The Transition to the Metallic State

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The most fundamental classification of the electronic properties of materials is in terms of metallic vs. nonmetallic properties. In perhaps its most widespread application, this classification forms the basis of the periodic table.[1,2] A most striking feature of the p-block series is the almost diagonal line separating metals from nonmetals. This natural demarcation of the elements under ambient conditions into metals and nonmetals is perhaps the most intriguing example of a metal–nonmetal (M–NM) transition.[2]

From a wider viewpoint, the M–NM transition in both disordered and crystalline systems is currently the subject of intensive experimental and theoretical investigation.[3] A wide variety of experimental techniques ranging from transport property measurements to magnetic properties have been employed to study the transition in expanded fluid metals,[4a] doped semiconductors[3] (e.g., P-doped Si), transition-metal oxides,[4b] alkali atoms in inert matrices (Ar, WO_3, etc.),[3b,c] solutions of metals in ammonia,[4d] and many other systems.

This Account outlines recent developments in the field that, we feel, have a direct bearing on current descriptions of the M–NM transition in condensed systems. Three prototype systems have been chosen for attention: the periodic table, expanded liquid metals, and metal–ammonia solutions.

The Periodic Table of the Elements—Why on Earth Do We Have Metals and Nonmetals?

This fundamental problem has attracted attention since the development of quantum-mechanical descriptions for electrons in atoms and molecules. The routine explanation in terms of electronic energy bands, viz., metals possess partly filled bands, nonmetals have empty or completely filled zones, can be traced back to the work of A. H. Wilson[5] in 1931. However, it is not generally recognized that the first semiquantitative rationalization of the problem dates back even further—to the work of D. A. Goldhammer[6a] in 1911 and K. F. Herzfeld in 1927.[6b]

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In simple terms[2] the Goldhammer/Herzfeld approach is concerned with the *mutual* polarization of an atom by the remaining atoms in the condensed phase. If this interaction is sufficiently large, a polarization catastrophe occurs; the electrons acquire itinerancy and the element itself takes on metallic status. The basis of the approach is as follows: For a nonmetallic material, the optical refractive index (n) and high-frequency dielectric constant (ϵ) are represented in terms of the Lorentz–Lorenz or Clausius–Mossotti relationships[7]

$$\frac{n^2 - 1}{n^2 + 2} = \frac{R}{V} = \frac{\epsilon - 1}{\epsilon + 2} \qquad (1)$$

where R is the molar refractivity of the gaseous atomic species and V is the molar volume of the element in the condensed state. For nonmetallic systems the ratio $(n^2 - 1)/(n^2 + 2)$ is necessarily always less than 1. However, if the ratio (R/V) is unity, we have $(\epsilon - 1) = (\epsilon + 2)$, a condition satisfied *only* if ϵ becomes infinite![6b,8] Therefore, at $R/V = 1$, the valence electrons, which before had been quasielastically bound to their atoms or ions, are now set free via mutual polarization. A dielectric catastrophe occurs, and the solid becomes a metallic conductor.[6] This simple criterion, therefore, defines the onset of a metallic state.

We have recently[2] used the Herzfeld criterion[6b] with measured molar refractivities of gases, and solid–state molar volumes, to predict which elements are metallic, which nonmetallic, and which borderline when in the solid state. Just how well the overall features of the periodic classification conform to the simple criterion

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(7) (a) Kittel, C. "An Introduction to Solid State Physics", 5th ed. Wiley: New York, 1976. (b) Ladd, M. F. C. "Structure and Bonding in Solid State Chemistry"; Ellis Horwood Ltd.: Chichester, 1979.

