JOURNAL OF SOLID STATE CHEMISTRY 88, 2–4 (1990)

Introduction: Mott Insulators, Correlated Metals, High-Temperature Superconductors

The physics of transition-metal compounds comprises three specific classes of solids: magnetic (Mott) insulators, (strongly) correlated metals, and high-temperature superconductors. Below we supply the principal definitions and list some of the basic questions pertinent to these three classes of solids. These definitions provide a perspective of specialized articles included in this volume.

1. Mott Insulators

The *magnetic insulators* are the systems which are insulating (or semiconducting) and which order magnetically below a certain critical temperature. They can be divided into two classes: *Mott insulators* and *Heisenberg magnets*. The Mott insulators order antiferromagnetically below the Néel temperature and undergo a transition to the metallic phase at T_N. The Heisenberg magnets are insulating in both the antiferromagnetic and the paramagnetic temperature regimes. Sometimes the Heisenberg magnets are regarded as being in the Mott insulating state in the whole physical range of temperatures; examples of the latter are NiO, CoO, MnO, Cr_2O_3, and many other compounds.

The Mott insulators are not diamagnetic; this feature distinguishes them from the band (Bloch–Wilson) insulators. The antiferromagnetic and paramagnetic properties below and above T_N cannot be explained by orbital effects; this is why those systems must contain uncompensated (unpaired) spin moments. The presence of the moments is rationalized by *Hund's rules*, which in present-day language are expressed in terms of ferromagnetic, intraatomic direct exchange interaction among the electrons located on different orbitals and belonging to the same $3d$ shell.

Although most of the thermal, transport, and magnetic properties of the Mott insulators have been studied extensively (for a review, see Ref. (*1*)), the fundamental question concerning the nature of the wave function of the $3d$ electrons has not as yet been answered adequately. The wave function cannot be of the Bloch type because such an approximation would invariably lead to a stable metallic ground state for systems with an odd number of electrons (MnO, CoO), if antiferromagnetic ordering is disregarded. Since this is not so, we must find a better way of expressing the *electron correlations*, i.e., the circumstance that the dynamics of a single electron is influenced by the degree of occupancy of the state involved.

To illustrate the last point let us note that the system containing N sites and one electron per site has 2^N available atomic configurations, and the number of single-particle states is N if the electrons are simply in configurations of localized moments (i.e., if no doubly occupied or empty site configurations are allowed). On the other hand, if the electrons with spin $\sigma = \uparrow$ are regarded as being independent of those with $\sigma = \downarrow$ (the assumption commonly made when Fermi–Dirac statistics is applied), then the number of available configurations is 2^{2N}, and the number of available single-particle states is $2N$. In other words, if the system containing N orbitals and N electrons is going to be a magnetic insulator, then half of the total number of magnetic single-particle

0022-4596/90 $3.00

states available for the electron gas configuration must become inaccessible for electrons constituting a Mott insulator. The exclusion of N states from the total $2N$ states exhibits the simplest form of strong electron correlations. In other words, in a correlated electron system a single-particle wave function must incorporate the conditional probability which expresses the dynamics in the presence of other electrons in the same shell.

In the actual situation of $3d$ compounds we usually cannot neglect the hybridization of $3d$ states with the states of anions (e.g., $2p$ or $3p$ oxygen states in the case of oxides). In this connection a distinction must be made between two types of magnetic insulators, namely charge-transfer (C-T) and Mott–Hubbard (M–H) insulators. In the C-T case the bandgap originates from cation–anion electronic (charge-transfer) transitions; in the M–H case the gap is determined by the d–d transitions. The nature of the electronic states in, e.g., $3d$ oxides is influenced by a combination of factors: intra-atomic (d–d) interactions, crystal-field splitting of the $3d$ levels, and $3d$–$2p$ hybridization. Models incorporating these three factors do not lead to unique conclusions, as can be seen from the discussions of the two papers included in this volume (*2*).

2. Metallic Phase of Correlated Electrons and the Metal–Insulator Transition

The description of the regime intermediate between simple metals and magnetic insulators constitutes a major challenge to solid state theorists, because in these systems the Coulomb interactions between electrons are comparable to their kinetic energies in the solid. This is also the regime in which spectacular metal–insulator transitions take place (see the two contributions on V_2O_3 (*3*)). The metallic phase, which under relatively small changes in either temperature, alloy composition, or pressure transforms into a Mott insulator, is called an *almost-localized Fermi liquid*. This electron liquid is characterized by a large effective mass (with the mass enhancement in the range 2–10), by a large T^2 term in resistivity at low temperatures, and by antiferromagnetic ordering with a small magnetic moment. The large effective mass will lead to the enhancement of the electronic specific heat and of Pauli paramagnetism.

