Strongly correlated electrons in solids

T. V. Ramakrishnan

Department of Physics, Banaras Hindu University, Varanasi 221 005, India, and Department of Physics, Indian Institute of Science, Bangalore 560 012, India

In this review, phenomena and ideas connected with strongly interacting electrons in condensed matter systems will be outlined. A simple picture which regards electrons as basically a free gas of quantum particles is the basis of our understanding of all electronic behaviour of metals and insulators. In the last few decades, families of systems have been explored in which the interaction energy is much larger than the energy of free motion, or kinetic energy. These include transition metal oxides with unfilled d electron shells, rare earth intermetallics with f electrons, etc. Their behaviour is rich and not well understood in terms of existing paradigms. I point out some experimental features common to these, e.g. that they are 'bad' metals with unusually low quantum coherence temperatures. I also briefly give illustrative examples such as cuprates (which are high temperature superconductors), manganites (exhibiting colossal magnetoresistance) and heavy fermions (rare earth intermetallics). Some of the ideas, theories and methods available for describing these sysytems are outlined. It is suggested that a new general approach may be needed for this qualitatively different regime of many electron behaviour.

Keywords: Cuprates, electron gas, heavy fermions, Hubbard model.

Introduction

WHEN atoms and molecules come together in large numbers (e.g. of the order the Avogadro number, i.e. about 6×10^{23}) such that distances between them are comparable to their natural sizes, the aggregation acquires new properties. Its physical behaviour is the subject of condensed matter (solid state or liquid state) physics. The standard paradigm for understanding the electron related properties of such systems regards the outer or incompletely filled shell electrons of the atoms as quantum mechanical particles moving about relatively freely in the medium constituted of other ions and electrons. In the last few decades or more, an increasingly large number of systems have been discovered and explored (including cuprates which are high temperature superconductors, manganites which exhibit colossal magnetoresistance, and families of rare earth intermetallics) whose novel properties are qualitatively different from expectations based on this standard paradigm. In these systems, it seems that

e-mail: tvrama2002@yahoo.co.in

electron motion is strongly correlated; the electron–electron repulsive correlation energy is (much) larger than the electron kinetic energy and is spatially strongly localized so that its effect cannot be treated as a mean field, as has been done hitherto. This (rather large) area, rich in phenomena and perhaps needing new organizing principles, is the subject of the present review. The field is also extremely active; for example, there has been a biennial conference on the subject for the last two decades or so, reporting both discoveries of novel systems and new results on old systems; in every meeting typically several hundred papers describe the findings[1]. It represents a great opportunity for research in terms of new materials, as well as physical properties and principles at different levels of description.

I start with an introduction which sets the background; then some experimental features common to strongly correlated metallic systems are pointed out. Solid state chemical realities of such systems are outlined, and some families are then described. I then outline sketchily some of the theoretical models and approaches developed for such systems, and conclude by mentioning obvious prospects.

Background

Towards the end of the 19th century, it became clear that electrons, the common constituents of all atoms (e.g. Thomson[2], 1897), determine the observed behaviour of condensed matter. Very soon thereafter, Drude[3] proposed (in 1900) the breathtakingly bold and simple hypothesis that electrons in solids form an *ideal* (i.e. completely free, noninteracting) classical gas of particles; their interaction can be neglected in comparison to their kinetic energy. This idea, and highly developed variants of it, dominate our thinking about the low energy electronic behaviour of all matter; e.g. the entire world of electronic devices is effectively and successfully viewed in this light. Particularly in the last three decades, however, an increasingly large number of families of materials (e.g. transition metal oxides, rare earth intermetallics) have been explored in which it appears that electron–electron interaction is much larger than the kinetic energy, and qualitatively affects the motion. These systems are host to a variety of rich and novel physical properties, often unlike those of solids (metals, insulators and semiconductors) we are familiar with. Possible new paradigms and

working models for this regime constitute one of the most active concerns in condensed matter physics; the field is characterized by the discovery of unexpected systems and phenomena.

There is very little here about the one family of systems in which strong electron interactions combine with high magnetic field, low temperature and low dimensionality (two dimensions) to produce the fractional quantized Hall effect and related phenomena. This is a fascinating, relatively well understood field. Also not mentioned are currently very active areas like the effect of correlations in quantum dots as well as in similar nanoscopic systems, strong interaction effects in cold atom systems, and graphene.

Free electron gas

Three years after the discovery of the electron, Drude[3] hypothesized that electrons in solids form an ideal classical charged gas of particles. He calculated electromagnetic properties of solids using this idea, and found that the results agreed well with those for metals. In hindsight, we would say that the electrons involved are those outside the filled atomic shells, and that being strongly influenced by the presence of other atoms in their close vicinity, they have broken free from their 'parent' atoms. They can therefore be regarded as moving freely throughout the solid. Drude realized that the large class of insulating solids cannot be described in this way; in them the outer electrons seem to be bound rather than free, though the number density of electrons seems to be about the same as in solids which are metallic (an example is diamond, which is a very good insulator, and has an electron density of about 6×10^{22} per cc, nearly twice that of aluminium, which is a metal). Nor can one understand the absence in a metal of the large extra temperature independent Dulong-Petit specific heat or heat capacity which should be associated with such a classical electron gas.

Both the above major failures of the Drude theory require the realization that electrons are matter waves, i.e. quantum and not classical particles. Again, very soon after de Broglie proposed the matter wave hypothesis in the early 1920s, Sommerfeld[4] worked out the consequences of a 'free electron quantum gas' model of metals (see below), and Wilson[5] proposed a classification of solids into metals and insulators (as well as semiconductors) based on the properties of electron waves moving in a medium constituted by atoms (positive ions) arranged in a periodic lattice.

Since the free electron gas model of solids is basic to our thinking about them, I briefly summarize it here; discussion of it (or equivalently, of the Fermi Dirac gas) can be found in almost any book on condensed matter physics or statistical mechanics. The fact that electrons are waves

and not classical point particles is not relevant if the characteristic de Broglie wavelength of electrons is smaller than the typical distance between them. For electrons at a temperature T, their rms speed (if thought of as constituents of an ideal classical gas) is $v_{rms} = \sqrt{3k_BT/m}$, so that the thermal de Broglie wavelength is $\lambda_{thermal} = h/mv_{rms}$. This needs to be smaller than the average interparticle spacing $r_{int} = (3/4\pi n)^{1/3}$ for the classical ideal gas description to be accurate, where n is the electron number density, i.e. the number per unit volume. The condition defines a degeneracy temperature T_d around which the behaviour of a noninteracting gas of particles of mass m and density n changes from classical (above T_d) to quantum (below T_d). In the quantum regime, which is inevitable for electrons under conditions typical of most condensed matter and most temperatures, the wave character of electrons is manifest in their properties. This condition is most simply visualized in the $T = 0$ limit. Electrons obey the Pauli exclusion principle, so that there is only one electron in a single quantum state (characterized in the present case by the propagation vector **k** of the electron wave, and by the orientation of its intrinsic angular momentum or spin which has two degenerate configurations in the absence of a magnetic field; the configurations are labelled by σ which takes these two values). At $T = 0$, the electrons occupy the lowest energy states one by one (Figure 1). Since the occupied states are all (in three dimensions) within a sphere of radius (say) k_F one has $N = 2\Omega(1/2\pi)^3(4\pi k_F^3/3)$ where Ω is the volume, and so the highest occupied state of energy ε_F (the Fermi energy) is related to electron density n and mass m by the equation:

$$\varepsilon_F = k_BT_F = (p_F^2/2m) = \{(hk_F/2\pi)^2/2m\} = (h^2/8m)(3n/\pi)^{2/3}$$

since $(k_F^3/3\pi^2) = n$. For typical electron densities (~ a few times 10^{22} electrons per cc), T_F is about 50,000 K, a large value, much higher than the room temperature of 300 K.
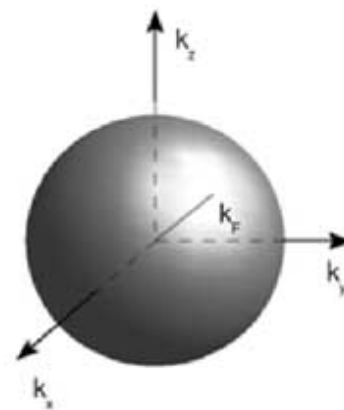

Figure 1. The Fermi sphere. In a free fermion gas (free electron gas) in three dimensions, all the states within the sphere (in k_x, k_y, k_z space) are occupied, and none above, at $T = 0$.

T_F, the intrinsic quantum energy scale of 'free' electrons in solids is very high; they form a highly degenerate quantum (Fermi Dirac) gas at most accessible temperatures. The temperature at which the electron gas crosses over from being classical to quantum, namely T_d, is about $(2\pi)^2 T_F$.

In the above approximation, the energy of the electron has a continuous distribution of values, i.e. it forms a continuum from zero upwards without a gap. Since the electrons are free particles, the energy $\varepsilon_k = (hk/2\pi)^2/2m$ where the state quantum numbers are $(\mathbf{k}, \sigma)$. Each state $(\mathbf{k}, \sigma)$ is thus occupied by one electron for $|\mathbf{k}| < k_F$, where k_F the Fermi wave vector is such that $\{(hk_F/2\pi)^2/2m\} = \varepsilon_F$, and by none for larger $|\mathbf{k}|$. This occupation discontinuity of unity defines the *Fermi surface*, which in this case is a sphere of radius k_F in quantum number or wave vector space. In general (i.e. in the presence of inevitable interactions between electrons) one expects a metal to have a Fermi surface with a discontinuity z_k less than one. If the occupied electronic states of the system are spatially localized, the occupation number distribution in reciprocal or wavevector space is smooth, i.e. has no discontinuity, and falls off for large $|\mathbf{k}|$ (Figure 2 shows these schematically).

In a periodic solid, several modifications occur. The energy levels are arranged in bands separated by gaps, and the relation between energy and wave vector is different. If the number of electrons is such that the highest energy occupied state is separated from the lowest unoccupied state by a gap, one has an insulator, because it requires the (nonzero) gap energy to excite and transport electrons across the solid for an electric current to flow. Such a gap is possible if the number of electrons per unit cell is even. If the number is odd, the highest band of electronic states is incompletely full (essentially due to spin degeneracy!) and the substance *has* to be a metal. The Fermi surface is not spherical, but has a shape symmetry appropriate to that of the crystalline solid, with
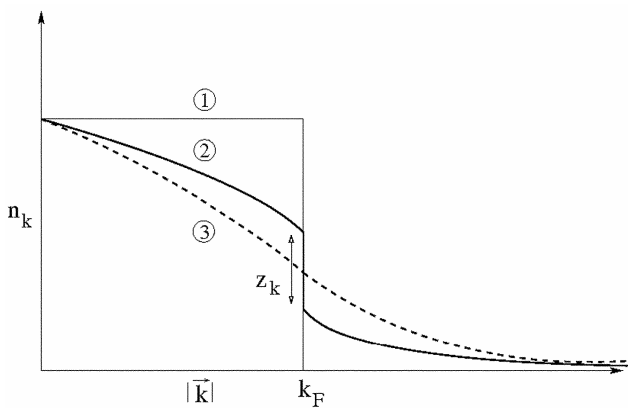
a deviation from spherical shape which increases with the size of the periodic potential, and with different parts of the surface being possibly in different Brillouin zones appropriate to the crystal symmetry into which $\mathbf{k}$ space (occupation number space) can be divided.

We notice that at $T = 0$, the electrons have a rather large (zero point) kinetic energy, namely large speeds of the order of $v_F \sim 10^8$ cm/s. Correspondingly, the pressure P is large as well, namely $P = (2/5)n\varepsilon_F$.

Elementary charge neutral excitations with respect to such a ground state consist of removing a particle from an occupied state and putting it in an unoccupied state; these are density or spin fluctuation excitations. The charged excitations consist either of adding electrons in unoccupied states, or of removing them from occupied states. For energies small compared to the Fermi energy ε_F or temperatures small compared to T_F, their density is proportional to energy $|\varepsilon - \varepsilon_F|$ of the excitation, or to the temperature T. As a consequence, for example, the specific heat of a degenerate free electron gas is proportional to temperature (it is approximately (T/T_F) times the Dulong-Petit value) and the paramagnetic spin susceptibility is independent of temperature (again, reduced by a factor of order (T/T_F) with respect to the value for a classical gas of magnetic moments). At most commonly accessible temperatures, i.e. for $T \ll T_F$, one has a dilute gas of excitations. These results are general, i.e. they are independent of whether the electron gas is free or interacting, since they depend only on the existence of a Fermi surface and Fermi energy scale for quantum degeneracy (Figure 3 shows the particle hole excitation spectrum of a free Fermi gas at $T = 0$).

Two major additional realities, namely interactions and disorder, are ignored in the above picture, and interestingly, both lead to the same qualitatively new consequence,
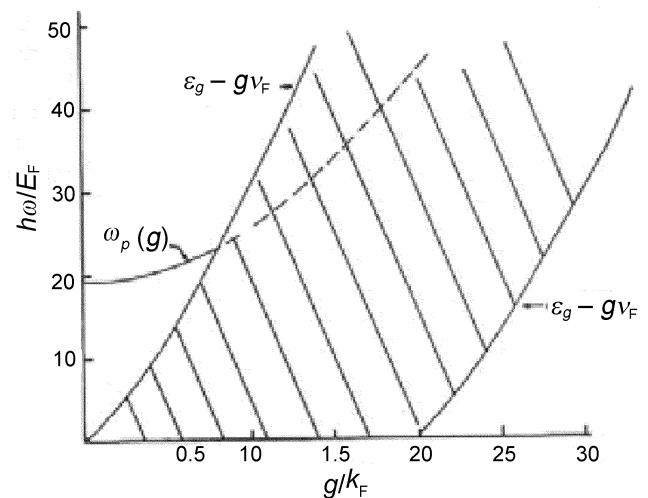

Figure 2. Occupation number $n(\mathbf{k})$ for an electron gas as a function of wave vector magnitude $|\mathbf{k}|$. (1) Free gas; (2) Interacting electron system which is a Fermi liquid (Fermi surface discontinuity $0 < z_k < 1$); (3) Strongly interacting electron system ($z_k = 0$, no Fermi surface).

Figure 3. Particle hole excitation spectrum of the free electron gas, in the frequency ω, wavevector $\mathbf{q}$ plane. They are in units of ε_F and k_F respectively.

namely that electronic states which are extended in the absence of interactions and disorder become localized when these are strong enough. Though this was realized more than five decades ago (by Mott[6] in the first case and by Anderson[7] in the second), the consequences of strong disorder were worked out much later, while the effects of strong interactions are being actively explored and not fully understood theoretically.

Interacting electron gas

Very sophisticated 'mean field' like theories have been developed for interacting electronic systems. In the early fifties, Bohm and Pines[8] considered the properties of a quantum gas of electrons interacting electrostatically with each other (Coulomb interactions) and showed that a characteristic effect of interactions is to introduce a new collective degree of freedom, the plasmon, which has a rather large energy at zero wave vector and does not change the low energy properties of the electron gas which continue qualitatively to be those of a free gas. This is formally described in terms of a canonical transformation involving the collective high energy 'plasmon' degrees of freedom acting on the electron states. The electron is thus not completely free; it drags along (coherently) a virtual plasmon cloud as it goes. In reality, there are low energy excited states of the degenerate electron gas not describable as plasmons; the coupling of an electron to these, via the same Coulomb interaction (as gives rise to plasmons) leads to incoherence in electron motion.

In extremely influential work, Landau[9] argued that the low energy excitations of a strongly interacting fluid of fermions (e.g. electrons) can be described in terms of interacting quasiparticles whose quantum numbers are in one to one correspondence with those of *free* fermions. This Landau Fermi liquid theory (see ref. 10 for an account) was derived using many-body perturbation theory (to all orders) by Luttinger and Nozieres[11] and others. It is the cornerstone of our understanding regarding electrons in solids, namely that their low energy (for example thermal) properties are *qualitatively* those of a degenerate quantum gas of free fermions. The origin of well-defined low excitation energy quasiparticles in solids where electrons interact with each other can be traced to the existence of a discontinuity in occupation of states (Fermi surface), and to the Pauli exclusion principle, which forbids transitions of electrons to states that are occupied. Because of this, the quasiparticles have a decay rate $\Gamma(\varepsilon) \sim (\varepsilon - \mu)^2$ much smaller than the excitation energy $|\varepsilon - \mu|$ (when the latter is small). They thus are sharply defined excitations. The energy of a Landau quasiparticle in a particular state $(\mathbf{k}\sigma)$ depends also on the distribution $\delta n(\mathbf{k}'\sigma')$ of quasiparticles in other states via their interaction with each other; this contribution is included in a mean field sense, namely as a product of $\delta n(\mathbf{k}'\sigma')$ and

$f(\mathbf{k}\sigma, \mathbf{k}'\sigma')$, the latter being the Landau interaction between quasiparticles. A nonzero distribution $\delta n(\mathbf{k}'\sigma')$ may arise from thermal excitation, from an external magnetic field acting differently on the two spin components, etc. The low energy properties of a Fermi liquid, namely properties for $(\mathbf{k}\sigma)$ and nonzero $\delta n(\mathbf{k}'\sigma')$ both in the vicinity of the Fermi surface, are qualitatively those of the free Fermi gas mentioned above. For example, the Pauli paramagnetic spin susceptibility is temperature independent (it goes as T^0 while for a classical paramagnet it would go as T^{-1}) and the specific heat is linear in temperature (namely, behaves as T^1 and not T^0 as in the Dulong-Petit law for a classical gas) though the coefficients are affected by interactions (the Landau or Fermi liquid parameters f). The effective mass $m*$ differs from m because of interactions between quasiparticles. Fermi liquid theories have been developed for superfluids[12], for electrons in a lattice periodic medium[13], and for disordered systems[14]. Spectacular examples of a Fermi liquid occur in rare earth intermetallics in which the rare earth f electrons are described as magnetic moments at high temperature. Below an exponentially low Kondo[15] temperature T_K the moments disappear because of hybridization of the f states with conduction electrons, and quantum f spin fluctuations, leading to a 'heavy' Fermi liquid of hybridized f and conduction electrons with a characteristic Fermi temperature of the order of T_K and an effective mass $m* \sim m(T_F/T_K) >> m$. Because of lattice coherence effects, the actual crossover temperature can be very different from the single impurity T_K (it is generally less). The Fermi liquid description of the low temperature properties of a Kondo impurity in a metal is due to Nozieres[16].

