Advances in the Theory of Correlated Materials Under Extreme Conditions

Summary: The change in the electronic state of a material with variation of, say, pressure and temperature is a fascinating process, especially if it entails a complete metamorphosis in many or all of the basic characteristics of a solid: conducting and magnetic behavior, optical properties (color), and sound and heat transfer. To achieve a microscopic description of such fundamental transitions in real materials is a grand challenge for computational scientists. Recently, the CMSN PCSCS collaborative research team has made important progress in meeting this challenge.

The Mott transition, in which electron states in solids evolve from localized to delocalized, the material converts from insulator to metal and changes color, and magnetism and volume may collapse abruptly, has been the subject of intense study for fifty years. The process involves the discontinuous change in electronic correlation effects – the manner in which electrons react to each other. Developing theoretical techniques for describing this process microscopically required decades (1950s to 1990s) of research for the case of a single electronic state per cell. Real magnetic materials, however, have several correlated states and usually several atoms per cell, which provide many additional possibilities and point to the challenge for the next decade. Conventional electronic structure theory models this process incorrectly as a continuous crossover from insulator to metal followed by a decrease in the moment, possibly culminating in a first-order volume change [1].

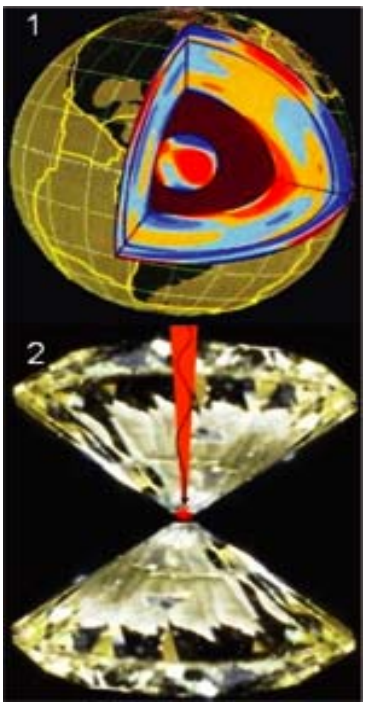

FIG. 1. Schematic cutaway of one octant of the earth's interior (top), showing layers with successively higher pressures and higher temperatures. The bottom panel shows a diamond anvil cell apparatus, in which extreme conditions can be created: pressures up to 2 Megabar and with laser heating temperatures up to 2000-3000 C. (From a drawing by K. Murphy, Salt Marsh Image Library.)

The classic Mott insulators are the transition-metal monoxides (MnO, FeO, CoO, NiO), with FeO being an important material for geophysicists because of its solubility in magnesiowüstite, which is believed to be a crucial constituent of the lower mantle [2]. The pressures at that boundary can be probed in the laboratory using diamond anvil cells, as suggested in pictorial form in Fig. 1. Another important monoxide is Li-substituted CoO, which is the active component in portable power supplies (batteries). Only recently has the Mott transition finally been observed in one

of these classic systems. High-pressure experimentalists at LLNL measured a conductivity increase by several orders of magnitude [3], and a second LLNL team that included UCD students in collaboration with PCSCS team members, observed a structural change, volume collapse, and magnetic moment collapse in MnO in the vicinity of 100 GPa [4]. A schematic of the pressure-temperature phase diagram is shown in Fig. 2.

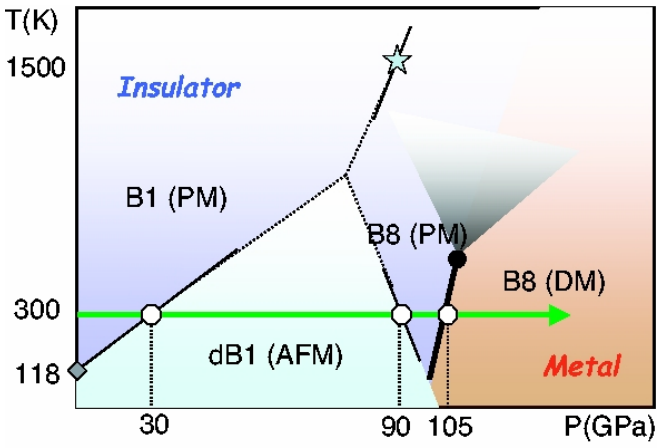

FIG. 2. A conceptual pressure-temperature phase diagram of MnO, based on data in the reference list. The heavy line around 100 GPa (100 GPa ≡ Mbar) denotes the Mott transition. B1 and B8 structures are rock salt and NiAs, respectively; dB1 is slightly distorted B1. PM, AFM, DM indicate paramagnetic, antiferromagnetic, and disordered magnetic, respectively. Figure from C. S. Yoo, LLNL.

