum then proceeds by analogy with the density functional theory. One proves the existence of a unique functional \( \Gamma_{\text{DMFT}}[G] \) such that \( \frac{\delta \Gamma_{\text{DMFT}}}{\delta G} = 0 \) at the physical local Greens function \( G \) [5]. Furthermore, this functional has the form,

\[
\Gamma_{\text{DMFT}}[G^L] = \Gamma_{\text{universal}}[G^L] + \int v_c(r) G^L(\tau = 0^-, r, 0^+, r)
\]
with the universal functional independent of the crystal potential, $v_c(r)$. This is proved using Legendre transformation techniques [5] and the existence proof is valid as long as certain invertibility condition is satisfied. Alternatively, one can formulate the problem in terms of a basic object $G^k(\tau, r, \tau', r') = -\sum_n \langle \psi(r + R_n, \tau) | \psi(\tau') \rangle$ related to the Greens function via the localization kernel $P(R_n) \equiv \int_{BZ} dke^{ikR_n}$.

From the point of view of a practical implementation, we need explicit forms to approximate the exact functional $\Gamma_{\text{DMFT}}$. One possibility is to express the full Hamiltonian in a complete basis of Wannier functions built from the solution of the Hartree Fock equations, truncating the dynamical part of the interaction leaving only the local terms and applying to the latter the standard dynamical mean field construction [2]. This procedure, is likely to be more accurate, the more localized the Wannier basis is. A different construction of an approximate functional which does not make reference to an explicit basis can be carried out using the cavity construction directly in the continuum [5].

The study of model Hamiltonians using DMFT, is by now a vast subject [2]. The continuum formulation goes beyond the treatment of model Hamiltonians because it allows the determination of the model Hamiltonian parameters in a self consistent fashion. This formulation necessary to describe the changes in the lattice parameters that accompany the metal to insulator transition.

**Insights From Dynamical Mean Field Theory** The DMFT, has systematized and unified seemingly different approaches to the study of correlated electron systems. Furthermore it has given rise to several surprising insights, that will guide us in the interpretation of experimental data [2]. The functional in eq. 2 is highly non linear and in certain region of parameters has multiple minima. The phase diagrams are constructed by comparing the free energies of these states. In the presence orbital degeneracy or other sources of magnetic frustration, DMFT has several states (or dynamical mean field solutions) with very different low energy properties which are very close in energy. It was found that in the presence of magnetic frustration, the phase diagram of the Hubbard Hamiltonian, has the same phases and topology of that of $NiSe_2S_{2-x}$ and $V_2O_3$[11]. Magnetic frustration suppresses magnetic long range order and allows a first order paramagnetic metal to paramagnetic insulator transition. The conjecture that the Hubbard model could produce the phase diagram of $V_2O_3$ was put forward long ago [9], however one lacked a thermodynamically consistent treatment of the model to demonstrate the point, and it was not clear that one needed a finite amount of magnetic frustration [1].

The origin of this magnetic frustration is very different in the two systems and reflects the different quantum chemistry of the two compounds. $V_2O_3$ is a Mott Hubbard system while, $NiSe_2$ is a charge transfer but this is not the main source of differences which lies in the different kind of orbital degeneracy. The minimal model for $V_2O_3$, due to Castellani et. al., involves one electron
in a doubly degenerate $a_{1g}$ orbital, so the Mott transition has to lift, not only the spin degeneracy but also the orbital degeneracy. The $NiSe_xS_{2-x}$system on the other hand is described by two holes in a twofold degenerate $e_g$ orbital. Hund's rule coupling favors parallel spins and both orbitals occupied, at each site lifting completely the orbital degeneracy. The source of frustration, in the $NiSe_xS_{2-x}$case, is the fact that the Ni ions in the pyrite structure occupy an fcc lattice which is strongly frustrated by the presence of nearest neighbor and next nearest neighbor exchange constants of similar order of magnitude. The source of magnetic frustration in $V_2O_3$, is tied to the orbital degeneracy, since the exchange among orthogonal orbits, is ferromagnetic, while the exchange among identical orbits is antiferromagnetic, the magnetic Hamiltonian in the ordered phase of $V_2O_3$ has both ferro and anti-ferro couplings, leading to magnetic frustration.

The finite temperature part of the phase diagram of $NiSe_xS_{2-x}$and $V_2O_3$ is qualitatively similar, its physics is captured by a simple one band Hubbard model with frustration. The low temperature phases, and the nature of the transition into the low temperature phases, on the other hand, is different. In $NiSe_xS_{2-x}$, the orbital degeneracy is totally removed and the spin ordering transition (Paramagnetic Metal to Antiferromagnetic Insulator or Paramagnetic Metal to Antiferromagnetic Metal) transition is of the second order. In the $V_2O_3$ system, the orbital degeneracy is lifted by orbital ordering, which causes the exchange constants to switch discontinuously [7].