Theories of electronic structure in which atomic and solid state realities are taken into account, have been developed and applied to a large variety of systems (e.g. density functional or DFT approaches[17]). These are essentially (self-consistent) independent electron theories, applied not only to periodic systems, but also to clusters, fluids, etc.[17]. A large amount of work is being done on grafting strong correlation effects on to density functional approaches, e.g. DFT + DMFT methods for electronic structure where the latter is an acronym for dynamical mean field theory which is a successful nonperturbative approach developed for strongly correlated systems in the last 15 years.

Strong correlations and the Hubbard model

It is well understood that in the theory of a Fermi liquid, one treats the average effect of all the other electrons on a particular electron. Such an approach is expected to work if the density of electrons is high or the effective interaction between them is of long enough range so that the highly mobile electron is simultaneously under the effect of a large number of other electrons, or if the energy

gained by motion, i.e. the kinetic energy, is larger than some sensible measure of the interaction energy. For a gas of electrons, the first means high electron density[18] and translates into $r_s < 1$. The second means that the screened Coulomb interaction should be smaller than the kinetic energy; this translates into approximately the same condition as the first. The third condition for a continuum $r_s < \sim 0.20$. For a lattice described by a tight binding Hamiltonian with intersite hopping parameter t_{ij} (a measure of kinetic energy) and onsite Mott Hubbard repulsion U the criterion[20] is $(U/D) \sim 2.4$.

The idea that it is qualitatively inadequate to consider effects of electron interactions via their average or static mean field value arose from the observation of de Boer and Verwey[21] that some transition metal monoxides, e.g. NiO are insulating, whereas according to one electron energy band theory, they ought to be incompletely filled band metals. It was immediately realized by Peierls[22] and by Mott[22] that this is a qualitative consequence of strong electron–electron interactions. They argued that if these are strong enough, electrons will 'stay home' with the parent atoms, since electron transfer or quantum mechanical hopping from site to site will lead to large additional local electron repulsion. If the number of electrons in the solid is commensurate with the number of atoms, e.g. one has one outer electron per atom, the system will be an insulator since that electron stays at its 'parent' site. Such a substance, which is an insulator because of electron correlation, is called a Mott insulator. If the lattice is such that there is an odd number of electrons (e.g. one) in a unit cell, such a system is necessarily a metal in one electron band theory, having an unfilled band (e.g. half filled for one electron per unit cell). In the late 1940s and early 1950s, Mott developed this idea further[23], using for example the model of a crystalline lattice of hydrogen atoms with a variable lattice constant a (the collection is constrained not to dimerize, namely not become a collection of hydrogen molecules) and arguing that at some critical $a = a_c$, the system becomes insulating (Mott transition). It is best described as a half filled band metal for $a \ll a_c$ and as an insulating collection of hydrogen atoms for $a \gg a_c$. This system has one electron per atom.

A simple lattice model with the minimum ingredients necessary for exploring the competition between kinetic energy and correlation was proposed by Hubbard in the 1950s and investigated by him in a number of papers[24]. He considered a system in which the electron (in a single 's' orbital at a given site i, with say zero site energy, and two spin orientations at each site) has an intersite hopping amplitude t_{ij}. Two electrons at a particular site (necessarily of opposite spin) repel each other with an energy U, the so-called Mott Hubbard repulsion or correlation energy. The average number of electrons per site is $(1 - x)$. The origin of U is finally the electrostatic or Coulomb interaction; it is the difference between the energy required to remove an electron from a site (ionization energy) and

the energy gained by putting it on the next site (electron attachment or affinity energy). For $t \gg U$, the system is a metal, and for $t \ll U$, an insulator at $x = 0$. The Hubbard Hamiltonian can be written as

$$H = \sum_{i\sigma}(\varepsilon_i - \mu)a_0^+ + \sum_{ij\sigma}t_i a_{i\sigma}^+ a_{j\sigma} + \sum_i U n_{i+} n_{i-}.$$

It is probably the most widely investigated quantum many body Hamiltonian[25,26].

Hubbard also investigated the single particle spectral density (namely the excitation energy spectrum for added or removed single particle states), and showed that it consists of two bands, now generally called the lower and upper Hubbard bands (Figure 4 shows the single particle spectral density in the Hubbard model). The former can be naturally connected with a 'free electron' like excitation spectrum and consists of states in which there is one or zero electron on each site. The latter is higher in energy by an amount of the order of U with respect to the lower Hubbard band and originates from many body excited states in which two electrons have a sizeable probability amplitude for being on the same site. If the two bands are separated by a gap, and if the electron number is such that the lower band is completely full, one has an insulator. This can be the description of a Mott insulator, since it does happen for large U and for $x = 0$ namely one electron per site. For $x \neq 0$, one can have a metal even for large U since there is necessarily a fraction x of sites unoccupied by electrons to which a nearby electron can hop, thus avoiding the extra energy cost U for transport. The low energy behaviour is determined by states in the lower
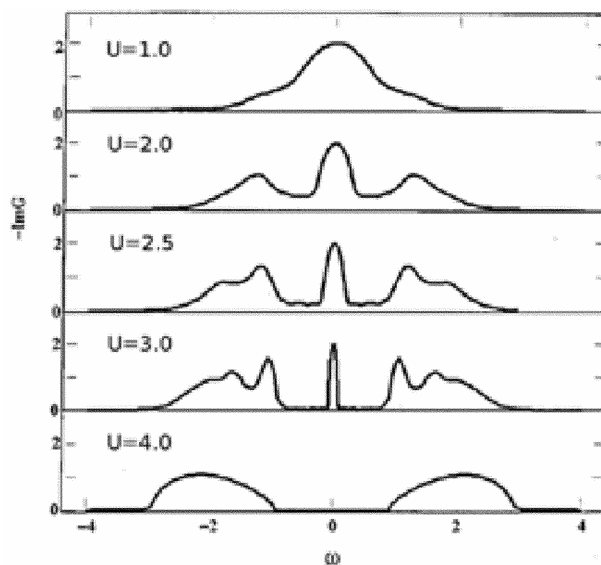

Figure 4. Single particle spectral density for the half filled Hubbard model, calculated in DMFT for increasing U in units of D the bandwidth. Notice the evolution of lower and upper Hubbard bands with increasing U.

Hubbard band. In this model, the phenomenon of strong correlations can be phrased as one of the Mott insulator (for $x = 0$), and of the strongly correlated metal which arises on doping the Mott insulator ($x \neq 0$). Interestingly, the above properties do not depend on lattice structure, but only on the existence of a spatially local strong correlation U. Whether the strongly correlated metal ($x \neq 0$) has special properties different qualitatively from that of a 'free' electron metal described above, and can at least qualitatively model (with additional realistic elements as necessary, e.g. site local features such as orbital degeneracy or electron lattice interaction and lattice structure) the many new families of systems some of which are described below, is the theoretical question addressed in this review.

The Hubbard model can be exactly solved in one dimension[27] where at half filling, the system turns out to be an insulator for the smallest U. The ground state is an antiferromagnet (it has strictly speaking, no long range order but power law antiferromagnetic correlations at zero temperature, a characteristic of one dimension). In two and higher dimensions, there is a metallic regime for small U, most likely with antiferromagnetic order (but this depends among other things on the lattice type) while the system is an insulator for large U; there is a discontinuous quantum ($T = 0$) metal insulator (Mott) transition at intermediate $U \sim U_c$. The phase transition has been widely investigated theoretically, e.g. using DMFT[28] (see below). A major effort at an analog realization of the Hubbard model, e.g. in two dimensions using cold atom lattices, and with varying effective interaction, has been mounted recently[29]. Though numerical calculations are plagued with the sign problem generic to fermions which necessarily have antisymmetric many body wave functions, there are many attempts in the literature[30] at simulating the behaviour of many electrons on a finite periodic lattice with the quantum dynamics described by the Hubbard Hamiltonian above. The regimes of the Hubbard model of the most interest are the Mott metal insulator transition region ($x = 0$) with $U \sim U_c$ and $T > \sim 0$, and the regime for large U and $x \neq 0$. The former may describe correlation driven metal insulator transition in the simplest way and the proximate metallic/insulating states, and the latter may be relevant for cuprates exhibiting high temperature superconductivity; these are often described by an effectively single band Hubbard model[31].

A related, strong correlation model which exclusively concentrates on the lower Hubbard band is the t–J model, first introduced[32] in the seventies. In this lattice system, there is nearest neighbour hopping with amplitude t_{ij}, and antiferromagnetic Heisenberg superexchange J_{ij} (originating as a consequence of eliminating the high energy doubly occupied states). The upper Hubbard band states (or more precisely all states in which sites are doubly occupied) are projected out. For nonzero x, electrons can hop to sites with no electrons present there, avoiding sites with electrons present, so that the system can be a metal. The relevant states are all in the lower Hubbard band. The t–J model, a strong correlation lattice model for electrons, has been extensively investigated in many ways, e.g. numerically[33] as well as in a slave boson gauge theory approach[34]. Whether the strong correlation Hubbard model or the t–J model have a d wave superconducting ground state and whether they have properties similar to those of cuprates in their normal/superconducting states, are very significant questions in the field.

Phenomena

Transition metal oxides[35] and rare earth intermetallics[36] are two large classes of solid state systems in which the electrons in the unfilled d and f shells respectively are close enough to the parent nucleus so that an atomic or ionic starting point is appropriate for usefully describing their properties. At this level of description, an ion has a fixed number of electrons so that it has a well-defined (integral) charge and an atomic magnetic moment. In a condensed matter environment, d or f electrons move in or out of a given site, so that the local charge and the local moment fluctuate. If the correlation energy U is large, these fluctuations are strongly suppressed. One can imagine two limiting cases. In the 'free' limit namely when U is small, the local moment fluctuations are rapid, as are charge fluctuations, while the local total average charge is fixed by the constraint of electrical neutrality (Friedel sum rule). In the opposite, strong correlation limit, electron motion takes place subject to strong local constraints on electron charge and magnetic moment. The time scales for the fluctuation of moments (spins) and charges can be very different. The system is strongly disordered dynamically, though homogeneous statically. Thus the problem can be viewed as one of the characteristic time scale of fluctuations. Kinetic energy, or the quantum mechanical hopping term in a tight binding model, causes the electron number on a site to fluctuate rapidly, on a time scale (h/t), while strong local correlations inhibit them. Thus the characteristic time scale changes from short to long with increase in local correlations. The dynamical structure of the site local self-energy changes with correlation; a successful and widely applied recent theoretical nonperturbative method for strong correlations (DMFT)[28] is based on this idea.

I describe below some systems with unfilled d and f shell electrons, whose properties are quite unusual. Whether these are natural consequences of strong correlation or various material complexities, is an intensely debated question. I begin by mentioning experimental features which seem to be common to this class of systems. Then a few illustrative families are described before giving an outline of theoretical approaches and open problems.

Some common features

Strongly correlated solids, especially metallic ones, exhibit electronic behaviour which is broadly common to them, and is different from that of metals we are familiar with. Some of these have been mentioned above. For example, the defining characteristic of an electron in a clean, perfectly periodic solid is that it has a definite momentum, and that such an electron with a definite momentum (not the bare electron, but in an interacting many electron system, a 'quasielectron' with the same momentum and spin quantum numbers as the bare electron) has a definite energy. This does not seem to be the case in strongly correlated systems, e.g. from electron spectroscopic measurements on high T_c superconductors (cuprates) it appears that in them, one does not have well-defined quasiparticles. Electrical resistivity depends on the 'relaxation' of electrons of a particular momentum (carrying a definite current) by scattering from either static imperfections or excitations (including other electrons) with energy less than the thermal energy $k_B T$. It has a characteristic dependence on temperature in clean or weakly disordered metals. In strongly correlated metals (which are generally 'bad metals' in terms of resistivity) the temperature dependence and the numerical value are quite different. Similarly the thermopower S in metals is small and (at least approximately) proportional to temperature, but in these systems, it is large and saturates at rather low temperatures to a 'classical' value. Again, in conventional metals, the paramagnetic spin susceptibility (the Pauli susceptibility) does not depend on temperature, but in correlated metals, it is strongly and peculiarly temperature-dependent. Electronic inhomogeneities also seem endemic.

The spectral density of occupied electronic states is measured by photoemission. If the momentum of the electron ejected from a solid by the incident photon is also measured, the experimental technique, called ARPES (Angle Resolved PhotoEmission Spectroscopy) directly gives (under several generally valid simplifying assumptions, and for electrons in the solid which can be probed by the photon, namely for electrons within a nanometre or so of the surface) the energy spectrum of an occupied electronic state of a given momentum. This general technique is a modern version of the photoelectric effect experiment; a photon removes an electron from the metal whose energy is measured. The angle and energy of the outcoming electron can now be measured to within about 0.2 degrees and a few meV respectively. The momentum of the outcoming electron could be a conserved quantity; for example, the inplane component of the momentum is conserved so that in a quasi 2d compound, one is doing the energy spectroscopy of an electron in an occupied state, which is believed to have a well-defined momentum. It is expected to have a well-defined energy for a gas of free electrons.

In an interacting electron gas whose low energy excitations, i.e. electronic states near the Fermi level are well-defined quasiparticles described by Landau's Fermi liquid picture the energy spectrum is nearly a δ function, and broadens as the excitation energy increases. This is indeed found to be the case for 'standard' metals, e.g. Au. In general, the 'spectral function' or the distribution of energies of an occupied electronic state of definite momentum is a curve having a single peak with the peak position at the quasiparticle energy and a width going as $\Gamma(\varepsilon) \sim (\varepsilon - \mu)^2$ for small excitation energies $|\varepsilon - \mu|$. The photoemission spectra of strongly correlated systems are qualitatively different. First, pioneering experimental work by Fujimori[37] showed that in a number of transition metal oxides there is indeed a well-separated lower Hubbard band, a specific electronic characteristic of strong correlations. A graphic example is the photoemission spectrum[38] of $SrVO_3$, (Figure 5). It is seen to additionally have a lower Hubbard band, and nonvanishing density of states near the Fermi energy. This is compared there with predictions form LDA, a realistic mean field theory which predicts a single large peak. Secondly, there are extensive ARPES studies[39] of cuprate high temperature superconductors (the present revolutionary energy and momentum resolution levels in ARPES have been directly fuelled by the drive to explore cuprate superconductors). They all show that, crudely, there are *no* quasiparticles in them, namely that in these systems electrons with a well-defined momentum in plane have a broad distribution of energies (Figure 6). Moreover, the energy spectrum becomes particularly broad for excitations near the nominal Fermi surface at the antinodal point. Interestingly, a quasiparticle peak appears in the superconducting phase. This spectroscopic technique shows that electronic states, even those near the Fermi energy, are incoherent in such systems.
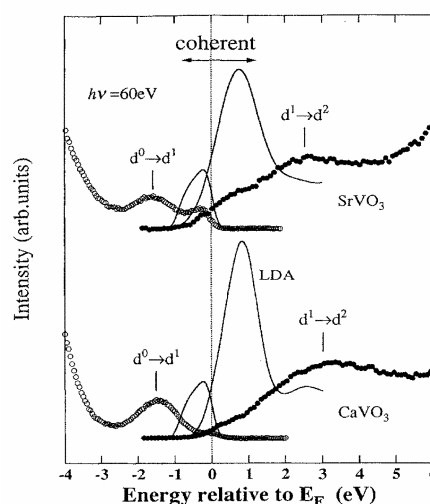

Figure 5. Photoemission spectral intensity as a function of energy for two vanadates. The LDA (local density approximation) electronic structure intensity curves are shown to emphasize qualitative differences due to strong correlation (from Morikawa *et al.*[38]).

The dc electrical resistivity is one of the most commonly measured properties of solids. It depends on the density and effectiveness of excitations which couple to electrons carrying a fixed current, and 'degrade' this current. These excited states need to be of excitation energy of order $k_B T$. Thus the electrical resistivity depends on the nature of low energy excited states which couple to electrical current. In this class of systems, it is very unusual in comparison to the metals and alloys we are familiar with. It is quite large, typically an order of magnitude or so larger than in 'conventional' metals, and ranges from a few hundred $\mu\Omega$ cm to a few mΩ cm, between temperatures of say 200 and 500 K. For example, the resistivity of $Ni_{0.98}S_{0.6}Se_{0.4}$ increases from 200 to 350 $\mu\Omega$ cm (Figure 7)[40] more or less linearly with temperature from $T = 100$ to 300 K. The observed electrical resistivity is often associable with a relatively low characteristic temperature T^* above (and often below) which the dependence is a simple power law, whose exponent could be zero (saturation of resistivity) or unity ('classical' behaviour in most metals, occurring above the quantum scale of temperature for the bosonic excitation which resistively scatters conduction electrons). T^* can range in strongly correlated metals from zero to a few hundred degrees absolute which is quite strange since the only obvious electronic energy scale is the Fermi energy ~ a few eV or ~10^4 K . Interestingly, the real ac electrical conductivity $\sigma(\omega)$ in correlated metallic systems has (in those cases where measurements have been made at the many relevant temperatures) a small Drude or low frequency peak whose strength diminishes rapidly with increasing temperature and which crosses over to a relatively flat curve as a function of ω above T^*. The lost spectral weight is generally transferred to a large region in frequency ω. The real part of the ac conductivity $\sigma(\omega)$ is also often characterized by a 'mid-infrared' peak. None of these features is expected. In the last few years, several semiphenomenological analyses of large resistivity in metals, some of which show obvious signs of saturation with increasing temperature, some not, have appeared[41]. They were inspired by the observation of resistivity saturation tendencies in a large number of metals and alloys, e.g. Nb and Nb_3Sn, around values not far from the Ioffe Regel or the Mott[42] limits. The former amounts to about 1.5 mΩ cm for a simple cubic lattice metal with one electron per unit cell of length 3 Å and the latter to about 190 $\mu\Omega$ cm[43].

