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Universality aspects of the metal-nonmetal transition in condensed media*

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Our objective in this paper is to provide a simple, conceptual, framework for describing the metal-nonmetal (MNM) transition in systems that can be viewed in terms of a lattice of impurity states embedded in a host matrix. From an extensive analysis of experimental data, we find that a particular (scaled) form of the Mott criterion, $n_c^{1/3} a_H^* = 0.26 \pm 0.05$, is applicable over a range of approximately 10^{10} in critical densities (n_c) and approximately 600 Å in Bohr radii (a_H^*). Here a_H^* is defined as an appropriate radius associated with a *realistic* wave function for the localized state in the low-electron-density regime. The systems of interest range from tight-binding (Frenkel) metal-atom states in the rare-gas solids to shallow (Wannier-like) states in the group-IV*a* semiconductors and indium antimonide. The possible origins of this apparent universality have been formulated from a consideration of Berggren's interpretation of the Hubbard model for the transition, as applied to condensed systems. In essence, it appears that the role of the host matrix in the phenomenon of MNM transition is important primarily in the sense that it determines the form of the radial distribution of the (localized) impurity state. We suggest that once these matrix-induced modifications to the (gas-phase) donor state are taken into account, the ensuing transition to the metallic state (at finite impurity concentrations) reduces to a one-electron problem in a suitably renormalized concentration grid.

INTRODUCTION

The phenomenon of the metallic condensation of a lattice of impurity centers in a host material has received a great deal of attention during the last three decades.[1-14] It was Mott,[6] in particular reference to the metal-nonmetal (MNM) transition in the group-IV semiconductors, who first derived a simple criterion relating the first Bohr radius (a_H) of an isolated (insulating) center to the critical density of centers (n_c) at the transition

$$n_c^{1/3} a_H = K , \tag{1}$$

where

$$a_H = \frac{K_{st} \hbar^2}{m^* e^2} \tag{2}$$

and K_{st} is the static (low-frequency) dielectric constant of the host material, m^* is the effective mass of an electron in the host conduction band, and K is a constant, typically[7] of the order 0.25.

Two aspects of this original formulation, perhaps not generally appreciated, merit attention:

(i) the model supposes that the electron-positive-ion interaction in the low-electron-density regime is screened by the static dielectric constant of the host material. The resulting one-electron wave functions are then constructed entirely from accesible (unoccupied) orbitals of the *host* matrix.[15,16] As such the approach should be rigorously applicable only to matrix-bound ground states whose eigenfunctions [$\psi(\vec{r})$] and eigenvalues (E) are truly Wannier-like, being totally independent of the peculiarities of the donor atom,[17]

$$\psi(\vec{r}) = (\pi a_H^3)^{-1/2} \exp(-r/a_H) , \tag{3}$$

$$E = \frac{-e^4 m^*}{2K_{st}^2 \hbar^2} = \frac{-e^2}{2K_{st} a_H} . \tag{4}$$

(ii) As a natural consequence of (i), n_c is expected to be independent of the nature of the donor atom for any particular host matrix.

Even in the case of the large-radius, Wannier-like, impurity states in the group-IV materials, these criteria are not rigorously upheld. Matrix-bound (localized) states display a slight donor dependence in both optical and magnetic properties,[15-17] and chemical shifts in n_c are well characterized in both silicon and germanium.[13,18] However, it is well established[12,19] that a criterion of the form given by Eq. (1) can be applied with considerable success to these materials, *provided* slight corrections to the donor eigenfunctions and eigenvalues are carried out. For example, if the isotropic Bohr radius is calculated from the *experimental* ionization energy (E_{expt}) of the localized state, via $e^2/2K_{st}E_{expt}$, rather than from the dielectric properties of the host material [Eqs. (2) and (4)]. In this manner, it is possible both to "fine-tune" the Bohr radius to a slightly more realistic value than that given by Eq. (2), and to introduce the required donor dependence into a_H and hence n_c.

Since Mott's original work,[2,6] our experimental spectrum of matrix-bound systems exhibiting a MNM transition has increased considerably and critical concentrations now span almost ten orders of magnitude, ranging from approximately 10^{22} cm^{-3} for alkali-rare-gas atom films[20-22] to ap-

TABLE I. Critical densities and Bohr radii for systems exhibiting a metal-nonmetal transition.

