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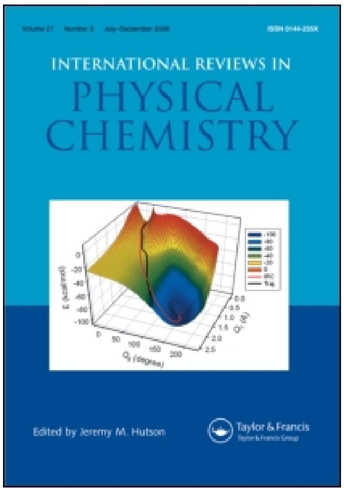

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What is a Metal?

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WHAT IS A METAL?

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ABSTRACT

A survey is given of simple predictive models and operational definitions of the metallic state. The purpose of this work is to highlight the essential features of electron localization versus itinerancy in both crystalline and disordered materials. Particular attention is given to systems that not only extend to the limiting insulating and metallic regimes, but also embrace the transition region between these two canonical states. Examples include the periodic table of the elements, doped semiconductors, metal solutions, expanded (supercritical) metals, transition-metal oxides, and small metallic particles or clusters. The necessary and sufficient conditions for metallic character in these systems are reviewed in terms of the Mott, Hubbard and Anderson views of the metallization process.

In addition, the concept of a polarization catastrophe at the metallization onset is introduced, with special reference to both its experimental realization and its predictive ability. The notion of a polarization, or dielectric catastrophe stems from a paper by Herzfeld in 1927, which seems to be the first consideration of metal-insulator transitions in condensed matter. In Mott's original theory of 1949, the transition from insulating to metallic behaviour takes place when an ionic potential, dielectrically screened to nearby atoms, now releases a valence electron. This suggests a connection between the Herzfeld/Mott views of the metal-insulator transition.

The corresponding transition in a disordered system is also described; here the concept of a minimum metallic conductivity separating localized and itinerant electron states is reviewed.

Finally, a section is devoted to a consideration of the electronic properties of small metallic particles. A preliminary qualitative description is given which centres around the corresponding question 'How many atoms maketh metal?'

1. PREAMBLE

Prior to Sir Humphry Davy's discovery and isolation of sodium and potassium in 1807, the established metals (iron, lead, gold, silver, etc.) were characterized as high-density elements possessing hallmark physical properties of unusual lustre, malleability, ductility and elasticity. Davy's monumental discovery of 1807 posed a major dilemma to this classification of metals since both sodium and potassium possessed many of the physical and chemical properties of the known metals, but had exceptionally low

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densities. Indeed, Erman and Simon in 1808 attempted to resolve this difficulty by proposing that sodium and potassium be termed 'metalloids'—meaning 'those that are like metals'—to indicate that they are similar to metals *only in certain respects* (Goldsmith, 1982).

In hindsight we can perhaps provide some resolution to the dilemma of the low-density alkali *metals* by considering the electronic properties of the isolated alkali *atoms*. The first ionization energy for the group I atoms ranges from 5.39 eV for lithium, to 3.89 eV for caesium. As ionization energies go, these are relatively small values. We recognize alkali atoms as monovalent species with one n*s* valence electron outside a closed shell, and this valence electron is relatively loosely bound and may easily be lost. These ideas have led quite naturally to an established picture of alkali metals as an agglomeration of monovalent metal cations with a permeating itinerant-electron gas of ionized valence electrons. In the metallic state, *all* the valence electrons have a parentage in *all* of the ions and consequently can move freely from one ion to another (*Fig. 1*). As Ziman (1964) has so persuasively put it '..., instead of having a cosy arrangement in which each ion has its "own" electron bound tightly to it, we have a sort of communist society ...'. Thus, itinerancy and mutual ionization of the n*s* valence electron in the alkali metal series are apparently achieved at quite low elemental densities in the condensed state.

In contrast, atoms far to the right of the periodic table have considerably larger ionization energies. For example, the first ionization energies of gold (9.22 eV) and

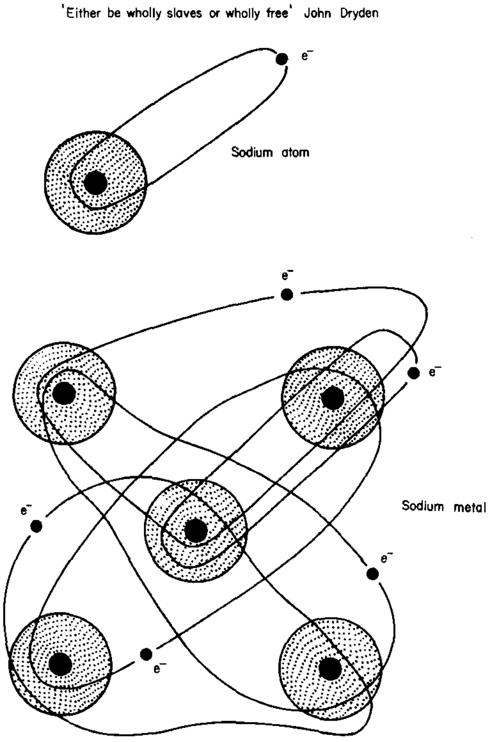

FIG. 1. Electrons in atomic and metallic sodium. Adapted from Ziman (1964). The quotation is from 'The hind and the panther', by John Dryden (1631–1700; first published 1687).

mercury (10.44 eV) are extremely high due to insufficient screening of the valence 6*s* electron in the atom by both the underlying d- and f-electron shells. Obviously single-atom ionization energies, when taken in isolation, provide no realistic guide to the occurrence of metallic character in the condensed state. In spite of these high ionization energies for the heavier atoms, metallic status in the condensed state of these elements probably arises quite simply because of their low atomic volumes. This intimate and all-important link between atomic properties, density and the metallic state was recognized some considerable time ago by K. F. Herzfeld (1927). Possibly because of the rapid advances in quantum physics around that period this simple idea based on atom size was lost (Cohen, 1968). In the last decade, however, a major development in the study of condensed phases has been the return to what one might term the 'atomistic' or 'real space' view of the metallic state and the associated problem of the transition from itinerant- to localized-electron regimes (Mott, 1974; Friedman and Tunstall, 1978; Edwards and Sienko, 1982). In this, the Herzfeld approach now has an important role to play.

With the advent of quantum mechanics a theory—developed by A. H. Wilson (1931)—emerged which set out metallic vs. insulating status in terms of the way in which atomic energy levels merged into bands as the atoms coalesced in the condensed phase. However, as we shall demonstrate in Section 2, the Wilson band theory does not allow an a priori prediction of metallic vs. insulating behaviour. In particular, it predicts to be metals some substances that are known in fact to be insulators! In addition, for the vast majority of real situations, randomness or disorder plays a central role in the detailed consideration of electronic properties. For these systems the loss of lattice periodicity has a disastrous effect on the traditional methodology of solid state physics (Section 4). The methods of group theory, in which one relies upon translational symmetry in a system, are no longer applicable. In fact a point of some concern is the continued use of traditional band theory results in the interpretation of experiments in random systems, in spite of their self-evident inapplicability (Elliott *et al.*, 1974). For these reasons we purposely neglect any detailed consideration of band theory, other than that required to highlight its deficiencies in real systems (Section 2). Our overall aim here is to bring out some of the essential physics of electron localization vs. itinerancy in both ordered and disordered systems. The orientation of this report is thus primarily qualitative and conceptual. Nevertheless, we shall also present experimental evidence to show that the various conceptual models of answering the question 'What is a metal?' are intrinsically sound and capable of precise mathematical treatment.

2. THE PROBLEM AT HAND: METALS vs. INSULATORS

A sharp distinction exists in nature between metals and insulators for temperatures approaching the absolute zero. In elemental metals, in certain compounds (e.g., ReO_3) and in heavily doped semiconductors, the electrical resistivity (ρ) tends to a finite value (or zero, in the case of superconductors) as the temperature tends to zero; in insulators (including certain compounds and lightly doped semiconductors) it tends to infinity. This fundamental distinction is illustrated quite dramatically in *Figure 2* by recent 'zero-temperature' conductivity studies on silicon doped with phosphorus (Rosenbaum *et al.*, 1980; Sasaki, 1980). The metal-insulator transition in P:Si occurs at a critical phosphorus density (n_c) of 3×10^{18} electrons cm^{-3}: for samples with $n < n_c$, the material is clearly insulating for $T \to OK$ ($\rho \to \infty$); for $n > n_c$ the material is metallic (ρ finite as $T \to OK$).

Therefore, the electrical conductivity of a material at the absolute zero of

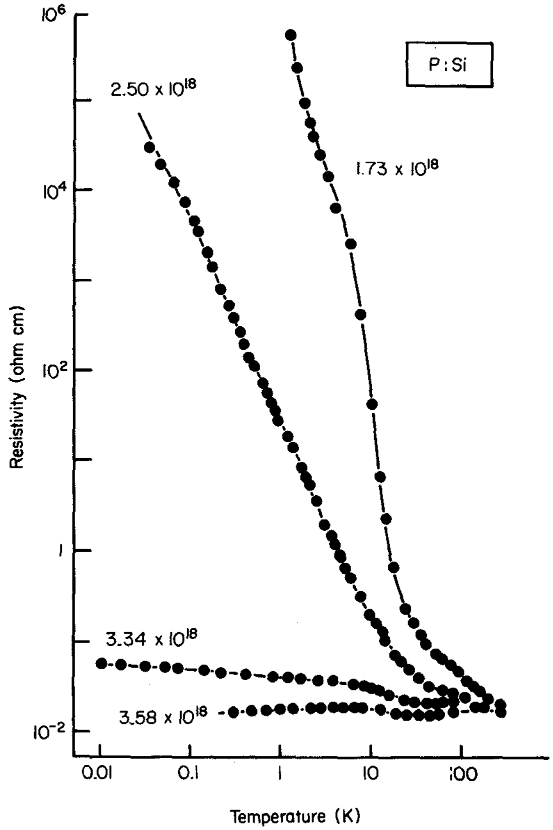

FIG. 2. The electrical resistivity of a series of phosphorus-doped silicon samples as a function of temperature. The curves are labelled with the net donor (*P*) density, *n*. For these materials, the metal-insulator transition occurs at a concentration between 2.50×10^{18}, and 3.34×10^{18} electrons cm^{-3}. Adapted from Sasaki (1980); *see also Figure 24*, which shows 'zero-temperature' conductivities of the P : Si system (Rosenbaum *et al.*, 1980).

temperature is a complete, operational definition of two canonical states of condensed matter, viz. metals and insulators. At temperatures above the absolute zero, this distinction becomes somewhat ambiguous, and subject to personal opinions and interests. Indeed a formal definition of a metal will invariably mean different things to different investigators. A physicist's view of a metal would probably be of a solid with a Fermi surface (Ziman, 1964; Kittel, 1971). Certainly the concept of the Fermi surface, as developed in quantum physics, provides a precise and elegant explanation of the main physical properties of metals. In this context we distinguish itinerant electrons in a metal from their localized electron counterparts in insulators by those properties that depend upon the existence of a Fermi surface, i.e., a finite density of non-localized states at the Fermi energy (Goodenough, 1967). Therefore, a metallic system should exhibit a sharp energy discontinuity in the occupied density of states function, $D(E)$, at the characteristic Fermi energy.

Photo-electron spectroscopy of solids can, under certain circumstances, monitor $D(E)$ directly. With monochromatic high-energy photons (e.g., He II excitation), the photo-electron spectrum of a solid should correspond simply to the density of occupied states (Orchard, 1977). *Figure 3* shows an elegant 'chemical' example of the use of photo-electron spectroscopy in the study of ruthenium valence electrons in a series of ternary ruthenates and perovskites (Egdell *et al.*, 1983). The photo-electron spectra of the lead, and bismuth ruthenate each show a signal from the ruthenium 4d band, consistent with their metallic status. However, the density of states at the Fermi energy decreases sequentially until $Y_2Ru_2O_7$, an insulating pyrochlore, which has a zero density of states. The photo-electron spectra of $SrRuO_3$ and $CaRuO_3$, two metallic perovskites (Goodenough, 1971), are included for comparison in the figure.

Many other elegant physical techniques, for example, the de Haas van Alphen effect, have been used to probe the geometric structure of the Fermi surface. However, the task of extracting detailed information from these types of measurements is a formidable one—and beyond the scope of this article. In addition, metals can be liquid or solid, amorphous or crystalline, one-, or multi-component materials, and the operational usefulness of such 'Fermiology' is perhaps questionable (Hurd, 1975).

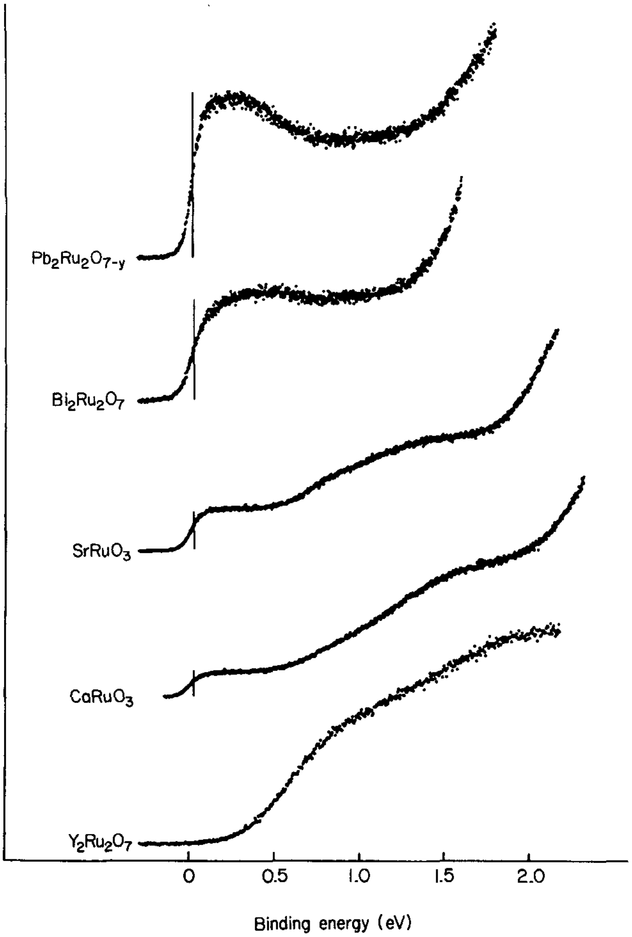

FIG. 3. The photo-electron spectra of ruthenium (4*d*) valence electrons in a series of ternary ruthenates ($M_2Ru_2O_7$), and perovskites, $SrRuO_3$ and $CaRuO_3$ (Egdell *et al.*, 1983).

Our interest in the following sections lies in attempting to provide certain operational definitions, and predictive models capable of characterizing the metallic state. An essential part of this scheme lies in precisely defining the boundary conditions between the two limiting electronic regimes, viz. localized- and itinerant-electronic states. For example, it is always possible, at least in principle, to transform any metallic system into an insulating (or semiconducting) state via expansion to low densities, or by alloying with a highly electronegative non-metal *or* metal (Warren, 1981). Conversely, it is possible to induce a transition from the insulating to metallic states by changing a basic thermodynamic variable such as temperature, density or composition. Therefore, our canvas here must be to include not only the experimental, operational properties of the metallic state, but we must also account for the precise conditions required for a metal-insulator transition. The two questions: 'What is a metal?' and 'When does a metal transform to an insulator?' are indeed inseparable.

To illustrate this viewpoint, we consider the periodic table of the elements (Edwards and Sienko, 1983). At pressures and temperatures found on the planet Jupiter, all elements, including hydrogen, are probably metallic (Metz, 1973). However, under ambient conditions imposed on our planet, the periodic table of the elements comprises both metals and insulators. In particular, an intriguing demarcation into these two canonical states occurs in the p-block elements (*Fig. 6*). Any predictive model for the metallic state should therefore be able to rationalize this type of behaviour of the elements in terms of a critical density/pressure beyond which metallization occurs.

Accordingly, the most appropriate systems for review are those that not only extend to the limiting insulating and metallic regimes, but also embrace the transition region between the two. *Table 1* shows a variety of systems in which the transition from metallic to insulating status, or vice versa, can be affected via changes in some thermodynamic, structural or compositional variable. This tabulation is meant to be representative, not exhaustive.

A preliminary experimental characterization

At the outset, it is apropos to describe briefly the salient physical properties of the metallic state. The following discussion implies several experimental characteristics associated with, but not exclusive to, elemental metals. Compounds, too, such as certain transition-metal oxides also may exhibit all the obvious traits of metallic character (Goodenough, 1967, 1971).

The most characteristic features of a metal lie in its electrical, optical, and magnetic properties. Of these properties, perhaps the single most outstanding characteristic that sets a metal apart from an insulator is its exceptional electrical conductivity. For example, the alkali metal series have conductivities approaching 10^5 ($\text{ohm}^{-1}\ \text{cm}^{-1}$) at room temperature. For a representative two-component system, saturated sodium-ammonia solutions have an equivalent conductance exceeding that of liquid mercury (Kraus, 1907). In these extreme situations, metallic status is surely undisputed. However, a fundamental question to pose is 'At what value of the electrical conductivity do we transform from itinerant- to localized-electron regimes?' The conductivity studies on the P:Si system clearly show an extremely sharp metal-insulator transition as the donor concentration is scanned through n_c (*Figs 2 and 24*). We will subsequently examine the background to this extremely important question, and discuss the theoretical and experimental basis for a possible, universal minimum metallic conductivity, σ_{min}, separating the two electronic regimes.

In addition to its absolute value at $T = OK$, the temperature dependence of the

TABLE 1. Examples of the metal-insulator transition

	Phase			
System	Metallic state	Non-metallic state	Variable physical parameter	Reference
Periodic table of the elements	sol. (Li) liq. (Si; T > 2000°C)	sol. (I_2) sol. (Si; T < 2000°C)	Atom polarizability, elemental density	Herzfeld (1927) Edwards and Sienko (1983)
Doped semiconductors P:Si, As:Ge, InSb, etc.	sol.	sol.	Change of donor concentration, or magnetic field (InSb)	Alexander and Holcomb (1968) Mott (1974)
Metal-rare gas thin films (4 K) Na:Ar, Pb:Xe	sol.	sol.	Change of metal concentration	Cate *et al.* (1970) Mott (1974)
Solid state oxide materials Na_xWO_3, $La_xSr_{1-x}VO_3$, etc.	sol.	sol.	Metal–metal interaction, electron density	Goodenough (1971)
Metals in non-aqueous solvents Li, Na:NH_3; Li:CH_3NH_2, etc.	liq.	liq.	Change of metal concentration	Thompson (1976) Edwards (1982)
'Expanded-metal' compounds $Li(NH_3)_4$, $Ca(NH_3)_6$, etc.	sol./liq.	sol./liq.	Density change/pressure/ temperature	Thompson (1976) Stacy *et al.* (1982)
Semiconducting alloys CsAu, Mg_3Bi_2	liq.	liq.	Change of concentration	Hensel (1971, 1980)
Metal-salt mixtures Cs:CsCl., etc.	liq.	liq.	Change of concentration	Warren (1981)
Se, Te and their mixtures Se_xTe_{1-x}, etc.	liq.	liq.	Change of chemical structure via temperature/pressure	Warren (1981)
Expanded metals Hg, Cs, Rb, K at high temperatures ($T > 2000°C$)	metallic liq. $-(T > T_c)^{*}-$ metallic liq. $-(T < T_c)-$	non-metallic liq. non-metallic vapour	Expansion to low elemental densities at high temperatures	Freyland (1981) Hensel (1981)

* T_c: critical temperature.

electrical conductivity is also of cardinal importance in determining the electronic status of a material. The transition from metallic to insulating behaviour is generally accompanied by a marked change in the temperature dependence of the electrical conductivity ($\partial\sigma/\partial T$). In a semiconductor, or insulator, the electrical conductivity increases with temperature, whereas in a normal metal it decreases—and at a rate roughly linear at moderate temperatures.