In strongly correlated metals, the resistivity can be of the order of or larger than the Mott or the Ioffe Regel limits and can be peculiarly temperature dependent. For example, in high T_c cuprates, the 'normal' state resistivity is linear in temperature over an astonishingly large temperature range, from essentially T_c (which could be as small as 10 K) to 500 or 600 K, for a wide range of doping; the highest value of the resistivity is comparable to or larger than the Mott limit (see e.g. Takagi *et al.*[44] and Figure 8). This is perhaps the defining characteristic of the optimally and slightly suboptimally hole doped cuprates (optimal doping is conventionally defined as the doping level at which the superconducting T_c is maximum). In many 'heavy fermion' systems, the resistivity often goes at low temperatures as a subquadratic power of temperature (this is non-Fermi liquid behaviour) and crosses over at very small 'coherence' temperatures T_{coh} of order but less than the single impurity Kondo temperature T_K[15] (typically 20–200 K) to a large generally temperature in-
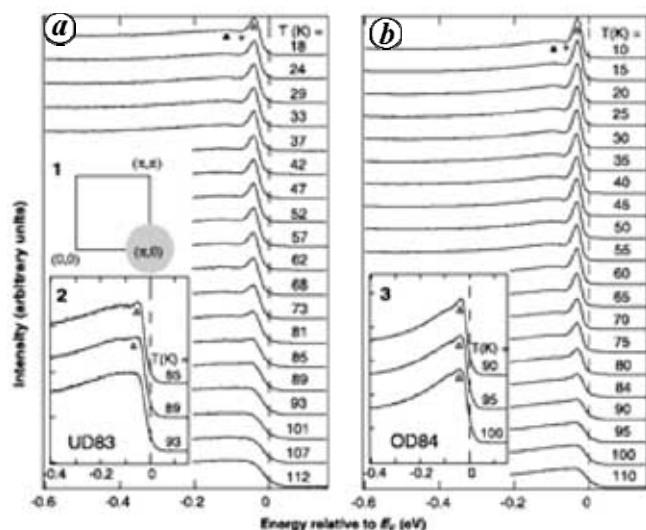

Figure 6. ARPES data for Bi–2212, with **k** at the $(\pi, 0)$ point, for two dopings (slightly underdoped, UD 83 with $T_c = 83$ K, slightly overdoped, OD84 with $T_c = 84$ K), at the various temperatures indicated. Note that the gap is nearly unchanged with T, and the broad spectrum above T_c.
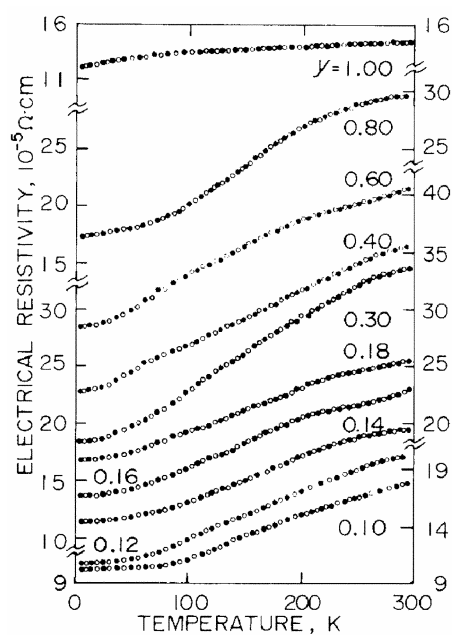

Figure 7. Electrical resistivity of $NiSe_{1-y}Sy$ as a function of T for different y. Note the resistivity scale and large variation with T. (From Matoba and Anzai[40].)

dependent value of order a few hundred $\mu\Omega$ cm (Figure 9)[45]. Kondo/Anderson lattice model theories and two fluid descriptions have been developed in this connection.
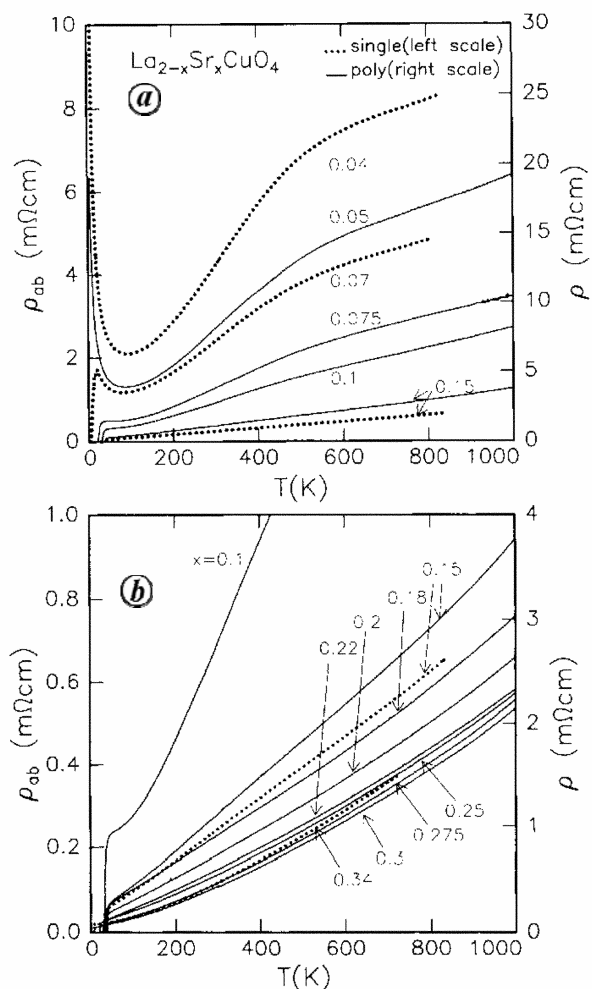

Figure 8. In plane resistivity ρ of single crystal $La_{2-x}Sr_xCuO_4$ for different values of x. Note the size of $\rho(T)$ and its nearly linear T dependence. Figures (*a*) and (*b*) are for different hole doping ranges. (From Takagi *et al.*[44].)
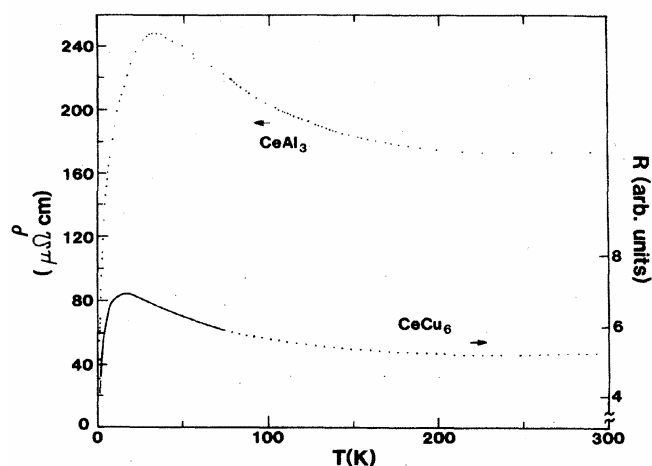

Figure 9. Resistivity ρ of single crystalline bulk $CeAl_3$ and $CeCu_6$ (From Stewart[45]).

The thermopower S of a metal is expected to be small for $T \ll T_F$ and to increase linearly with temperature; the generic reason is that the electric current due to a temperature gradient is connected with the thermal entropy of the charge carriers. This is of order $(T/T_F)k_B$ because only a fraction $\sim (T/T_F)$ of electron states have an occupation number different from unity or zero and hence contribute to entropy. Consequently, the thermopower is expected to be $\sim S_{cl}(T/T_F)$ where S_{cl} is the classical value (k_B/e). In strongly correlated systems however, S is observed to be rather large, not linear in temperature, and often saturates at rather low temperatures ~ 200 K to a value of order S_{cl}. It is as if quantum coherence of electrons persists only till such temperatures, and above this incoherence sets in (consistent with resistivity behaviour). For example, the misfit cobaltite $Ca_3Co_4O_9$ has a saturation thermopower of order -120 μV/K above 150 K (Figure 10). The thermopower of sodium cobaltite Na_xCoO_2 saturates to $+120$ μV/K at about the same temperature (Figure 11).

The paramagnetic spin susceptibility χ due to electrons in a metal is independent of temperature (Pauli susceptibility). This is indeed the case for conventional metals. However, in strongly correlated metals, χ is invariably strongly temperature dependent, in different ways. For example, the high T_c cuprate $La_{2-x}Sr_xCuO_4$ (often abbreviated as 214 or doped 214) has a spin susceptibility which decreases dramatically[48] with temperature below about 200 K, in the normal state above T_c (Figure 12). An extreme Curie Weiss temperature dependence is found in metallic Na_xCoO_2 (Figure 13)[49] with a Weiss temperature of order 150 K, while the characteristic free electron degeneracy temperature is expected to be ~ 5000 K, from the bandwidth corresponding to the bare intersite hopping amplitude of 0.15 eV.

A very interesting characteristic of strongly correlated systems is the observed nearly generic coexistence of two
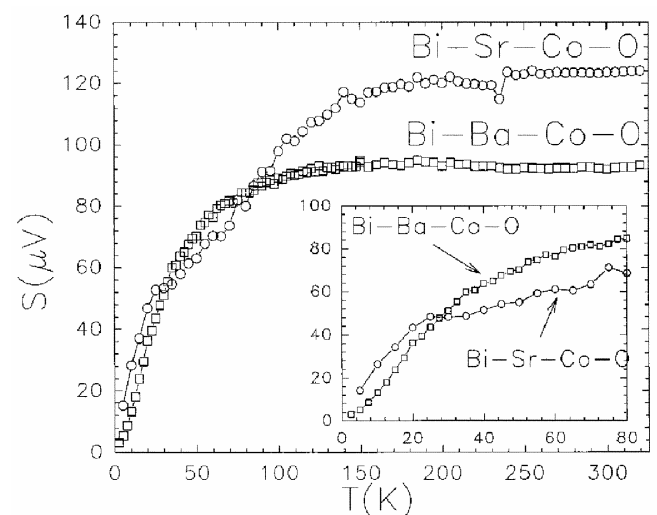

Figure 10. Thermopower of misfit cobaltates Ba–Al–Co–O, where Ak = Sr or Ba. Note the large saturation value and its low temperature scale.

very different 'phases'[50]. The 'phases' are not thermodynamic or large volume phases in the strict sense because the observed patches are often very small, nanoscopic in size. The two kinds of patches have a very different organization of electron charges or spins (Figures 14 and 15). For example, in cuprates, especially the relatively underdoped hole concentration regime ($x < 0.12$), there is evidence for large nanoscopic inhomogeneities in x. Since the $x = 0$

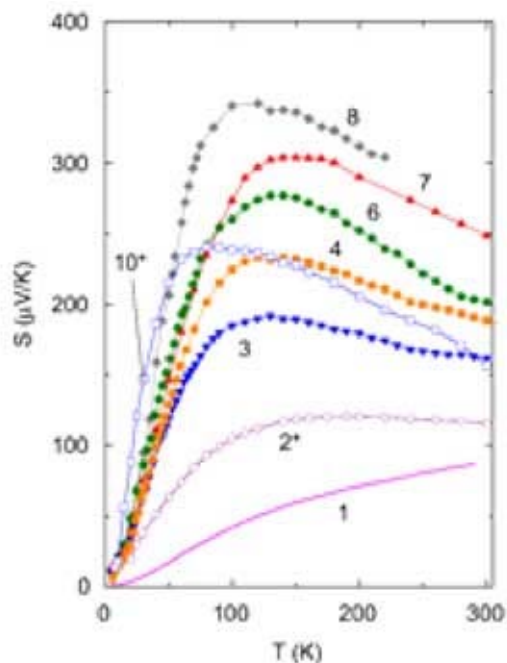system is an undoped Mott insulator, ordered antiferromagnetically, while the $x \neq 0$ cuprate is most likely to be

Figure 11. Thermopower of Na_xCoO_2 for different values of x (decreasing in the order 10^{-1})[95].

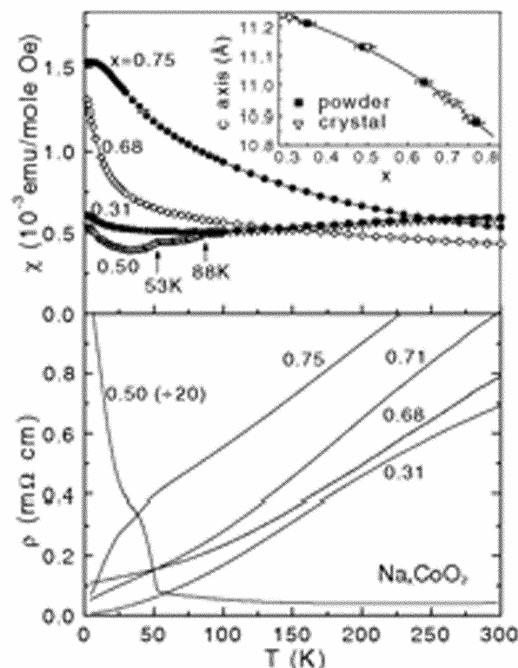**Figure 13.** Spin susceptibility and in plane resistivity of Na_xCoO_2 as a function of temperature (From Foo M.-L. *et al.*[97]).

Figure 12. Spin susceptibility of $La_{2-x}Sr_xCuO_4$ as a function of temperature T (Nakano *et al.*[48]).
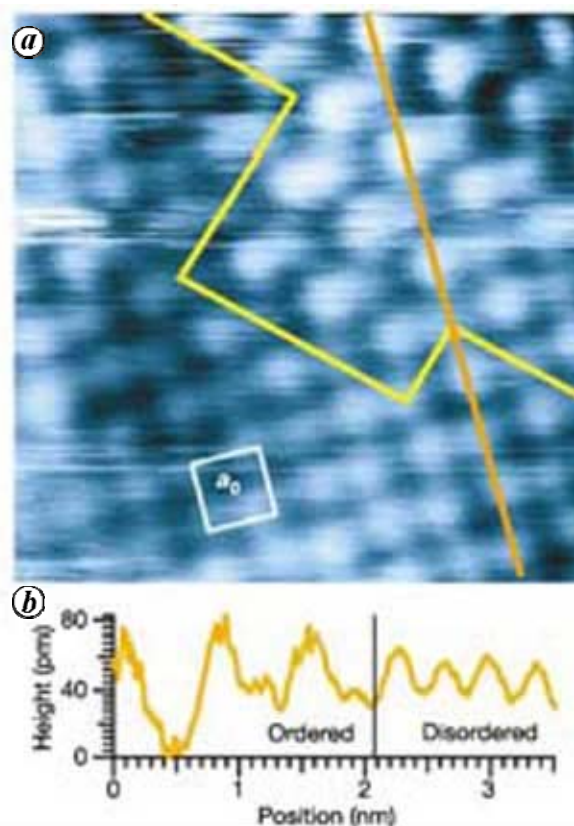

Figure 14. Real space STM photograph of $BiCaMnO_3$ (From Renner *et al.*, *Nature*, 2002).

a metal (with a superconducting ground state) a system with an inhomogeneous x can have insulating magnetic and metallic nonmagnetic phases coexisting. The widely observed 'stripe' phases[51] in hole doped 214 are possibly long range ordered examples of this. In many cases the stripes are static; in others, dynamic, while in many cuprates there is no experimental evidence for stripes. Local measurements like scanning tunneling spectroscopy show that superconductivity is extremely inhomogeneous, especially for small x. Phase separation is endemic in manganites, where the 'surprising proximity of metallic and insulating phases' has been remarked on[52]. In manganites, coexistence of insulating (orbitally and charge ordered?) and metallic phases has been observed in scanning tunneling microscopy (STM; Figure 14) and in real space STM imaging (Figure 15), over a length scale ranging from several nanometers to microns. The explanations range from frustrated phase separation of competing thermodynamic phases with competing order parameters, to Coulomb interactions muting separation of such phases with different electronic charges or charge distributions[52]. A novel 'strong correlation' explanation argues that at an atomic or local level, there are two different kinds of states with close energies in strongly correlated systems. Their segregation is frustrated at nanoscopic length scales by Coulomb interactions or the need for the electrochemical potential
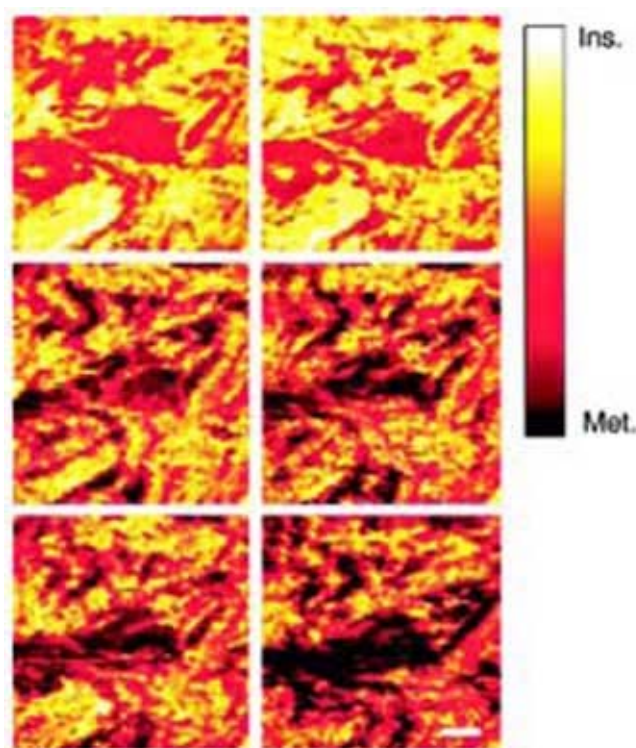
to be the same throughout the solid. The frequent observation of micron scale inhomogeneities[53] (Figure 16) is perhaps associated with frozen strains and their effects, and may thus be extrinsic, e.g. the relative stability of the two states or 'phases' depends on the local strain. The implication here is that when local correlation effects are strong, energies of globally different phases satisfying local constraints can be close to each other.