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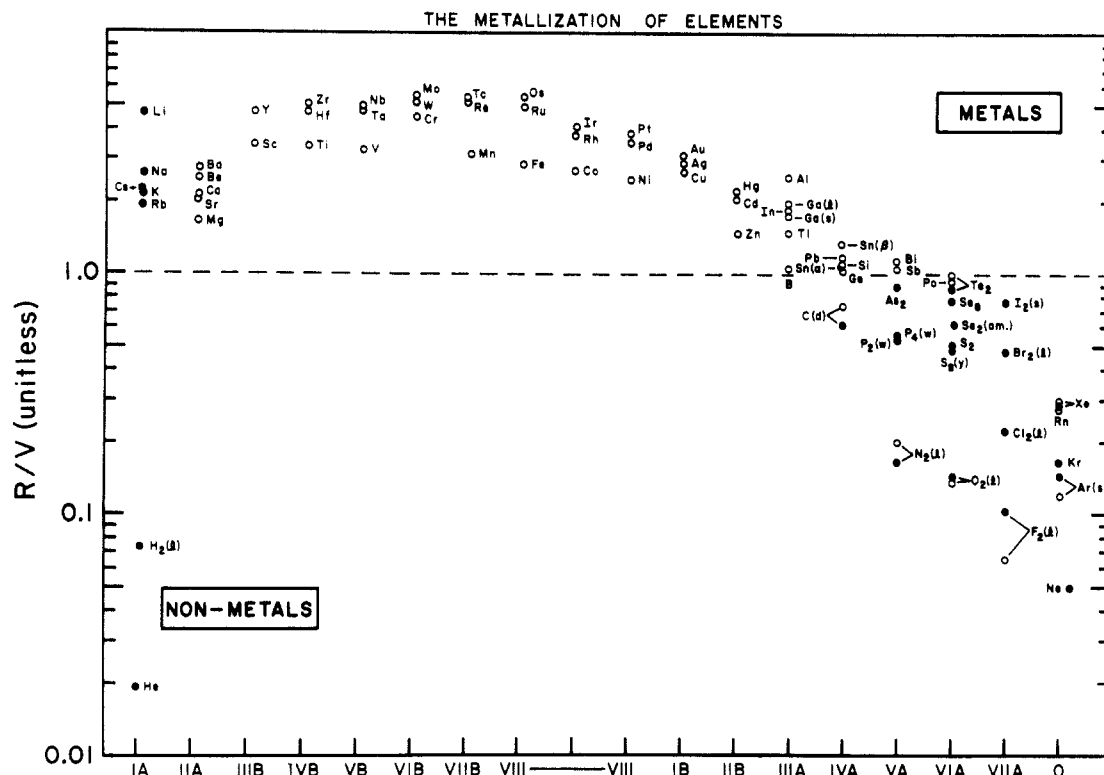
Figure 1. Metallization of elements under the ambient conditions imposed on this planet. The figure shows the ratio (R/V) for elements of the s, d, and p blocks of the periodic table. Here R is the molar refractivity and V is the molar volume; see text. The shaded circles represent elements for which both R and V are known experimentally. The open circles are for elements of which only V is known experimentally, and R is calculated. Taken from ref 2.

can be seen by referring to Figure 1 which shows the data[2] for the naturally occurring elements at their normal densities.

As an example, the group 7A elements have (R/V) < 1; we anticipate nonmetallic behavior for the entire halogen series. Moving down the group, the ratio (R/V) increases, leading, at normal densities, to transition to the solid at I_2 and, at higher densities, to the metallic state. From a wider viewpoint, groups 3A–6A effectively straddle the dividing line between metallic and nonmetallic. The success of the criterion, even in its simplest form,[2] illustrates the importance of *atomic* properties in dictating the nature of the *element* in the condensed state.[6b]

There has recently been considerable interest[9] in the experimental detection of an impending "polarization catastrophe" in two-component systems which transform from nonmetallic to metallic behavior at some critical composition. Figure 2 shows typical results for Na–NH$_3$ solutions[10] and P donors in silicon.[9a] Both systems show large enhancement in the dielectric constant as the M–NM transition is approached. Another important application of the Herzfeld criterion has been in the prediction of the critical conditions necessary for conversion of molecular to metallic H_2. Ross[8] has used eq 1 to predict metallization onset at a density of 1.02 g cm^{-3}. The recent experiments of Hawke et al.[11] show that H_2 becomes metallic at $\rho \sim 1.06$ g cm^{-3}, corresponding to a pressure of some 2 Mbar.

Expanded Fluid Metals—A Probe of the Microscopic Features of the Transition

In fluid alkali metals, transition between metallic and nonmetallic states can be continuously studied by expansion of the metallic liquid up to supercritical conditions.[12] Despite the extreme conditions, a detailed picture of the electronic properties is now emerging.[4a] These systems offer the distinct advantage of a M–NM transition in an array of simple s-electron states uncomplicated by presence of a host matrix. Such a system is important also in that it illustrates a fundamental breakdown in the Wilson criterion for metallic character.[13]

Consider an array of cesium atoms on a lattice characterized by spacing d which may be varied.[13] For finite d, overlap of the 6s wave functions gives rise to a half-filled band, and according to the Wilson picture, the system should be metallic—*however far apart the atoms might be.* As Mott[13] has pointed out, ".... this is against common experience, and, one might say, common sense". It is clear, therefore, that for large d the Wilson picture is not valid, essentially because it neglects "correlation" due to Coulombic interactions between electrons. These tend to localize electrons at distinct lattice sites. Therefore, for large d, we have an array of isolated, neutral Cs atoms. For conduction to occur in this nonmetallic regime, one electron has to be transferred from its home site to another, producing Cs⁻. In the limit, $d \to \infty$, this excitation energy is the ionization energy of the Cs atom (3.89 eV) minus the