Thermal excitation of electrons across the energy gap, E_G, of an insulator or semiconductor into the lowest unoccupied band can lead to electrical conduction in a sample. The fraction of electrons excited across the gap at temperature T is roughly $\exp(-E_G/2kT)$, where k is the Boltzmann constant. With $E_G \approx 4$ eV at room temperature ($kT \simeq 0.025$ eV), this factor is $e^{-80} \approx 10^{-35}$, and essentially no electrons can be excited across the gap. For an energy gap of 0.25 eV, then the factor $e^{-5} \simeq 10^{-2}$, and observable conduction may occur. The number of electrons excited thermally into the conduction band varies exponentially as $1/T$; hence the electrical conductivity of a semiconductor should increase rapidly with increasing temperature. Compare this with the behaviour for metals where the conductivity is given by

$$\sigma = \frac{ne^2\tau}{m^*}$$

where n is the density of carriers, e is the charge on the electron, m^* its effective mass and τ is the relaxation time for the electron, i.e., the time between resistive scattering events. Thus, the conductivity of a metal decreases with increasing temperature since all the temperature dependence comes from τ, which generally decreases with increasing temperature because of the increase in electron-lattice (phonon) scattering (Meaden, 1966).

A typical metallic one-dimensional inorganic or organic complex exhibits the temperature dependent conductivity illustrated by (TTF)(TCNQ) or (NMP)-(TCNQ) in *Figure 4* (*a*). The common feature is that both prototype materials exhibit a metallic state, i.e. $(\partial\sigma/\partial T) < 0$, at higher temperature and both complexes reach a conductivity maximum at lower temperature. Thus, a metal-insulator transition occurs at a particular temperature, and this is accompanied by a change in the temperature dependence of σ (Miller, 1978). In *Figure 4*(*b*), the logarithm of the electrical conductivity is plotted vs. the reciprocal temperature in a series of liquid Cs–Au mixtures. At a concentration of approximately 0.44 atom fraction Au, corresponding to a conductivity of about 100 ohm^{-1} cm^{-1}, the temperature dependence changes from negative to positive, as the liquid metal transforms to the charge-transfer insulator Cs^+Au^- close to the stoichiometric composition (Hensel, 1980).

Another important characteristic of the metallic state lies in its optical properties. Itinerant electrons in a metal exhibit a reflectance spectrum with a sharp cutoff at the plasma frequency (Kittel, 1963). This reflectance is responsible for the characteristic metallic glitter, although for a variety of reasons, this *single* observation cannot be judged to be an unambiguous hallmark of metallic character* (Anex and Simpson, 1960). However, metallic reflectivity from an itinerant-electron material can indeed be viewed as a manifestation of an infinite dielectric constant (or refractive index), and this aspect is the basis of a simple, but important, predictive criterion for determining when an element or material will exhibit metallic conductivity. Indeed, probably the first detailed consideration of the question 'What is a metal?' was based on the concept of a 'dielectric catastrophe' at the metallic onset (Goldhammer, 1913; Herzfeld, 1927).

The magnetic properties of localized unpaired electrons differ significantly from their

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* All that glitters is not gold . . .', W. Shakespeare, Merchant of Venice, Act II, Sc. 7, 1. 65.

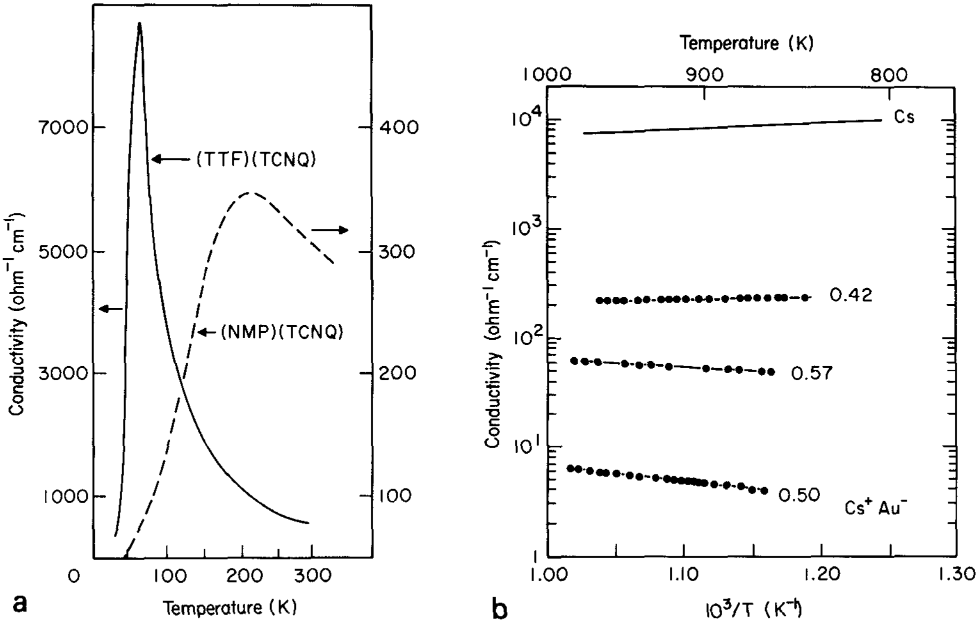

FIG. 4. The electrical conductivity of (a) the organic one-dimensional complexes, tetrathiofulvalenium-7,7,8,8-tetracyano-*p*-quinodimethanide, (TTF) (TCNQ), (b) liquid Cs–Au mixtures as a function of the reciprocal temperature at different Au-concentrations (given in atom fraction of Au). Note that in both cases the metal-insulator transition is accompanied by a change in the temperature dependence of the electrical conductivity, *see* text. Adapted from (a) Miller (1978), and (b) Hensel (1980).

itinerant-electron counterparts in a metal; *Figure 5* illustrates schematically two limiting types of temperature dependence in the magnetic susceptivity, viz. Pauli- and Curie-type behaviour.

Itinerant electrons are not spatially localized, nor, because of the stringent constraints of the exclusion principle, do they respond independently to the magnetic field. In contrast to the magnetic susceptibility of paramagnetic ions given by the Curie law, the Pauli susceptibility of itinerant electrons is essentially independent of temperature (*Fig. 5*). The Curie law form of the (molar) magnetic susceptibility of localized, non-interacting electrons is given by

$$\chi_m = N_A\left\{\frac{(g_e\mu_B)^2}{3}\frac{J(J+1)}{kT}\right\} \tag{1}$$

where N_A is the Avogadro number, g_e and μ_B are the electron g-factor and the Bohr magneton, respectively, k is the Boltzmann constant, and J is the spin angular momentum.

A simple way of comparing Pauli paramagnetism with the Curie form for magnetic ions is to note that the Pauli susceptibility can be transformed into the Curie law form (Eq. (1)), but with a fixed, characteristic temperature of the order of the Fermi temperature, T_F, taking the role of T (Ashcroft and Mermin, 1976). For typical metals, e.g., sodium, $T_F \approx 37\,000\ K$; thus the Pauli susceptibility is considerably smaller than the corresponding Curie value, even at room temperature, and essentially temperature

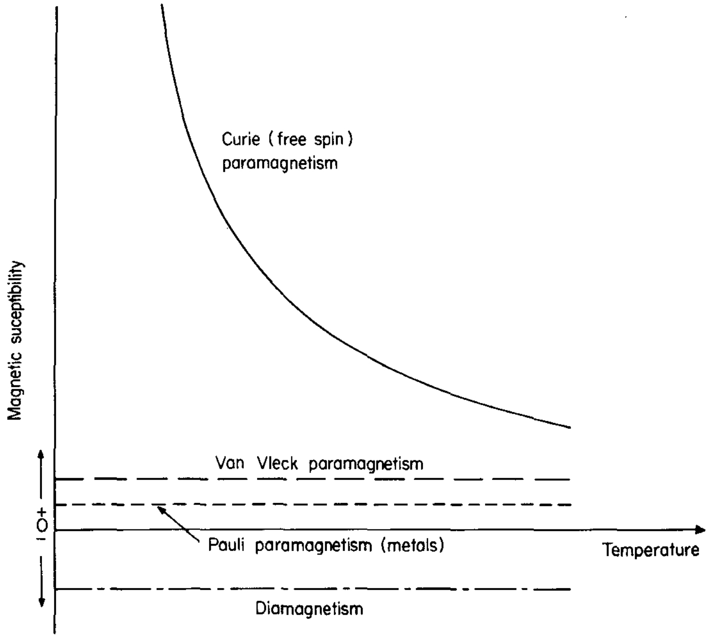

FIG. 5. Characteristics of magnetism in localized- and itinerant-electron systems (After Kittel, 1971).

independent. However, it is important to note that electron–electron interactions, even in metallic systems (e.g., Ti, Cr, Pd), give rise to a variety of magnetic interactions which can result in a marked temperature dependence in the Pauli paramagnetic susceptibility (Kittel, 1963; Ashcroft and Mermin, 1976). Indeed, this enhancement of susceptibility may be generally symptomatic of the impending transition from metallic, to insulating states as one proceeds across the periodic table (Chakraverty, 1980).

These types of experimental considerations form the basis of at least a first-order description of a metal. In perhaps its most widespread application, this classification forms the basis of our systematization of the elements within the framework of the periodic system. In *Figure 6* we show that some 79 of the 103 elements are, on the basis of the various definitions outlined earlier, metals in their solid and/or liquid states at ambient pressure. Four others, Si, Ge, Se, and Te, are semiconducting in the solid state but become metallic when molten. Therefore, as far as the elements are concerned, metallic behaviour is the rule rather than the exception. Clearly, the rationalization of the periodic table in terms of metallic vs. insulating character must be one of the primary goals of this review.

The independent electron view

The fundamental problem as to the precise reasons for the metallic vs. insulating status of elements, and indeed materials in general (*Table 1*), has attracted considerable and sustained attention since the beginnings of quantum mechanics (Mott and Jones, 1936; Mott, 1974). An early explanation of the difference between these two canonical states arose out of the pioneering work of A. H. Wilson (1931), based on the free-electron picture of F. Bloch.

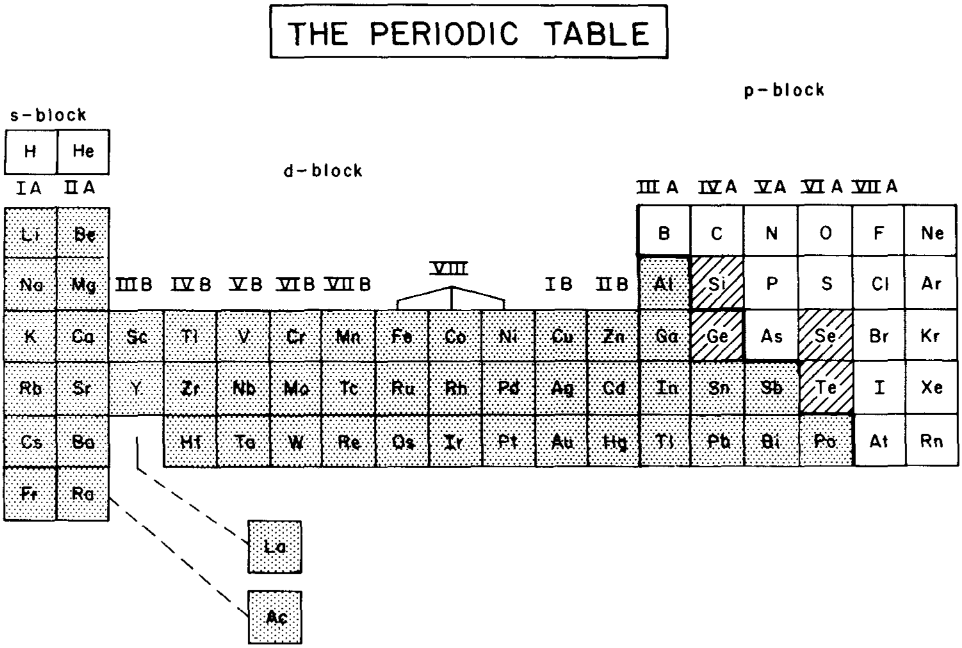

FIG. 6. A periodic table of the elements. For the sake of simplicity, the *f*-block elements have been omitted; for the remainder, we identify metallic elements in their solid and liquid states at normal pressure (hatched). Four are semiconducting in the solid state but become metallic when molten (Si, Ge, Se and Te, cross hatched). We have assumed that Tc probably has a metallic phase.

Consider an electron moving in a potential $U(\boldsymbol{r})$ which is periodic with the lattice. All solutions of the Schrödinger equation for an electron subject to this periodic field of potential $U(x, y, z)$; namely:

$$\nabla^2\Psi + (2m/\hbar^2)\{E - U(x, y, z)\}\Psi = 0 \tag{2}$$

are of the form

$$\Psi = \exp(i\boldsymbol{kr})u(x, y, z) \tag{3}$$

where $u(x, y, z)$ has the same period of the lattice. Each wavefunction is then characterized by a wave vector $\boldsymbol{k}$, and represents an electron moving through the lattice without being scattered.

The periodic boundary condition requires that

$$u_k(\boldsymbol{r}) = u_k(\boldsymbol{r} + \boldsymbol{R}), \tag{4}$$

and although the full set of levels can be described with $\boldsymbol{k}$ restricted to a single primitive cell, it is often useful to allow $\boldsymbol{k}$ to range through all of $\boldsymbol{k}$-space. In addition, the imposition of periodic boundary conditions requires that the set of all wavefunctions and energy levels for two values of $\boldsymbol{k}$ differing by a reciprocal lattice vector must therefore be identical. We therefore assign indices n to the levels in such a way that for a given n, the eigenstates and eigenvalues are periodic functions of $\boldsymbol{k}$ in the reciprocal lattice representation:

$$\Psi_{n,k+K}(\boldsymbol{r}) = \Psi_{nk}(\boldsymbol{r}) \tag{5}$$

$$\varepsilon_{n,k+K} = \varepsilon_{nk} \tag{6}$$

where K is a reciprocal lattice vector.

The Wilson approach leads to a description of the energy levels of an electron in terms of a family of continuous functions, ε_{nk} each possessing the periodicity of the lattice. An important result to emerge from this work is that an electron in a level specified by a band index, n, and wavenumber, k has a non-vanishing mean velocity. This leads to the remarkable fact that stationary levels for an electron subjected to a periodic potential involve a movement of the electron forever, *without any degradation of its mean velocity* (Ashcroft and Mermin, 1976). On this basis, then, all electrons in a perfect crystalline solid can be considered as free. However, this does not require that every crystalline solid ought to be a metal! The symmetry of the zone, or band of electron energies ensures that for every electron state with wavenumber k there is a corresponding one with $-k$. Consequently, a completely filled zone cannot show a preponderance of electron waves in any direction, i.e., there can be no electric current. An external electric field induces a current by exciting some electrons into higher energy states. In a completely filled zone, there are obviously no accessible vacant sites into which excitation of electrons can occur (*Fig. 7b*). True, we will probably have empty states in the next highest band, but, if these are of a considerable energy difference, no excitation can occur until very high temperatures (Hurd, 1975; Wilson, 1979).

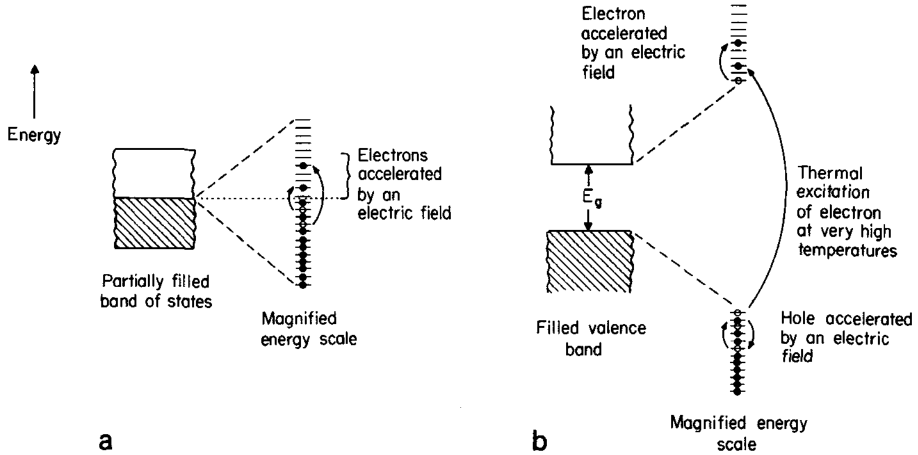

FIG. 7. Energy bands in solids in the region of the highest-energy electrons (a) for metallic systems; (b) for semiconducting (small energy gap) and insulating (large energy gap) materials. Adapted from Wilson (1979).

In contrast, an electric current flow can occur in partially filled bands in the presence of an external electric field. Here the electron energy can be raised via the excitation of the electron by the external electric field into vacant, accessible energy states (*Fig. 7a*), and a net change in electric momentum is produced.

Therefore, on the Wilson (1931) scheme, two distinct configurations exist (*Fig. 8*):

1. An insulator is a material in which the energy bands which contain electrons are completely full.
2. A metal is a material in which the highest-lying occupied band is partially filled.

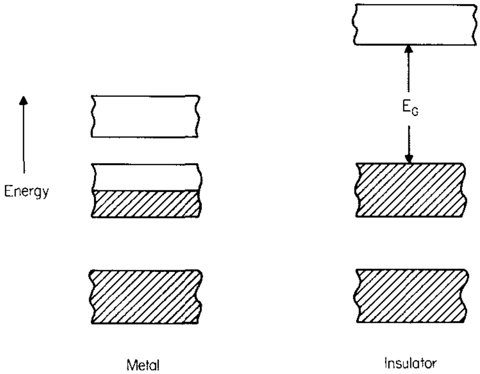

FIG. 8. On the Wilson scheme, electrons in solids occupy levels that divide into bands. On this view *all* materials having partially occupied bands are metallic. In semiconductors, accessible thermal energy is generally sufficient to excite electrons from the top of the full band into an empty band. In an insulator, this thermal energy is insufficient to bridge the energy gap at all but the highest temperatures.

In perfect crystals at $T=OK$, *provided that the independent-electron approximation is valid*, this model provides a completely rigorous theoretical criterion for distinguishing between the two regimes.

According to Wilson (1931), criterion (2) has universal applicability. However, as Sir Nevill Mott (1949, 1961) has pointed out, this is unfortunately *not* the case; the Wilson scheme predicts metallic status for materials that are known in fact to be insulators! The first indication of the breakdown of this theory came in 1937. At a conference chaired by Mott on the electrical conduction processes in solids (Mott, 1937), de Boer and Verwey (1937) presented electrical conductivity data for a variety of transition metal oxides, including NiO, CoO, MnO, Fe_2O_3, Fe_3O_4, Mn_3O_4 and Co_3O_4. With the exception of Fe_3O_4, all of these compounds showed conductivities in the range 10^{-10} to 10^{-7} (ohm^{-1} cm^{-1}), indicating that they are insulators. De Boer and Verwey considered these results very surprising, for the following reasons. Consider the transition metal monoxides, MnO, CoO and NiO, all of which have the NaCl (rocksalt) structure. *Figure 9* is a schematic representation of the (100) plane of the rocksalt structure. By symmetry, the five 3d orbitals of the octahedral site metal cation are split by the crystal field into two groups: a twofold-degenerate group of e_g symmetry, which is directed toward near-neighbour anions, and a threefold-degenerate group of t_{2g} symmetry, which is directed *toward near-neighbour metal cations*. Here the e_g orbitals overlap strongly with the p_σ orbitals of the oxygen anions, whereas the t_{2g} orbitals are orthogonal to the anionic p_σ orbitals and overlap strongly the p_π orbitals. In the solid state, these t_{2g} energy levels will broaden into a band which contains the essential ingredients for electron transport via direct metal–metal interactions (Goodenough, 1971).