The behavior in the paramagnetic phase, near the Mott transition, can be described in terms of a two fluid picture. The spectral function of correlated electron systems contains two kinds of features, quasiparticles, and incoherent features. They both play a crucial role at finite temperatures, near the Mott transition. When the Mott Transition is approached, as a function of a control parameter (temperature, pressure, etc) spectral weight is transferred from low energy to high energy. Several spectroscopic measurements in $NiSe_xS_{2-x}$ and $V_2O_3$ are consistent with these ideas. Optical measurements [11] in the metallic phase of $V_2O_3$ can be interpreted as a result of anomalous transfer of spectral weight from low to high energies. Recent photoemission experiments by the group of Z. X. Shen [8] in the $NiSe_xS_{2-x}$ system have provided direct evidence that the temperature driven metal to insulator transition point can indeed be described as the evaporation of the quasiparticle peak, in the one particle spectra. Theoretically, the anomalous temperature dependence of the single particle spectra was first studied in the paramagnetic phase [2]. However this seems to be a very robust feature of the strongly correlated metallic regime near a frustrated paramagnetic insulator and also occurs in antiferromagnetic metallic phases [10] [6]. The transfer of spectral weight as the mechanism driving the Metal to Insulator transition, is quite different from the opening of Slater gap, which conserves the k integrated low energy spectral weight. Finally it is worth mentioning that a comparison between the photo emission
spectra of the paramagnetic metal and the anti ferromagnetic insulating phase of $V_2O_3$, is also consistent with the transfer of spectral weight from low energies to extremely high energies [12].

**Mass Enhancement** In $V_2O_3$ the mass increases as a function of pressure until the metal to insulator transition is reached. On the other hand in $NiSe_xS_{2-x}$ the mass increases as pressure is applied, and starts decreasing after it entered the metallic anti-ferromagnetic phase [3] [4]. To understand this contrasting behavior, it is useful to start from general Fermi liquid considerations, in a metallic phase with magnetic long range order. The one particle Green’s function, is separated into a singular part and a smooth incoherent part.

$$G_{\sigma\alpha}(\omega, k) \approx \frac{Z_{k\sigma\alpha}}{\omega - E_{k\sigma\alpha}} + G_{inc,\sigma\alpha}(\omega, k)$$ (3)

The Fermi Surface, is defined by the locus of zeros of the quasiparticle energy, i.e. $E_{k\sigma\alpha} = 0$ and has multiple sheets in orbitally degenerate systems, $\sigma$ and $\alpha$ are spin and orbital indices. The linear term of the specific heat is proportional to the quasiparticle density of states

$$\gamma \propto \sum_{\sigma, k} \delta(E_{\sigma, ka}) = \sum_{\sigma} A_{\sigma\alpha} < m^*_{\sigma, ka} >$$ (4)

Here we have defined an effective mass by, $rac{\partial E_{k\sigma\alpha}}{\partial k_{||}} = \frac{k_F(\theta)}{m^*_{\sigma\alpha}(\theta)}$, $A(x)_{\sigma\alpha}$ denotes the area of the Fermi surface parametrized by the angle $\theta$, and $<>$ denotes an average over the Fermi surface.

The basic physics controlling the behavior of the specific heat near the AM to AI phase boundary is the competition between the increase of $< m^*_{k\sigma\alpha} >$ and the decrease of the Fermi surface area $A$. Quantitative calculations of the specific heat displaying these tendencies have been performed in a frustrated version of the one band Hubbard model [6]. In the anti-ferromagnetic phase, $m^* \propto [1 - \frac{\partial \Sigma(\omega, \theta)}{\partial \omega}] = Z^{-1}$ and its increase is cut off by staggered magnetization [6]. On the other hand, $A$ decreases due to self consistent change in band structure. When the staggered magnetization is large the change in area is the dominant effect, whereas the first effect dominates when the magnetism is weak.

The different behavior of the mass enhancement as the AM (antiferromagnetic metal) to AI (anti-ferromagnetic insulator) boundary is approached can be understood if we assume that the metallic magnetism is stronger in $NiSe_xS_{2-x}$ than in $V_2O_3$. The first effect dominates in $V_2O_3$ while the second effect dominates in $Ni(SSe)_2$ as a result $\gamma$ increases (decreases) as the MIT is approached in the two materials respectively. This is consistent with the larger size of the magnetic moment of the $NiSe_xS_{2-x}$ compared with the $V_2O_3$ system.
as observed in neutron scattering [13]. This is also consistent with the DMFT interpretation of the low temperature Hall coefficient measurements which are given by the Boltzman formula, using $E_{k\sigma}$ as the quasiparticle energy. In $V_2O_3$ the low temperature Hall coefficient depends very weakly on pressure, while in $NiSe_xS_{2-x}$ the Hall coefficient increases dramatically as the pressure driven MIT is approached.

**Conclusion** The main shortcoming of the dynamical mean field approximation is the neglect of short range magnetic correlations in the paramagnetic phase. It is most reliable when the effective magnetic interactions are frustrated or small. The local approximation might also be an appropriate starting point to describe the recently discover metal to insulator transition in two dimensional mosfets [14], in the accessible temperature range. In the low density regime of the electron gas and in the presence of disorder, the exchange constants in the insulating phase are very small and frustrated. It is interesting to notice that the conductivity data in Mosfets [14] and in the $NiSe_xS_{2-x}$ system [3] are remarkably similar, once we recognize that in the $NiSe_xS_{2-x}$ system the bare kinetic energy is a two orders of magnitude larger.

**References**

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