Some solid state chemical realities

While simple models of strongly correlated systems, e.g. the Hubbard model, have at each lattice site a single non-degenerate orbital, actual systems are quite complex. The variety of phenomena observed may be due to or at least be influenced by this complexity.

As an example of local solid state chemical realities, the case of an Mn ion in a solid state environment, e.g. in solid $LaMnO_3$ is described here. The Mn^{3+} ion (this is the configuration one expects from simple electron count and chemical valence arguments) at a particular lattice site, namely at the octahedron centre, has four 3d electrons (the sp electrons are assumed to be part of an uncorrelated

Figure 15. STM picture of mesocale inhomogeneity in LCMO just below the Curie temperature T_c, for increasing magnetic fields. Note the nanoscale inhomogeneity and the increasing metallic fraction with increasing magnetic field. (From Fath *et al.*, *Science*, 1999, **285**, 1540.)
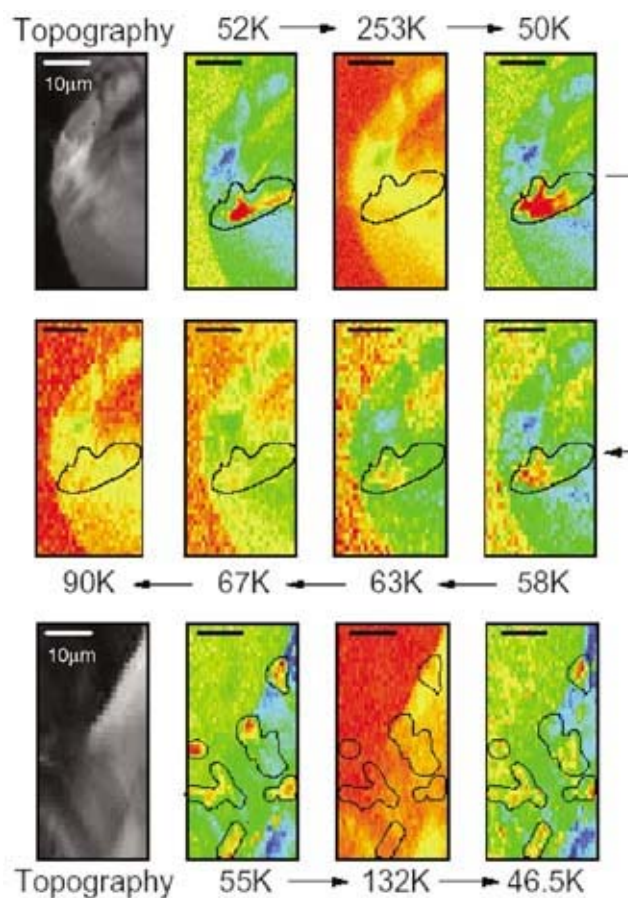

Figure 16. Position sensitive ARPES picture of reversible 'domains' in LPCMO on a micron scale (From Sarma *et al.*[53]).

conduction band, and may, if needed, be so described). In the octahedral environment of the perovskite crystal $LaMnO_3$, the five-fold orbitally degenerate d levels split into three-fold degenerate t_{2g} and two-fold degenerate e_g manifolds (Figure 17 shows the situation of octahedral symmetry). The former are lower in energy than the latter by the crystal field splitting Δ which could be of the order of an eV or more. The distribution of the four d electrons in this scheme of energy levels depends on the size of the effective Coulomb interaction when two electrons are in the relevant d orbitals on the same site, with respect to the crystal field splitting Δ. Phenomenologically the effect is described qualitatively by the Hund's rule in atomic physics, which states that the ground state of many electrons in an atom has the maximum possible total spin or angular momentum consistent with the Pauli exclusion principle. In the present crystal field case, it turns out that the effective interorbital Coulomb interaction is larger than Δ, so that the three t_{2g} states corresponding to different orbitals (d_{xy}, d_{yz}, d_{xz}) are all occupied (this minimizes electron repulsion) and the collection has a total spin $S = (3/2)$. The Hund's rule effect for the fourth d electron is described quantitatively and effectively by a ferromagnetic coupling J_H between the spin of this electron (which is in the e_g manifold) and the three t_{2g} electrons with total spin $S = (3/2)$. In the present case J_H is much larger than Δ, so that it is energetically favourable for the four d electron system to have 'high spin' $S = 2$, and for the fourth electron to be in the e_g state. A number of low spin possibilities for the ground state, which arise when $J_H < \Delta$, are realized in other systems; when this difference is relatively small, high spin–low spin transitions and admixtures, thermal well as quantum, occur (e.g. in solids with the Co^{3+} ion[54]). Further, in a solid state environment, electrons move in and out of a given site. For example, in the above case, if the system is 'hole' doped, i.e. has $(4 - x)$

Figure 17. Schematic arrangement of La, Mn and O ions in $LaMnO_3$. Octahedral crystal field levels e_g and t_{2g}, and the Jahn–Teller distortion of the octahedron which removes the two fold degeneracy of the e_g level are also shown.

d electrons per site on the average, one has, in the ground state (and for low energy states, with large U) necessarily an admixture of Mn^{3+} and Mn^{4+} in the proportion $(1 - x)$ to x. This is what is believed to happen for example in rare earth manganites doped with alkaline earth ions, i.e. in $Re_{1-x}A_xMnO_3$. This means that one has a mixture of configurations with one e_g electron (probability $(1 - x)$) and none (probability x), *and* a spin $S = (3/2)$ at each site. For U not large, the Mn^{2+} configuration with five 3d electrons is also significantly present in the ground state. This configuration may have two e_g and three t_{2g} electrons or one e_g and four t_{2g} electrons per site depending on the relative sizes of J_H and Δ.

Hopping of a d electron from one site to the next occurs via admixture with the surrounding oxygen p ligand. An important question is whether for describing, say, the low energy behaviour of the system, these p states can be integrated out, leading to an effective 'd' band behaviour and a corresponding renormalized Hamiltonian, or whether the p states need to be kept, so that the effective Hamiltonian is more complex. This question can also be phrased as one of having a band originating from the oxygen p state at and near the Fermi level. Thus in general, local ionic configurations and their energetics in addition to quantum mechanical hopping and the Pauli exclusion principle determine quantum many body dynamics.

The above description emphasizes the fact that the actual chemical nature of the particular family of systems can be crucial for its physical properties; e.g. in the above case, the t_{2g} and e_g orbitals are the relevant states in terms of which one needs to describe the physics. The three different orbitals of the t_{2g} states are always occupied so that they can be described by a spin $S = (3/2)$. There is a two-fold degeneracy of the e_g orbital states. This, it turns out, is necessarily removed by a Jahn Teller distortion which removes the local octahedral symmetry in which the d ion is placed. The distortion leads to two levels, one lower and one higher in energy by the same amount with respect to the original e_g level. For a system with one e_g electron, the lower level is occupied, so that there is necessarily a lowering of energy due to the Jahn Teller distortion. The phenomena in $La_{1-x}Ca_xMnO_3$ depend on whether the Jahn Teller distortion (and the corresponding energy lowering) is large or small. If the relevant electronic configurations have many degenerate or nearly degenerate orbitals on a particular site (as can happen in this case with e_g and t_{2g} orbitals) novel kinds of orbital correlations and ordering are possible. The Hilbert space of low energy states is larger; e.g. in the above case, the two-fold orbital states e_g and the spin states $S = (3/2)$ at each site originating from the t_{2g} state may all need to be kept; this kind of e_g, t_{2g} description is a consequence of the nature and size of the crystal field. In many cases, the oxygen p orbitals and their hybridization with d orbitals need to be explicitly kept. The effects of strong correlation are played out in this chemical arena.
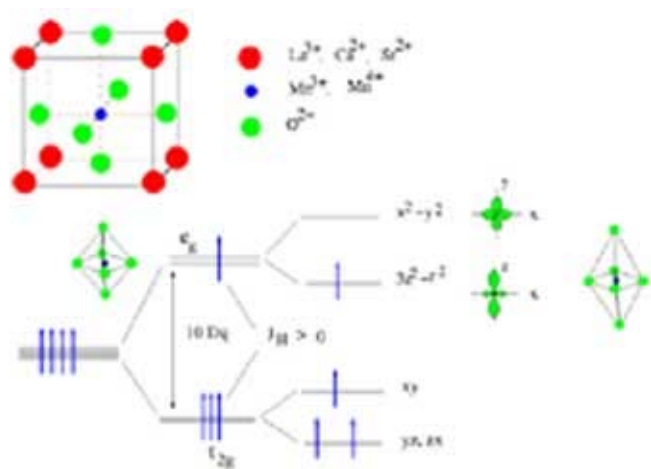
Systems

There is a large and increasing number of families of systems whose electronic properties are attributed to strong electron correlation effects. Given their wide variety, we mention here only a few common illustrative examples. As mentioned earlier, two major classes are transition metal oxides and rare earth intermetallics. Most such oxides are insulating; this insulating state itself may arise from strong electron correlation (Mott insulators) especially in the 3d series, because in them, the d electron is closest to the parent nucleus. There are however a large number of strongly correlated oxides which are metallic, superconducting, undergo metal insulator transitions, etc. One large family whose properties we describe below is cuprates, home to high temperature superconductivity. Manganites, or more specifically alkaline earth doped rare earth manganites $Re_{1-x}A_xMnO_3$ exhibit a bewildering variety of phases and phenomena with different doping x and different rare earth/alkaline earth ions. They have metal insulator and paramagnetic ferromagnetic transitions, charge/orbital ordering, colossal magnetoresistance, etc. Na_xCoO_2, the best studied cobaltate is a metal which shows quite unusual properties for large x (~0.75), e.g. large thermoelectric power and Curie Weiss magnetic susceptibility with a small Curie temperature. There are many oxides exhibiting metal insulator transitions; historically, V_2O_3 (doped with Cr) has been investigated for the last five decades as the archetypical Mott transition. In many other transition metal systems, e.g. titanates and Sr_2CuO_4, the presence of many d orbitals with energies close to each other is very important. There are a very large number of reviews which deal with these systems or with classes of phenomena in them[55]; here only a very sketchy outline in the perspective of strong correlations is presented.

Cuprates

Subsequent to the discovery of superconductivity in hole doped cuprates by Bednorz and Muller in 1986 at unprecedented temperatures, their physical properties have been explored very actively. Today, they are probably the most extensively investigated family of condensed matter systems. Part of the interest has been fuelled by the occurrence of high temperature superconductivity in them and the consequent possibility of revolutionary applications. It was clear from the very beginning that superconductivity entered the industrial age in 1986–87. However, it is also the fact that these systems are strongly correlated, as pointed out by Anderson[56] immediately after the experimental discovery of high temperature superconductivity. Strong correlations were proposed by him to be directly connected with its superconductivity. Here we outline some of the properties of cuprates from this perspective. A number of articles and books describe various experimental features and connected theoretical ideas[57]. Overall, the phase diagram of the doped cuprates and their unique physical properties (some mentioned below) make sense only from the point of view that these are doped Mott insulators[31]. Further, they seem to be systems for which the single band Hubbard model can be a credible description[31]. From this point of view, cuprates exemplify starkly the properties of a strongly correlated lattice system of electrons.

The cuprates, e.g. $La_{2-x}Sr_xCuO_4$, can be thought of structurally as perovskite variants (Figure 18). The CuO_6 octahedron is split with well separated 'top' and 'bottom' pyramidal halves, resulting in electronically active square planar Cu–O layers which have strongly correlated d shell electrons. The (La,Sr) ions (and the remaining O^{2-} ions) inhabit the spaces between the split octahedra. Substituting trivalent La ions with divalent Sr ions in $La_{2-x}Sr_xCuO_4$ removes electrons from (adds holes to) the square planar Cu–O layer, very much like the δ doping of semiconductors. Crudely, the charge reservoirs are spatially removed from the 2d Cu–O sheets which are being doped. Different cuprates differ in the degree (and manner) of coupling between these layers, and in the arrangement of the other oxygen and rare earth/alkaline earth ions. All of them have interlayer coupling small compared to the intralayer interactions, as evidenced for example by the large resistance anisotropy (which varies from thirty to a million). Some have close layers separated substantially from other such parallel layers; for example, YBCO ($YBa_2Cu_3O_{7-x}$) has two Cu–O layers close to each other (a bilayer) and there is an oxygen chain between bilayers.

The cuprates are strongly correlated. For example, the parent or undoped compound La_2CuO_4 is a Mott insulator. Above its antiferromagnetic transition which occurs at T_N, around 300 K, the square planar unit cell has only
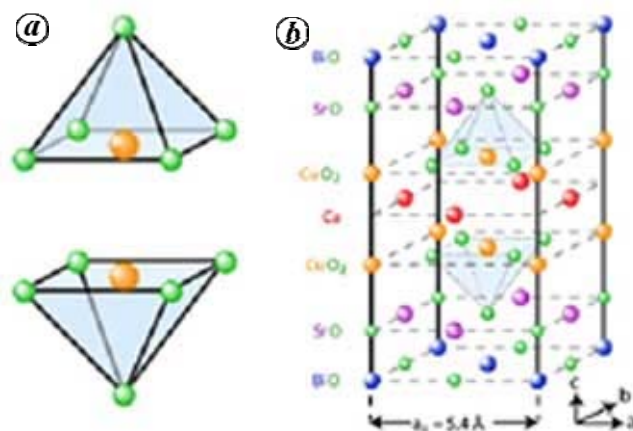

Figure 18. Crystal structure of cuprates, showing the split octahedron, and the planar Cu–O arrangement.

one Cu^{2+} ion with a d^9 configuration or one d hole per unit cell, so that the system ought to be a half-filled band metal. (Below T_N, the unit cell is doubled and there are two Cu^{2+} ions and so an even number of electrons; the system can be a semiconductor or insulator. This is not so above the Neel temperature; the unit cell has one Cu^{2+} ion.) However, the system continues to be an insulator through the Neel temperature, even though the number of electrons per unit cell changes from even to odd; this insulating nature is a strong correlation effect. Quantitatively, careful analysis of the observed Cu 2p core level XPS, XAS and Auger spectra, a local property, via cluster calculations[58] leads to a U in the range of 7–10 eV while LDA band calculations[59] suggest a t of the order of 0.6–0.8 eV so that one has $U \sim 12t >> W = 4t$. One is thus clearly in the strong correlation regime. The presence of O2p valence electron states implies d–p charge transfer; the charge transfer gap is estimated[60] to be ~1.5–1.8 eV so that strictly, La_2CuO_4 is a charge transfer insulator in the scheme first proposed by Sawatzky et al.[61]. A major issue from the eighties has been whether the p orbitals (specifically, the p_x, p_y orbitals) should be explicitly present in a low energy description of electronic states in addition to the d states (a three band theory) or whether the p states can be integrated out, and one can work with a single d like band with renormalized coupling constants. A detailed discussion of this question is given in a recent review of the t–J model by Ogata and Fukuyama[60]. They point out for example that because the added hole (which is in the oxygen p band) forms a bound state with the d^9 state which it surrounds in the Cu–O plane, as shown first by Zhang and Rice[62], this singlet bound state can be thought of as a spinless hole in the d^9 band. Thus an effective two dimensional, one d band, Hubbard-like model is appropriate for low energy behaviour. A three-band model (with oxygen p states explicitly included) has been actively developed by Varma and collaborators[63]. Interestingly, this model has a time reversal symmetry breaking phase above the superconducting transition.

The parent compound, e.g. La_2CuO_4 orders antiferromagnetically below a T_N of about 200 K as shown by Ganguly and Rao[64] who first investigated this system and recognized its near two dimensionality. On hole doping this Mott insulator, the antiferromagnetic LRO is lost quickly (for $x \sim 0.03$ or so) and a metal with a superconducting ground state is formed (for $x \sim 0.05$ and beyond). The transition temperature T_c has a parabolic dependence on doping (Figure 19 shows the surprisingly generic phase diagram of the cuprates). The metallic state above T_c is unusual. Its (x, T) regime can be divided into three broad parts, the 'pseudogap' region for small x (underdoped with respect to the optimum for which the T_c is maximum), the 'strange metal' phase for intermediate values of x and a more 'normal' (i.e. conventional) metal for large x, i.e. the overdoped region. This last region is not as well characterized as the first two, which exhibit

many signatures of strong electronic correlations. These regimes are briefly described below.