This leads to the following electronic configuration for the monoxides:

$$\mathrm{NiO}(t_{2g}^6e_g^2);\ \mathrm{CoO}(t_{2g}^5e_g^2);\ \mathrm{MnO}(t_{2g}^3e_g^2)$$

Clearly, the CoO and MnO systems, in particular, would be expected to possess partially filled 3d bands in the solid state (*Fig. 10*), and according to the conventional Wilson band picture, both of these compounds should be metallic. In fact, both oxides are insulators! This is even more intriguing in view of the relatively small differences

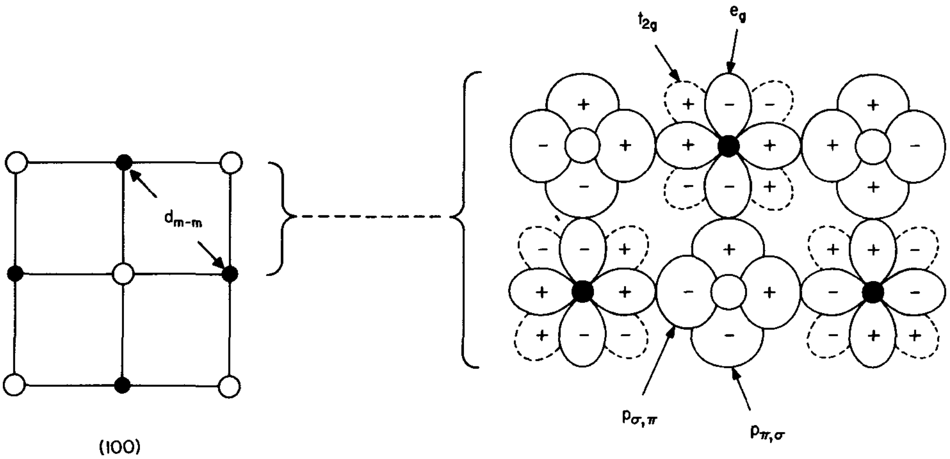

FIG. 9. Schematic representation of transition metal cations and anions in the (100) plane of a rocksalt crystal showing cationic orbitals of t_{2g} and e_g symmetry and anionic p orbitals. Anionic p-orbitals σ-bond to some cations and π-bond to others, as noted by the subscripts $p_{\sigma,\pi}$. Adapted from Goodenough (1967). Here d_{m-m} is the metal–metal separation in the crystal.

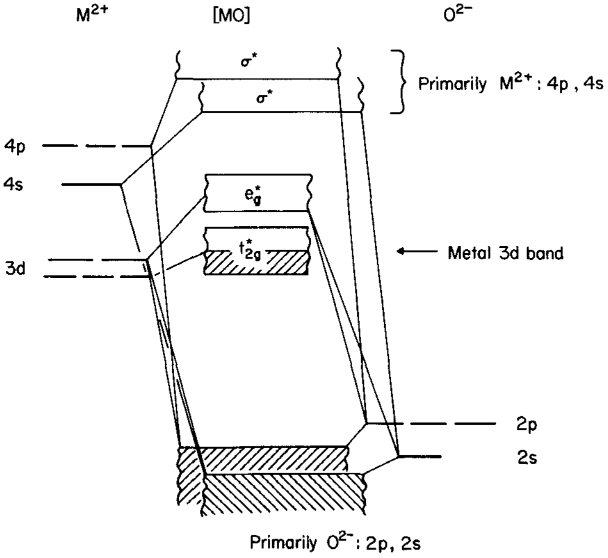

FIG. 10. Construction of one-electron energy diagram for a transition-metal monoxide with the rocksalt structure. Adapted from Goodenough (1971).

between the metal-metal distances (d_{m-m}) in the transition metal monoxides and the corresponding (highly conducting) elemental metals:

System	Co (metal)	CoO	Mn (metal)	MnO
d_{m-m}/Å	2.50	3.01	2.74	3.14

Furthermore, it now transpires that TiO, a superconductor below 1.5 K, possesses itinerant 3d electrons and is clearly *metallic*; $d_{m-m} = 2.94$ Å (TiO). In the discussion following de Boer and Verwey's paper, R. E. Peierls (1937) built upon some of their insightful remarks to suggest that the Coulomb repulsion between d-electrons was causing the electron localization at individual lattice sites. This identification of the complete breakdown of the conventional Bloch–Wilson theory lay dormant for more than a decade. Mott, however, in a determined campaign starting in 1949, as Brandow (1976, 1977) has put it, '... urged that this problem be recognized for what it was—a fundamental challenge to the existing conceptions of solid state theory'.

3. METALS vs. INSULATORS: BEYOND THE INDEPENDENT ELECTRON APPROXIMATION

To illustrate the precise origins of the breakdown of the Bloch–Wilson scheme, we consider an assembly of alkali atoms, e.g., caesium, at various densities. At high densities, the metal–metal separation, *d*, is small, and a considerable overlap of the valence electron 6*s* wavefunctions occurs, giving rise to a half-filled band, itinerant electrons and metallic conductivity. *Figure 11* illustrates the basic idea of band formation via the agglomeration of isolated, one-electron Cs atoms. In solid-state physics terminology, this is the so-called 'tight-binding' approach to band formation (Ashcroft and Mermin, 1976). Its chemical counterpart is the molecular orbital (MO) treatment (Goodenough, 1963).

Within the independent-electron scheme, we describe the valence electrons in high density Cs metal as Bloch-like extended states (Eq. (3)). Although the width of this 6*s* band would be expected to decrease with decreasing density (increasing *d*), the lowest-

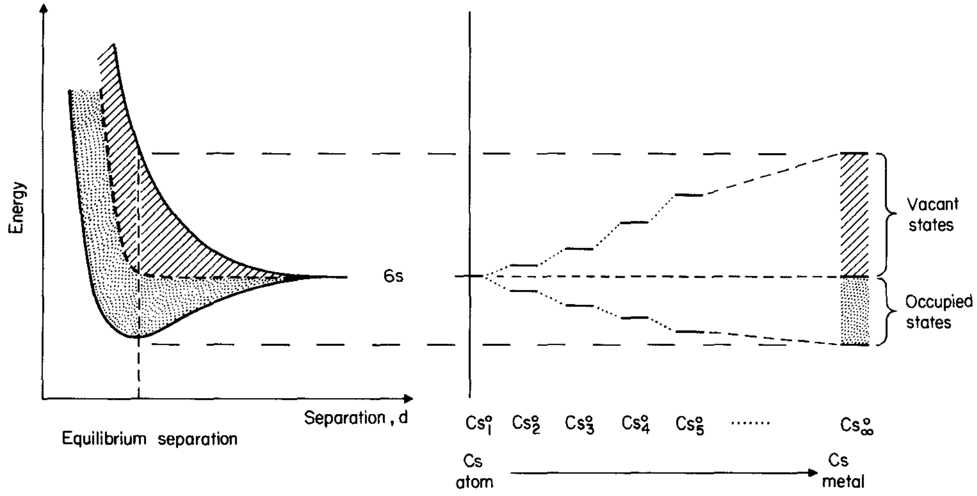

FIG. 11. Schematic representation of the evolution of energy bands in metallic caesium from atomic caesium. The figure shows the variation of energy with (average) caesium–caesium separation, *d*, and the corresponding energy levels for the bonding and anti-bonding combinations of the 6*s* states of caesium atoms in the intermediate regime; Cs_2°, Cs_3°, Cs_4°, etc. with the limiting cluster, Cs_∞°, identified with metallic caesium.

lying excited states above the ground state would still, in principle, lie infinitesimally close and metallic status would be predicted—*however far apart the atoms might be.* As Mott (1961) has pointed out, '... this is against common experience, and, one might say, common sense'. From the experimental standpoint, the breakdown in metallic status as Cs metal is continuously expanded is unquestionable. *Figure 12* shows high-temperature ($T = 2000°C$) conductivity data for expanded (supercritical) caesium at various densities (Hensel, 1971), while *Table 2* shows similar data for 'expanded sodium' in Na:Ar thin films at low temperatures, c. 4K (Cate *et al.*, 1970).

Thus, the Bloch-Wilson scheme, based as it is on an independent-electron approach, is inappropriate for any 'global' considerations of metallic status. It is inappropriate primarily because it generally neglects to take into account the very strong

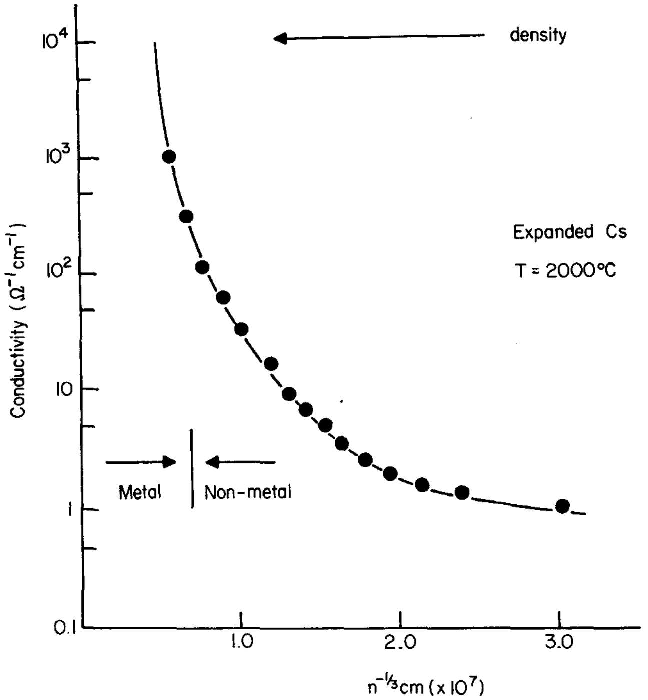

FIG. 12. Electrical conductivity of elemental caesium traversing the metal-insulator transition. The concentration of caesium is given in terms of the cube root of the reciprocal number (electron) density, *n*. The density of the system increases from right to left. Reprinted with permission from Hensel (1971). The appropriate location of the transition is indicated.

TABLE 2. Resistance of as-deposited films of sodium dispersed in argon (4 K), in the region of 15% sodium* (After Cate *et al.*, 1970)

Per cent Na	14.3	14.8	14.9	15.6	15.7
Resistance/ohms	2×10^5	2×10^5	0.6	0.6	0.6

* Probable error in composition ±0.9%.

electron–electron repulsion a second electron exerts at a given Cs site when another electron is already there. In the metallic state, this interaction is completely reduced, or screened via the degenerate gas of itinerant electrons (*Fig. 1*). However, in the low-density regime, electron–electron interactions, or correlations, become of paramount importance. Thus, an appropriate description at large atomic separations *must* recognize the localization of individual electrons as caesium atoms in disconnected regions of space. The independent-electron picture fails to do this. The failure of the independent-electron approximation in the present context is directly analogous to the well-recognized failure of the independent-electron approximation to describe accurately the hydrogen molecule (Coulson and Fischer, 1949; March, 1978). Indeed, it is interesting to note that the landmark papers by Mott (solids), and Coulson and Fischer (molecular hydrogen), both appeared in 1949!

Coulson and Fischer noted that the usual molecular orbital (MO) treatment of the H_2 molecule, in the linear combination of atomic orbitals (LCAO) approximation, took the spatial part of the ground state wavefunction to be

$$\Psi_{\mathrm{MO}}=[\Psi_\alpha(1)+\Psi_\beta(1)]\,[\Psi_\alpha(2)+\Psi_\beta(2)] \tag{7}$$

$$=\{\Psi_\alpha(1)\Psi_\beta(2)+\Psi_\alpha(2)\Psi_\beta(1)+\Psi_\alpha(1)\Psi_\alpha(2)+\Psi_\beta(1)\Psi_\beta(2)\} \tag{8}$$

where $\Psi_\alpha(1)$ is the wavefunction of electron (1) on the hydrogen atom α, etc. However, they noted a deficiency of this wavefunction in that it gives *ionic* configurations such as $\Psi_\alpha(1)\Psi_\alpha(2)$, i.e., $H_\alpha(1, 2)H_\beta^{\oplus}$, the same weighting as the so-called Heitler–London terms $\Psi_\alpha(1)\Psi_\beta(2)$ and $\Psi_\alpha(2)\Psi_\beta(1)$. These ionic terms in the MO function permit the possibility of *both* electrons being on one of the hydrogen atoms at the same time, i.e., the MO treatment starts by neglecting electron correlation. The description of the hydrogen molecule in terms of ionic structures $H_\alpha^{\oplus}(1,2)H_\beta^{\ominus}$, a hydride ion and a bare proton, is clearly non-physical in the limit of large internuclear separation.

The analogous situation in the many-body, infinite lattice problem envisaged in *Figure 11* is that of narrow energy bands, and here also the effects of electron–electron correlations are equally dramatic (March, 1978; *see also* Gutzwiller, 1963, 1964). In the limit of widely separated monovalent Cs atoms, the Bloch-Wilson model still provides for the finite probability of a *ground state configuration* in which two valence electrons are localized on the *same* Cs site (cf. *Fig. 1*).

The Hubbard model

Hubbard (1963, 1964) has proposed a scheme which attempts to come to grips with this problem, and contains the essential features necessary to yield *both* band-like, and localized behaviour in the respective high-, and low-density limits. Returning again to the lattice of Cs atoms, we have two competing factors to take into account:

1. For conduction to occur in the low-density insulating regime, a 6*s* electron has to be transferred from its home site to another, distant site. Without the simultaneous transfer of the other 6*s* electron on the distant site, a substantial amount of correlation energy will build up. In the very low density limit, such a charge transfer naturally leads to the production of both a Cs^+ and Cs^- ion, requiring an energy input

$$U=(IE-EA), \tag{9}$$

where IE is the ionization energy of the Cs atom, and EA is its electron affinity. This energy difference, customarily denoted by U, is then a measure of the instability associated with putting two electrons, of antiparallel spin,* on the same atom. For caesium, this *on-site* Coulomb repulsion energy can also be estimated to be (Berggren, 1973; Brandow, 1976)

$$U \sim \left\langle \phi_{6s}\phi_{6s} \left| \frac{e^2}{r_{12}} \right| \phi_{6s}\phi_{6s} \right\rangle \tag{10}$$
$$= \frac{5}{8}\left(\frac{e^2}{a_H^*}\right)$$

where a_H^* is the Bohr-orbit radius of the Cs atom, and $U \sim 3.4$ eV.

Therefore, in the limit of large d, this considerable Coulomb instability serves to localize the 6s valence electrons *in a quota of just one per Cs atom*, and also leads to a Cs° ground state configuration detached by a finite energy (U) from the excited state configuration, Cs^- (cf. Section 2). This is clearly a correct description for $d \rightarrow \infty$.

2. However, this complete localization cannot be strictly correct for finite d, for the following reason. When two or more atoms are brought together, a certain orbital overlap occurs permitting a possible electron transfer from the mth to the nth atom. In quantum mechanics this electron transfer is generally specified by an overlap or hopping integral (Slater, 1963). It is this interaction which leads to molecular binding in diatomic states, and to a characteristic *bandwidth*, Δ, for electron energy levels in the solid state. This effect, then, opposes the preceeding factor, U, and tends to *delocalize* electrons.

The formalization of this state of affairs was embodied in a specific Hamiltonian by Hubbard (1963, 1964). A reasonable approximation within the Hubbard scheme is to include only the electron–electron correlation term for intra-atomic interactions, i.e., for two electrons on the same atom. The articles by Hubbard (1963, 1964) should be consulted for the computational details. Specific interpretations may differ, but there seems to be little doubt that within the Hubbard picture the essential features of both the limiting insulating, and metallic regimes do indeed come to the fore (Cyrot, 1972a,b; Berggren, 1973; Mott, 1974; Coey, 1977). Thus, at large d, Coulomb repulsion dominates, electrons are localized in disconnected spatial regions and the system is an insulator. For small d, considerable orbital overlap occurs relieving any electron excess on any one atom. This is the '*broad band*' limit, where conventional independent-electron theory is applicable. Here the entire spectrum of metallic properties is found. In addition, an important new feature emerges. Given these two limiting descriptions, it is reasonable to anticipate that in the range of intermediate values of the overlap matrix element, the two atomic levels at ε_{at} and $\varepsilon_{at} + U$ will each broaden into bands with increasing density until at some critical density, n_c, the energy gap between these bands goes continuously to zero, as illustrated in *Figure 13*. Thus the criterion for band splitting, and hence a metal-to-insulator transition is then

$$\Delta \lesssim U; \tag{11}$$

and detailed estimates give

$$(\Delta/U)_{\text{crit}} \sim 1.2 \tag{12}$$

as the critical condition required for metallization (Hubbard, 1963; Caron and Kemeny, 1971). The use of Eq. (12), together with certain approximations, leads to a

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* According to the Pauli principle, two electrons with parallel spin cannot be on the same atom in the same caesium 6s orbital.

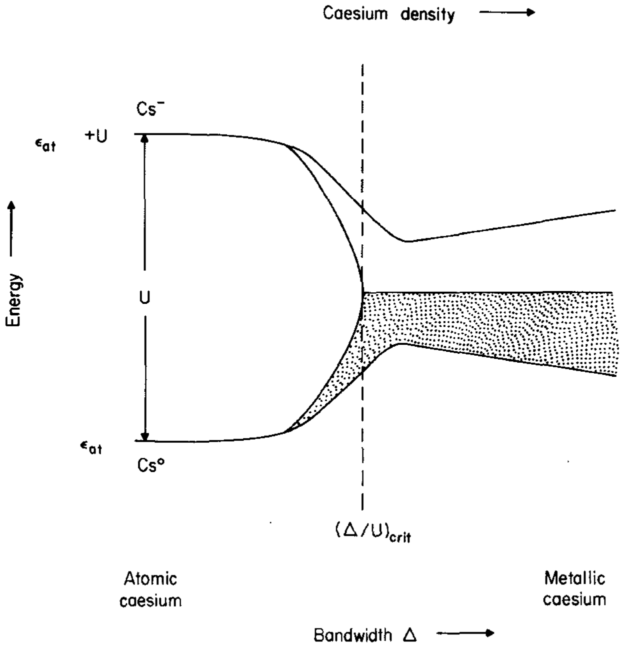

FIG. 13. A representation of the variation of electron energies in the transition from atomic to metallic caesium. The metal-insulator transition occurs at the critical density dictated by $(\Delta/U)_{\text{crit}}$; here the one-electron (metallic) band splits into the upper (Cs^-) and lower (Cs°) Hubbard bands, with the limiting case being caesium atoms and caesium anions. This scheme neglects the (stabilizing effect of the Cs^+-Cs^- interaction at low elemental densities (*see* below).

simple, explicit expression for the critical (electron) density, n_c, for metallization, viz.

$$n_c^{1/3}a_H^* \sim 0.2 \tag{13}$$

for

$$(\Delta/U)_{\text{crit}} = 1.0,$$

where a_H^* is the Bohr-orbit radius of the localized state in the low-electron density regime. We outline briefly two applications of the Hubbard model which are chosen to illustrate the predictive aspects of the approach.

The metal-insulator transition in doped semiconductors

A very interesting formulation of the Hubbard Hamiltonian is that due originally to Berggren (1973), who studied the metal-insulator transition in doped germanium and silicon in terms of a so-called tight-binding (atomic) model. Berggren utilized an approach somewhat similar to Slater's solution (1963) for the H (1*s*) integrals in the hydrogen molecule, and obtained explicit expressions for the one-electron band width, Δ, and Coulomb repulsion energy, *U*, for a regular array of centres,

$$\Delta = 2zT \tag{14}$$

where *z* is the coordination number for a particular arrangement of centres, and *T* the hopping or transfer integral between two adjacent orbitals is given by

$$T = \int \mathrm{d}\boldsymbol{r}\Psi^*(\boldsymbol{r})\mathrm{H}_1\Psi_j\Pi\boldsymbol{r}) \tag{15}$$

where H_1 is the one-particle Hamiltonian including the kinetic energy operator and the electron-donor interactions.

Specifically,

$$T = \frac{e^2}{\kappa_{st}a_H^*}\left\{-\frac{1}{2}S - \left[\frac{d}{a_H^*} + 1\right]\exp\left(-\frac{d}{a_H^*}\right)\right\} \div \sqrt{N} \tag{16}$$

and

$$S = \left\{1 + \left(\frac{d}{a_H^*}\right) + \frac{1}{3}\left(\frac{d}{a_H^*}\right)^2\right\}\exp\left(-\frac{d}{a_H^*}\right) \tag{17}$$

where κ_{st} is the static (low-frequency) dielectric constant of the host semiconductor, d is the separation between donor states, and N is the number of conduction band minima in $\boldsymbol{k}$-space. In addition, a simplification introduced was to assume that the intradonor repulsion energy

$$U = \frac{5}{8}\left(\frac{e^2}{\kappa_{st}a_H^*}\right), \tag{18}$$

was independent of composition (cf. Eq. (10)).

