METAL-INSULATOR TRANSITIONS

The problem with spins

The metal–insulator Mott transition, which has been extensively studied by means of charge transport, is now detected through the electron spins in a two-dimensional organic conductor.

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Understanding the electronic properties of metals in terms of electron-energy bands was a chief success of quantum mechanics in condensed-matter physics in the 1930s. According to the band picture, open-shell orbitals of metal atoms should lead to partially filled energy bands in crystalline compounds, a situation that favours high electron conduction as the density of electron states at the highest occupied state in the band (also called the Fermi energy) would be finite. However, this successful model has its limitations in many transition-metal compounds, which behave like insulators in spite of the conduction band being partially filled.

This unexpected behaviour was explained by Nevill Mott, who described the role of Coulomb repulsion between carriers as a powerful factor responsible for electron localization. He thus introduced a new concept known as the Mott insulator, which can be modelled by the so-called Hubbard Hamiltonian with the addition of an on-site Coulomb repulsion added to the usual hopping term. This energy represents the price to be paid for the presence of two carriers on the same atomic site, a prerequisite for their delocalization over the whole sample.

Mott also recognized that this insulator can undergo a sharp transition towards a metallic state provided the screening of the Coulomb potential becomes weak enough to prevent the formation of bound states between electrons and holes (that is, electron vacancies). Consequently, Mott was the first to predict that the transition between the two states is discontinuous (first order) as the pressure is varied, with the existence of a phase-coexistence regime (metallic and insulating) limited by spinodal lines on both sides of the first-order line that ends at a critical point in the pressure–temperature phase diagram (Fig. 1). Such a picture is actually reminiscent of the conventional liquid–gas transition. Reporting on page 880 of this issue, Fumitaka Kagawa and co-workers have now extended the Mott problem to the spins.

In the 1960s, the existence of Mott insulators received much support experimentally from studies of the electronic transport of vanadium sesquioxides \( (V_2O_3) \) either under pressure or doped with isovalent atoms of chromium. Since the discovery of high-temperature superconductivity, understanding the properties of Mott insulators has become of primary importance because the cuprate superconductors all originate from half-filled band insulators that become metallic and superconducting with doping. The transport properties on both sides, as well as through the transition have been described successfully by the dynamical mean field theory (DMFT). According to DMFT, the electrons change their behaviour depending on the timescale of the measurements. At very short timescales they are localized by correlations, which correspond to the ‘bad metal’ region with a mean free path not larger than the intermolecular distance at high temperatures, whereas they can be considered to be delocalized at longer timescales (the usual Fermi-liquid domain at low temperatures).

The work of Kagawa et al. addresses another aspect of the Mott transition, namely the change in the spin degrees

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**Figure 1** Pressure–temperature phase diagram of the Mott transition. The spinodal lines \( (U_i, U_M) \) defining the light-blue coloured region of coexistence of insulating (paramagnetism of localized spins) and metallic phases (Pauli paramagnetism) are indicated (where the thick continuous line is the virtual boundary between the two phases). The stability of the phases is governed by the ratio \( U/W \), which is pressure dependent. The invisible first-order Mott line where the free energies of both phases are equal is situated within the coexistence regime and becomes second order (dotted line) beyond a critical end-point (the bright spot near the centre of the chart). A discontinuity of the spin relaxation is observed only at temperatures lower than the critical temperature. The compound \( \kappa - \text{Cl} \) shows a long-range antiferromagnetism below 25 K on the insulating side (AF) and a superconducting order below 12 K on the metallic side (SC).
of freedom accompanying the change of conductivity at the transition. They focus on the layered conducting organic salts based on the electron-donor molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF), in particular k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl, hereafter called k-Cl, where k signifies a particular polymorph of these compounds. As already shown by one of the authors, k-Cl is a member of a broader family of compounds in which the ionic radius of the halogen atom provides a means of fine tuning the internal pressure. However, the main interest of the present work performed on a single compound lies in the use of hydrostatic helium gas pressure to monitor the stability of the different phases at low temperature. The use of helium pressure as the control parameter is a significant improvement over alloying techniques because it enables the fine adjustment of the experimental conditions, minimizes the role of impurities that could affect the transition, and allows both isothermal and isobaric sweeps. The application of pressure on the two-dimensional (2D) conductor enhances the overlap between molecular orbitals of neighbouring molecules and, in turn, increases the bandwidth W of the 2D conductor. The net effect of pressure amounts to a reduction of the ratio $U/W$, that is, the strength of the correlations.

Previous studies of the same material only dealt with charge transport, $^1$H NMR and alternating-current-susceptibility experiments. They established that in several respects k-Cl can be thought of as a prototype compound for the study of the Mott transition, supporting the early conjectures of Mott — in particular, the existence of a critical point at the end of the first-order line of transitions. Until now, hardly anything was known about the behaviour of the spin degrees of freedom through the transition. Using $^{13}$C-enriched molecules, Kagawa et al. managed to follow the electron-spin susceptibility by means of the $^{13}$C Knight shift and their spin–lattice relaxation throughout the Mott transition, sweeping either temperature or pressure.

As the establishment of metallicity can be related to an increase in the probability of the occurrence of doubly occupied sites, switching localized spin into delocalized electrons (becoming Pauli paramagnetic), a discontinuity is expected when crossing the first-order Mott line in both static and dynamic properties of the electron spins. Phase transitions can be classified according to the critical exponents of various observable quantities around the critical end-point. DMFT predicts that the three-dimensional Mott transition is in the regime of the liquid–gas phase change, in common with the magnetization of the Ising spin model in statistical mechanics. However, Kagawa and co-workers claim that a similar criticality exists in both magnetic and conductance experiments. This feature supports the existence of an unusual criticality for the Mott transition of 2D materials, in contrast with the situation encountered in chromium-doped V$_2$O$_5$, where the order parameter behaves in the critical regime like the order parameter of the liquid–gas transition.

A new criticality for the 2D Mott transition is admittedly a very exciting prospect because it has been proposed that it could characterize the situation of ‘marginal’ quantum criticality. Once more, these results have shown how helpful organic conductors can be for our understanding of basic phenomena of condensed matter.

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References
1. Mott, N. F. Metal to Insulator Transitions (Taylor & Francis, 1974).