The superconducting state in a cuprate is a coherent superposition of Cooper pairs as in conventional superconductors. However, many other characteristics are qualitatively and quantitatively different. For example, the cuprates are 'd wave' superconductors, namely the Cooper pair amplitude is anisotropic in a specific, d wave symmetric manner. Whereas in conventional superconductors the amplitude Δ_k of a Cooper pair $(k\uparrow, -k\downarrow)$ is generally independent of k (i.e. $\Delta_k = \Delta \neq 0$ below T_c), in the cuprates Δ_k is strongly dependent on k (for say k close to the Fermi surface) and has nodes, i.e. vanishes at some points. A correct approximate two-dimensional representation of Δ_k is $\Delta_k = \Delta_0(\cos(k_x a) - \cos(k_y a))$. This can arise in a lattice system for nearest neighbour pairing such that the pair amplitudes along x and y pair bonds are the same, but the phases differ by π. A gap function of this kind implies a substantial density for nodal electronic excitations or quasiparticles at $T \neq 0$, and related characteristic electronic behaviour below T_c, e.g. C_v (electronic) α T^2; this is observed. The cuprate superconductor is characterized by a relatively small superfluid stiffness. The superfluid density ρ_s for small doping goes as x as also does T_c. This Uemura[65] scaling between ρ_s and T_c is unlike that in clean conventional superconductors, where there is no such relation, and where ρ_s is large and T_c is very small. The related penetration depth λ_{ab} (where $\lambda_{ab}^{-2} \alpha \rho_s$ the superfluid density) is large, of order 1500 Å at $T = 0$. The Cooper pair coherence length ξ_0 on the other hand is ~15 Å is rather small, only a few lattice spacings. This is again very different from conventional clean supercon-
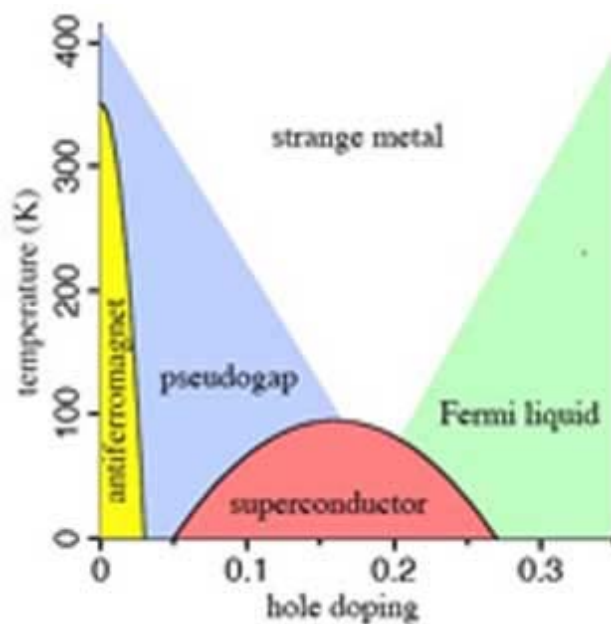

Figure 19. 'Phase' diagram of the hole doped cuprate in the hole doping (x) and temperature T plane.

ductors, which have $\xi_0 \sim 10^4$ Å. A few other unusual characteristics of the superconducting state are the following. Many measurements point[66] to the existence of two 'gaps' in the electron excitation spectrum, one of which can loosely be connected with Δ_0 (the prefactor of the anisotropic gap) and the other with T_c or the superconducting coherence temperature. The electron excitation spectrum as measured by ARPES shows a coherent quasiparticle peak below T_c; interestingly, its strength seems proportional to the nonzero superconducting order parameter. Recently, much excitement has been generated by the observation[67] well below T_c, of magnetoconductivity (deHaas Shubnikov) and diamagnetic susceptibility (deHaas van Alphen) oscillations as a function of $(1/H)$ in clean $YBa_2Cu_4O_8$. In conventional metals, this is believed to be due to well defined quasiparticles at the Fermi level and is a very powerful method for exploring their **k** space structure (actually the extremal Fermi surface). Does the observation of these oscillations imply the existence of well defined quasiparticles and Fermi surface pockets – as is naturally assumed? Another novel characteristic of the superconducting state is the presence of a well-defined magnetic collective excitation[68] probed by inelastic neutron scattering. The excitation is sharply defined below T_c, has an energy ~ 40 meV, and a wave vector $\mathbf{Q} = \{\pi/a, \pi/b, \pi/c\}$. The energy scale seems to track T_c, and the dispersion $\omega(\mathbf{Q})$ is bell shaped.

Perhaps the greatest difference between conventional superconductors and the cuprates concerns the *mechanism* of superconductivity. In the former, there is considerable experimental evidence (e.g. from tunnelling) that retarded electron electron attraction mediated by phonons provides the glue that binds electrons into Cooper pairs and leads to superconductivity. It has been more or less clear from the very early days of the field that the phonon glue is not strong enough to produce the high T_c's observed, and further that the existence of d wave symmetry in pairing is also unlikely in a simple phonon mechanism. This is in spite of considerable evidence for phonon-related effects in cuprate electronic spectra, e.g. ARPES kinks[69] and isotope effect in many physical quantities[70]. The pairing agency is then of electronic origin, and a naieve faith in the necessity of 'something' which mediates pairing, a la phonons, has led to the search for many electronic candidates, e.g. spin fluctuations or the 41 meV resonance. The necessity of such a glue for strongly correlated systems has been questioned[71]; pure strong on site repulsion leads quantum mechanically to a nearest neighbour antiferromagnetic superexchange J. This favours nearest neighbour spin singlets (and hence such Cooper pairs) energetically; this is the application of the RVB[56] idea. The superexchange arises, as is well known, from electronic states in the upper Hubbard band. If such states are eliminated to obtain an effective low energy Hamiltonian (as in the t–J model), this exchange interaction in its RVB avatar[56,60] is the 'glue'. It can be traced to high energy or high frequency bosonic fluctuations (involving the upper Hubbard band) and is thus nearly instantaneous. The question of the frequency structure of the effective pairing interaction has been explored recently[72]. That strong correlation effects are important in pairing is clear from a wide variety of observations; for example, the Δ_0 inferred from experiments in the superconducting state[73,66] is very large in comparison to $k_B T_c$ and the two depend on hole doping in very different ways, whereas in the mean field or BCS theory of superconductivity, $(2\Delta_0/k_B T_c) = 3.5$.

The metallic state above T_c seems unlike any conventional system in its properties; as emphasized above the latter have universal qualitative features. This fact is specially pronounced in the underdoped region. Here, it has been known for more than a decade from ARPES experiments[74] that the electron excitation spectrum has a pseudogap, one which moreover has the four-fold symmetry (in **k** space) of d wave superconductivity. Experimentally the pseudogap is seen to develop below a crossover temperature $T^*(x)$. This temperature is large (~ 600 K) for $x \sim 0$, and decreases with increasing hole concentration x, and appears to join T_c near the optimum x at which T_c is maximum. A number of other measured quantitites, e.g. $\chi(T)$, T_1^{-1}, ρ_{ab}, $\mathrm{Re}\,\sigma(\omega)$, show an anomalous decrease below T^*, as if low energy electronic states are being removed, i.e. there is a gap in the density of electronic states that sets in smoothly below T^*. Experiments on some of these quantities gave first indications of a characterstic T^*, an energy scale small compared to electronic energies but of order J_{ij} the nearest neighbour superexchange AF coupling. Two classes of explanations for T^* are prevalent. In one, T^* is regarded as the temperature below which incoherent Cooper pairs exist (while T_c is the temperature below which they are globally phase coherent). In another, T^* is the temperature below which true long range order of some kind (not superconductive LRO) sets in. This could be a $(d + id)$ kind of density wave or charge order[75], or loop current order[63]. Experiments have been interpreted according to these alternative pictures; local STS measurements of electron density of states have been described in terms of local pairs. The observation above T_c of a large temperature and magnetic field dependent Nernst effect (namely electric current perpendicular to the thermal gradient when both of these are in the ab or Cu–O plane of the cuprate and there is a magnetic field perpendicular to both) by Ong and co-workers[76] in the pseudogap phase, is another unexpected discovery. The Nernst signal observed is about two orders of magnitude larger than expected in a metal, and is most simply interpreted in terms of transverse motion of short lived superconducting vortices in a thermal gradient. This interpretation, and the fact that the temperature range above T_c where the effect is significant is not the same as T^* but is substantially lower, with a shape in the (x, T) plane similar to $T_c(x)$ rather than to

$T*(x)$, point to a new regime of short range phase order above T_c.

Another unusual feature of the pseudogap regime is the absence of a Fermi surface but the presence of a Fermi *arc* above T_c. ARPES experiments do not show a quasiparticle peak above T_c, but the observed Fermi surface crossings instead of forming a curve in the BZ centred around the (π, π) point and touching the Brillouin zone edges, form a symmetric arc which is a part of this curve, and whose arc length decreases with increasing T, perhaps linearly[77]. The absence of a Fermi surface, and the occurrence of a temperature-dependent Fermi arc which terminates abruptly in k-space and therefore does not seem to enclose any states, is difficult to understand for a degenerate Fermi gas.

The optimally hole doped cuprate, i.e. with x such that one is close to the maximum T_c, has a characteristic electrical *ab* plane resistivity depending linearly on temperature, over a wide temperature range, e.g. from above T_c to 600 K or so. Another novel and universal feature is that the room temperature ρ_{ab} ($T = 300$ K) per layer is about 500 $\mu\Omega$ cm. This linear T dependence[44] is one of the most prominent long recognized features of the cuprate, something not fundamentally understood, and is generally associated with strong correlations in the system. It is well known that electron interaction in Fermi liquid systems leads to a T^2 dependence of resistivity, unlike what is observed in optimally doped cuprates. Interestingly, with increasing doping, the temperature dependence is of the form $\rho_{ab} \alpha T^\beta$ with β increasing smoothly from 1 to 2 as the hole concentration x increases from optimum to overdoped. This behaviour is also not understood, but presumably can be broadly described as due to the system changing from a strongly correlated non-Fermi liquid to interacting electron Fermi liquid. A number of power laws for transport properties have been noticed; e.g. the Hall angle θ_H is of the form[78], $\cot(\theta_H) = a + bT^2$.

Manganites

Alkaline earth doped rare earth manganites $Re_{1-x}Ak_xMnO_3$ constitute a large family of essentially cubic perovskites ABO_3 with corner sharing $(Mn–O_6)$ octahedra. They exhibit a surprising range of intertwined electronic, structural and magnetic phases, briefly described below (this is the subject of many review articles and books[79,80]). The origin of these properties has been a matter of debate for the last decade or so; they are generally attributed large Hund's rule coupling involving the d electrons of Mn (leading to double exchange, see below), and strong electron lattice coupling leading to polarons (small?Jahn Teller?). I describe these two features below, and argue that Mott Hubbard correlation is not only large, but very important for a number of their physical properties. A strong correlation model, namely the *lb* model developed

by some of us[81] incorporating all these strong local interactions and used to explain qualitatively and quantitatively a number of properties of the manganites, is also outlined.

The elementary solid state chemical background of the manganites (mentioned already in the section 'some common features' above) is as follows. The parent compound $LaMnO_3$ has only Mn^{3+} ions; these have four 3d electrons at each site of which three are in the three different energetically degenerate t_{2g} orbital states and the fourth is in the higher, doubly degenerate e_g state[82]. At doping x, one necessarily has Mn in a mixed valent state, namely a fraction $(1 - x)$ of ions in the Mn^{3+} state and a fraction x in the Mn^{4+} state. The former has one e_g electron while the latter has none; both have three t_{2g} electrons.

Because every site has three t_{2g} electrons in different orbital states and maximal spin state due to the large Hund's rule exchange coupling J_H, the collection can be described as a spin $S = (3/2)$. Thus at each site there is either one electron or none (in one of the two degenerate e_g states) at each site, and a spin $S = (3/2)$ also. Hund's rule (a shorthand for local interorbital Coulomb interaction effects) operates as a large ferromagnetic coupling between the t_{2g} spin $S = (3/2)$ and the e_g electron spin s $(= (1/2))$. Since the e_g electrons hop from site to site in the presence of this strong ferromagnetic coupling, their effective intersite hopping amplitude and hence the e_g electron kinetic energy depends on the relative orientation of the t_{2g} spins on these sites. This is the famous double exchange associated with Zener[83] and clearly articulated by Anderson and Hasegawa[84]. The other coupling believed to be prominent in manganites[85], from the 1950s is between the d electron and the lattice ion on site, or electron phonon coupling. This necessarily leads to a Jahn Teller distortion of the $Mn–O_6$ octahedron, removing the twofold degeneracy of the e_g level, lowering the energy of one combination of the e_g orbitals, which becomes polaronic. It is largely believed that the phenomena and phases of manganites can be described entirely in terms of the consequences of these two local strong interactions. The effect of U (local effective repulsion between electrons in the e_g orbital states) is not often considered to be qualitatively significant. However, there are several broad features of manganites which can be understood only if U is large. An example is the fact that stoichiometric $LaMnO_3$ is a Mott insulator. It is insulating *above* T_{JT} at which long range antiferrodistortive (Jahn–Teller) order sets in. On application of pressure, it appears that this substance, which has one e_g electron per unit cell, turns metallic at about 20 kbar[86]. A characteristic which manganites share with strongly correlated systems is that they are all 'bad metals', namely their resistivity in the metallic state (not near $T = 0$ K but near the Curie point of about $T = 150–300$ K) is quite high, about 1–5 mΩcm. Electronic inhomogeneity or 'phase' separation on a scale varying from nanometres to microns

is endemic in the manganites. In the *lb* model proposed by the author and colleagues[81], the (immobile) *l* polaron and the *b* electron repel each other on site with a strength *U* which is large ($U \sim 6$ eV). Therefore, the *b* electrons form small puddles, effectively surrounded by *l* polarons whom they avoid strongly. This phase separation is muted by long-range Coulomb interaction effects[50,87]. I discuss below the *lb* model and its strong correlation character after mentioning the phenomena found in doped manganites.

Figure 20 shows the phases of $La_{1-x}Ca_xMnO_3$ in the *x*–*T* plane. The doped manganite at ambient pressure continues to be insulating, with an antiferromagnetic ground state which changes to a ferromagnetic ground state at $x = x_{c1} < x_c$. This becomes metallic beyond $x = x_c$ which is about 0.20. The metallic ferromagnet undergoes a $T \neq 0$ Curie transition to a paramagnetic state which is generally insulating, i.e. the metal insulator transition is coincident with the ferromagnetic paramagnetic transition. The metallic and insulating phases exist over a rather broad range of doping, approximately from $x = 0.20$ to $x = 0.50$. This unusual 'persistent proximity of metallic and insulating phases' has been remarked on[52]. At and beyond $x = 0.50$, an insulating phase with charge and orbital ordering and a related characteristic pattern of lattice distortions is observed. The magnetic ground state is an antiferromagnet. At $x = 0.5$, where one expects an equal concentration of Mn^{3+} and Mn^{4+} ions, a simple long range ordering of these charges was hypothesized by Goodenough[88] in the 1950s. Very active questions in the field are the extent of charge order, its connection with orbital order, the effect of disorder or randomness on it, 'melting' of the charge order into a metallic state in a magnetic state, the gap or pseudogap in the charge ordered state, etc. Beyond $x = 0.5$, a question is whether commensurate charge ordering found for $x = 0.5$ continues, interspersed with discommensurations. Experimental evidence seems to point to incommensurate charge order, with a lattice periodicity going as $(1 - x)$[89].

Though the compounds were first identified in the 1950s by Jonker and van Santen, the present surge of interest in their properties can be dated to the 1990s, when it was realized that[90] thin films of these have a colossal magnetoresistance. Near $x = 0.3$ or so, where there is no orbital or charge order, the electrical resistivity near T_c is greatly reduced by application of a magnetic field, the effect being two or more orders of magnitude larger than in a typical metal. The origin of this cmr, and its harnessing for applications, were till recently among the major questions in the field.

While manganites are broadly similar in the kinds of phases they exhibit, they also exhibit quite characteristic systematic differences. For example, LSMO (common shorthand for $La_{1-x}Sr_xMnO_3$) becomes metallic for relatively small x_c, and its Curie transition (paramagnetic to ferromagnetic) is a metal–metal transition. In LCMO, x_c is somewhat larger, and the Curie transition is an insulator to metal transition. PCMO does not have a metallic state, and the charge order, which occurs in the other manganites only at and beyond $x = 0.5$, is seen in PCMO well before $x = 0.5$, starting from $x = 0.37$. This progression is generally associated with their decreasing bandwidth.

As mentioned above, a proper description of manganites must include the effect of three strong onsite local correlations, namely electron lattice coupling, Hund's rule interaction J_H and Mott Hubbard correlation U. It is widely recognized that the former leads to Jahn–Teller distortion of the local ion positions and Jahn–Teller polarons. While this was realized very early[85], in the sixties (e.g. the work of Kanamori[91] on manganites), the essentiality of polaronic effects (in addition to double exchange[83,84] arising from Hund's rule and electron motion) was emphasized by Millis *et al.*[92] in the mid-nineties after the current revival of interest in mabganites. These authors dealt with the polaronic distortion as a classical lattice displacement. However, quantum effects of lattice motion effectively localize the polaron: its intersite hopping is reduced by an exponential Huang Rhys factor $\exp(E_{JT}/\omega_{ph})$. It is thus plausible that the J–T polaron is described as a site localized fermionic object l_i^+. At each lattice site, the two-fold orbital level e_g gives rise to another possible state which can be labelled b_i^+. This has an undiminished intersite hopping amplitude t_{ij}. This is the two fluid *lb* model for manganites proposed by Ramakrishnan *et al.*[81]. In this model, the strong electron–phonon interaction is taken into account by means of reorganizing the electron fluid into two, a site localized polaron fluid *l*, and a band fluid *b*. The other interactions, namely *U* (acting between *l* and *b* when they are on the same site) and J_H are kept explicitly. Since the two fluids must be in mutual equilibrium, i.e. have the same chemical potential μ, the latter must be such that $\langle n_l + n_b \rangle = (1 - x)$
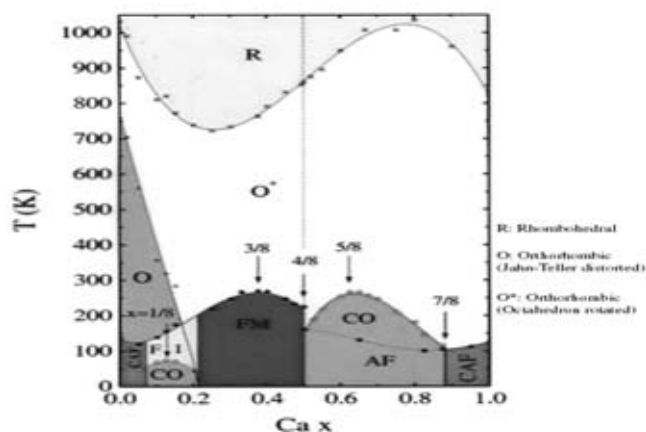

Figure 20. Phase diagram of the manganite $La_{1-x}Ca_xMnO_3$ in the *x*–*T* plane.

at every site, where x is the concen-tration of holes. Clearly, the quantum admixture between l and b (via e.g. intersite hopping) leads to a single hybridized fluid at low temperatures. This is neglected in present versions of the theory, which is therefore a high temperature theory of this strongly correlated system. The authors show that a variety of unusual effects in manganites, e.g. cmr, persistence of the metallic and insulating phases, anomalously low carrier concentration, tendency for two phase existence, insulating ferromagnetic ground states, can be qualitatively and quantitatively understood in this microscopic two fluid picture.