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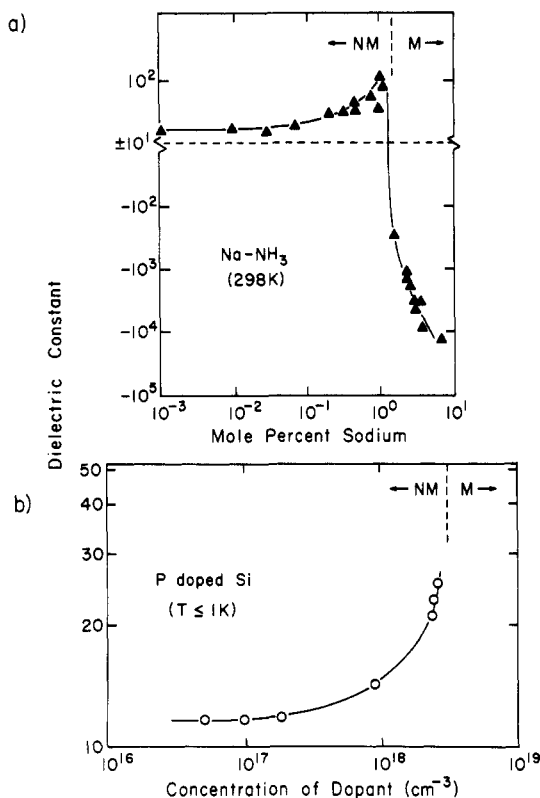
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Figure 2. Dielectric constant for two systems exhibiting a polarization catastrophe at the M-NM transition. (a) The real part of the microwave frequency (10 GHz) dielectric constant vs. Na concentration in fluid Na-NH$_3$ solutions. (Reprinted with permission from ref 10. Copyright 1968, American Institute of Physics.) (b) The static dielectric constant as a function of excess donor concentration of Si doped with P. (Reprinted with permission from ref 9. Copyright 1975, American Institute of Physics.) In both instances, the approximate location of the M-NM transition is indicated.

electron affinity (0.47 eV), i.e., 3.42 eV. This energy difference, customarily denoted by U, is a measure of the instability associated with putting two electrons, of antiparallel spin, on the same atom. For s-like orbitals it can also be estimated by

$$\left\langle \phi_{6s}\phi_{6s} \left| \frac{e^2}{r_{12}} \right| \phi_{6s}\phi_{6s} \right\rangle = \frac{5}{8} \frac{e^2}{a_H^*} = 3.4 \text{ eV} \qquad (2)$$

where a_H^* is the radius of the Cs 6s orbital.[3c] For finite lattice spacings, the electronic energies should be broadened by a characteristic bandwidth, Δ, representing the orbital overlap between constituent atoms. The actual excitation energy for conduction is then $U - \Delta$. Thus, at large lattice spacings (small Δ), Coulomb repulsion dominates, electrons are localized, and the system is nonmetallic. For small d, orbital overlap (Δ) dominates, and the system is metallic.[3c] Between these regimes, a M-NM transition must therefore occur. Figure 3 shows conductivity data for expanded (supercritical) Cs at various densities.[14]

The formalisation of the above was embodied in an explicit Hamiltonian by Hubbard.[15] The reasonable approximation was that the (repulsive) electron-electron correlations are important only when two electrons, with antiparallel spin, are present on the same atom.
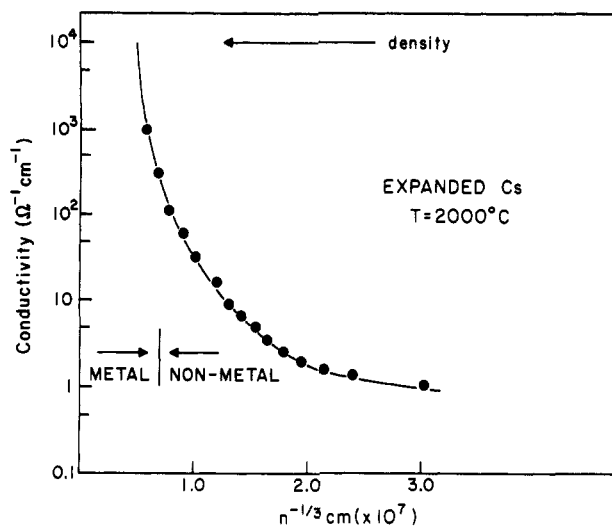
Figure 3. Electrical conductivity of elemental cesium traversing the M-NM transition. The concentration of cesium is given in terms of the cube root of the reciprocal number (electron) density, n. (Reprinted with permission from ref 14. Copyright 1971, Verlag Chemie.)