Critical concentrations (Eq. (12)) for the doped Si and Ge systems were in good agreement with experimental values. Further details can be found in the articles by Berggren (1973, 1978).

Edwards and Sienko (1978) re-examined Berggren's formulation and suggested an apparent universality in the treatment of the metal-insulator transition driven by electron correlation effects. Utilizing Hubbard's estimate of 1.15 for the critical value of $(\Delta/U)_{\text{crit}}$ at the transition, they computed transition densities as a function of a_H^*, the isotropic Bohr-orbit radius of the isolated- (localized-electron states. *Figure 14* shows a comparison of their numerical calculations with experimental results for both donor and acceptor states in various systems.

In addition, the calculated values of $n_c^{1/3}a_H^*$ from this Hubbard approach were 0.20–0.25 (for different N) over the entire range, which agree very well with the value 0.26 ± 0.05 obtained from experimental data (Edwards and Sienko, 1978).

More recent investigations of the doped semiconductor materials and expanded liquid metals have led to a more realistic picture of the transition region in terms of an amended Hubbard scheme (Rice, 1978; Bhatt and Rice, 1980, 1981; Freyland, 1980, 1981). In particular, the original Hubbard picture effectively neglected the possible stabilizing effect of the Coulomb interaction between the positive 'hole' (Cs^+) and the negatively charged carrier (Cs^-). In addition recent experimental data for alkali atoms in the vapour phase show that a relatively high concentration of molecular clusters form as the density of metal increases (Herrmann *et al.*, 1978). These clusters have an ionization energy substantially reduced from the single atom values (Foster *et al.*, 1969). Furthermore, recent theoretical treatments by Bhatt and Rice (1981) and Rice (1978) suggest that large multinuclear clusters of four or more donors in the P:Si system may also possess very large electron affinities. Both features serve to increase the effective probability of electron transfer from an isolated atom to a large cluster, and so naturally reduce the Hubbard correlation energy, U, (Eq. (9)), as more and more

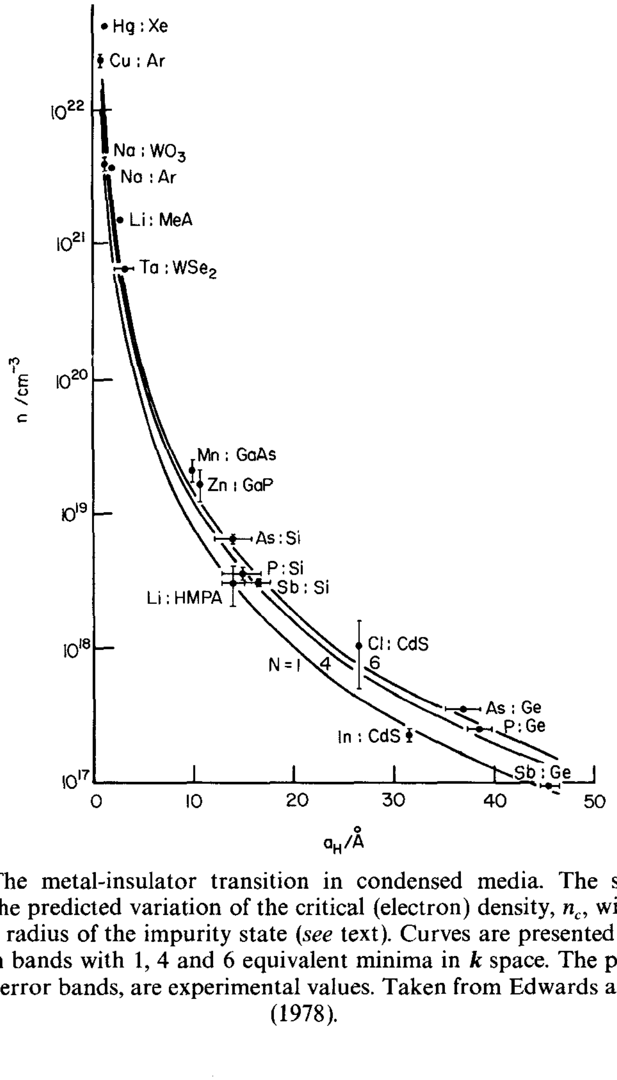

FIG. 14. The metal-insulator transition in condensed media. The solid lines represent the predicted variation of the critical (electron) density, n_c, with a_H^*, the Bohr orbit radius of the impurity state (*see* text). Curves are presented for (host) conduction bands with 1, 4 and 6 equivalent minima in $\boldsymbol{k}$ space. The points, and associated error bands, are experimental values. Taken from Edwards and Sienko (1978).

clusters form. A recent contribution by Monecke (1981) attempts to take into account the additional (attractive) Coulomb interaction between positive and negative states. He predicts a critical condition, $n_c^{1/3}a_H^* \approx 0.23$, for the appearance of metallic properties in the doped semiconductor materials.

The reader is referred to the recent reviews by Thomas (1980), Bhatt and Rice (1981), Castner and Thomas (1980), Freyland (1981) and the present authors (1982) for a more detailed discussion of the problem (*see also* Section 5).

Electrons in transition-metal monoxides

Figure 10 shows the one-electron energy-band scheme for transition-metal monoxides with the rocksalt structure. Here the 3d-states fall within the energy gap so that at normal temperatures the electrical and magnetic properties of the oxides are *primarily imparted by the d-electrons.* The isostructural series of monoxides have at least one member (TiO) which exhibits the properties of itinerant electrons (high conductivity, superconductivity at low temperatures, etc.) and other members in which the physical properties are characteristic of localized electrons. Pertinent physical properties of the first transition-series monoxides are summarized in *Table 3* (Goodenough, 1967, 1971). Now arising from our earlier discussion, whether the *d*-electrons in these materials are localized or itinerant depends critically upon the magnitude of the overlap integral and repulsion energies for *d*-orbitals on neighbouring cations. Goodenough (1967) has made extensive use of this type of approach to predict a critical overlap integral or bandwidth, Δ_c such that *d*-electrons are localized if $\Delta < \Delta_c$, or itinerant if $\Delta > \Delta_c$. The magnitude of the direct cation–cation bandwidth (*Fig. 10*) in the monoxide series varies sensitively with d_{m-m}, the observed metal–metal separation in the crystal, and Δ_c may be transformed to give a critical separation, d_c, separating the two electronic regimes. The column d_c in *Table 3* shows the values for d_c obtained from the empirical formula (Goodenough, 1967)

TABLE 3. Some physical properties of the monoxides of first-row transition metals (After Goodenough, 1967)

	d_{m-m}/Å	d_c/Å*	Transport	Colour	Magnetic§
TiO	2.94	3.02	Metal	Gold	Pauli
VO	2.89	2.92	S.C.$\rightleftharpoons$Metal	Steel grey	Weakly T-dependent
CrO	Unstable	2.80	S.C.†	—	—
MnO	3.14	2.66	S.C.	Green	C-W (122 K)‡
FeO	3.03	2.95	S.C.	Dull black	C-W (198 K)
CoO	3.01	2.87	S.C.	Olive green	C-W (291 K)
NiO	2.95	2.77	S.C.	Green	C-W (440 K)

* $d_c^{3d}(M^{m+}\text{-oxides})$.
$=\{3.20-0.05\,m-0.03(Z-Z_{\mathrm{Ti}})-0.04\,S_i(S_i+1)\}$; *see* Eq. (19).
† S.C.; Semiconducting behaviour.
‡ Curie-Weiss (C-W) law obeyed for temperatures above the Néel temperature (T_N, given in parentheses).
§ For typical magnetic behaviour in the limiting regimes, *see Figure 5*.

$$d_c^{3d}(M^{m+}\text{-oxides}) = \{3.20 - 0.05\ m - 0.03(Z - Z_{\mathrm{Ti}}) - 0.04S_i(S_i+1)\}\text{Å} \qquad (19)$$

where S_i is the total spin quantum number of the ion. Clearly TiO, which is superconducting below 1.5°K, has itinerant electrons. Furthermore, the radial extension of the *d*-orbitals decreases, and therefore the critical cation–cation separation d_c decreases, on passing to the heavier elements of the first-row series. In addition, a contraction of *d*-orbitals necessarily implies an increase in the intradonor repulsion energy (recall $U \propto 1/a_H^*$) across the period. Therefore it is perfectly consistent with known periodic trends to find itinerant *d*-electrons in TiO and VO, but localized electrons in MnO, FeO, CoO, and NiO.*

Ionization and screening

A fundamentally different approach to the problem of metals vs. insulators was presented by Mott in 1949; again, the basic origins of these ideas evolved from the 1937

* See also the work of Sheldon (1964) in attempting to predict a critical separation for metal–metal bonding in transition-metal halide clusters.

conference on conduction processes (Mott, 1937). Mott's model is based on the dielectric screening properties of a uniform electron gas, and is thus independent of any particular arrangement of constituent atoms.

The Mott transition

Consider again the collection of Cs atoms at various densities. For an isolated Cs atom, the 6*s*-valence electron and the caesium cation attract each other with a force for which the potential energy at large distances is of the form

$$V(r)=\left(-\frac{e^2}{r}\right) \tag{20}$$

where r is the electron–cation separation. Therefore, a non-conducting atomic state exists when the valence electron is trapped in this long-range (attractive) Coulomb field, and a continuum of bound, localized states will result (*Fig. 15*). Under these circumstances, an ionization process requiring some 3.89 eV is necessary for electron excitation, and hence electrical conduction. This state of affairs *cannot* exist in a metal, as was first discussed by Mott (1938). Here the attractive interaction between the two oppositely charged particles is reduced, or screened, via the (Fermi) sea of electrons. According to the so-called Thomas–Fermi prescription, this screened potential may now be written

$$V(r)=\left(-\frac{e^2}{r}\right)\exp(-qr), \tag{21}$$

where q^{-1} is a characteristic screening length, dependent upon the electron density, n, of the uniform electron gas, via

$$q^2=\frac{4me^2(3n/\pi)^{1/3}}{\hbar^2}. \tag{22}$$

In a metal, the screening length is sufficiently small (usually of the order of an atomic spacing) that the screened potential is too weak to produce a bound state (*Fig. 15*). Thus, metallic status is achieved by having a sufficiently high electron concentration so that the ionization energy of any particular 'atom' in the system then disappears. Coming from the metallic side, the model predicts a *first-order*, *discontinuous*, metal-insulator transition when the screened potential in Eq. (21) starts to have *bound localized* states. Such states appear when

$$qa_H^* \approx 1, \tag{23}$$

giving

$$n_c^{1/3}a_H^* \approx \tfrac{1}{4} \tag{24}$$

as the Mott criterion for metallic character.* We stress that the Mott transition requires a first-order transition between the two regimes—at $T=OK$, electrons are *either* localized *or* itinerant.

On the theoretical front, although the early Mott picture probably represents an oversimplification of the *details* of the screening process, there appears to be little doubt that the basic concept is intrinsically sound. On the experimental front, there can be no

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* Later work suggests that this condition may need to be amended in the light of more accurate calculations based on bound states of the static screened Coulomb potential (Rogers *et al.*, 1970; Popielawski, 1978).

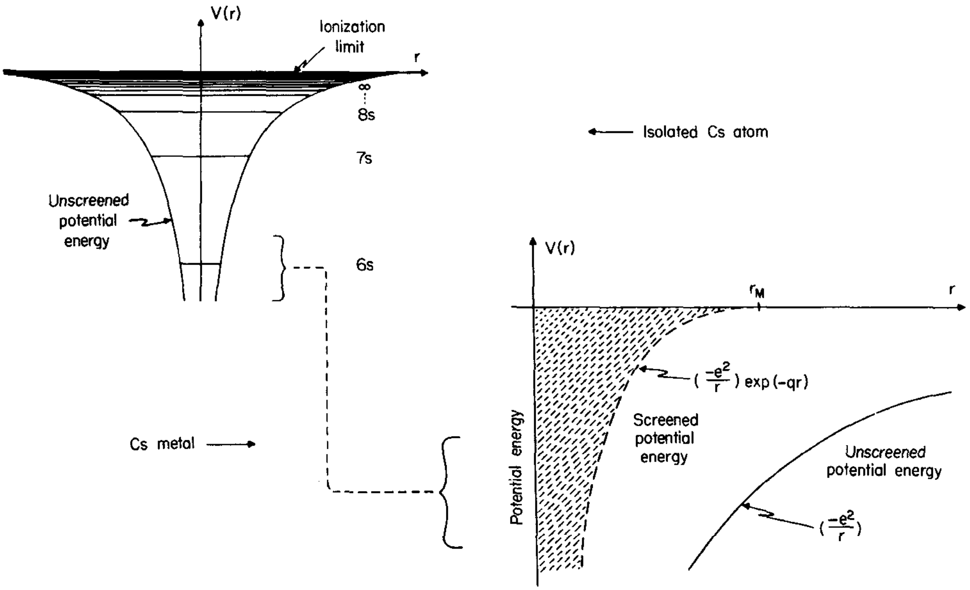

FIG. 15. Schematic representation of screened and unscreened Coulomb potentials of a Cs$^+$ ion core as seen by an electron; (a) an isolated Cs atom, (b) a Cs 'atom' in a metallic system. In the former, the potential is long range; in the latter, short range. Here r_m is the (radial) extent of the screening in the metallic state; it is typically less than 1 Å in most metals.

doubt as to its applicability, perhaps even its universality, in predicting the critical conditions for metallization. From an extensive analysis of experimental data (*Fig. 16*) we find that the Mott criterion

$$n_c^{1/3}a_H^* = 0.26 \pm 0.05, \qquad (25)$$

describes the onset of metallic character for a wide variety of systems spanning a range of c. 10^{10} in critical densities and approximately 600 Å in a_H^* (Edwards and Sienko, 1981). The important feature of this analysis was that a determined effort was made to obtain a realistic, experimental value for a_H^*. Therefore, Eq. (25) illustrates an experimental correlation between n_c and a_H^*. In addition, the validity of the screening mechanism has been confirmed by optical studies on various systems moving through the metal-insulator transition. *Figure 17* illustrates just two examples taken from the literature (Wilson and Yoffe, 1969; Acrivos *et al.*, 1971; Raz *et al.*, 1972). These show the broadening and ultimate disappearance of the well-known Wannier exciton series corresponding to transitions between the ground ($n = 1$) and excited states ($n = 2, 3$, for Hg:Xe), converging to the continuum limit at the bottom of the (host) conduction band. In this regard, Popielawski (1978) has also generalized the Mott criterion (Eq. (24)) for the disappearance of bound states to the case of higher excitonic states of the type found in Hg:Xe thin films (*Fig. 17*).

It is important to note again that since Mott's model for the metal-insulator transition is based on the dielectric screening properties of a uniform gas, it is therefore independent of any particular arrangement of the constituent atomic states. In contrast, the original Hubbard picture starts from an assembly of atomic-like states, and consequently exaggerates crystalline order. Yet the two models predict similar

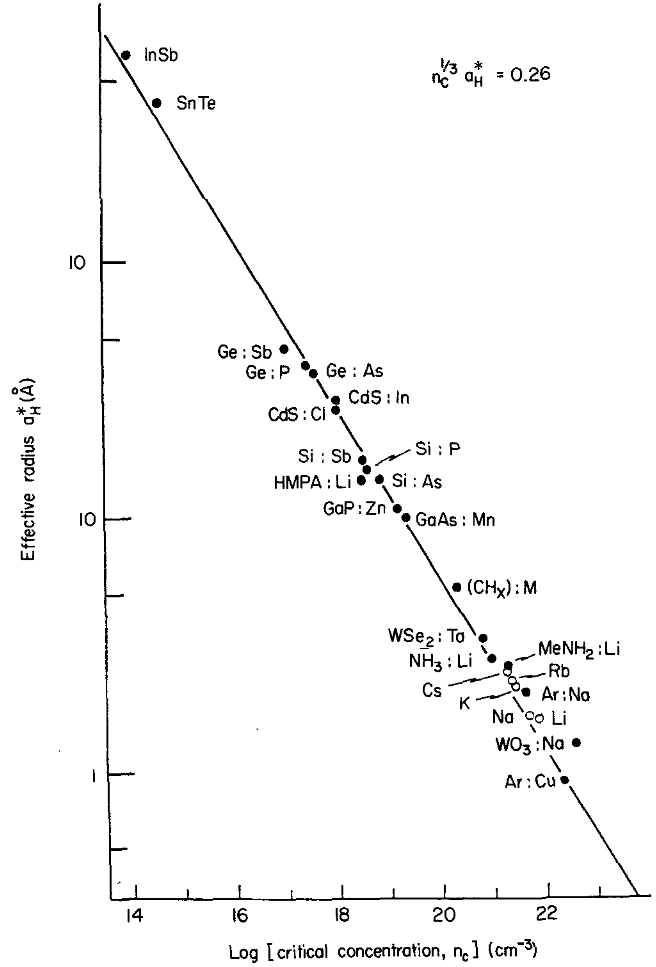

FIG. 16. A logarithmic plot of the effective Bohr-orbit radius, a_H^*, vs. the critical concentration for metallization, n_c, in a variety of doped semiconductor systems. Open circles represent experimental data for the supercritical alkali metals. The solid line is $n_c^{1/3} a_H^* = 0.26$. Taken from Edwards and Sienko (1981).

critical densities for metallization which agree well with observed values for a wide variety of systems (Edwards and Sienko, 1978). Possible origins of this convergence are discussed by Berggren (1973) and Mott (1978).

Therefore, from both the Hubbard and Mott schemes, we see the emergence of two characteristic parameters, the Bohr-orbit radius, a_H^*, and the critical density, n_c, which are obviously extremely important in any consideration of metallic vs. insulating status. The former is a parameter characteristic of the atomic, or localized-electron regime; the latter is a measure of the (electron) density in the condensed state under critical conditions for metallization. In the following section we explore this correlation further, and resurrect a simple criterion for determining when an element will show metallic conductivity: namely, a discussion of *atomic* properties which make an *element* a metal.

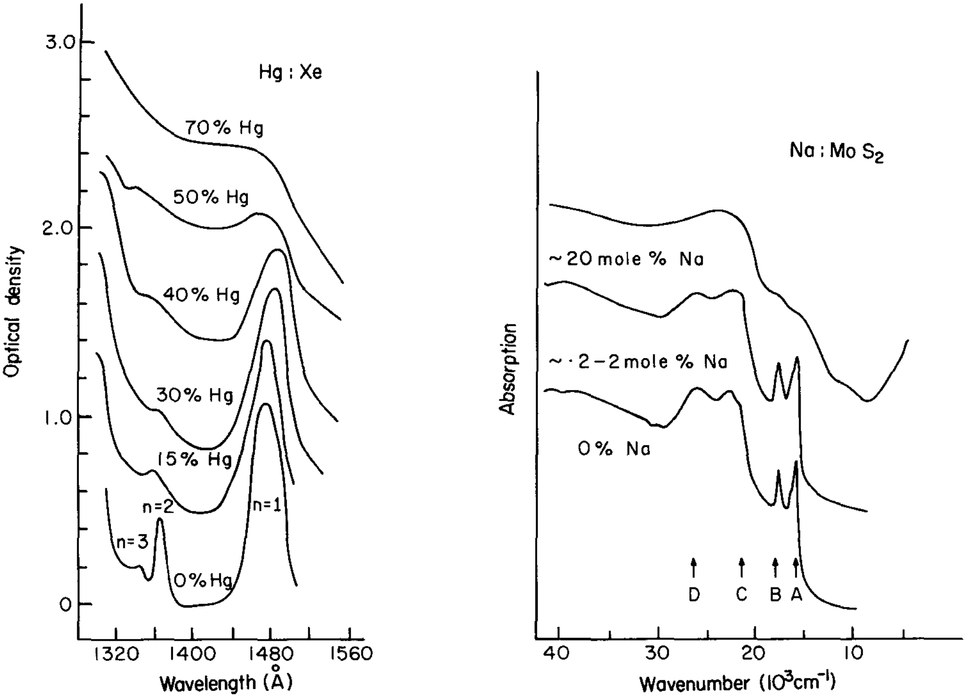

FIG. 17. The screening of excitons in mercury–xenon mixtures, and sodium-intercalated MoS_2 crystals. Exiton lines are identified in both systems, together with the compositions of the dopant (Hg and Na). Taken from Raz *et al.* (1972) and Acrivos *et al.* (1971).