Cobaltates

Na_xCoO_2 is a member of the unusual cobaltate family; the end member CoO_2 with Co being in the 4^+ state and five 3d electrons seems to be a strongly correlated metal[93]. $NaCoO_2$ with Co^{3+} configuration and therefore six 3d electrons and a filled t_{2g} subband can be thought of as a band insulator. In the last several years, there has been enormous experimental and theoretical activity in the exploration of Na_xCoO_2 essentially because of the unusual phases and phenomena associated with different doping regimes (Figure 21). For $x > \sim 0.75$ the system is a very peculiar metal, at $x \sim 0.5$, there is a charge ordering of the Na^+ ions, and at $x \sim 0.3$, there is superconductivity (upon hydration). All this happens in a system which can be electronically approximated by a two-dimensional triangular lattice in which the low energy degrees of freedom arise from electrons (or holes) in the tight binding a_{1g} orbitals (of the t_{2g} states which lie lower than the e_g^π orbitals for the kind of local coordination present). The intrinsically frustrated structure can host novel phases; e.g. the nearest neighbour AF superexchange is more likely to lead to an RVB superconductor than to

Figure 21. Phase diagram of Na_xCoO_2 in the x–T plane.

magnetic LRO. In actuality, the properties of Na_xCoO_2 may be quite complex not only because of intraorbital strong correlation U (e.g. as in the cuprates) or strong electron lattice coupling (both seen to be important for manganites) or structural frustration but also because of orbital degeneracy as well as thermal/quantum fluctuations between high/intermediate/low spin states of the Co^{3+} ion, a phenomenon whose effects have been studied for decades[54] in $LaCoO_3$. The phenomena in say Na_xCoO_2 are indeed quite unusual and share a family resemblance with those in other strongly correlated systems, and cannot be rationalized in an independent electron framework. The tasks of theoretical modelling and experimental unravelling of their peropeties, as well as delineation of the precise role of the Mott–Hubbard like correlation, are quite unfinished (see, however, ref. 94). I therefore make only a brief mention of some of the effects observed in Na_xCoO_2.

The most striking property of Na_xCoO_2 for large x is its thermopower[95] which is quite large, strongly x as well as T dependent, showing a tendency to saturate at a large positive value (100–300 μV/K) at about 300 K, with the saturation value increasing with x. The resistivity is strongly anisotropic, with $\rho_c/\rho_{ab} \sim 10^4$. The inplane resistivity itself is large and varies from a few hundred μΩ cm to a few mΩ cm with temperature and doping[95]. The Hall number[95,96] R_H increases strongly with temperature (by a factor of three to four between say 4 and 300 K). The spin susceptibility is large, strongly temperature dependent and has a Curie Weiss form for large x with a Weiss temperature[96] θ_W of order 100–200 K. The simplest interpretation is in terms of local moments with an interaction energy of order θ_W. How such a moment continues to exist in a metal, especially if the magnetism is to be associated with d electrons whose intersite hopping amplitude is ~0.15 eV is an unanswered question. Large positive magnetoresistance[95] is another peculiar property for large x. At $x \sim 0.5$, there are clear signs of Na^+ ordering[97]. The discovery of superconductivity[98] for small $x(\sim 0.2$–0.3) at very low temperatures ($T_c \sim 3$ K) and its possible non s-wave or conventional nature was exciting as the latter strongly hinted at a non phonon mechanism. Only hydrated cobaltates are superconducting. ARPES measurements[99] and low temperature resistivity[95] which goes as T^2, both require rather small effective degeneracy temperatures. Theories with spin state transitions have been proposed[94].

Other oxides

The description above of some oxides which appear to be strongly correlated is heavily influenced by ideas and results connected with the orbitally non-degenerate strong correlation lattice model, namely the Hubbard model. Of the oxides described, probably the high temperature superconducting cuprates are the closest to it. It is clear that orbital degeneracy and other strong local interactions
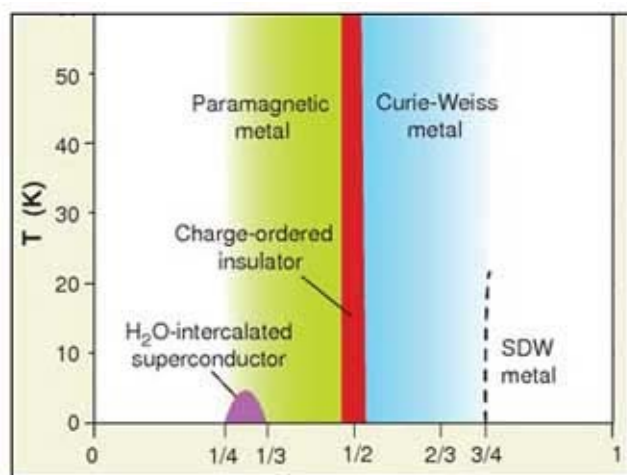
(e.g. electron lattice interaction/polarons) play an important role in manganites so that a naieve Hubbard model like description is inadequate. In cobaltates, the picture is less clear; multiorbital effects and high (intermediate) spin-low spin admixtures seem to be present, but a comprehensive alternative theoretical model is lacking (see, however ref. 94, for a recent attempt). I mention a few other oxide systems including titanates and vanadates[100] where strong correlation effects occur. These have different 'chemical realities' and manifestations.

Titanates and vanadates. The number of d electrons in the unfilled d shell of transition metal oxides depends obviously on their formal valence. Titanates and Vanadates are specially interesting in that this number can vary from zero to two so that a relatively simple one or two (or three!) orbital per site description is natural. For example, in $BaTiO_3$ (Ti^{4+}) and V_2O_5 (V^{5+}) the d shell is empty. Systems with one or two d electrons have also been extensively studied. They have Mott insulating phases, orbital long and short range order, and metal insulator transitions. For example, $ReTiO_3$ where Re is a trivalent rare earth ion, e.g. $YTiO_3$ is a Mott insulator[101] which, unusually, has ferromagnetic long range order. The former implies strong correlation since that is the only way such a stoichiometric compound (half filled band metal) can be insulating. In the orbitally nondegenerate Hubbard model, only AF order is possible for half filling. However, in the orbitally degenerate Hubbard model, ferromagnetic Heisenberg like intersite coupling is possible. Interestingly, in mixed $Re_{1-x}Re_xTiO_3$, e.g. $La_xY_{1-x}TiO_3$, there is a systematic change from AF to F order with increasing x (chapter V of ref. 100). Many titanates show orbital long range order. The compound $YTiO_3$ is a perovskite; the ($Ti–O_6$) octahedral share corners and are distorted (mainly rotation around the O ion with the Ti–O–Ti angle being consequently ~140° rather than 180° as in the undistorted perovskite structure). The five-fold orbital degeneracy is lifted in the cubic perovskite and one has three-fold degenerate t_{2g} states which can be further split for a noncubic structure, opening up to a_{1g} (nondegenerate) and (doubly degenerate) e_g^π orbitals. This splitting can be small (or even zero!). Thus, if one has the configuration d^1 or d^2 (Ti^{3+} or V^{3+} respectively) in the perovskite, the single d electron can be in one of several (two or three) orbitally degenerate or nearly degenerate states. Inter orbital Coulomb interactions, onsite and intersite hopping involving different orbitals are new and important ingredients and liquid and solid interorbital phases are possible.

The doped titanate $Y_{1-x}Ca_xTiO_3$ in which each substituent Ca contributes a hole has an insulator to metal transition at x increases to about $x_c = 0.4$. In the $La_{1-x}Sr_xTiO_3$ series, the transition occurs at $x_c = 0.05$. Interestingly, physical properties near x_c, on the metallic side, are similar to those obtained for the half filled ($x = 0$) orbitally nondegenerate

Hubbard model, e.g. the way physical properties change as U increases towards U_c. The increase in paramagnetic spin susceptibility χ, linear specific heat coefficient γ, and the T^2 coefficient of resistivity (commonly denoted as A) are examples. It is interesting that a multiorbital, paramagnetic, strongly correlated metal away from half filling has properties similar to those of a single orbital correlated half filled metal $x = 0$ and $U < U_c$ (presumed critical value for the metal insulator transition). It is also a fact that $La_{1-x}Ca_xVO_3$ which has a paramagnetic metal to AF insulator transition as x decreases to the value $x_c = 0.176$, has a metallic critical behaviour different from that of the doped titanates; the resistivity at low temperatures goes for example as $T^{1.5}$ rather than T^2. The differing properties in the vicinity of the insulator metal QCP argue for a 'relevant' diversity in the low energy description.

The insulator metal transition in V_2O_3 has been investigated for more than five decades[102]. In the seventies and later[103], it was considered a textbook example of the Mott transition in a Hubbard-like model, driven by strong correlation. The phase diagram of V_2O_3 as a function of pressure (positive physical pressure and electronic substitution considered equivalent to negative or positive 'chemical' pressure) and temperature, terminating in a critical point marking a continuous metal insulator transition (Figure 22) is well known. It is becoming clear over the last few years, from strong correlation effectively multiorbital electronic structure calculations[104] that the transition is actually very different. For example, there is evidence that the transition is driven by redistribution of spectral weight for the two d electrons in the crystal field split a_{1g} and e_g^π suborbitals of the t_{2g} orbital.
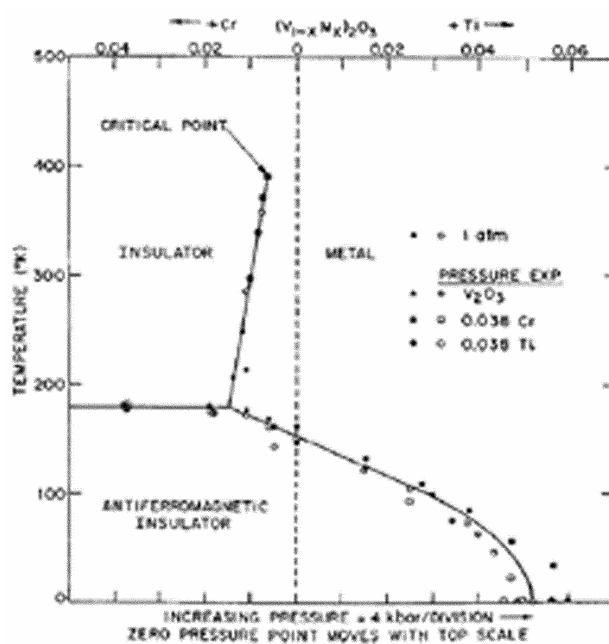

Figure 22. The metal insulator transition in $(V_{1-x}M_x)_2O_3$ and in V_2O_3 under pressure.

MnO. Canonically, rocksalt structure monoxides such as MnO are antiferromagnetic Mott insulators. Under pressure (~ 100 GPa), MnO becomes metallic. This insulator metal transition is argued not to be a simple single orbital Hubbard model transition but a multiorbital transition from high spin to low spin (moment collapse) with again a change in partial orbital occupancy[105].

Heavy fermions

Metallic systems with rare earth ions are intrinsically unusual in that two very different types of electronic states necessarily coexist in them. One is the s, p (or even d) electrons which are basically itinerant and free. The other is f electrons whose local number is integral and is constrained to have a particular value (for example, Ce^{3+} has one f electron $4f^1$, and Nd^{3+} has the configuration $4f^4$); there is an associated magnetic moment. The two states hybridize weakly. In a real sense, these are examples of orbitally selective Mott systems. The f orbitals are in the strong correlation regime, and the others are not. For small concentrations of the rare earth ions or the f electron moment, it is known that at around an exponentially small temperature, namely the single impurity Kondo temperature[15] T_K, the moment disappears essentially because of the hybridization between the conduction band electrons and those constituting the moment and related fluctuations in the spin of the latter. When the f electron concentration is large, as happens in rare earth intermetallics, the local moments are quenched as temperature is lowered in a process perhaps not unlike the Kondo effect. The (resulting) low temperature system has remarkable properties, including heavy fermion, non Fermi liquid behaviour and superconductivity close to the disappearance of the magnetic moment and of magnetic

Figure 23. Resistivity of CeCoIn$_5$ with temperature. The thick black line is the phenomenological fit alluded to in the text. (From Nakatsuji *et al.*[118].)

order. This is a central continuing low temperature activity; e.g. there has been for more than two decades a biennial conference on strongly correlated electron systems[1] in which the main theme continues to be heavy fermion related physics. There are several recent reviews of the field[106,107]. I therefore, do not describe in any detail the observed phenomena in this diverse family, but only briefly sketch them in the context of strong correlations.

Broadly, rare earth intermetallics show a high temperature phase with f electron derived magnetic moments and conduction electrons. As temperature decreases below say T^* (typically 10–100 K) the f moment disappears smoothly, and an f electron related band forms, with an energy scale related to T^*. This is the heavy Fermi system, with an effective mass $m^* \sim m(T_F/T^*)$. The discovery[108] of CeAl$_3$ in the 1970s, a compound with no long-range order at low temperature, but apparently a free fermionic ground state, started the field. Its specific heat coefficient $\gamma = C(T)/T$ is very large, ~1.6 J/mol K^2 which is about a thousand times larger than that of typical metals. This and the corresponding enhancement in susceptibility χ are the hallmarks of the 'heavy' fermion state. An early review by Stewart[45] describes the phenomena observed. It had been pointed out by Nozieres[16] that the magnetic impurity whose moment has disappeared because of coupling with conduction electron, can be regarded as a local Fermi liquid. The nature of this Fermi liquid was described by him, and detailed numerical renormalization group calculations of Wilson[109] substantiated this, showing among other things that the ratio (γ/χ) (now known as the Wilson ratio) is not enhanced, and has the value of unity in units of $(\pi^2 k_B^2/3\mu_B^2)$. Various possibilities for the impurity ground state were discussed by Nozieres and Blandin[110]. Early work on heavy fermions was entirely described in this language. An obvious generalization for a lattice of rare earth atoms is to a two uncorrelated (renormalized parameter) band model, with an 'f' band hybridizing with the conduction band, the hybridization energy or coupling being of the order of the Kondo scale[111]. Recent experiments on optical conductivity in a large number of rare earth intermetallics find[112] that they all have a peak in Re $\sigma(\omega)$ at a frequency ω which goes as $\sqrt{a/\gamma} \, \gamma_0$, where γ is the linear specific heat coefficient (highly enhanced) of the heavy fermion and γ_0 is the band electron specific heat coefficient. The quantity a depends on the degeneracy of the f state. The fit, extending over more than a decade in frequency, is identical to what is expected in a simple band model of the sort mentioned above, and arises from a hybridization gap of order $\sqrt{T_K W}$, where W is the width of the electron band. Another Fermi liquid property is the Kadowaki–Woods ratio, namely the ratio of the coefficient (A) of the T^2 term in the low temperature resistivity to γ^2. This is expected to be nearly the same for all heavy fermions (except for orbital degeneracy factors), though both A and γ are highly enhanced. There is considerable evidence
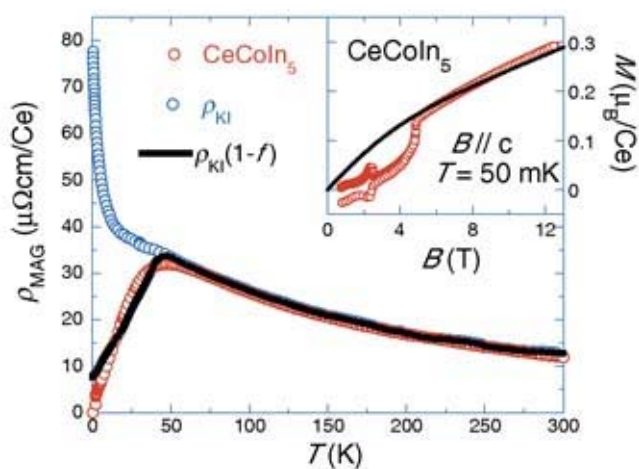
that this is so[113]. An early support to the existence of well-defined quasiparticles at the Fermi energy in rare earth intermetallics was the observation[114] in them of deHaas van Alphen oscillations in magnetic susceptibilty as a function of $(1/H)$ with a period close to what is expected of extremal orbits from electronic structure theory. The effective mass though (estimated from the Dingle temperature) turns out to be high. The Gruneisen parameter $\Gamma \sim V^{-1}C(T)^{-1}(\partial V/\partial T)$ is known to be very large in heavy fermions and is singular as a function of temperature near, e.g. the quantum critical point (measurements for the cubic compound $CeIn_{3-x}Sn_x$ are reported in ref. 115).