The energy ($U-\Delta$) is generally called the Hubbard gap, and materials which are nonmetallic because of a Hubbard gap are called "Mott-Hubbard" insulators. The criterion for a M-NM transition is then[3b,c]

$$\Delta \sim U$$

A number of recent studies on expanded liquid metals and doped semiconductors has led to a more realistic picture of the transition region in terms of an amended Hubbard scheme.[4a,12,14,16,17] The original Hubbard picture[15] neglected the stabilizing effect of Coulomb interaction between the positive "hole" (Cs$^+$) and the negatively charged carrier (Cs$^-$) formed during excitation. Recent experimental data[4,18] for alkali atoms in the vapor phase show that a relatively high concentration of molecular associates forms as the density of metal increases. These clusters have ionization energy substantially reduced from the single atom value of 3.89 eV. Furthermore, recent theoretical treatments by Bhatt and Rice[17] suggest that large multinuclear clusters may also possess high electron affinity. This effectively increases the probability of electron transfer from an isolated atom to a large cluster.[19]

The general conjectures,[4a] then, for the energy spectrum of Cs undergoing a M-NM transition are summarized in Figure 4. For isolated atoms, charge transfer requires considerable energy. As the density of Cs increases, larger clusters form; charge transfer becomes easier, forming complexes Cs$_n{}^-$. As $n \rightarrow n_c$ at the M-NM transition, energies of Cs$_n$ and Cs$_n{}^-$ overlap, and facile conduction proceeds.

Freyland[20] has recently measured the magnetic susceptibility of elemental Cs from saturated liquid up to near the critical point (1750 °C and 114 bar). Figure 5 contains his data. The dashed curve gives the calculated paramagnetism assuming monatomic Cs vapor.

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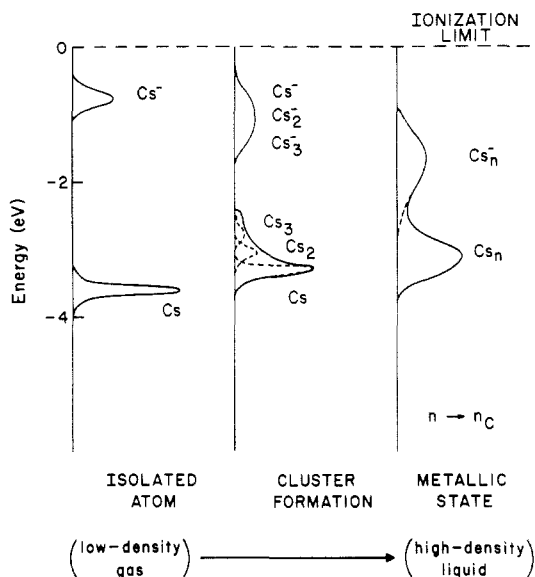(15) Hubbard, J. *Proc. R. Soc. London, Ser. A* 1963, 276, 238; 1964, 281, 401.
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(19) Rice, T. M. In ref 3b, p 369.
(20) Freyland, W. *Phys. Rev. B: Condens. Matter* 1979, 20, 5104.

Figure 4. A schematic representation of the "microscopic" structure during the M–NM transition in expanded fluid Cs metal. The energy zero refers to the ionization limit. The system moves from a low-density gas (composed predominantly of isolated atomic states) to a high-density liquid, at the critical metal (electron) density, n_c. (Adapted with permission from ref 4a. Copyright 1981, Gordon and Breach Science Publishers, Inc.)
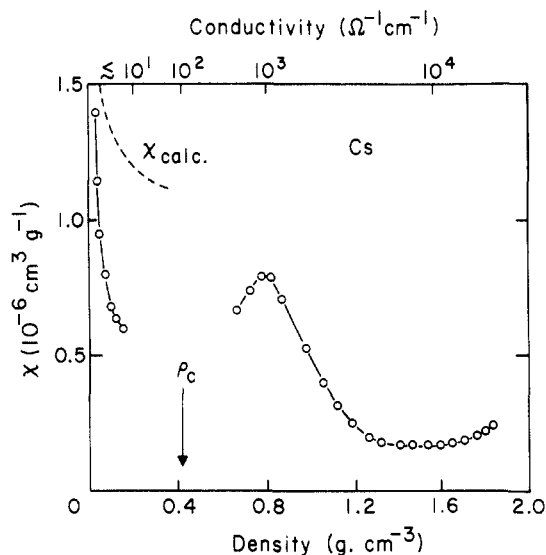
Figure 5. The magnetic susceptibility χ liquid and vapor phase Cs. The dashed curve is the calculated Curie paramagnetism on the basis of a purely atomic vapor. (Reprinted with permission from ref 20. Copyright 1979, American Institute of Physics.)