The Herzfeld theory of metallization

Approached from the metallic state, the Mott transition takes place when the (ionic) potential of the parent site becomes insufficiently screened via the electron gas, and a bound state results (*Fig. 15*). Approached from the insulating state, a similar transition would occur if the binding energy of the localized electron–cation pair was reduced to zero, i.e., at the critical density n_c, the valence electron is ionized and hence acquires itinerant status. This is completely equivalent to a polarization or dielectric catastrophe at the critical density, when the Coulomb potential, $V(r)$ (Eq. (20)), is now replaced by

$$V(r) = \left(\frac{-e^2}{\kappa r}\right) \tag{26}$$

where κ is an effective dielectric constant of the material, and for

$$\kappa \to \infty;\ V(r) \to 0$$

at the critical density, n_c, for metallization.

This simple, and very attractive idea was the basis of a milestone contribution by Herzfeld in 1927 entitled 'On atomic properties which make an element a metal', which seems to be the first detailed consideration of the metal-insulator transition in condensed matter (Berggren, 1974, 1978; Edwards and Sienko, 1983a,b). The idea was the following: consider an element in the condensed state, be it liquid or solid. If an atom or molecule is placed in a Lorentz cavity in a dielectric medium, an external field $\boldsymbol{E}$ will give rise to an internal field, $\boldsymbol{E}_{\text{loc}}$, at the centre of the cavity,

$$\boldsymbol{E}_{\text{loc}} = \boldsymbol{E} + \tfrac{4}{3}\pi \boldsymbol{P} = \boldsymbol{E} + \tfrac{4}{3}\pi N p \tag{27}$$

where $\boldsymbol{P}$ is the polarization of the surrounding medium (representing the total electrostatic dipole moment per unit volume of material), p is the electric dipole moment of an atom or molecule, and N is the number of atoms per cm.

On classical grounds Herzfeld (1927) argued that the equation of motion of the valence electrons in an isolated atom would be

$$m\ddot{p} + 4\pi^2 m v_0^2 p = e^2 f \boldsymbol{E} \tag{28}$$

where f is the number of bound (valence) electrons and v_0 is their characteristic frequency. At the finite densities encountered in the condensed state, Eq. (28) must be replaced by

$$m\ddot{p} + 4\pi^2 m v_0^2 p = e^2 f \{\boldsymbol{E} + (\tfrac{4}{3})\pi N p\} \tag{29}$$

The net result is that the characteristic frequency v_0 of the bound electrons, representing a measure of the force holding the valence electrons in the isolated atom or molecule, is diminished at finite densities to the value

$$v = v_0 \{1 - (R/V)\}^{1/2} \tag{30}$$

where V is the molar volume in the *condensed state*, and R is the molar refractivity of the *gaseous atomic state*. Here $R = (4/3)\pi N \alpha_A$, where N_A is the Avogadro number, and α is the polarizability.

If

$$(R/V) = 1, \tag{31}$$

then the resultant force (Eq. (30)) on the valence electron vanishes; the electron becomes itinerant and the system acquires metallic status.

The previous statements can also be recast in terms of the Lorentz–Lorenz or Clausius–Mossotti relationships (Herzfeld, 1927; Ross, 1972).

$$\frac{(n^2-1)}{(n^2+2)} = \left(\frac{R}{V}\right) = R\left(\frac{D}{M}\right), \tag{32}$$

where n is the index of refraction, and n squared is the (high-frequency) dielectric constant arising from the electronic polarizability. Now it is clear that the left side of Eq. (32) cannot be larger than 1. However, Herzfeld argued that if we start with a substance of large refractive index (polarizability) in the gaseous state and compress it, increasing the density (D) such that the ratio (R/V) reaches unity, then for

$$\left(\frac{R}{V}\right) = 1,$$

$$n^2 - 1 = n^2 + 2, \tag{33}$$

a condition only satisfied when n is infinite! This polarization, or dielectric catastrophe means that the valence electrons, which before have been quasi-elastically bound to their atoms or ions, are now set free via mutual polarization in the condensed state and the solid becomes a metallic conductor. Note again the link with the basic Mott picture for the metal-insulator transition.

There has recently been considerable interest in the experimental detection of an impending 'polarization catastrophe' in single-, and multicomponent systems which undergo a metal-insulator transition (Castner, 1980; Ortuno, 1980; Thomas *et al.*, 1980). Capacitance and other measurements on the P:Si system at various donor concentrations reveal the onset of a probable polarization catastrophe as n_c is approached from the insulating state. Similar results have also been reported for amorphous Au:Si alloys, *n*-type Ge, sodium-ammonia solutions, and Hg-Xe thin films (for detailed references, *see* Edwards and Sienko, 1982). In *Figure 18* we show recent results for P:Si samples at millikelvin temperatures (Hess *et al.*, 1982); clearly, giant dielectric constants characterize the approach to the metallic state! We can use these data for P:Si to illustrate further the basic physics underlying the Herzfeld metallization idea.

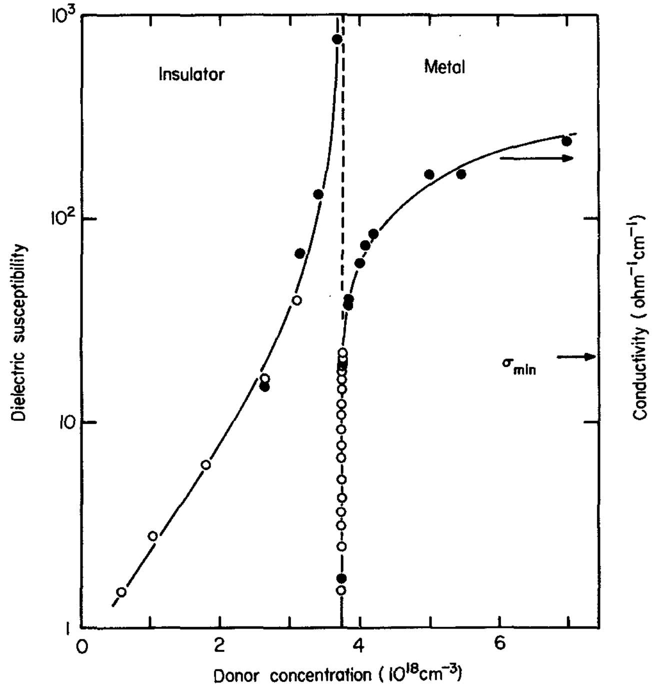

FIG. 18. Giant dielectric constants at the approach to the insulator-metal transition. The figure shows the divergence of the $T=OK$ donor (P) dielectric susceptibility $4\pi\chi$ in the insulating regime, and the corresponding $T=OK$ conductivity as a function of phosphorus donor density, *n*. Taken from Hess *et al.* (1982). σ_{min} represents the calculated value (Eq. (43)) of the electrical conductivity for the transition between the two electronic regimes (*see also* Section 4).

For isolated donor states in P:Si the additional (valence) electron from the phosphorus moves in the field of the donor ion (P^+) in much the same way as an electron moves about the proton in a hydrogen atom (Kohn, 1957). However, because the P^+ cation is itself embedded in a host (Si) dielectric medium, the force of attraction is reduced from $(-e^2/r)$ to $(-e^2/\kappa r)$ via the background dielectric constant of the Si lattice ($\kappa \approx 13$ for *pure* Si). As a result, the electron moves in a highly expanded 'Bohr orbit' whose radius (a_H^*) is considerably larger than that of a 1*s* electron in a hydrogen atom,

$$a_H^* = \frac{\kappa \hbar^2}{m^* e^2} \tag{34}$$

where m^* is the effective mass of an electron in the Si conduction band, and $\hbar$ and e have their usual meaning. For silicon doped with phosphorus, $a_H^* \approx 16$ Å. In addition, the ground state binding energy (E) is considerably reduced compared to the hydrogen atom 1*s*-value, and

$$E = \frac{-e^2}{2k a_H^*} \tag{35}$$

or

$$E \approx 0.08 \text{ eV for the P:Si system.}$$

Figure 19 shows a representative band structure of P:Si over a range of donor concentrations. As the donor concentration increases, band formation occurs and

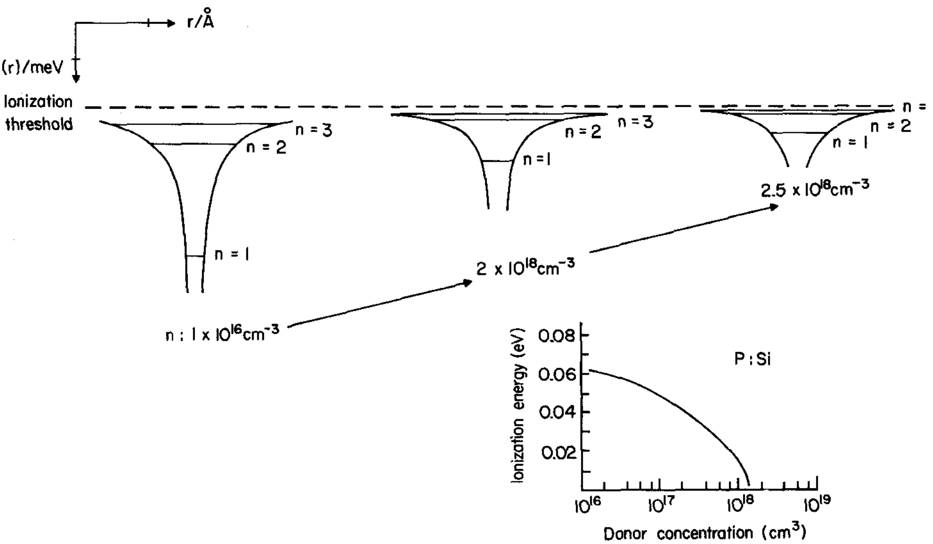

FIG. 19. A schematic representation of the variation in ground ($n = 1$) and excited-state ($n = 2, 3$) energies for a series of phosphorus-doped silicon samples approaching the metal-insulator transition at c. 3×10^{18} donors cm^{-3} (*see* text). Also included is the approximate dependence of the ($n = 1 \rightarrow$continuum) ionization energy of the impurity centres upon density (Shockley, 1950).

above a critical phosphorus concentration of c. 3×10^{18} elec. cm^{-3}, electrons within the donor or impurity band conduct in much the same way as do electrons in a metal. We can now see quite clearly the effect of the extremely large increase in the measured dielectric constant for densities close to n_c (*Fig. 18*); binding energies decrease considerably, and the initially discrete '1*s*' ground state level is pushed into the continuum or ionization limit, close to the critical density (*Fig. 19*). For comparison, we include also the corresponding experimental data for the 1*s*-continuum ionization energies at different donor concentrations (Shockley, 1950).

In summary, experimental data for a wide variety of systems certainly lend credence to the Herzfeld idea of an impending polarization catastrophe at the critical density for metallization.

This simple criterion (Eq. (31)), then, was utilized by Herzfeld over 50 years ago, in a predictive role to determine which *elements* are metallic, which are non-metallic, and which are borderline in the condensed state. However, as M. H. Cohen (1968) has pointed out 'The degree of sophistication then extant was such that these (Herzfeld's) remarks were not picked up at the time, and they have become lost'. This no longer is the case (Herzfeld, 1966; Ross, 1972; Berggren, 1974; Edwards and Sienko, 1982).

The Herzfeld criterion (Eq. (31)) predicts that a material will show metallic behaviour if the molar volume is reduced below the value R, the molar refractivity obtained at standard (i.e., low density) conditions. This criterion, at varying levels of complexity, has been applied to systems exhibiting *induced* metal-insulator transitions in order to predict the critical experimental conditions for metallization (Berggren, 1974)—no more so than in the realm of high-pressure experiments (Ross, 1972). While the criterion is arrived at by classical arguments, it is known to give predictions which agree with experiments as well as with estimates derived from ambitious quantum mechanical calculations. For example, the reported transition volumes (the critical volumes at which metallization begins) of Ar, Xe (calculated and experimental) and of TlI, I_2, NaCl, KCl and KBr (experimental) and those calculated via the Herzfeld criterion generally differ by, at most, 15% (Vaišnys and Žmuidzinas (1978). M. Ross (1972) has employed the criterion to predict the required volume reduction for the metallization of elemental and molecular hydrogen. On the basis of the measured refractive index of liquid hydrogen at −252.80°C, Ross utilized the Herzfeld criterion to predict a metallization onset in condensed hydrogen at a density of 1.02 g cm^{-3}. The recent experiments of Hawke *et al.* (1978) at Berkeley now reveal that hydrogen becomes metallic at a density of about 1.06 g cm^{-3}, corresponding to a calculated pressure of about 2 Mbar. Similarly, Berggren (1974) has successfully utilized the metallization criterion to predict critical compositions for the metal-insulator transition in n-type Si and Ge, electron-hole droplets, metal atoms in rare gas matrices, and even the supercritical alkali metals.

It seems clear, therefore, that the following simple criterion appears to be a necessary and sufficient condition for predicting metallic or insulating behaviour in the condensed state (Herzfeld, 1927):

$$(R/V) \geqslant 1 \quad \text{(metal)} \tag{36}$$

$$(R/V) < 1 \quad \text{(insulator).} \tag{37}$$

Figure 20 illustrates just how well the overall features of the periodic classification of the elements conform to this criterion (Edwards and Sienko, 1982). The group I metals all have $(R/V) > 1$ and metallic character is predicted for all the members. Typical explicit results for the alkali metals and for copper, silver and gold are given in *Table 4*.

We have outlined the possible viewpoint that the insulating, or non-metallic

TABLE 4. Values of R and V for certain elements (After Herzfeld, 1927)

	Na	K	Cu	Ag	Hg†
Molar refractivity* (R/cm^3)	61	107	18.95	19.4	13.74
Molar volume* (V/cm^3)	23.6	45.4	7.1	10.3	14.22 (sol)
First ionization energy (IE/eV)	5.1	4.34	7.6	7.57	10.4

* Taken from Herzfeld (1927).

† For solid Hg (R/V) is 0.966 and the metallic state, which requires $(R/V) > 1$ can be accounted for by a real change in R; as Herzfeld (1927) puts it, a 'deformation', e.g., via the formation of Hg_2 dimers. This viewpoint has now been confirmed (Pitzer, 1979).

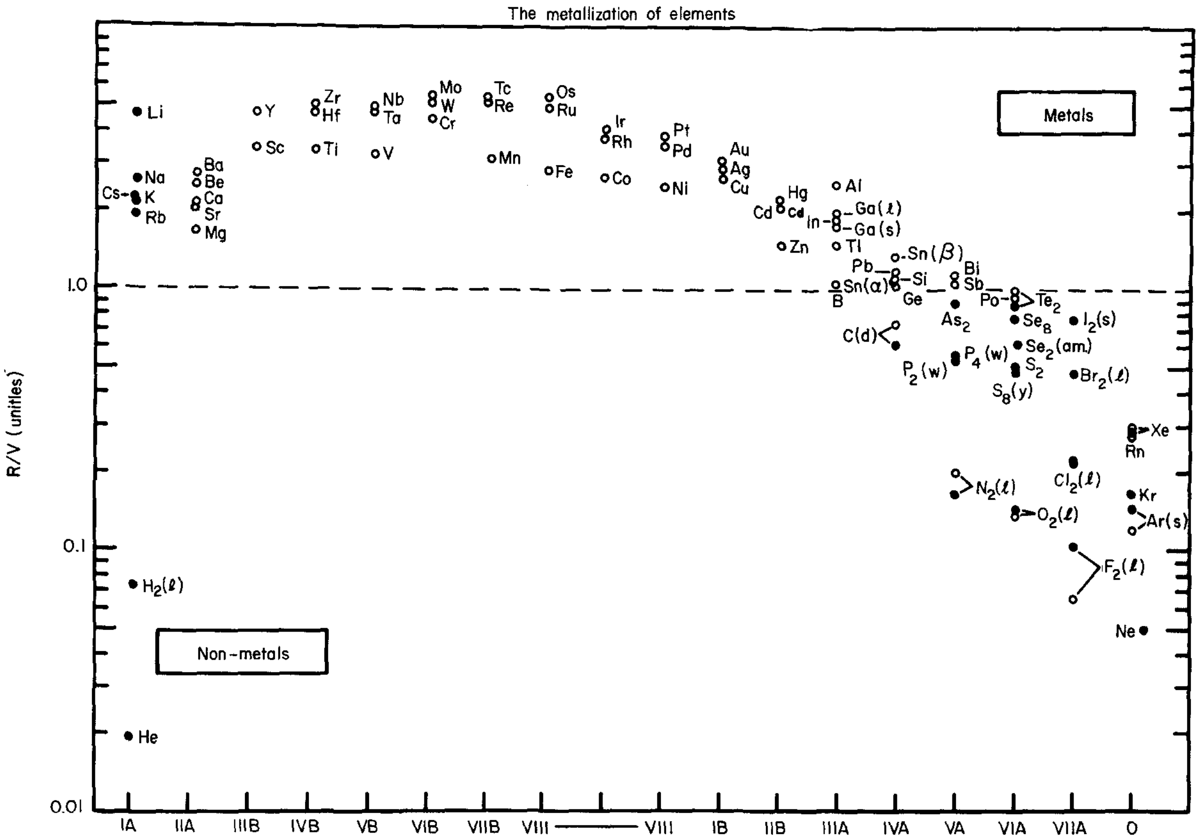

FIG. 20. The metallization of elements under the ambient conditions imposed on this planet. The figure shows the ratio (R/V) for elements of the s, p, and d blocks of the periodic table. Here R is the molar refractivity and V is the molar volume. The shaded circles represent elements for which both R and V are known experimentally. The open circles are for elements for which only V is known experimentally, and R is calculated. Taken from Edwards and Sienko (1982).

character of an element might be determined simply by the ionization energy of the individual atoms, or, as Herzfeld (1927) puts it, the force which holds the electron in place. However, we see now that the real determining factor is the ratio of this force to the *density of the valence electrons in the solid* (*Table 4*). Mercury, for example, has 2 electrons in its valence shell and an extremely large ionization energy (10.4 eV), approximately three times that of caesium. A mercury *atom* therefore holds its valence electrons much more strongly than do the atoms of the alkali metals. Nevertheless, it is a metal quite simply because of the extremely high density in the condensed state, giving a low molar volume, and consequently

$$R > V$$

As Herzfeld points out, if mercury had, in the solid state, the large molar volume of say an alkali atom (e.g., potassium c. 45 cm^{-3}), it would *not* be a metal. Indeed, mercury expanded above a certain critical density, either as a supercritical material (Hensel, 1980, 1981) or as a thin film (Cheshnovski *et al.*, 1977, 1981) certainly transforms from the metallic to the insulating state. On the other hand, argon with a very small value of R requires very high pressures to sufficiently reduce its molar volume to the critical value for metallization (Ross, 1972). Similarly, the ultra-high pressure experiments on molecular hydrogen attest to its very small R value (Hawke *et al.*, 1978).

Consider the elements of group VIIA. All the halogens have $(R/V) < 1$; consequently we expect insulating behaviour at ambient conditions. Moving down the group (R/V) increases; consistent with the well established physical picture of increasing polarizability of atoms leading, at normal (ambient) densities, to the transition to the solid material at I_2, and, at higher densities, to the metallic state. In fact it is well known that liquid iodine at normal densities exhibits various traits of metallic character (Sienko and Plane, 1974).

Groups IIIA–VIA of the periodic table are perhaps the most intriguing. Note that these elements effectively straddle the dividing line between localized- and itinerant-electron behaviour. We argue elsewhere that these elements may well take on the appellation 'transition elements' (Edwards and Sienko, 1982)! In addition, two features of this area of the periodic table are particularly interesting.