A broad PCSCS collaboration of eleven scientists from seven institutions, using four separate but related computational approaches to the correlated electron problem [5], have chosen MnO as the system of choice for applying the methods and comparing results. Collaborations of this type are rare, but can be very helpful, especially in areas where developments are occurring rapidly and differing approaches need to be contrasted. There were considerable variations in the predictions of the four methods in some properties (critical pressure, amount of volume collapse), reflecting the importance of correlation corrections and sensitivity to how they are included. However, all four methods agreed on one unanticipated feature: the moment collapse is from a (spin) S=5/2 state to a S=1/2 state, rather than to a nonmagnetic state (S=0), as in the common scenario of a Mott transition. A recent interpretation of x-ray emission spectroscopy on MnO in the 100 GPa regime supports a S=1/2 state of the Mn ion [6] in the collapsed phase at high pressure.

One of the correlated band methods [5, 7] provided an especially novel low-spin state: each Mn 3*d* orbital is still singly occupied as in the large volume, high-spin states, but two of the orbitals have flipped their direction of spin. Isocontour plots of the spin density (distribution of the magnetization per unit volume) on the Mn ion before and after the moment collapse are pictured in Fig. 3. Because such a state was so unanticipated, two accurate and independent codes (FPLO [8, 9] and Wien2K [10]) were used to establish it as a robust solution. Analysis of the

energetics [7] has revealed the microscopic mechanism: the two orbitals that flip their spin retain the most anisotropic Coulomb interaction energy on the Mn ion, they maximize bonding with the oxygen 2*p* states, and keeping each Mn *d* orbital polarized retains much of the magnetic exchange energy. These predictions, which suggest clear changes in the Mott transition between room temperature (no magnetic order) and at low temperature in the antiferromagnetic phase, can be tested using Mössbauer spectroscopy (which can be done in a pressure cell). The occurrence of such spin-flip states could occur in other correlated systems at ambient pressure, where they would be much easier to study experimentally.

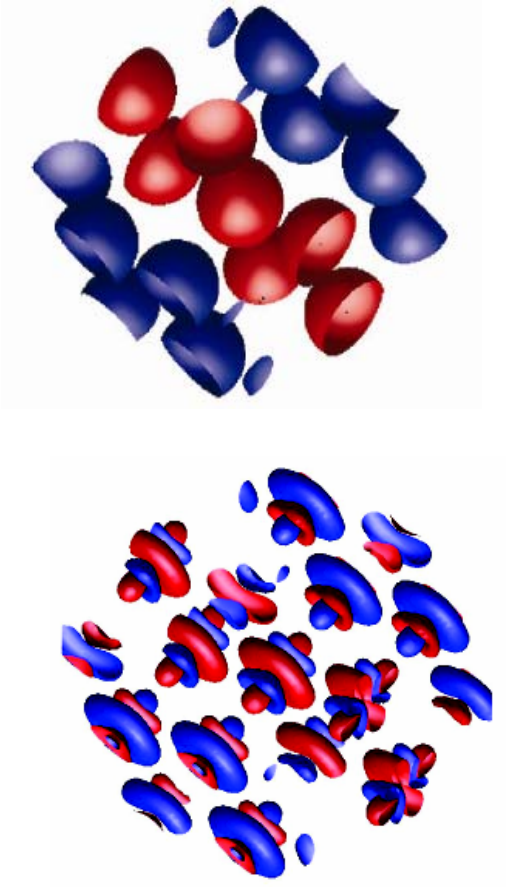

FIG. 3. Isosurface plots of Mn ion spin density, with red and blue indicating opposite sign. Top: before collapse, showing the spherical S=5/2 ion, with (111) layers of aligned spins. Bottom: after collapse, displaying the extreme anisotropy of the spin density of the S=1/2 state. The magnetic order is unchanged: alternating directions of cubic (111) layers in the rock salt structure, of (0001) layers in the hexagonal NiAs structure.

Our PCSCS team is in the process of addressing this “signature challenge” (microscopic theory of the Mott transition in real materials) with additional techniques. A new auxiliary field quantum Monte Carlo technique that samples the many-electron wave function directly has been found to provide accurate energies for the MnO molecule (as well as in simpler molecules) [11] and will soon be applied to crystalline MnO. An all-electron dynamical mean-field-theory code developed by the team that includes the effect of dynamic behavior within the Mn ion is currently being applied to MnO under pressure [12]. The PCSCS team is applying additional techniques to MnO and related correlated materials, and substantial breakthroughs in quantifying what happens at the Mott transition are expected in the next 2-3 years.

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