The deviation at low density is attributed to spin pairing of electrons in diamagnetic Cs_2 molecules, or larger molecular aggregates. We note, in passing, the superficial similarity of this spin-pairing interaction to that observed in, say, $Na–NH_3$ solutions, as the concentration of Na is increased.[21] However, in the latter system, the spin pairing is usually viewed in terms of a long-range (almost antiferromagnetic) interaction between isolated electron units. In liquid Cs, spin pairing occurs via formation of discrete dimers or higher polymeric aggregates.[20]

The pronounced maximum in χ just on the metallic side of the transition is generally attributed to a large

(21) Edwards, P. P. "The Electronic Properties of Solutions of Metals in Ammonia and Related Solvents"; *Adv. Inorg. Radio Chem.*, in press.

enhancement in the spin susceptibility, the "Brinkmann–Rice enhancement",[3c,22] for materials in which the Hubbard energy U is comparable with Δ. Recent studies[23] of fluid $Li–NH_3$ solutions reveal a similar slight enhancement just above the M–NM transition.

A Closer Look at the Transition

The Actual Location of the M–NM Transition— the Mott Criterion. For an isolated Cs atom, the 6s valence electron and cesium cation attract each other with a force for which the potential energy is given by $V = -e^2/r$. It is well recognized that under the influence of this interaction (Figure 6) a continuum of bound, localized states will exist.[3c] This state of affairs *does not* exist in the metal. Here the attractive Coulombic interaction between the two oppositely charged particles is reduced or "screened" via the (Fermi) sea of metallic electrons. The potential may now be written, according to the Thomas–Fermi prescription, as[3c]

$$V(r) = -(e^2/r) \exp(-qr) \tag{3}$$

where q is a characteristic screening length given by

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

and n is the (metal) electron concentration.

Such a potential in a metallic system does not necessarily lead to a bound state for the electron. Indeed, at high Cs concentrations, screening via metallic electrons *prevents* the formation of bound states.[3c,7a] As electron concentration is reduced, screening diminishes, and ultimately the ionized cesium atom is capable of capturing the electron that has been removed from it. These considerations were the basis of Mott's original thesis[3c,13] for the transition from the metallic to the nonmetallic state. Mott went further and argued that the changeover between regimes must be sharp[24]— indeed, first order; electrons are *either* localized *or* itinerant. Although the experimental realization of a true (i.e., first order) Mott transition remains elusive,[25] a large number of systems show extremely rapid changes in conductivity as some experimental parameter (e.g., pressure, temperature, composition, etc.) is varied. Figure 7 shows results from three representative systems: Cu–Ar thin films,[26] the oxide VO_2,[27] and iodine-doped polyacetylene.[28]

Mott first predicted that the M–NM transition should occur at a critical electron concentration, n_c, given by

$$n_c^{1/3} a_H \simeq 0.25 \tag{5}$$

where a_H is an effective radius for the *isolated* center in the low-electron density limit; i.e., in the nonmetallic regime far from the transition. From an extensive