1. The marked tendency to form polyatomic molecules under ambient conditions, e.g., S_8, Se_8, As_4, etc.; similar clustering phenomena in other systems traversing the metal-insulator transition are indeed well recognized (Mott, 1974; Friedman and Tunstall, 1978; Freyland, 1981).
2. The very large dielectric constants found, for example, in the group VA 'semi-metals' (Chakraverty, 1980).

Thus, the preponderance of polymeric states, and large dielectric constants for elements in this area of the periodic table may well be generally symptomatic of the *impending* transition to the metallic state under more stringent conditions (viz. $(R/V) \geqslant 1$) achieved at high pressure. The periodic table itself, then, must surely be one of the most dramatic examples of the metal-insulator transition in condensed systems.

Pauling (1983), in a recent communication, has pointed out that an *approximate* measure of the radius of the outermost valence electrons in a (gaseous) atom is the cube root of the molar refractivity, R. If this is approximately equal to the cube root of the molar volume (V) in the condensed state, then the outer orbitals from one atom will overlap with those from an adjacent atom and, unless there are filled shells, covalent bonds will be formed. If there is a metallic orbital, the covalent bonds will show unsynchronized resonance (Pauling, 1949; Harcourt, 1974), and the system will exhibit metallic properties. Pauling suggests that one can therefore expect metallic orbitals to be at hand except when approaching the completion of a shell. Accordingly, most elements are metals!

In summary, the fact that there exists a recognizable, diagonal demarcation between elements of the *p*-block series strongly suggests, once again, the fundamental importance of the atomic characteristics in dictating metallic vs. insulating status. Here, one would argue, the well-recognized orbital contraction of individual atoms as one proceeds across the periodic table must eventually lead to insulating behaviour. Chakraverty (1980) has recently drawn attention to two additional symptoms which usher the transition from metallic to insulating status in the periodic table:

1. A large paramagnetic susceptibility in magnetic metals (e.g., Pd, Pt, etc.), which is characteristic of large repulsive interactions between electrons (the Hubbard *U* term) in the 'narrow-band' regime (Section 3).
2. The phenomenon of superconductivity which results from strong electron–ion interactions close to a metal-insulator transition.

Which physical interaction dominates is clearly a rather delicate balance; indeed, in certain instances superconductivity and magnetism can coexist (Maple, 1981).

4. ELECTRONS IN DISORDERED SYSTEMS

Our discussion so far has centred around the tacit assumption that the systems of interest are periodic in nature. This quite naturally leads to a one-electron theory of crystalline materials in which long-range order, i.e., periodicity, is the key factor (Section 2). It allowed, within fairly stringent constraints (i.e., the independent electron viewpoint), a first-order microscopic explanation of the differences between metals, semiconductors and insulators in terms of the concepts of energy bands and gaps (Wilson, 1931). Within this periodic framework, electron–electron interactions bring about a fundamental change in the collective behaviour of the electrons (Mott, 1961, 1974). As Yonezawa and Cohen (1981) have recently pointed out, 'Perhaps because of this history, there existed an implicit, vague idea that bands and gaps arose from long-range order'.

The inadequacy of this assertion has become apparent over the past two decades. In particular, Anderson (1958) has shown that an analogous phenomenon of localization or itinerancy exists, even within a one-electron situation, if the electron moves in a disordered material (*see also* Anderson, 1974; Mott, 1974). Two idealized models have evolved for this sort of situation:

1. Percolation, in which actual physical disconnection occurs between metallic and insulating regions.
2. Anderson localization of electrons due to a sufficient degree of randomness or disorder; here there is no question of actual physical disconnectedness, the effect is purely quantum-mechanical in nature (Chakraverty, 1983).

Percolation treats the conduction process on a *classical* level in terms of linkages among metallic sites distributed throughout the inhomogeneous material; a typical example would be a heterogeneous system such as metallic globules embedded in a non-conducting matrix (Kirkpatrick, 1971, 1973; Shante and Kirkpatrick, 1971; Abeles *et al.*, 1975). A system will exhibit metallic conductivity if the concentration of metallic sites is large enough to sustain a conducting path which spans the sample. The percolation concept might be judged as a mathematical, and not a physical model for defining a metallic state in a heterogeneous system (Thouless, 1978). In particular, it provides few clues to the fundamental problem of deciding when the individual *microscopic* regions may be judged metallic or insulating. The model, when applied to a discussion of metal-insulator transitions, has also been sharply criticized by Mott (1972, 1974), whose principal argument is that an electron is not classical, and hence will tunnel from one metallic region to the next, thereby essentially wiping out the possibility of the coexistence of metallic and insulating regions at any given energy. This model will not be pursued further here; however, we note its considerable success in rationalizing the properties of macroscopically inhomogeneous materials traversing the metal-insulator transition (Cohen and Jortner, 1973).

If the condensed medium is homogeneous, and disorder extends down to the microscopic level, then the individual wavefunctions may be profoundly modified in the Anderson sense. In particular, it is now well established that the introduction of sufficient disorder in a solid can effectively transform the material from a metal to an insulator. This idea was first suggested by P. W. Anderson in 1958 in his classical paper on 'Absence of diffusion in certain random lattices'. Anderson (1972) himself characterizes the paper as 'often cited but seldom read'. The disorder-induced transition from itinerant- to localized-electron states is now universally known as the Anderson transition. To understand how this works, we go back to the Schrödinger equation for an electron subject to a periodic field of potential $V(x, y, z)$. Anderson considered the potential energy function shown in *Figure 21*. In the absence of disorder, solutions of the Schrödinger equation would be of the type discussed earlier (Section 2), viz.

$$\Psi = \exp(i\boldsymbol{kr})u(x, y, z)$$

with u being periodic with the period of the crystal potential. In the tight-binding approximation

$$\Psi = \sum \exp(i\boldsymbol{ka}_n)\Psi_n(x, y, z) \tag{38}$$

where $\boldsymbol{a}_n$ denotes the lattice sites and Ψ_n are functions for the individual potential wells. Under these circumstances each electron wave will be periodic and will extend throughout the entire system. Given a finite density of interacting centres, the wavefunction overlap leads to a corresponding band width, Δ, as outlined earlier (Section 3). Anderson in 1958 asked the question: what happens if the potential wells are now made random, as in *Figure 21*? If contributions randomly drawn from a range

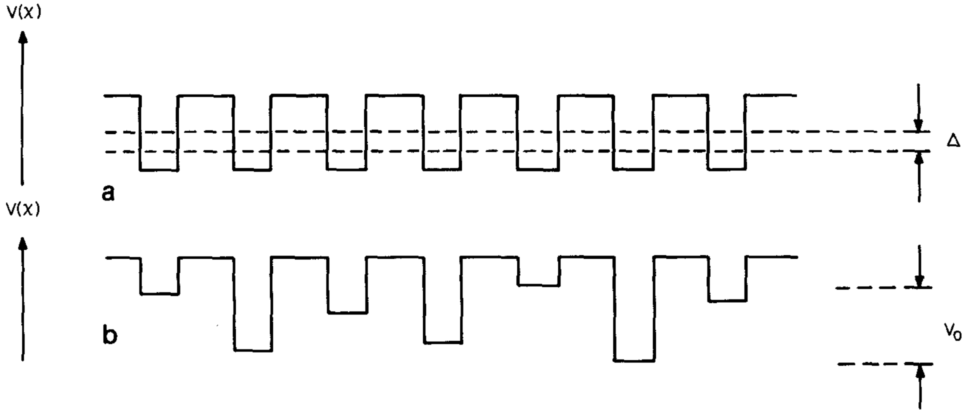

FIG. 21. The potential energy of an electron within (a) a periodic field, and (b) a random potential field. Δ is the one-electron bandwidth in the absence of the random potential V_0.

$-V_0/2$ to $+V_0/2$ are added to the potential well depths, then the energy V_0 is a measure of the extent of the local disorder. For a nominally disordered system in which the random potentials are so weak (viz. $V_0 \ll \Delta$), then the valence electrons are still essentially free to propagate throughout the system, with only minor perturbations on their mobility; eigenstates of the system are superpositions of Bloch waves of the same energy (*Fig. 22a*). If we now gradually increase the disorder potential, $V_0 \lesssim \Delta$, then the electron scattering becomes even stronger. In a 'free-electron' picture this would have the effect of shortening the electron mean-free path. The amplitude of these extended states begins to fluctuate through the system, varying in phase over a distance of the order of the wavelength of the Bloch wave, and losing phase coherence over a distance identified as the mean-free path (*Fig. 22b*).

Eventually when the disorder increases sufficiently, the mean-free path of the electron is shortened such that it becomes comparable to the average interatomic distance, *d*, between potential wells. If the scattering (disorder) becomes even stronger, the electron wavefunction will become localized in a discrete region of space, viz. their amplitude will fall off exponentially with distance, so that an envelope of a typical wavefunction would appear as *Figure 22c*. These exponentially localized states are

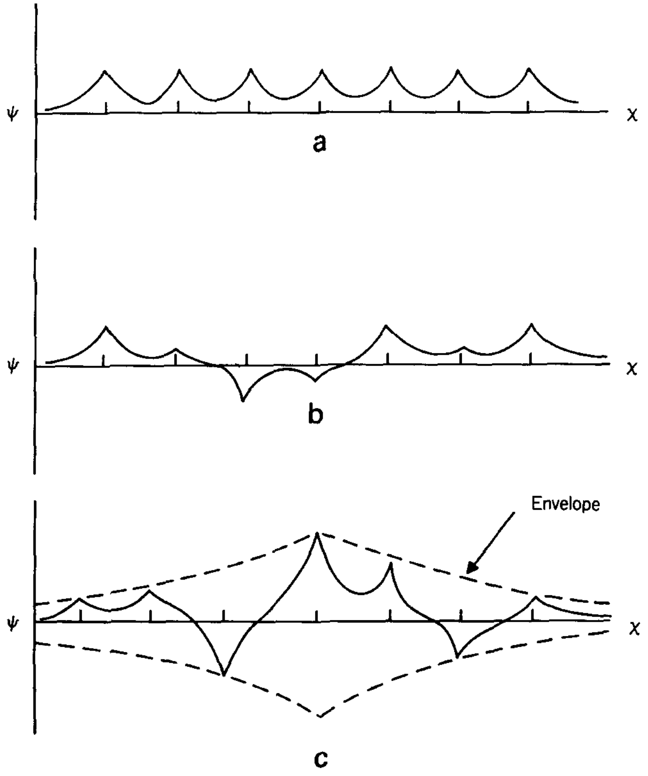

Fig. 22. A typical wavefunction Ψ in an Anderson lattice: (a) an extended wavefunction of Bloch character, with a mean-free path far exceeding the separation between potential wells, and $\Delta \gg V_0$; (b) extended wavefunction subject to disorder potential and $\Delta > V_0$; (c) a weakly localized function for which $\Delta \sim V_0$. The overall form of the envelope function is outlined. Adapted from Mott (1974).

expected to have a maximum amplitude at some point falling off as $\exp(-r/\beta)$, where β is some localization distance.

According to Anderson (1958), there exists a critical value $(V_0/\Delta)_{\text{crit}}$, for which, at zero temperature, electron diffusion is impossible, and a *nominally* metallic system becomes insulating.

Under these circumstances, the eigenstates of the system for all values of the energy then take the form shown for exponentially-decaying functions (*Fig. 22c*). The crucial aspect here is obviously to determine the exponential rate at which the wavefunction falls off from the centre of localization, and the degree of disorder necessary to bring about the stabilization of the localized state—or the destruction of the delocalized state. Although the basic idea of disorder-induced localization is conceptually simple (*Fig. 21*), the evaluation of the critical condition $(V_0/\Delta)_{\text{crit}}$ is extremely difficult to calculate exactly, since it depends both on the coordination number and on the detailed form of the distribution function for the energies V_0. Numerical studies suggest a value of about 2 for typical *s*-state systems, but considerable problems remain in obtaining precise numerical results (Weaire, 1981).

However, Mott has made extensive and very effective use of the so-called Ioffe–Regel criterion (1960) as a predictive guide for the onset of disorder-induced localization in a metallic system (Mott, 1972, 1974, 1982). The basic argument is as follows: Since the mean-free path (l) of an electron is the distance over which an electron wavefunction loses phase coherence, and the wavelength (λ) is the distance over which the phase changes by 2π, then it does not make sense for a metallic system to have a wavelength which is substantially longer than the mean-free path. The Ioffe–Regel criterion for metallic behaviour is therefore

$$l > \lambda \tag{39}$$

or

$$lk_F > 1, \tag{40}$$

where k_F is the electron wavenumber $(1/\lambda)$.

When the criterion (40) is violated, viz.

$$lk_F \leqslant 1, \tag{41}$$

then the electronic states are taken as localized.

In *Figure 23*, we show room-temperature resistivity data for a series of sodium-tungsten bronzes (Na_xWO_3); values of lk_F are indicated, and the Ioffe-Regel criterion does indeed monitor the onset of electron localization at a critical sodium concentration ($x \sim 0.2$) (Holcomb, 1978).

In 1972 Mott utilized the Ioffe–Regel criterion (Eq. (41)) and Anderson's prediction of a certain critical value of the disorder necessary for localization, to propose the existence of a finite minimum conductivity $\sigma_{\min}$ in a metallic three-dimensional disordered system. Thus, at the zero of temperature one cannot have a *non-zero* value of the conductivity less than $\sigma_{\min}$, where

$$\sigma_{\min} = \frac{\pi}{4z}\frac{e^2}{\hbar d_c}\{(\Delta/V_0)_{\text{crit}}\} \tag{42}$$

where d_c is the distance between centres *at the metal-insulator transition*, and $(\Delta/V_0)_{\text{crit}}$ is just the value of Δ and V_0 where electron localization sets in.

If $(\Delta/V_0)_{\text{crit}} \simeq \frac{1}{2}$, and $z=6$, this gives

$$\sigma_{\min} = \frac{0.026e^2}{\hbar d_c} \tag{43}$$

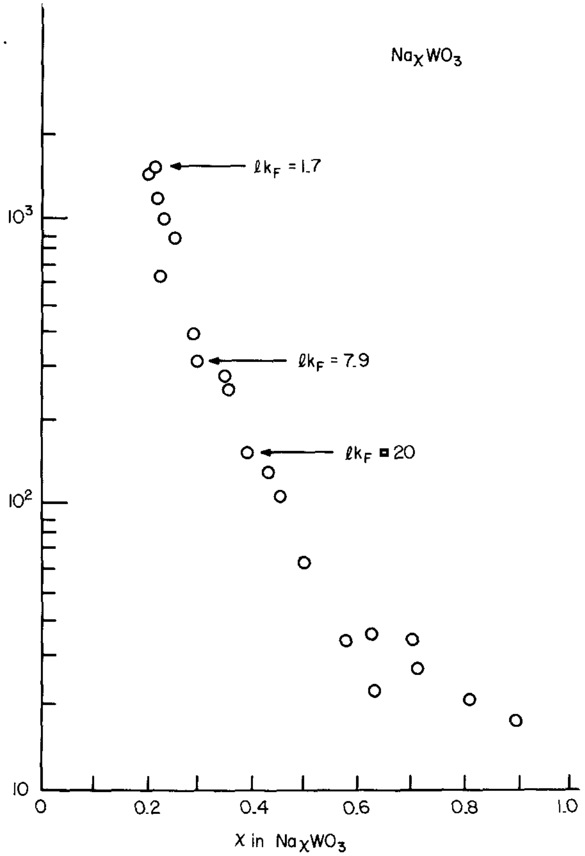

FIG. 23. Room-temperature resistivity data for the sodium tungsten bronze system, Na_xWO_3. The various locations of lk_F are also indicated for comparison with the Ioffe-Regel condition, $lk_F = 1$. Adapted from Holcomb (1978).

Therefore, if (V_0/Δ) increases through the critical value, the conductivity at zero temperature jumps *discontinuously* from the value $\sigma_{\min}$ to zero.

For a typical system, e.g., P:Si, $d_c = 64$ Å at $n_c(3 \times 10^{18}$ elec. cm$^{-3})$ giving $\sigma_{\min} = 20$ (ohm^{-1} cm^{-1}), as indicated in *Figure 24*, and this value is in excellent agreement with the experimental value of the zero temperature conductivity when metallic conduction $(\partial\sigma/\partial T < 0)$ transforms to thermally activated conduction characteristic of localized electrons (Rosenbaum *et al.*, 1980).

We have already pointed out the general applicability of the Mott criterion (Eq. (25)) in predicting the metallization onset. Mott's expression for the minimum metallic conductivity (Eq. (43)) seems to be based on similarly universal arguments (Fritzsche, 1978). *Figure 25* shows a comparison with the experimental data in a wide range of materials. Here, the value for the minimum metallic conductivity was either estimated from the value of σ at which the activation energy disappears, or from the extrapolation to $1/T = 0$ of the curve showing ln σ vs. $1/T$ (Mott, 1982). As Fritzsche (1978) has pointed out, $\sigma_{\min}$, the experimental value of the conductivity for which the activation energy disappears, agrees well with the general formula.

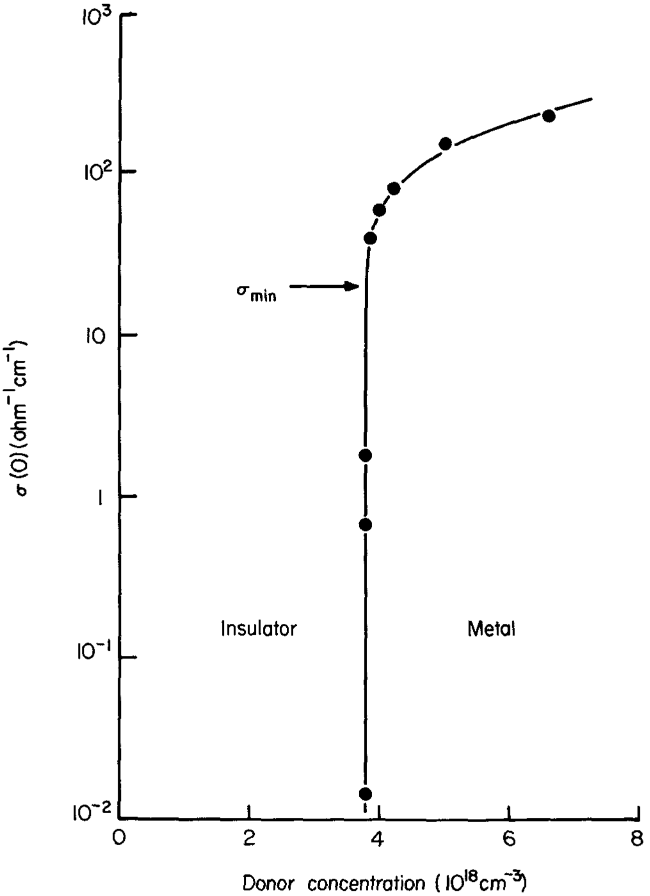

FIG. 24. The zero-temperature electrical conductivities of phosphorus doped silicon samples traversing the metal-insulator transition. Taken from Rosenbaum *et al.* (1980).

$$\sigma_{\min} = \frac{Ce^2}{\hbar d_c} \tag{44}$$

where C is a constant in the range 0.025 to 0.05.

Given that the experimental data for $\sigma_{\min}$ are considerably sensitive to the presence of uncontrolled impurities, the agreement between experiment and Eq. (44) is taken as good experimental evidence for the concept of a minimum metallic conductivity.

However, this beautiful result (Eq. (43)) is still controversial. In particular, recent work on the scaling theory of localization casts doubt on the theoretical basis of the minimum metallic conductivity. Thouless (1982), in a recent review of current theories of electrons in disordered systems, goes so far as to state '... I regard the concept of minimum metallic conductivity as one of the creative errors that helped the progress of science'.