In the last decade or so, evidence continues to accumulate that the low temperature state of heavy fermion metals is not (generally) a Fermi liquid, that the system is near quantum criticality and that a superconducting ground state is common. I very briefly touch on these major (connected) areas here. It is likely that the connection has to do with strong correlations in the f orbital. The observed non-Fermi liquid properties are reviewed, for example by von Loheneysen et al.[106] and Stewart[46]. The resistivity of many heavy Fermi systems goes as a power of temperature different from and less than two, the only exponent possible for resistive scattering arising from electron interactions in a Fermi fluid. Often the exponent is unity; in some systems it is about (3/2) or (5/3), values expected in weak coupling theories of magnetic order in the electron fluid near the magnetic transition, in the paramagnetic phase. The exponent of unity is what one generically expects above the quantum critical point (for $T \neq 0$). The surprising fact is both the ubiquity of the behaviour and the large temperature range over which it is seen. The specific heat coefficient γ depends on tempe rature; it increases logarithmically as temperature decreases. This was most clearly noticed in $CeCu_{6-x}Au_x$ by von Loheneysen[116] who also showed that this logarithmic increase smoothly disappears with increasing magnetic field. An interesting experimental observation is that two measured quantities, namely the Knight shift K and the spin susceptibility χ are not proportional to each other (i.e. this ratio is not a temperature independent constant as expected in a Fermi liquid). This implies for example either an emergent single non-Fermi liquid or a two fluid system.

Many heavy fermion systems order magnetically at low temperatures (AF, F or spiral order). The ordering temperature can be changed smoothly by some physical/ chemical parameter, e.g. pressure, doping, magnetic field, and can go to zero. This 'quantum critical point' separates a magnetically ordered phase (interacting moments) and a paramagnetic phase of degenerate strongly correlated fermions. The nature of this critical point in rare earth intermetallics is a subject of great activity and significance[106,107]. I mention some ideas below. One question of interest is the carrier density near the transition. If on one side, there are magnetic moments which do not contribute e.g. to the transverse Hall current, but on the other side, they do, the carrier density if measurable by the Hall effect, will show a discontinuos decrease. On the other hand, if the magnetic order is an electron spin density wave, the effective carrier density will smoothly increase as one approaches the QCP. Both the possibilties seem to be realized in heavy fermion systems[117]. Experimentally, it appears that the system is a non-Fermi liquid around the QCP. For example[116], the specific heat of $CeCu_{6-x}Au_x$ divided by temperature is not constant as expected for a Fermi liquid, but increases logarithmically as temperature decreases. The electrical resistivity increases as T^α with temperature, where the index α is in the range of 1–1.5, distinctly less than 2 which is the value expected if electron–electron interactions are the source of resistive scattering. The static magnetic susceptibility is strongly temperature dependent.

In several members of the family, the observations can be described quantitatively in a two fluid model[118]. One fluid is the Kondo gas, namely a system with the properties of a collection of independent Kondo impurities and the other is the Kondo liquid, a collective state formed by the interaction between moments (this is a fraction $f(T)$). Assuming this, the electronic specific heat and the magnetic susceptibility can be written as

$$C_{mag}(T)/T = [1 - f(T)]C_{KG}(T)/T + f(T)C_{KL}(T)/T]$$

and

$$\chi(T) = [1 - f(T)]\chi_{KG}(T) + f(T)\chi_{KL}(T).$$

If the Wilson ratio $\alpha\chi_{KL}(T)/\{C_{mag}(T)/T\}$ is assumed to have the strong correlation value 2 at all temperatures (where $\alpha = (\pi^2 k_B^2/3\mu_B^2)$), one can find $f(T)$ which turns out to grow linearly with decreasing T and to be characterized by a crossover temperature T^*. For example, from measurements on the compound $Ce_{1-x}La_xCoIn_5$ one finds that $f(T)$ saturates at about $T \sim 2$ K and that $T^* \sim 45$ K, where the single impurity Kondo temperature is known to be $T_K \sim 1.7$ K and $T_{CEF} \sim 12$ K. The fact that $T^* \gg T_K$ is quite unexpected in that the coherence temperature can be argued to be less than the single impurity T_K which is the characteristic energy scale at which the coupling between the local moment (a strong correlation indicator) and the conduction electron causes the 'screening' of the moment. If one takes this screening literally in the sense of one conduction electron forming a singlet with one local spin there is an 'exhaustion' of conduction electrons[119] in a lattice of moments. The coherence of conduction electrons and local spins to form a many fermion singlet should occur at a temperature lower than T_K. This is a one fluid model. On the other hand, hybridization models[111] lead to a characteristic 'mid-infrared' energy or temperature $T^* \sim T_{coh} \sim \sqrt{T_K W} \gg T_K$. In many 'Kondo lattice' systems, indeed $T_{coh} < T_K$. This

difference suggests that there is more than one moment quenching quantum fluctuation process, e.g. one in which only spin fluctuations are relevant (localized spin in a conduction electron bath as for the Kondo impurity) and another which can occur in a lattice of electrons whose hopping or local charge fluctuations quenches their spins. A microscopic strong correlation theory with these possibilities is desirable.

The phenomenological two-fluid model, which is inspired by the two-fluid model of He^4 (a bosonic system) where the coherent superfluid condensate is one fluid and the quantum fluctuations or excitations are another, may not be an appropriate microscopic low temperature model for a many-fermion system. However, it is very successful in unexpected ways. For example, the Knight shift K, which depends on local susceptibility, breaks away from the uniform susceptibility, χ below about T^*. The divergence can be described well in the two fluid picture. The resistivity behaviour of heavy fermion lattice systems (Figures 9 and 23) is regarded simply as due to the fraction $(1 - f(T))$ of the Kondo gas! Superconductivity in heavy fermions was discovered nearly three decades ago[120] in $CeCu_2Si_2$. The occurrence of superconductivity is likely near the QCP, because there the system makes a transition from one kind of ground state to another, so that quantum fluctuations, especially spin fluctuations, are quite likely to be prominent. Lonzarich and collaborators have explored this idea systematically at Cambridge, taking special care that the system is clean (no disorder) and approaching the QCP with pressure. They (and now, several other groups) have found a number of low temperature superconducting transitions in heavy fermion systems near the QCP. A clear example of super-conductivity near the AF-paramagnetic metal QCP was discovered by Mathur and co-workers[122] and that near the F-paramagnetic metal QCP by Saxena and co-workers[123]. In many cases, the metallic (non ordered) system is a non-Fermi liquid. The magnetic fluctuations have been quantitatively described (e.g. as input into a BCS like superconductivity calculation) in a weak coupling nearly magnetic metal model. Since the forms of the fluctuation spectrum for small q and ω are generic, the spectrum might equally well characterize fluctuations in a strongly correlated system near the QCP. The weak coupling model (i.e. fermionic quasiparticle system) coupled to such fluctuations makes predictions, e.g. for transport pro-perties near the QCP. The electrical resistivity is expected to go as a power α of the temperature, with $\alpha \sim 1.5$. However, the observed non-Fermi liquid exponents are often different from these, and I believe this points strongly to correlation effects. One interesting feature of superconductivity in heavy fermions is f electron hole asymmetry e.g. there are many Ce (f^1) based super-conductors but only one Yb($f^{13} = f^{14-1}$) based super-conductor[124] β-$YbAlB_4$. The superconducting T_c is enhanced by valence fluctuations; namely heavy fermion

systems with valence (local charge?) fluctuations can have high optimum T_c's. A theory in which pairing is mediated by such fluctuations has been developed[125].

I mention some of the ideas developed to describe heavy fermion phenomena. In the early period well into the nineteen nineties, inspired by the description of the Kondo ground state of the local moment as an impurity Fermi liquid, the low temperature behaviour of rare earth intermetallics was taken to be a latticized version of the same. In the eighties, Doniach argued that in these systems the competition among the interaction between f moments and their quenching by the single site Kondo effect can lead to two phases. This leads to a quantum critical point separating a magnetically ordered metallic phase (generally with Ne'el order) and a nonmagnetic metal. The nature of this quantum criticality is the subject of intense activity. A theory in the image of the order parameter or Ginzburg Landau approach to phase transitions, taking into account temporal fluctuations of the order parameter in addition to spatial fluctuations, was first proposed by Hertz[126] and has been developed in great depth and detail (e.g. the book on quantum phase transitions by Sachdev[127]). However, the properties of the QCP in heavy fermions are different from those expected in a quantum Ginzburg Landau theory. For example, there seems to be a dramatic change in the number of electrons within the Fermi surface[117] across the QCP, as inferred from de Haas van Alphen oscillation periods. This means that the description of the transition only in terms of a (bosonic) order parameter is inadequate; the underlying low energy fermionic degrees of freedom also undergo a change at the transition. A detailed theory of local quantum criticality, involving coupled fermionic and the bosonic degrees of freedom, and focusing on the critical dissolution of the local moment (Kondo effect) has been developed[128]. It has been argued that long range gauge field interactions will emerge[129] at the QCP ('deconfinement') so that an order parameter theory is necessarily inadequate. In rare earth intermetallics, the f electrons are always in the strongly correlated regime, and weakly hybridize with the uncorrelated (spd) electrons. The low energy excitations are associated with the lower Hubbard band of the former. If the fermionic degrees of freedom could all be integrated out and cause only local bosonic degree of freedom coupling constants, one has the Ginzburg Landau theory. Including explicitly the small (q, ω) fluctuations of a Fermi quasiparticle system, and treating fluctuation effects in the Gaussian approximation leads to the approach associated with Moriya and collaborators[130]. A model low energy fermion boson field theory, with bosonic degrees of freedom for the localized spins has been developed by Qimiao Si and co-workers[128]. They find a 'local' critical point at which the Kondo moment disappears necessarily coincident with the disappearance of long range magnetic order. A field theory which focuses on the gauge degrees of

freedom associable with strong correlations leads to emergent quantum criticality[130]. A microscopically motivated low energy field theory for a strongly correlated Fermi system and its consequences near the QCP might be different from all of the above!

Theories

Since the explicit formulation of the strong correlation problem by Hubbard[24] in the 1960s in its simplest form (one nondegenerate orbital on each lattice site), an enormous effort has been made in this field. One of these is the dynamical mean field theory (DMFT)[28,131] in which the site local effects of strong correlation namely the lectron self energy are explored nonperturbatively, and another is an auxiliary field (slave fermion/boson) approach[34,132].

The dynamical mean field theory[34] due to Georges and Kotliar (see also Georges[131] for an insightful perspective) is based physically on the fact that strong correlation is local. For example, in a lattice model, the strong correlation acts on the fermionic degrees of freedom at the same site. The electron self energy $\Sigma_{ij}(\omega)$ (or the generalized electron energy shift) resulting form this correlation is predominantly local, namely $\Sigma_{ij}(\omega) \sim \Sigma_{ii}(\omega)$ with corrections of relative order $(1/d)$, where d is the spatial dimensionality of the system. A systematic $(1/d)$ expansion was obtained by Muller-Hartmann[133] and by Metzner and Vollhardt[134]. Thus for $d = \infty$, the self-energy is entirely site local; it is a single dynamical (frequency dependent) mean field and can be usefully thought of as a generalization of the classical static mean field idea to a many body interacting quantum system. This formulation and development as dynamical mean field theory is due to Georges and Kotliar[135]. They showed that the locality of the self energy implies, for the Hubbard model, the self-consistent solution of an Anderson impurity model (AIM). This describes a strongly correlated impurity or a magnetic moment in a metal (Anderson[136]). An electron (a 'd' electron in a single nondegenerate orbital with energy ε_d and local repulsive correlation $Un_{d\sigma}n_{d-\sigma}$ hybridizes with the conduction electrons $|\mathbf{k}\sigma\rangle$ with a strength $V_{d\mathbf{k}}$. The latter gives rise to a width $\Gamma(\varepsilon_d) = 2\pi\Sigma_{\mathbf{k}\sigma}|V_{d\mathbf{k}}|^2\delta(\varepsilon_d - \varepsilon_\mathbf{k})$. In the AIM implementation of the DMFT, $\Gamma(\varepsilon_d = \omega)$ (which is a measure of the coupling of the 'impurity' to the 'bath') is determined self consistently. The Anderson impurity has a magnetic moment for large U which disappears at exponentially low temperatures (the Kondo effect[15]). Self-consistent calculations using various 'impurity solvers' describe how the lattice system crosses over as temperature is lowered, from a collection of magnetic moments to a strongly correlated quantum fluid.

In the last nearly two decades, this method has developed into the most significant theoretical approach to strongly correlated systems. Among the several directions of continuing development, a few are the following. There is a considerable effort in developing impurity solvers, namely (mostly numerically implemented) methods for solving the Anderson impurity problem, that are simultaneously accurate for both low and high temperatures. Examples are iterated perturbation theory (IPT, see e.g. ref. 28) which is a simple approximation for the site local fermion self energy with an arbitrary bare propagator and arbitrary U; the quantum Monte Carlo method[137,138] in which $\Sigma_{ii}(\omega)$ is obtained by Monte Carlo sampling of different 'times' or 'frequencies', the NRG or numerical renormalization group first used by Wilson[109] for the Kondo problem, the local moment with Gaussian fluctuations method pioneered by Logan and co-workers[139], the quantum rotor model of Florens and Georges[140] which focuses on local charge fluctuations, etc.

Another direction is the consideration not of a single site, but a cluster of sites immersed in a fermionic bath, and self-consistent solution of this problem. This direction is important because many low energy properties of strongly correlated systems depend on intersite correlations. Perhaps the best known example is d wave superconductivity in cuprates. In a d wave superconductor, the nearest neighbour Cooper pair 'bond' amplitudes have a definite phase relation with each other; the x and y bond amplitudes have opposite signs. Many kinds of cluster theories have been developed[141].

At a formal level, the free energy functional of the DMFT and the Luttinger Ward functional[142] of many body theory have been related and this has inspired novel approaches[143].

A very promising direction in which there has been a great deal of progress in the last few years is the effort to develop realistic electronic structure approaches to strongly correlated systems. This is an important and urgent necessity because many such systems show mean field electronic structure features (e.g. even though the Fermi surface is often not sharp, its shape is as expected from such calculations) while differing qualitatively in several ways from weakly interacting systems (as described above in many cases). An example of recent progress in the field is the calculation[144] of the anisotropic electron spectral density, and the coherent to incoherent crossover in $CeCoIn_5$ at very low temperatures, by Kotliar and co-workers) using a composite electronic structure and DMFT approach.

The power of the DMFT approach is that it describes the largely local effect of strong correlations over a vast energy scale ($\sim U$ to zero) self-consistently and nonperturbatively. Early implementations had serious limitations regarding low temperature behaviour, nonlocal properties, etc. But with increasingly sophisticated impurity solvers and numerical methods, as well as greater computer power, this limitation is being overcome. The approach remains entirely numerical, though a large number of features of the results are understood physically.

One of the early successes of the DMFT method was a quantitative description of the Mott metal insulator transition in the Hubbard model at half filling ($x = 0$) with increasing U. It was shown that as U increases, the spectral density splits into a lower and an upper Hubbard band (Figure 4) and spectral intensity develops at the Fermi level (lying between these two peaks). With further increase in U, there is, at U_{c1}, a sudden (first order) metal to insulator transition. Between U_{c1} and $U_{c2} > U_{c1}$ one has a peculiar coexisting metallic and insulating mixed phase very much like what happens for the classical liquid gas transition. This is the situation at $T = 0$. As temperature increases, the two critical U's come together and at a critical temperature, there is a critical point. Here, the metal insulator transition becomes continuous, like the critical point of the liquid–gas transition. Both the general transition, and the actual values of the transition lines, critical correlation, etc. are well known (refs 20 and 145 describe some recent results).

Another approach for strongly correlated systems is of introducing auxiliary fields which enable local strong correlation constraints to be described simply and approximated. For example, with $U = \infty$, a site can have one electron or none. This can be described in terms of local fermions f and bosons b; the total number at a site is constrained to be one, namely $\langle \sum_\sigma f_{i\sigma}^+ f_{i\sigma} + b_i^+ b_i \rangle = 1$. This kind of slave boson theory which implies a local gauge principle (the physical fermion creation operator is $f_{i\sigma}^+ b_i$ which is invariant if b_i changes to $b_i \exp(i\varphi_i)$ and $f_{i\sigma}^+$ to $f_{i\sigma}^+ \exp(-i\varphi_i)$) has been developed in great depth and detail for cuprates by Lee and co-workers[132]. This is again a nonperturbative approach. It expands the Hilbert space but constrains its occupation.

Prospect

The review above of correlated electron metallic systems is brief and patchy. I have tried in it to bring out the following. The systems are quite diverse, share some broad common features and are not described in several essential ways by the prevalent, vastly successful ideas/theories of interacting electrons. This has been recognized for some decades now, and enormous effort has gone recently into a nonperturbative description of correlation effects. These have been fairly successful, but unexpected discoveries of new phenomena only emphasize how incomplete our understanding is. I believe that there is need for a new paradigm (e.g. as a zero order theory) which can hope to play for strongly correlated systems the role which the free electron gas plays for all the electronic systems and phenomena that are understood today. Perhaps systematic development of such a new paradigm will enable us to make full sense of the variety and novelty of strong correlation effects especially at low temperatures. Meanwhile, phenomenological correlations, broadening and deepening of existing theoretical approaches, as well as novel systems and phenomena will continue to keep this a lively and central area of condensed matter physics.