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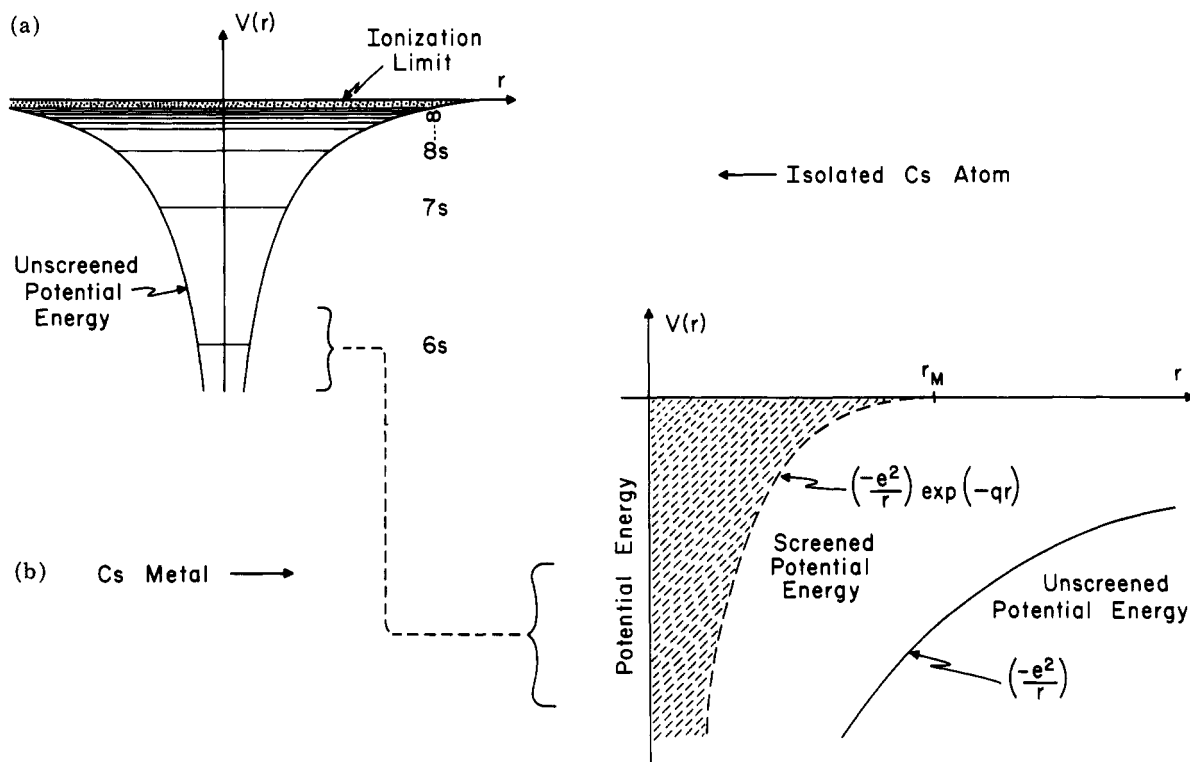
Figure 6. Schematic representation of screened and unscreened Coulomb potentials of a Cs^+ ion core as seen by an electron. (a) Isolated Cs atom; (b) Cs "atom" in a metallic system. In the former, the potential is long range; in the latter, short range. r_M is the (radial) extent of the screening in the metallic state; it is typically less than 1 Å.
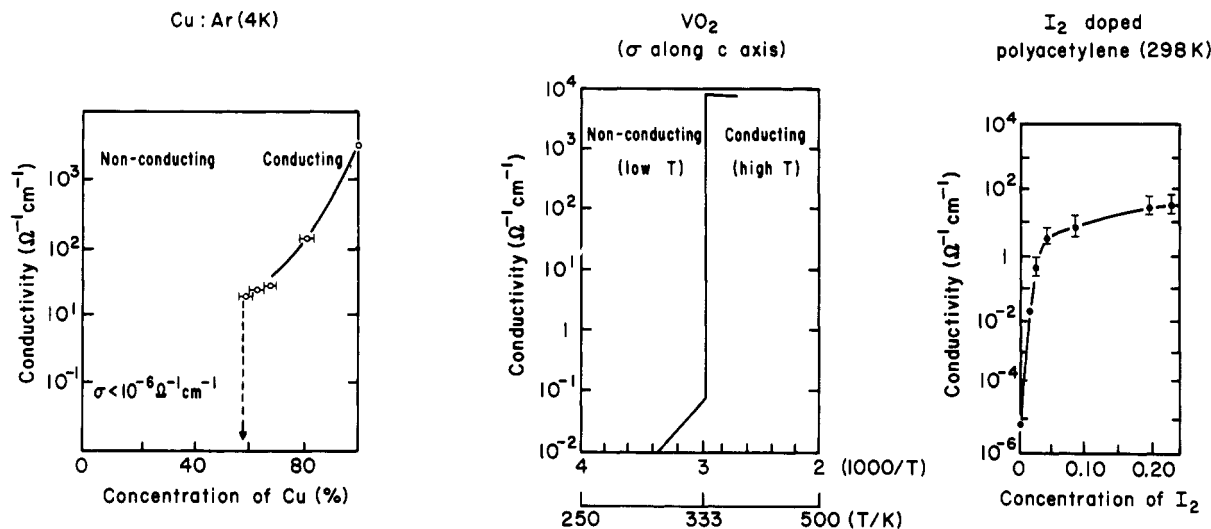
Figure 7. Transition to the metallic state in three representative systems. (1) Cu:Ar thin films; (2) VO_2; (3) I_2-doped $(CH)_x$. (Reprinted with permission: (1) ref. 26; copyright 1973, Physical Society of Japan; (2) ref 27; copyright 1969, Pergamon Press; (3) ref 28; copyright 1978, American Institute of Physics.)

analysis of experimental data, we have recently shown[29] that a particular form of the Mott criterion,

$$n_c^{1/3} a_H^* = 0.26 \pm 0.05 \tag{6}$$

exhibits apparent universality in that it describes the onset of metallic character for systems spanning a range of ca. 10^9 in critical densities and approximately 600 Å in a_H^*. The important feature here is that a_H^* is now characteristic of a *realistic* wave function for the isolated species. (The original Mott derivation calculates a_H^* for a simple hydrogen-like atom in a dielectric medium. For systems in which the dielectric constant

(29) Edwards, P. P.; Sienko, M. J. *Phys. Rev. B: Condens. Matter* **1978**, *17*, 2575.

is large, ca. 16 in Si, this approximation is adequate. For low-dielectric systems, a more realistic wave function recognizes the peculiar chemical characteristics of the various matrix-bound species.[29]) For the majority of systems a_H^* is obtained directly from experimental measurements which characterize the localized-electron state. The data given in Figure 8 range from doped semiconductors through metal–ammonia and –methylamine solutions to thin films of Na in Ar at 4.2 K. Also included are expanded alkali metals in the gas phase.[30] For the latter systems onset of *metallization occurs at the same metal (electron) density as the liquid–vapor critical point.*[4a,31] We return to this observation later.