The Mott transition is associated with a transformation of itinerant electrons composing an almost localized Fermi liquid into a lattice of localized magnetic moments. On the metallic side the concepts such as the Fermi surface or quasi-momentum are still applicable. On the insulating side they lose meaning. Also, the metal–insulator boundary represents the borderline for applicability of the Fermi–Dirac distribution since no double occupancies of the same orbital state are allowed in the Mott insulating phase. Thus, the Mott transition specifies a dividing line: On the metallic side the concept of Bloch (itinerant) states is applicable to the $3d$ electrons, while on the insulating side atomiclike (soliton?) $3d$ states are realized in the solid state.

One of the principal problems concerning this metal–insulator transition is envisaging how a thermal stimulus of 150 K (in the range of 10 meV) could induce radical changes in the nature of electronic states on the scale of electronvolts. It turns out that in systems like V_2O_3 the positive Coulomb repulsion and the negative band energies are of comparable magnitude and therefore almost compensate each other. Hence, much smaller exchange energy, or entropic (thermal) or atomic disorder contributions to the total free energy produce qualitative changes in the nature of the many-electron states. The detailed calculations (*4*) allow one to theoretically construct the full diagram for systems like V_2O_3. A more complete theory requires the inclusion of the

lattice effects in these electronic phase transitions. A simple workable approach including lattice effects has not yet been constructed.

3. High-Temperature Superconductors

The study of the entire area of transition metal compounds (mainly oxides) has gained enormous interest since the discovery of high-temperature superconductivity. Three basic properties of these systems should be mentioned: (i) the close connection between antiferromagnetism and superconductivity; (ii) the metal–insulator transition as a function of stoichiometry (e.g., for $La_{2-x}Sr_xCuO_4$ for $x \approx 0.05$); and (iii) the onset and subsequent disappearance of the superconducting phase as a function of the nonstoichiometric parameter x ($0.05 \lesssim x \lesssim 0.30$ for $La_{2-x}Sr_xCuO_4$).

The crucial point for these systems is that the parent compounds are antiferromagnetic insulators (cf., e.g., La_2CuO_4, Nd_2CuO_4, and YBa_2CuO_6), and can be regarded as Mott insulators. The presence of antiferromagnetic ordering may prove to be as important as the isotope effect in classic superconductors. Namely, this circumstance points to the antiferromagnetic interaction (5) and spin fluctuations as a mechanism for the singlet pairing that produces the superconducting state in the liquid-nitrogen (and above) temperature range. The principal attractive feature of this mechanism is that one can treat antiferromagnetism, metal–insulator transitions, and superconductivity on the same footing and within a single theoretical framework of the *theory of correlated electrons in narrow-band systems*. The field of high-temperature superconductivity forces us to unify such concepts as superconductivity, antiferromagnetism, Hubbard subbands, and correlated electron states, which have been regarded as completely disparate so far.

The fundamental difficulty in understanding the high-temperature superconductors arises from the fact that we do not know the exact nature of the metallic phase in the normal state. Is it a correlated Fermi liquid or is it a new type of spin liquid in which the energy associated with exchange interactions among electrons is comparable to, or even larger than, their kinetic energy? Does this mean that the localization we encounter in $La_{2-x}Sr_xCuO_4$ for $x \leq 0.05$ is induced by antiferromagnetic interactions? What is the role of disorder introduced by Sr atoms or oxygen nonstoichiometry? These types of basic questions must be answered if we are to be able to synthetize new systems with improved characteristics such as a higher value of the transition temperature or high critical currents.

We hope that the present volume summarizes at least some aspects of research of the rapidly developing field of correlated electron systems and in particular high-temperature superconductors.

JOZEF SPAŁEK

References

1. N. F. MOTT, "Metal–Insulator Transitions," 2nd ed. Taylor & Francis, London, 1990; B. H. BRANDOW, *Adv. Phys.* **26**, 651 (1977); J. B. GOODENOUGH, *Prog. Solid State Chem.* **5**, 145 (1971); P. W. ANDERSON, *in* "Frontiers and Broderlines in Many-Particle Physics" (R. A. Broglia and J. R. Schrieffer, Eds.), North-Holland, Amsterdam, 1988.
2. J. ZAANEN AND G. A. SAWATZKY, *J. Solid State Chem.* **88**, 8 (1990); B. H. BRANDOW, **88**, 28 (1990).
3. M. YETHIRA, *J. Solid State Chem.* **88**, 53 (1990); J. SPAŁEK, **88**, 70 (1990).
4. J. SPAŁEK, A. DATTA, AND J. M. HONIG, *Phys. Rev. Lett.* **59**, 728 (1987).
5. P. W. ANDERSON, *Science* **235**, 1196 (1987).