1. See, e.g. the conferences on Strongly Correlated Electron Systems (SCES), the latest of which was held in 2007 in Houston, Texas, USA (SCES2007). Its proceedings appear in *Physica*, 2008, **B403**.
2. Thomson, J. J., *Philos. Mag.*, 1897, **44**, 295.
3. Drude, P., *Ann. Phys.*, 1900, **1**, 566.
4. Sommerfeld, A., *Z. Physik*, 1928, **47**, 1.
5. Wilson, A. H., *Proc. R. Soc. London*, 1931, **A133**, 458; 1931, **134**, 277.
6. Mott, N. F., *Proc. Phys. Soc. London*, 1949, **A62**, 416; See also *Metal Insulator Transitions*, Taylor and Francis, London, 1990.
7. Anderson, P. W., *Phys. Rev.*, 1958, **109**, 1492.
8. Bohm, D. and Pines, D., *Phys. Rev.*, 1952, **85**, 338; 1953, **92**, 609.
9. Landau, L. D., *Sov. Phys. JETP*, 1957, **3**, 920.
10. Baym, G. and Pethick, C. J., *Landau Fermi Liquid Theory, Concepts and Applications*, Wiley-VCH, New York, 1991.
11. Luttinger, J. M. and Nozieres, P., *Phys. Rev.*, 1962, **127**, 1431.
12. Leggett, A. J., *Phys. Rev.*, 1965, **140**, 1869 as well as 1966, **147**, 119.
13. Pethick, C. J., *Phys. Rev.*, 1970, **B2**, 1789.
14. Castellani, C., Kotliar, G. and Lee, P. A., *Phys. Rev. Lett.*, 1987, **59**, 323.
15. See e.g. the book by Hewson, A. C., *The Kondo Effect to Heavy Fermions*, Cambridge Univesity Press, Cambridge, UK, 1993. (The Kondo temperature for a magnetic impurity coupled with strength J to the spin of a conduction electron with bandwidth D is $T_K = \sqrt{DJ} \exp(-1/J\rho)$ which is exponentially small for $J\rho \ll 1$ where ρ is the electron density of states at the Fermi energy.)
16. Nozieres, P., *J. Low Temp. Phys.*, 1974, **17**, 31.
17. Dreizler, R. M. and Gross, E. K. U., *Density Functional Theory*, Springer-Verlag, Berlin, 1990; also Gross, E. K. U. and Dreizler, R. M. (eds), *Density Functional Methods in Physics*, Plenum, New York, 1995.
18. Measured by r_s namely the radius of a sphere that holds one electron on the average in units of the Bohr radius a_0; for high electron density, r_s is small and vice versa.
19. This was proposed by Mott as the criterion for the electron density at which a metal to insulator transition occurs, and is known to be quite accurate for an astonishing range of electron densities in the doped semiconductor metal insulator transition; see for example Edwards, P. P. and Sienko, M. J., *Acc. Chem. Res.*, 1982, **15**, 87.
20. See for example Miranda, E. *et al.*, *Physica*, 2008, **B403**, 1465.
21. de Boer, J. H. and Verwey, E. J. W., *Proc. Phys. Soc.*, 1937, **A49**, 5.
22. Mott, N. F., *Proc. Phys. Soc. London*, 1937, **A49**, 72.
23. Mott, N. F. in ref. 6, and *Can J. Phys.*, 1956, **34**, 1356.
24. Hubbard, J., *Proc. R. Soc. London*, 1964, **A281**, 401 is the first of a series of papers.
25. Montrosi, A. (ed.), *The Hubbard Model, A Collection of Reprints*, World Scientific, Singapore, 1992.
26. Baeriswyl, D. (ed.), *The Hubbard Model*, Plenum, New York, 1995.
27. Giamarchi, T., *Quantum Physics in One Dimension*, Oxford University Press, Oxford, 2003.
28. Georges, A. *et al.*, *Rev. Mod. Phys.*, 1996, **68**, 13.
29. See e.g. Cho, A., *Science*, 2008, **319**, 118.
30. For a review of numerical work in two dimensions, see Scalapino, D. J., In *Handbook of High Temperature Superconductivity* (ed. Schrieffer, J. R.), Springer-Verlag, Berlin, 2006, Ch. 13.

31. See e.g. the book by Anderson, P. W., *The Theory of Superconductivity in Cuprates*, Princeton University Press, Princeton, 1997.
32. A recent retrospective is, Spalek, J., *Acta Phys. Polonica.*, 2007, **111**, 409.
33. Jaklic, J. and Prelovsek, P., *Adv. Phys.*, 2000, **49**, 1.
34. Lee, P. A. and Nagaosa, N., *Phys. Rev.*, 1992, **B46**, 5621.
35. Rao, C. N. R. and Raveau, B., *Transition Metal Oxides*, VCH Publishers, New York, 1995.
36. Misra, P., *Heavy Fermion Systems*, Elsevier Science, New York, 2007.
37. Fujimori, A., *J. Phys. Chem. Solids*, 1992, **53**, 1595; Fujimori *et al.*, *Phys. Rev. Lett.*, 1992, **69**, 1796.
38. Morikawa, K. *et al.*, *Phys. Rev.*, 1995, **B52**, 13711.
39. Damascelli, *et al.*, *Rev. Mod. Phys.*, 2003, **75**, 473; Campuzano, J. C. *et al.*, In *The Physics of Superconductors* (eds Benneman, K. H. and Ketterson, J.), Springer-Verlag, Berlin, 2004; Shen, K. M. and Shen, Z.-X., In *Photoemission* (ed. Hufner, S.), Springer-Verlag, Berlin, 2007.
40. Matoba, M. and Anzai, S., *J. Magn. Magn. Mater.*, 1987, **70**, 213.
41. Gunnarsson, O., Calandra, M. and Han, J. E., *Rev. Mod. Phys.*, 2003, **75**, 1085; Hussey, N. E., Takenaka, K. and Takagi, H., *Philos. Mag.*, 2004, **84**, 2847.
42. The Ioffe-Regel and Mott limits corresponds the electron mean path l being equal to the interatomic spacing or $(2\pi/k_F)$ respectively.
43. To put these results in perspective, the electrical resistivity in clean metals is believed to be due to inelastic scattering of electrons from lattice vibrations and is generally small, of the order 10 $\mu\Omega$ cm or less. It is temperature dependent, going as a high power of temperature below the characteristic quantum temperature of the lattice vibrations namely phonons (which scatter electrons resistively) with the Debye temperature θ_D, and linearly with temperature above it. In disordered interacting metals, the resistivity at low temperatures goes as T^2, due to electron–electron collisions.
44. Takagi, H. *et al.*, *Phys. Rev. Lett.*, 1992, **69**, 2975.
45. Stewart, G. R., *Rev. Mod. Phys.*, 1984, **56**, 755. An update is ref. 46.
46. Stewart, G. R., *Rev. Mod. Phys.*, 2001, **73**, 797; *Rev. Mod. Phys.*, 2006, **78**, 743.
47. Hervieu, M., *et al.*, *Phys. Rev.*, 2003, **B67**, 045112.
48. Nakano, T. *et al.*, *Phys. Rev.*, 1994, **B49**, 16000.
49. Foo, M. L. *et al.*, *Phys. Rev. Lett.*, 2004, **92**, 247001.
50. Shenoy, V. and Rao, C. N. R., *Philos. Trans. R. Soc.*, 2008, **A366**, 63; Dagotto, E., *Science*, 2005, **309**, 257.
51. Tranquada, J. M., arXiv.cond-mat 0510792v1, 2005.
52. Mathur, N. D. and Littlewood, P. B., *Phys. Today*, 2003, **56**, 25.
53. Sarma, D. D. *et al.*, *Phys. Rev. Lett.*, 2004, **93**, 097202.
54. See e.g. Rao, C. N. R., Matin Sheikh Md. and Chandrabhas, N., *Topics Curr. Chem.*, 2004, **234**, 1.
55. Maekawa, S. *et al.*, *Physics of Transition Metal Oxides*, Springer-Verlag, Berlin, 2004.
56. Anderson, P. W., *Science*, 1987, **235**, 4196.
57. The *Reviews of Modern Physics* has carried, for the last half a dozen years, review articles on different aspects of cuprate high temperature superconductors.
58. Fujimori, A. *et al.*, *Phys. Rev.*, 1987, **B35**, 8814.
59. Hybertsen, M. S., Schluter, M. and Christensen, N. E., *Phys. Rev.*, 1989, **B39**, 9028.
60. Ogata, M. and Fukuyama, H., *Rep. Prog. Phys.*, 2008, **71**, 036501.
61. Zaanen, J., Sawatzky, G. A. and Allen, J. W., *Phys. Rev. Lett.*, 1992, **68**,1054.
62. Zhang, F. C. and Rice, T. M., *Phys. Rev.*, 1988, **B37**, 3759.
63. Varma, C. M., *Phys. Rev.*, 1997, **B55**, 14554; *Phys. Rev. Lett.*, 1999, **83**, 3538.
64. Ganguly, P. and Rao, C. N. R., *J. Solid State Chem.*, 1984, **53**, 193.
65. Uemura, Y. J., *Physica*, 1997, **C282–287**, 194; Uemura, Y. J. *et al.*, *Phys. Rev. Lett.*, 1989, **62**, 2317.
66. Hufner, S. *et al.*, *Rep. Prog. Phys.*, 2008, **71**, 062501.
67. Doiron-Leyraud, N. *et al.*, *Nature*, 2007, **447**, 565.
68. Bourges, P., In *Gap Symmetry and Fluctuations in High Temperature Superconductors* (eds Bok, J. *et al.*), Kluwer, New York, 2006, Ch. V.
69. Lanzara, A. *et al.*, *Nature*, 2001, **412**, 510.
70. See e.g. Khasanov, R. *et al.*, arXiv:0710.5053v1[cond-mat.suprcon]
71. Anderson, P. W., *Science*, 2007, **316**, 1705.
72. Maier, T. A., Poilblanc, D. and Scalapino, D. J., *Phys. Rev. Lett.*, 2008, **100**, 23701.
73. Sutherland, M. A. *et al.*, *Phys. Rev.*, 2003, **B67**, 175420.
74. Ding, H. *et al.*, *Nature*, 1996, **382**, 51.
75. Chakravarty, S. *et al.*, *Phys. Rev.*, 2001, **B63**, 094503.
76. See e.g. the forthcoming review, Wang Yayu and Ong, N. P., *Rep. Prog. Phys.*, 2008 (to appear).
77. Kanigel, A. *et al.*, *Nature Phys.*, 2006, **2**, 447.
78. Harris, Yan, Y. F. and Ong, N. P., *Phys. Rev.*, 1992, **B46**, 14293.
79. Chatterji, T., *Colossal Magnetoresistive Manganites*, Springer-Verlag, Berlin, 2004.
80. Salamon, M. B. and Jaime, M., *Rev. Mod. Phys.*, 2001, **73**, 583.
81. Ramakrishnan, T. V. *et al.*, *Phys. Rev. Lett.*, 2004, **92**, 157203.
82. As is well known, the five-fold degenerate d orbital state split in the octahedral environment of the Mn ion into a three-fold degenerate t_{2g} and a two-fold degenerate e_g level with the former being lower in energy.
83. Zener, C., *Phys. Rev.*, 1951, **82**, 403.
84. Anderson, P. W. and Hasegawa, H., *Phys. Rev.*, 1955, **100**, 675.
85. Finch, G. I., Sinha, A. P. B. and Sinha, K. P., *Proc. R. Soc. London*, 1957, **A242**, 48.
86. Loa, I. *et al.*, *Phys. Rev. Lett.*, 2001, **87**, 125501.
87. Shenoy, V. *et al.*, *Phys. Rev. Lett.*, 2007, **98**, 097201.
88. Goodenough, J. B., *Phys. Rev.*, 1955, **100**, 564.
89. Loudon, C. *et al.*, cond-mat.0308581.
90. von Helmolt, R. *et al.*, *Phys. Rev. Lett.*, 1993, **71**, 2331.
91. Kanamori, J., *J. Appl. Phys. Suppl.*, 1960, **31**, 145.
92. Millis, A. J., Littlewood, P. B. and Shraiman, B. I., *Phys. Rev. Lett.*, 1995, **74**, 544.
93. de Vaulx, C. *et al.*, *Phys. Rev. Lett.*, 2007, **98**, 246402.
94. Khaliullin, G. and Chaloupka, J., *Phys. Rev.*, 2008, **B77**, 104532.
95. See e.g. Lee, M. *et al.*, *Physica*, 2008, **B403**, 1564 for recent work.
96. Lang, G. *et al.*, *Phys. Rev.*, 2005, **B72**, 094404.
97. Foo, M. L. *et al.*, *Phys. Rev. Lett.*, 2004, **92**, 247001.
98. Takada, K. *et al.*, *Nature*, 2003, **422**, 53.
99. Hasan, M. Z. *et al.*, *Phys. Rev. Lett.*, 2004, **95**, 146401.
100. Maekawa, S. *et al.*, *Physics of Transition Metal Oxides*, Springer-Verlag, Berlin, 2004, Ch. V.
101. Katsufuji, T., Taguch, Y. and Tokura, Y., *Phys. Rev.*, 1997, **B56**, 10145.
102. See e.g. Morin, F., *J. Phys. Rev. Lett.*, 1959, **3**, 34.
103. McWhan, D. B. and Rameika, J. P., *Phys. Rev.*, 1970, **B2**, 3734.
104. Keller, G. *et al.*, *Phys. Rev.*, 2004, **B70**, 205116.
105. Kasinathan, D., Koepernik, K. and Pickett, W. E., *N. J. Phys.*, 2007, **9**, 235.
106. von Loheneysen, H. *et al.*, *Rev. Mod. Phys.*, 2007, **79**, 1016.
107. Gegenwart, P., Si Qimiao and Steglich, F., *Nature Phys.*, 2008, **4**, 186.
108. Andres, K., Grabner, J. E. and Ott, H. R., *Phys. Rev. Lett.*, 1975, **35**, 1779.
109. See e.g. Wilson, K. G., *Rev. Mod. Phys.*, 1975, **47**, 773.
110. Nozieres, P. and Blandin, A., *J. Phys. (Paris)*, 1980, **41**, 193.
111. Garner, S. R. *et al.*, *Phys. Rev.*, 2000, **B62**, R4778.
112. Okamura, H. *et al.*, *Physica*, 2008, **B403**, 761.

113. Tsujii, N. *et al.*, *Phys. Rev. Lett.*, 2005, **94**, 0572; Canfield, P. C. *et al.*, *Physica*, 2008, **B403**, 844.
114. Lonzarich, G. and Taillefer, L., *Phys. Rev. Lett.*, 1988, **60**, 1570.
115. Kuchler, R. *et al.*, *Phys. Rev. Lett.*, 2006, **96**, 256403.
116. von Loheneysen, F., *J. Phys. Cond. Mat.*, 1996, **8**, 9689.
117. Paschen, S., *Physica*, 2006, **B378–380**, 28.
118. Nakatsuji, S., Pines, D. and Fisk, Z., *Phys. Rev. Lett.*, 2004, **92**, 016401; Curro, N. J. *et al.*, *Phys. Rev.*, 2004, **B74**, 235; Yang Yifeng and Pines, D., *Phys. Rev. Lett.*, 2008, **100**, 096404.
119. Nozieres, P., *Ann. Phys.* (*Paris*), 1985, **10**, 19; Vidyadhiraja, N. S. *et al.*, *Europhys. Lett.*, 2000, **40**, 459.
120. Steglich, F. *et al.*, *Phys. Rev. Lett.*, 1979, **43**, 1892.
121. Steglich, F., *J. Phys. Soc. Japan*, 2005, **74**, 1.
122. Mathur, N. D. *et al.*, *Nature*, 1998, **394**, 39.
123. Saxena, S. S. *et al.*, *Nature*, 2000, **406**, 587.
124. Nakatsuji, S. *et al.*, *Nature Phys.*, 2008, **4**, 603.
125. See e.g. Miyake, K., *J. Phys. Cond. Mat.*, 2007, **19**, 125201.
126. Hertz, J. A., *Phys. Rev.*, 1974, **B14**, 1165.
127. Sachdev, S., *Quantum Phase Transitions*, Cambridge University Press, Cambridge, UK, 1999.
128. Si, Qimiao, *J. Phys. Condens. Matter*, 2005, **17**, R1025.
129. Senthil, T. *et al.*, *Science*, 2004, **303**, 1490.
130. See e.g. Moriya, T., *Proc. Jpn. Acad.*, 2006, **B82**, 1.
131. Georges, A.,arXiv: cond-mat/ 0403123.
132. Lee, P. A., Nagaosa, N. and Wen, X.-G., *Rev. Mod. Phys.*, 2006, **78**, 17.
133. Muller-Hartmann, E., *Z. Phys.*, 1989, **B74**, 507.
134. Metzner, W. and Vollhardt, D., *Phys. Rev. Lett.*, 1989, **62**, 324.
135. Georges, A. and Kotliar, G., *Phys. Rev. B*, 1992, p. 5, 6079.
136. Anderson, P. W., *Phys. Rev.*, 1961, **124**, 41.
137. See for example Blumer, N., 0801.12222 v1 (cond-mat str-el)
138. Hirsch, J. E. and Fye, R. M., *Phys. Rev. Lett.*, 1906, **56**, 2521.
139. Logan, D. E., Eastwood, M. P. and Tusch, M. A., *J. Phys. Condens. Mat.*, 1998, **10**, 2673.
140. See e.g. Florens, S. and Georges, A., cond-mat/ 04043342 v2.
141. Maier, J. *et al.*, *Rev. Mod. Phys.*, 2005, **77**, 1027.
142. Luttinger, J. M. and Ward, J. C., *Phys. Rev.*, 1960, **118**, 1417.
143. Potthoff, M., arXiv: cond-mat/0511729v1/[cond-mat.str-el].
144. Shim, J. H., Haule, K. and Kotliar, G., *Science*, 2007, **318**, 1615.
145. Jacob, D., Haule, K. and Kotliar, G., arXiv: cond-mat 08051383 (cond-mat str-el).