(30) Edwards, P. P.; Sienko, M. J. *J. Am. Chem. Soc.* **1981**, *103*, 2967.
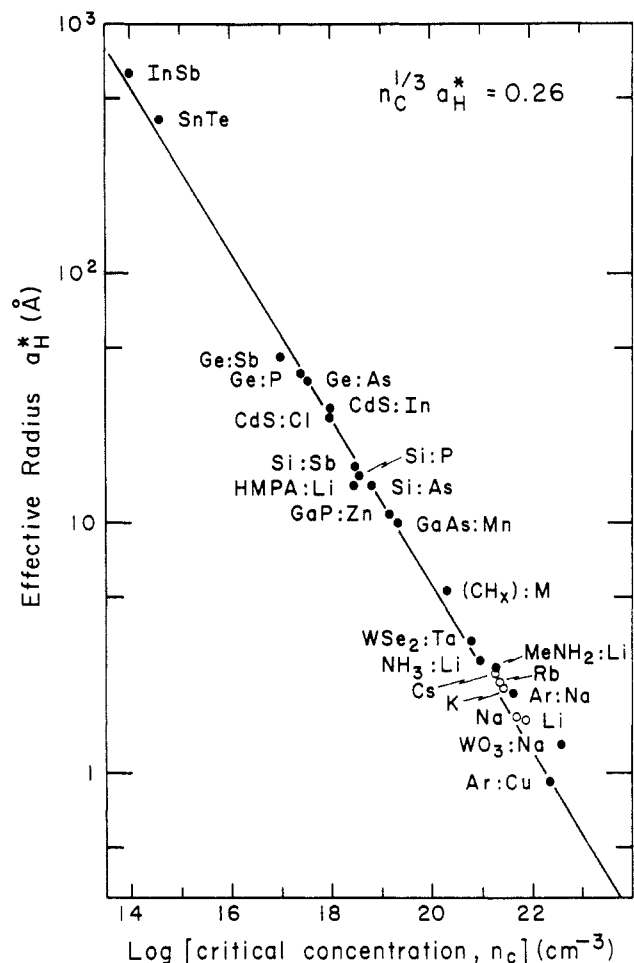
Figure 8. Transition to the metallic state. A logarithmic plot of the effective radius, a_H^*, of the localized-electron state vs. the critical concentration for metallization, n_c, in a variety of systems. Taken from ref 30.

Table I

| system	$a_H^*/Å$ (estimated, eq 6)	$a_H^*/Å$ (empirical atomic radii, Slater)
Si–Au	1.35	1.35
Si–Mn	<1.27	1.40
Si–Fe	<1.30	1.40
Si–Co	1.33	1.35
Si–Ni	1.39	1.39

This plot highlights an interesting, and recurrent, theme in the M–NM transition; viz, the "size" of the *isolated* species appears to be important in dictating the threshold density of metallization. Indeed, the mere form of the periodic table is probably the most intriguing example of this![2] Orbital contraction as one proceeds across the table may lead to insufficient overlap to produce the metallic state.

Another interesting (almost reverse!) application of the Mott criterion is given by Morigaki in a recent paper.[32] He uses eq 6 to obtain estimates of a_H^* from experimental values of the critical density n_c in amorphous alloy systems. His results are compared with empirical atomic radii from Slater[33] in Table I.

(31) Freyland, W. *J. Non-Cryst. Solids* **1980**, *35*, *36*, 1313.
(32) Morigaki, K. *Philos. Mag.* **1980**, *B42*, 979.
(33) Slater, J. C. "Quantum Theory of Molecules and Solids"; McGraw-Hill: New York: 1965; Vol. 2, p 103.
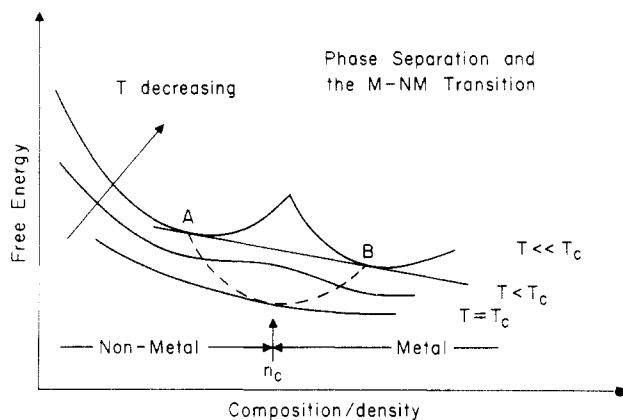
Figure 9. Thermodynamic consequences of a M–NM transition. Anticipated form of the free energy of a system showing a M–NM transition as a function of some compositional parameter, e.g., density. T_c is the critical temperature below which a thermodynamic phase transition accompanies an electronic transition.