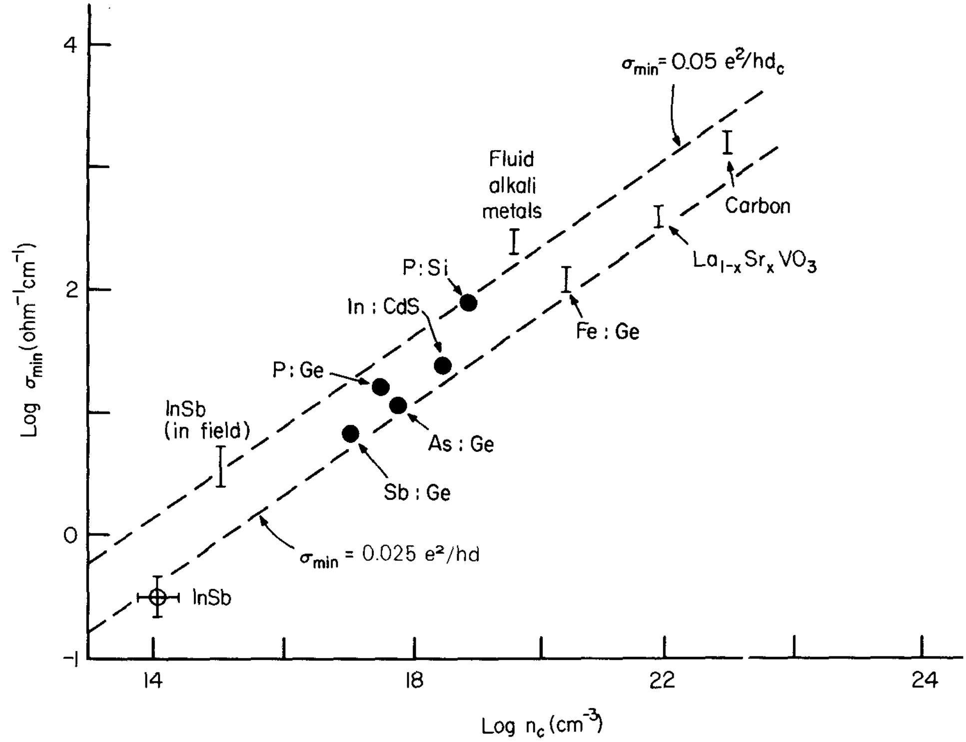

FIG. 25. A comparison of experimental values of Mott's minimum metallic conductivity, σ_{min}, with theory. The data are taken from Fritzsche (1978) and Mott (1982). The plot is a function of n_c, the critical density, in electrons cm^{-3} at the metal-insulator transition. The lines are for $\sigma_{min} = Ce^2/\hbar d_c$, with $C = 0.025$ and 0.05, and d_c, te average distance between impurity centres at n_c, is about 4 a_H^*, according to Eq. (25). Adapted from Mott (1982).

5. HOW MANY ATOMS MAKETH METAL?

Clustering and the metal-insulator transition

The preceding descriptions of the metal-insulator transition are based on the assumption that most systems are essentially homogeneous—at both the microscopic and macroscopic levels—on either side of the critical conditions for metallization. For example, the 'Mott transition' described earlier is only expected to be a first-order transition in an infinite lattice of interacting atoms (Mott, 1961). However, it might be argued that this viewpoint somewhat overlooks the important question of microscopic clustering, or inhomogeneities in the transitional region. Consider our earlier discussion of the Hubbard model for the transition from metallic to atomic caesium (Section 3; *Figs 11, 13*). As indicated, there is now a considerable amount of experimental data for alkali atoms in the vapour phase which show a relatively high concentration of molecular associates and cluster species (Herrmann *et al.*, 1978; Freyland, 1981). These alkali clusters have an ionization energy substantially reduced from the single atom value and a high electron affinity. Both factors obviously increase the probability of electron transfer from an isolated atom to a high-nuclearity cluster, and these microscopic features must clearly be part of any detailed consideration of the

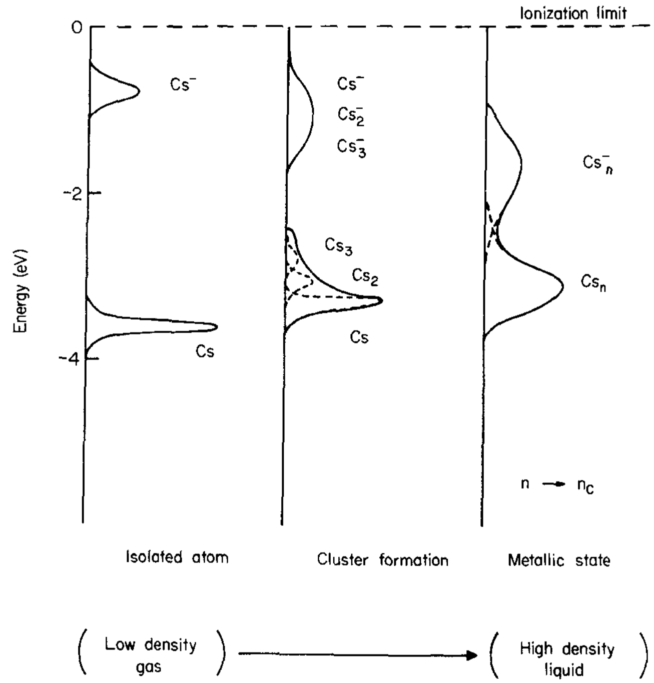

FIG. 26. A schematic representation of the 'microscopic' structure of expanded fluid caesium metal at various densities. The energy zero refers to the ionization limit, and the system moves from a low density gas to a high density liquid, at a critical metal (electron) density. Adapted from Freyland (1981) by Edwards and Sienko (1982).

metal-insulator transition in this system (Freyland, 1980, 1981). The general conjectures, then, for the energy spectrum of supercritical caesium are summarized in *Figure 26*. For isolated atoms (the low density regime) electron transfer requires an energy input of some 3.24 eV (Section 3). As the density of caesium increases, larger clusters form and charge-transfer processes become increasingly favourable. Within the Hubbard formulation (*Figure 13*), this is tantamount to the broadening of both upper (Cs^-) and lower (Cs^0) bands. As the caesium density approaches n_c, the energies of the cluster bands overlap, and facile conduction now proceeds. Therefore, this microscopic view incorporating cluster formation quite naturally leads to the conventional picture of band broadening and ultimate merging at some critical density for metallization. Bhatt and Rice (1981) have also discussed the question of clustering in the approach to the metal-insulator transition in the doped semiconductors P:Si and Sb:Ge. They argue that in these 'multi-valley' semiconductors, large clusters are sufficiently electronegative to attract an electron from isolated donor states and go so far as to suggest that there is no limiting Mott-Hubbard gap (U) due to electron correlation in these disordered systems!

Therefore, microscopic clustering and/or lattice distortions are always inextricably linked with the macroscopic problem of the metal-insulator transition in an infinite lattice. In this macroscopic problem, we are dealing with continuum physics in which the limiting effective particle interactions and sample dimensions approach the thermodynamic limit of an infinite system.

The electronic properties of small metallic particles

There is another equally important aspect of the problem, now much discussed in both the chemistry and physics literature, which considers the evolution of cluster units in isolation (Baetzold, 1981; Borel and Buttet, 1981; Löwdin, 1981; Davis and Klabunde, 1982). This description involves, to first-order, the neglect of inter-cluster interactions and deals primarily with the genesis of isolated, microscopic cluster states. Representative systems include:

1. Ultra-finely dispersed metal catalyst dispersed on various oxide, or zeolite substrates (Bourdon, 1980).
2. 'Naked' transition metal clusters formed via the controlled aggregation of metal atoms in low-temperature inert materials (Ozin, 1980).
3. Inorganic cluster compounds, e.g., the transition metal carbonyl clusters, of generic formula $M_m(CO)_n^{2Q-}$ ($Q \geqslant 0$, $n > m$) in particular those of osmium, rhodium and platinum, representing metallic fragments essentially isolated from adjacent cluster units by an inert sheath of carbonyl ligands (Johnson, 1980).

The considerable interest in these systems stems partly from their high catalytic activity (Muetterties *et al.*, 1979; Bourdon, 1980; Hugues *et al.*, 1981), but also from their position as intermediaries between the atomic and metallic regimes (Baetzold, 1981). With these systems in mind, our original question 'What is a metal?' must now be recast into the more appropriate form 'How many atoms are needed in an aggregate or cluster of atoms to effectively mimic the bulk properties of a metal?' At the outset we stress that the answer to this question must obviously depend upon which particular property of the metal one wishes to describe (Section 2). Consider, for example, the requirements attached to metallic status in terms of magnetic and transport properties, e.g., conductivity, Hall effect, etc. For the latter, the appellation 'metallic' suggests the creation and subsequent transport of itinerant electrons across the sample. Such a process is generally viewed in terms of the free ionization of an electron from its parent (atomic) site. Under these conditions, complete delocalization of the electronic wavefunction occurs over the particle and conventional transport measurements would, in a sufficiently large sample, monitor the onset of metallic characteristics, viz. high conductivity. However, the onset of *spin* rather than *electron* (*charge*) delocalization within a cluster or aggregate species is a different question. In systems composed of large numbers of interacting species (c. 10^{18}–10^{20} elec. cm^{-3}) it has been recognized for some time that magnetic resonance properties (and in particular ESR) detect what appears to be the onset of 'delocalization' effects at considerably lower concentrations than those inferred from transport property measurements (Alexander and Holcomb, 1968; Holcomb, 1978; Edwards *et al.*, 1979). In this regard, Silsbee (1968) first made the important point that, for example, ESR measurements are sensitive not only to complete delocalization of the wavefunction (i.e., free ionization of carriers), but also to *partial* delocalization effects which might involve the extension of the (primarily localized) electron wavefunction over several sites. The latter process—spin delocalization—almost certainly occurs *without* the formation of free (ionized) carriers, and *without* the concomitant changes in charge-transport properties. The primary responsibility for this type of effect lies in the typical energies associated with the various types of measurements. Therefore, modifications to the inter- and intra-site exchange energy in the metal cluster as the nuclearity increases need only be of the order of magnitude of the magnetic Zeeman or hyperfine energies (both typically in the range 10^{-4} eV) for noticeable changes to be detected in, say, the characteristic ESR properties. In contrast, transport properties require as a prerequisite for the detection of metallic character, the *complete* ionization of an electron from its parent site. This process typically involves energy changes in the range 10^{-1} to 10 eV. These types of experimental considerations are fundamental in any consideration of 'metallic' characteristics in these systems. Hamilton (1980), Baetzold (1981) and others (Demuynck *et al.*, 1981), have suggested as a criterion for 'bulk' properties the width of the *d*-band in clusters, as determined by photo-electron spectroscopy. Such a criterion obviously involves large energy terms in the 1–10 eV range. This type of approach may overlook or obscure many interesting magnetic and optical properties of clusters in the small-particle regime. Similarly, quantum mechanical calculations aimed at reproducing the bulk-metal *d*-band width in clusters would obviously require several hundreds of atoms before metallic status would be conferred on the aggregate. Magnetic measurements may well signal the onset of some aspect of metallic behaviour at considerably lower nuclearity (Benfield *et al.*, 1982; Johnson *et al.*, 1983).

Having recognized these experimental considerations, one can now suggest several important domains in the evolution of molecular clusters and higher aggregates. These are summarized in *Figure 27.* Here the appropriate compositional parameter, *m*, is the cluster nuclearity.

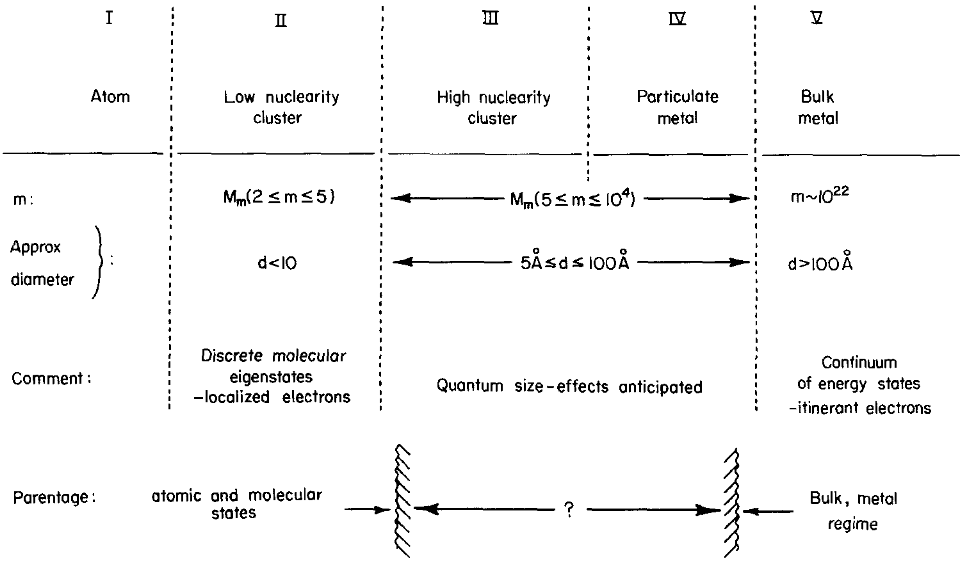

FIG. 27. Possible electronic regimes for the evolution of particulate and bulk metals from atomic aggregates. Electronic regimes are indicated by an approximate nuclearity, *m*.

The composite low nuclearity clusters, $m=1$, and $2 \leqslant m \lesssim 5$ represent monotomic and higher nuclearity clusters extending to an *arbitrary* upper limit, the pentanuclear cluster, M_5. Here we anticipate a relatively smooth transition from discrete metal atoms to higher aggregates. The essential features for this regime are obvious and distinguishable atomic and molecular properties. This is certainly the case for silver and alkali clusters in the rare-gas solids (Ozin, 1980; Thompson and Lindsay, 1981), and for low-nuclearity transition metal cluster carbonyls (Johnson *et al.*, 1983).

The term high-nuclearity cluster implies a microcluster within the appropriate bounds $5 \lesssim m \lesssim 100$. The number of atoms in a spherical sodium particle of diameter d' with bcc structure is $\frac{4}{3}\pi(\frac{1}{2}d')^3/(\frac{1}{2}a_0^3)$, where a_0 is 4.225 Å, and for this metal the terminology 'high-nuclearity cluster' extends to sodium particles of approximate diameter 10 Å. Here the atomic structure for the naked (matrix-isolated) clusters is generally not known, but may be more akin to the short range order found in liquid or disordered materials. Similarly details of the electronic properties of these high nuclearity clusters are uncertain, although we anticipate that the electronic structure can vary considerably with the shape and size of the microcluster.

At the upper limits of the 'high-nuclearity' regime (*Fig. 27*)—or at some slightly higher nuclearity—we anticipate a transition to what we term a 'particulate metal'. We stress that the interfacial region between III and IV (*Fig. 27*) is not to be viewed as a rigorous demarcation; the details of this transitional region in fine metallic particles are still imprecisely known. For the present purposes we define a particulate metal as a fragment of metal in which the finiteness, or localization of the electronic wavefunction within the cluster fragment brings about quite considerable changes in the electronic states of the *parent* (*bulk*) *metal*. Therefore, our view of low and intermediate cluster states based on *atomic* properties is no longer strictly applicable, and parentage may now be sought in the electronic properties of the condensed phase bulk metal—but with several fundamental differences (Fröhlich, 1937; Kubo, 1962, 1977; Marzke, 1979).

In a bulk metal, the one-electron energy levels are quasi-continuous, and a sum over the electronic states is generally interpreted in terms of a properly defined density-of-electronic states, which is independent of the boundary conditions imposed on the wavefunction. In brief, this standard picture must be dramatically modified when we deal with particulate metals or high-nuclearity clusters (regions III and IV, *Fig. 27*). The finite extension of the wavefunction now brings about two distinct effects on the electronic states of a metal particle. The first is a surface effect due to imposed boundary conditions. As the surface-to-volume ratio increases, so the effective density-of-states will be modified. We shall, however, be primarily concerned here with the second effect, namely the changeover of the electron levels from quasi-continuous to discrete. The direct consequences which arise from such a discrete energy level structure in a nominally 'metallic' system are generally termed *quantum size effects* (Kubo, 1962). For example, in a particle containing N atoms, the spacing of adjacent electronic levels, denoted by δ, will be of order E_F/N, E_F being the Fermi energy. This will amount to c. 10^{-3} to 10^{-4} eV if the particle contains, say 10^4 atoms. In the case of sodium, this corresponds to a particle of approximate diameter 100 Å. In considering bulk metallic properties, the spacing δ is considerably smaller than any of the relevant energy parameters, i.e., in practice, we have a quasi-continuous spectrum of energy levels. However, for metal particles of sufficiently small dimension, the level spacing δ may no longer be small in comparison with experimental energy parameters. Under these circumstances, magnetic susceptibility, magnetic resonance, optical, and many other properties (Marzke, 1979) may be quite different from bulk properties if we work at sufficiently low temperatures ($\delta \gtrsim kT$) or, in the case of magnetic experiments, at sufficiently weak fields so that $\delta \gtrsim \mu_B H$, where $\mu_B H$ is the Zeeman energy. In addition, dynamical responses of particles at a frequency ω so low as to satisfy the condition $h\omega \lesssim \delta$ may be completely different from those of the bulk system. This is certainly the case for the magnetic relaxation characteristics of small metallic particles; the Elliott mechanism for electron spin relaxation, and the Korringa mechanism for nuclear spin relaxation will both be suppressed (Kubo, 1977). In the case of a particulate metal, the inelastic spin-flip scattering is prohibited because the energy conservation cannot be fulfilled when δ is much larger than the Zeeman energy.

These types of effects have been discussed by a number of authors who have shown that, under the condition $\delta > kT$, the behaviour of the magnetic susceptibility as a function of temperature will be very different depending upon the parity of the ensemble of itinerant electrons (Kubo, 1969; Denton *et al.*, 1971, 1973). Predictions in behaviour vary according to the statistical ensemble employed in the calculations (Marzke, 1979). However, a transition from Pauli- to Curie-type behaviour in the magnetic susceptibility (*Fig. 5*) at low temperatures has been predicted for particles with an *odd* number of electrons, and, depending on the assumptions made regarding the distribution of electronic energy levels, an expectation of an enhanced paramagnetism for particles containing an *even* number of electrons. Curie-type behaviour with enhanced susceptibility at low temperatures has been observed recently in small particles of odd-electron metals such as lithium (Borel and Millet, 1977), and even-electron metals such as magnesium (Millet and Borel, 1981), platinum (Marzke *et al.*, 1976), and even the high-nuclearity molecular cluster, $H_2Os_{10}C(CO)_{24}$ (Benfield *et al.*, 1982).

The transition, or interfacial region separating III/IV in *Figure 27* is at present poorly understood. As well as the transition from Pauli to Curie-law behaviour in the magnetic susceptibility, it may well signal the appearance of exotic physical properties in the particulate metals, including extremely large dielectric constants (Bergman and Imry, 1977) and intriguing optical properties (Marzke, 1979). Kreibig *et al.* (1977) have studied the optical properties of very small silver particles ($\lesssim 25$ Å) in glassy matrices and find evidence for quantum size effects from the dependence of several features of the absorption spectra upon particle size. Okumara *et al.* (1982) have recently reported the near-infrared absorption spectra of $[(Mo_6Cl_8)Cl_6] \cdot 6H_2O$ which shows absorption peaks attributed to the electronic transitions between the energy levels in this small metallic particle ($\delta \approx 5000$ cm^{-1}).

In this transitional range (*Fig. 27*) the variation of the dielectric properties may, once again, play a crucial role in dictating the critical conditions (cf. Section 3). They may similarly provide a basic experimental criterion for distinguishing between the cluster/particulate-metal/bulk metal regimes. Grannan *et al.* (1981) have recently reported the observation of a dielectric singularity, or catastrophe at the percolation threshold of a granular composite of small silver particles randomly dispersed throughout a KCl host. This dielectric catastrophe occurs quite close to the (classical) critical volume fraction of metal corresponding to the conduction threshold. However, it is clear that there are considerable differences in the precise critical behaviour between this classical percolation system, and the corresponding behaviour of the dielectric constant of heavily doped semi-conductors (e.g., P:Si). For the latter system the dielectric enhancement at the transition (*Fig. 18*) is considerably larger than that expected from classical percolation theories, and is dominated by quantum effects near the metal-insulator threshold (Capizzi *et al.*, 1980).

These differences once again amplify our comments at the beginning of this section concerning the continuum vs. microscopic physics of the metal-insulator transition (à la Mott), and the particulate metal problem (à la Fröhlich, Kubo).