Thermodynamic Consequences of the M–NM Transition. If we take a reasonable estimate of a_H^* for an isolated Cs atom (e.g., from the ionization energy,[31] or from the principal maximum in the radial distribution function[30]) and use eq 6 to predict the critical concentration for a M–NM transition, we find $n_c \sim 1.1 \times 10^{21}$ cm^{-3}. This is actually very close to the density of Cs at its critical point.[34] The general consensus now[30-32,35,36] appears to be that for the monovalent liquid metals, the liquid–vapor transition at the critical temperature ($T_c = 2023$ K for Cs) and density ($\rho_c = 0.42$ g cm^{-3}) is indeed coincident with the M–NM transition. This is important not only theoretically but also technologically in view of the continuing interest in dense metal vapors and their possible applications to energy-conversion devices.

Any M–NM transition requires a gross change in the nature of electronic interactions between atoms. Such changes in *electronic* properties are apparently sufficient to influence the *thermodynamic* features of the system, in particular, the electronic contribution to the total free energy. The conditions, therefore, appear conducive for a thermodynamic phase transition to accompany an electronic transition at the critical density for the M–NM transition.[35,36] The realization of this connection dates back to the work of Mott[13a] and Krumhansl.[35] Similar arguments for narrow d-band materials (e.g., transition-metal oxides) were elegantly developed by Goodenough.[37] Mott[38] consistently argued that for a true discontinuous (i.e., first order) M–NM transition, a plot of the total free energy against composition will be as shown in Figure 9. The familiar condition for a first-order phase transition is that there be two points of common tangency at constant T. Clearly, then, a system in the region between A and B will separate into two phases.[38] For pure alkali metals, the liquid–vapor transition is a direct manifestation of the electronic constitution change at the M–NM transition.[35] The Mott criterion (eq 6) is fullfilled *at* the

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(37) Goodenough, J. B. In "New Developments in Semiconductors"; Wallace, R. R., Hams, R., Zuckermann, M. J., Eds.; Noordhoff International Publishing: Leyden, 1971; Chapter III, p 107.
(38) Mott, N. F. *Philos. Mag.* **1978**, *37*, 377.

critical densities (Figure 8). This again demonstrates the fundamental importance of the atomic characteristics in dictating the threshold for both electronic and thermodynamic transitions.

The "matrix-bound" congener of this phenomenon apparently is responsible for properties close to a M–NM transition. In the liquid state, one of the most spectacular examples of this is in metal–ammonia solutions. Na–NH_3 solutions in the transition region (~ 4 mol % Na) undergo a striking liquid–liquid phase separation below 232 K.[39] The solutions physically separate into two distinct layers: a low-density bronze metallic phase floating on a more dense, less concentrated, blue phase. In 1958, Pitzer,[40] in a remarkable contribution which appears to have been the first theoretical consideration of this phenomenon, likened the liquid–liquid phase separation to the critical condensation of an alkali-metal vapor in the gas phase. His idea[40] was remarkable in that it preceded almost all the experimental investigations into dense metal vapors. It was also in advance of the realization[13a,35] of the link between this type of critical phenomenon and the M–NM transition. It turns out that Pitzer's suggestion represents a particularly apt description of the liquid–liquid separation in these systems.[30] Here again, critical densities are in agreement with the Mott criterion (eq 6).

Similar effects can arise in solid-state materials. Goodenough[37] has suggested that instability close to a M–NM 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 notable example can be found in the spinel system $Li_{1+x}Ti_{2-x}O_4$ ($0 \le x \le {}^1/_3$), which has attracted attention[41] because of its high superconducting transition temperature, ca. 11 K. The material appears unstable to disproportionation into nonmetallic and metallic superconducting regions. The latter form percolating networks throughout the sample. Superconductivity appears to be suppressed if the system falls below the percolation threshold for conductivity.[42]

Concluding Remarks

Our aim in this Account has been a brief, introductory survey of the M–NM transition in condensed systems. With incursion into solid state physics of numerous "chemical" systems, the need arises[43] for a "....new kind of partnership between chemists and physicists". Both areas clearly benefit from a healthy fuzziness between disciplines. It is hoped that the present survey shows at least some of the physical background and chemical guidelines important in the *transition to the metallic state.*

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