Nevertheless, we suggest that the dielectric behaviour of high nuclearity clusters and particulate metals will be a particularly fruitful and interesting area for future study. We again return to the basic Herzfeld idea (Section 3), which has proved quite successful in so many areas (Ross, 1972; Berggren, 1974; Edwards and Sienko, 1983), to provide some approximate estimate of the critical cluster nuclearity at which *some* metallic properties may well be evident. We have chosen as a prototype system the transition metal carbonyl clusters.

The metallization of inorganic cluster compounds

In a recent review, Marzke (1979) pointed out that *the* basic experimental problem in the study of particulate metals (*Fig. 27*) was still the production of pure, well characterized samples. Major experimental problems include; spurious paramagnetic contaminants, unavoidable particle-size distributions, sintering of particles into larger crystallites during preparation, and the usual necessity for ultra-high vacuum conditions to avoid contamination with oxide species (Knight, 1973; Bourdon, 1980). In contrast, the transition metal carbonyl cluster compounds are structurally very well characterized materials, obtainable in exceptionally high purity and representing metal aggregates of uniform nuclearity and geometry (Johnson, 1980; Benfield *et al.*, 1982). The cluster carbonyls exhibit many different geometries (*Fig. 28*) that are fragments of extended metallic lattices (hcp, fcp, bcc) or resemble other types of close-packing that are theoretically favourable for particles containing a few dozen atoms (polytetrahedral, icosahedral, etc., *see* Hoare and Pol, 1964). The carbonyl ligands themselves exhibit a variety of terminal and bridging coordinations, resembling carbon monoxide adsorbed on a metal surface, and it is anticipated that the physical properties of cluster carbonyls may closely model those of their highly catalytically active, ligand-free analogues. In the present context, we feel they are ideal model systems for monitoring the development of the electronic structure of a particulate metal from that of an individual high-nuclearity cluster molecule.

In a small cluster, for example, $Os_3(CO)_{12}$, the electrons are paired in closed shells of localized molecular orbitals, yielding a diamagnetic ground state with a large energy gap (Woolley, 1981). In contrast, a large cluster will have many closely spaced electronic energy levels which may well be characteristic of a small metallic particle—homogeneous in both size and shape—in the quantum size effect regime. Indeed, recent magnetic susceptibility measurements on the decanuclear osmium cluster $H_2Os_{10}(CO)_{24}$ (Benfield *et al.*, 1982) show intrinsic paramagnetisms below 70 K, as expected for an osmium particle of approximate overall diameter 10 Å exhibiting electronic quantum effects.

The early application of the Clausius-Mossotti expression (Eqs (36), (37)), using measured gaseous molar polarizabilities and known solid densities provided Herzfeld (1927) with a reasonably accurate prediction of which *elements* were metallic, and which insulating in the solid state. It is interesting to extend Herzfeld's application of the Clausius-Mossotti result to the cluster carbonyls of osmium and rhodium and suggest an *approximate* nuclearity for the threshold for metallization, or a corresponding singularity in dielectric properties (Benfield and Edwards, 1983).

In bulk, metallic osmium each atom occupies a volume of approximately 14 Å. The Herzfeld criterion (*Fig. 20*) suggests that bulk osmium could be expanded to an upper limit of a volume of approximately 70 Å before ceasing to be metallic. Crystals of high nuclearity osmium cluster carbonyls contain overall metal atom concentrations of up to one per 100 Å (*see Fig. 29*, which also contains the data for rhodium clusters) approaching the level at which, in *the absence of ligands*, metallization of the sample would be expected. Obviously the presence of the carbonyl 'sheath' will have an effect on the metallization process. Woolley (1981) has recently modelled the bonding mechanism in the M–CO bonds of cluster compounds in terms of Anderson's theory (1975) of the electronic structure of amorphous semiconductors. Here, metal-carbonyl bonding effectively localizes cluster electron density via non-periodic vibronic interactions and this, we anticipate, may well retard the onset of the metallization process (*Fig. 29*). Clearly, however, transition-metal cluster carbonyls of nuclearity

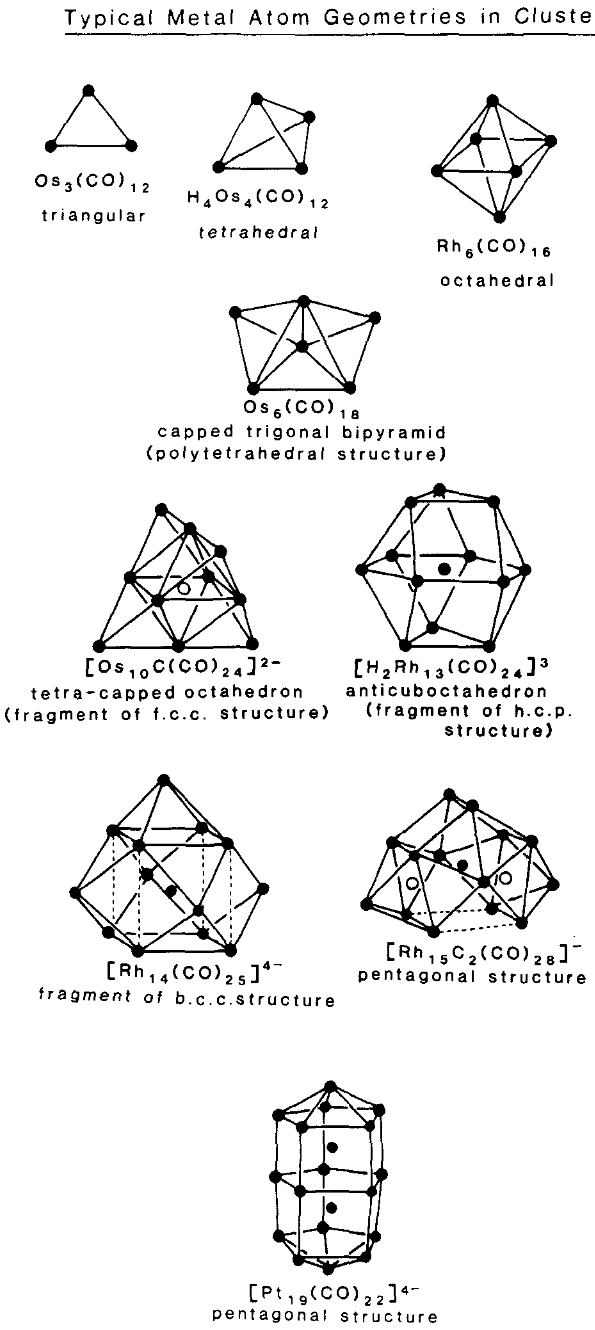

FIG. 28. A representation of typical metal atom geometries in transition metal carbonyls. For clarity, the carbonyl ligands have been omitted. Open circles denote carbon atoms in the cluster compound. Taken from Benfield and Edwards (1983).

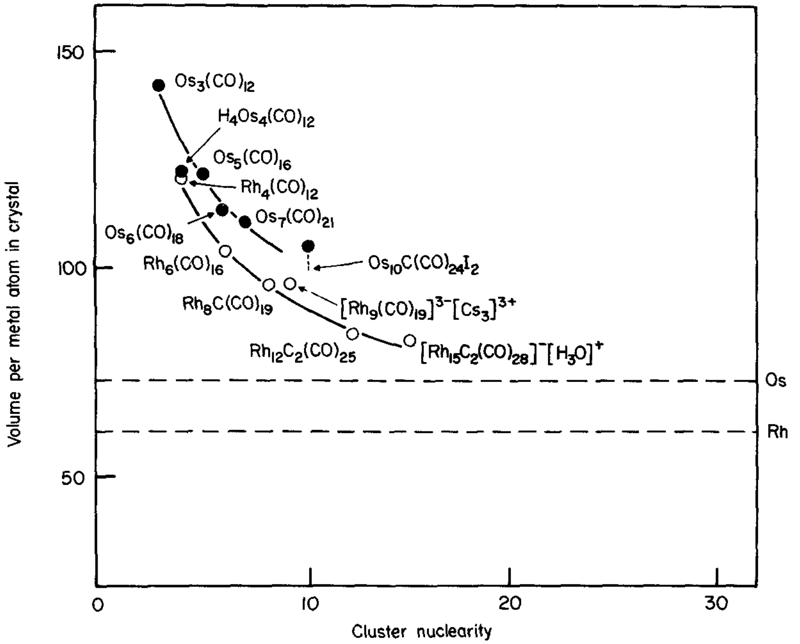

Fig. 29. The metallization of inorganic cluster compounds. The figure shows the volume occupied per metal atom in crystals of rhodium and osmium cluster carbonyls, as a function of the cluster nuclearity. The dotted lines show the approximate values at which, according to the Herzfeld criterion, the metallization of an assembly of single atoms in the absence of ligands would be anticipated. Taken from Benfield and Edwards (1983).

slightly higher than those currently available should show particularly interesting electronic properties, possibly arising from the onset of a polarization catastrophe within the cluster units.

6. CONCLUDING REMARKS

In this review we have tried to bring together a collection of simple predictive models and operational definitions of the metallic state. Our coverage has been representative, rather than exhaustive. For example, we have omitted here any detailed discussion of the role of dimensionality and the metallic state. In the past decade or so there has been considerable interest in the electronic properties of so-called one-dimensional materials that possess an extended columnar structure and anisotropic physical properties in the solid state. Several one-dimensional materials exhibit high room-temperature conductivity (generally some 10^{12} times larger than typical inorganic and organic insulators), and a metal-insulator transition at lower temperature (*Fig. 4a*).

The highly conducting materials are represented by

1. Organic metals, e.g. (TTF) (TCNQ), tetrathiofulvalenium-7,7,8,8-tetracyano-p-quinodimethanide.
2. Inorganic complexes, e.g., $K_2Pt(CN)_4Br_{0.3}$.

3. Main group elemental polymers, e.g., poly(sulfurnitride), SN_x. 4. Organic polymers,
4. Organic polymers, e.g., iodine-doped polyacetylene ($CHI_{0.25}$).

No attempt has been made here to discuss the detailed electronic properties of these materials, and the reader is referred to the reviews by Miller and Epstein (1976), Miller (1978), Underhill and Watkins (1980) and Day (1978) for accounts of present-day activity in this area. However, the considerations outlined in the present review can provide a useful framework for any discussion of the metallization process in one-dimensional materials. For example, many one-dimensional metals exhibit anisotropic reflectivity such that the component of the reflectivity parallel to the chain axis exhibits a Drude edge in the optical spectrum. This is once again a manifestation of an extremely large (high-frequency) dielectric constant in the solid state. For (TTF) (TCNQ), the dielectric constant measured along the chain axis is greater than 3200; perpendicular to the chain axis, the dielectric constant is 6! It would be very interesting to modify the simple Herzfeld criterion (Eq. (31)) to take into account anisotropic polarizabilities in the condensed state. Similarly, the chemical criteria for the design of highly conducting one-dimensional substances rely on precisely similar considerations as those developed earlier in our discussions on the Mott-Hubbard and Anderson models of the metallization process: viz. large overlap between repeat units, reduced on-site electron–electron repulsion, minimum random disorder, etc. (Miller and Epstein, 1976).

We can summarize our present thinking as follows. If a transition from insulating to metallic status occurs, by what changes in property will it be recognized? From the experimental standpoint, the usual answer is electrical conductivity, and in this context a system may be *suspected* of having acquired metallic status when:

1. The electrical conductivity σ tends to a finite value as the temperature approaches zero; by insulating behaviour is meant that σ tends to zero, or ρ tends to infinity. Mott has long maintained that at the limit of low temperature ($T=0$) there can be *no* intermediate state between the two electronic regimes (Mott, 1978). The 'zero-temperature' conductivity studies of silicon doped with phosphorus from the Tokyo, and Bell-Lab groups certainly suggest an extremely sharp transition between the metallic, and insulating states (*Fig. 2*).
2. $\sigma \geqslant \sigma_{\min}$, where $\sigma_{\min}$ is settled empirically (*see*, e.g., Allgaier, 1969), or theoretically (*see*, e.g., Mott, 1972). Note $\sigma_{\min}$ may range from a few hundred ($\text{ohm}^{-1}\,\text{cm}^{-1}$) to several thousand ($\text{ohm}^{-1}\,\text{cm}^{-1}$) (*Fig. 25*), depending upon the nature of the localized-electron states, and hence n_c, the critical density for metallization (*Fig. 16*).
3. $(\partial\sigma/\partial T)_V < 0$: The temperature dependence of the electrical conductivity (at constant volume) will therefore change from the explicit form characteristic of the insulating, or semiconducting state

$$\sigma \sim \sigma_0 \exp(-E_G/kT)$$

   to that anticipated for the phonon-scattering of high-velocity itinerant electrons (*Fig. 4*).

   Corresponding changes in characteristics would also be expected in other transport properties; for example, in the thermoelectric power, and in the Hall coefficient which would now approach the typically metallic value of approximately $(ne)^{-1}$, where n is the electron number, and e its charge.
4. In addition to changes in characteristic transport properties, an insulator-metal transition implies a fundamental change from metallic to other interatomic forces, e.g., van der Waals forces, etc. Therefore, the change in *electronic* character across the transition region suggests that a *thermodynamic* phase change may frequently,

but not necessarily, accompany the onset of metallic conductivity (Krumhansl, 1965; Mott, 1978). Part of the considerable post-War interest in insulator-metal transitions stems from the realization that, when electron-electron interaction is taken into account, the transition in a crystalline system *must* always be discontinuous (Mott, 1961, 1978, 1982). If so, and if the thermodynamic free energy is plotted against the appropriate parameter that 'drives' the transition (either composition or volume), curves such as those of *Figure 30* will be obtained. If the parameter x is the volume, then there will be a discontinuous change of volume, or if x is the composition, a two-phase region and an associated critical temperature T_c (*see Table 1*). Above this critical temperature, an electronic transition occurs *without* a thermodynamic transition; the density at which this occurs is essentially that at which the thermodynamic phase change occurred below T_c. In the case of a discontinuous volume change, it may well prove impossible to observe the volume (AB) at which a sudden appearance of metallic/insulating behaviour occurs (Mott, 1978).

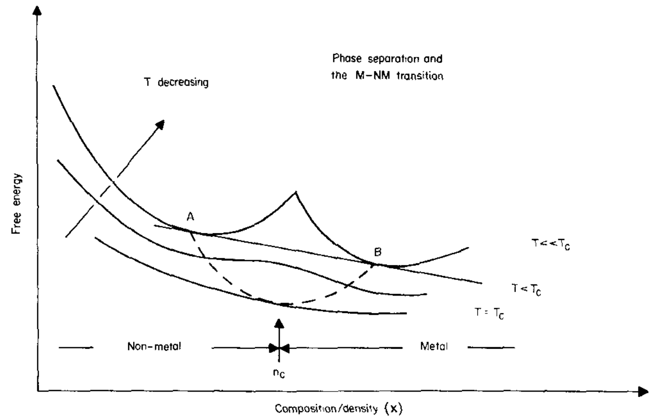

FIG. 30. Thermodynamic consequences of a metal-insulator transition. The anticipated form of the free energy of a system showing a transition between the two electronic regimes as a function of some compositional parameter, e.g., density. T_c is the critical temperature below which a thermodynamic phase change accompanies an electronic transition. Taken from Edwards and Sienko (1982).

There has been much effort devoted to the possible concurrence of the electronic and thermodynamic transitions in condensed phases (Krumhansl, 1965; Cusack, 1978; Mott, 1978; Hensel, 1981). For example, in divalent elemental mercury, the insulator-metal transition occurs at densities well above the critical density, but in the monovalent alkali elements this is not so. Near the critical point of elemental caesium, the very rapid decrease of σ suggests that the critical density is indeed very close to that of the insulator-metal transition, as originally proposed for the alkali metals, and sodium-ammonia solutions by Krumhansl (1965; *see also* Edwards and Sienko, 1981; Hensel, 1981). Similar arguments for narrow *d*-band materials (e.g., transition-metal monoxides) were elegantly developed by Goodenough (1971). He argued convincingly that the instability close to an insulator-metal transition is *the* fundamental reason for the difficulty in preparing model experimental systems which attempt to span the intermediate region between the two limiting regimes. A recent notable example can be found in the spinel system $Li[Li_xTi_{2-x}]O_4 (0 \leqslant x \leqslant 1/3)$, which has attracted attention because of its high superconducting transition temperature (c. 11 K), and a composition induced insulator-metal transition for $x \approx 0.1$ (Johnston, 1976). Close to the critical composition the material appears unstable to disproportionation into insulating regions and metallic superconducting regions (Harrison *et al.*, 1983). The latter form percolating networks throughout the sample, and superconductivity appears to be suppressed if the system falls below the percolation threshold for conductivity.

Naturally to pose the basic question 'What is a metal?' is to suggest many others. Is it, for instance, possible to obtain some reasonable estimate of the critical conditions for metallization, without invoking complicated band structure calculations? In this context, we have made extensive use of the simple Herzfeld theory of metallization. As Ross (1972), Berggren (1974) and Vaišnys and Žmuidzinas (1978) have pointed out, the Herzfeld model gives predictions in a wide variety of experimental systems which are as good as any other estimates derived from ambitious quantum mechanical calculations. Throughout, we have resurrected and applied the original Herzfeld criterion in its most simple, literal sense. We have, with others (e.g., Berggren, 1974), used polarizabilities for free atoms. Obviously, large deformations may be expected as the (gas-phase) atom is condensed into the dense state. An example of this might be mercury, forming Hg_2 units in the condensed state (Herzfeld, 1927). In addition, the molar refractivity, R, has been treated as a constant for all densities up to the metallization onset. One feature which a more rigorous approach would obviously have to take into account is the possible variation in R as a result of interatomic interactions in the approach to the metallic state. Castner (1979) has recently developed this type of self-consistent approach. However, one might argue, with Berggren (1974), that with such elaboration the present criterion does indeed lose some of its immediate and attractive simplicity. Indeed, even in its present form (Eqs (36), (37)) the original Herzfeld criterion does give a reasonable *first-order* description of which elements are metallic, which insulating, and which are borderline in the solid state (*Fig. 20*).

In conclusion, we again return to the long-standing question of the metallic status of the alkalies. Sir Humphry Davy, in his 2nd Bakerian Lecture (1808), first addressed the controversial problem of whether the newly discovered elements sodium and potassium could justifiably be called metals, Davy remarked that 'The great number of philosophical persons to whom this question has been put, have answered in the affirmative. They agree with metals in opacity, lustre, malleability, conducting powers as to heat and electricity, and in their qualities of chemical combination'. Concerning their low elemental density, Davy suggested that '. . . their low specific gravity does not appear a sufficient reason for making them a new class; for amongst the metals themselves there are remarkable differences in this respect, platina, being nearly four times as heavy as tellurium'. In his major work 'The principles of chemistry', Mendeleeff (1869, 1905) also drew attention to the important periodic nature of the atomic, or molar volumes of the elements. In particular, he stressed the link between the large molar volume of the alkalies, their metallic status, and their high chemical reactivity. He contrasted this with the corresponding inertness of the low molar volume metals iridium, platinum and gold. About this time, Meyer's paper on the periodic variation of molar volume also appeared (1870). It was left to Herzfeld (1927) in a beautiful, but somewhat obscure paper, to fully emphasize the fundamental link between atomic properties, density and the metallic state. However, the 1920s and 1930s period in physics and chemistry was dominated by the major advances in quantum mechanics, and this simple, attractive idea was lost for some considerable time (Cohen, 1968).

It is therefore amusing and, we suggest, possibly comforting to chemists, to note that events have now come full circle! The breakdown of the one-electron band theory of solids still remains one of the fundamental problems in solid-state science (Goodenough, 1971; Mott, 1982). The last few years have indeed revealed an increased awareness of the 'atomistic' or 'real space' view of the metallic state (*see*, for example, Davis, 1980). The basis of this approach is the fundamental importance of the *atomic properties* in dictating the threshold density for the onset of *metallic properties* in the condensed state. The periodic table of the elements (*Fig.* 6) still remains the most fundamental and intriguing example of this (Davy, 1808; Herzfeld, 1927).

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