System	Critical density (cm^{-3})	Isotropic Bohr radius, a_H^* (Å)	Obtained from
Xe:Hg	$(4-4.5)\times10^{22}$ [a]	1.3	Excitonic spectra [a]
Ar:Cu	$(2.2-2.6)\times10^{22}$ [b]	0.9	Pseudopotential theory as applied to the isolated donor (Ref. 24)
WO_3:Na	$(4\pm0.5)\times10^{22}$ [c]	1.3	See footnote d
Ar:Na	3.7×10^{21} [e]	2.08	Pseudopotential theory (Ref. 31)
MeA:Li	$(1.8\pm0.3)\times10^{21}$ [f]	2.88	Obtained by fitting optical ($1s\rightarrow2p$) transition of the isolated center to a polaron model (Ref. 52)
WSe_2:Ta	6.6×10^{20} [g]	3.4 ± 0.9	Optical spectra: (i) taken directly from Ref. 53 (ii) utilizing data from Ref. 54, and and incorporating central-cell corrections for excitonic spectra (Ref. 55)
GaAs:Mn	$(2.1\pm0.4)\times10^{19}$ [h]	10.1	Quantum-defect approach for deep and intermediate impurity states (Ref. 56)
GaP:Zn	$(1.7\pm0.5)\times10^{19}$ [i]	10.8	Experimental ionization energy in the low-concentration limit (Ref. 57)
HMPA:Li	$(3\pm1)\times10^{18}$ [j]	14.1 ± 1.2	Kohn-Luttinger effective-mass theory (Ref. 32)
Si:P	$(3.5\pm0.4)\times10^{18}$ [k]	15.2 ± 1.7	For both Si and Ge, a_H^* obtained from two approaches: (i) the Coulomb result (ii) quantum-defect approach Details given in Refs. 18 and 32
Si:As	$(6.4\pm0.5)\times10^{18}$ [k]	14.1 ± 1.9	
Si:Sb	$(3.0\pm0.2)\times10^{18}$ [k]	16.6 ± 1.3	
CdS:Cl	$(0.5-1.6)\times10^{18}$ [l]	26.7	Experimental ionization energy in the low-concentration limit (details given in Ref. 48)
CdS:In	$(2.2\pm0.2)\times10^{19}$ [m]	31.6	
Ge:P	2.5×10^{17} [n]	38.7 ± 1.2	See details for doped Si systems
Ge:As	3.5×10^{17} [n]	37.0 ± 1.8	
Ge:Sb	0.95×10^{17} [n]	45.5 ± 1.0	
InSb	$(0.7-1.25)\times10^{14}$ [o]	640	Reference 60

[a] References 22 and 51.

[b] N. E. Cusack, private communication to K.-F. Berggren, cited in Ref. 24.

[c] B. R. Weinberger and D. F. Holcomb (private communication).

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[e] Reference 20.

[f] Reference 61, methylamine (MeA).

[g] References 53 and 62.

[h] Reference 56.

[i] Reference 57.

[j] Reference 58, hexamethylphosphoramide (HMPA).

[k] Reference 18.

[l] Reference 59.

[m] Reference 63.

[n] Reference 19.

[o] Reference 23 and references therein.

proximately 10^{13} cm^{-3} for indium antimonide.[23] (Table I contains data collected from a wide range of experimental systems.)

At first sight the documented MNM transitions occurring in the low- and intermediate-dielectric materials would be expected to present considerable difficulties in an application of the Mott criterion.[24,25] For the rare-gas systems in particular, both magnetic resonance[26,27] and optical properties[28,29] of the isolated impurity center are generally consistent with the picture of a small-radius (Frenkel) ground state,[30] a situation far removed from the lattice of Wannier-like states envisaged in Mott's original formulation.[2,6,7] However, Berggren and Lindell[31] were able to predict a realistic transition concentration for the argon-sodium system on the basis of a scaled (variational) form of the Mott criterion

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

in which a_H^* replaces a_H [Eq. (2)] and now represents an appropriate radius (~2 Å for Ar:Na) associated with a *realistic* wave function [not necessarily of the type given by Eq. (3)] for the localized state.

We point out that Eq. (5) is just the adaptation of the Mott criterion discussed earlier in regard to the transition in the doped group-IV semiconductors.

The success of this particularly simple criterion in these two extreme situations led us to enquire whether its applicability extends to the wide range of systems which exhibit a MNM transition, as one of us has recently suggested.[32]

APPARENT UNIVERSALITY OF A SCALED (VARIATIONAL) FORM OF THE MOTT CRITERION

In Table I we have assembled experimental values of transition concentrations and Bohr radii for matrix-bound systems which undergo a MNM transition. Bohr radii (a_H^*) were typically obtained from *experimental* parameters which characterize the localized state; details are given in Table I. If a relation of the type (5) is indeed generally applicable,[32] we would expect a plot of $\frac{1}{3}\log n_c(x)$ versus $\log a_H^*(y)$ to yield a straight line of slope −1, and intercept K' ($\equiv \log K$). We show a plot in Fig. 1, comprising data from systems in which the n_c and a_H^* are known from experimental studies. The resulting linear correlation, described by the relation

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

extends over a range of approximately 10^{10} in critical concentration and approximately 600 Å in Bohr radii.

We suggest that this scaled form of the Mott criterion can be used as a simple but accurate guide in predicting the onset of a MNM transition in a condensed medium.

It is not immediately apparent why such a simple criterion should be so successful in this respect. In Mott's original model,[6,7] a MNM transition occurs when a dielectrically screened Coulomb potential starts to give rise to bound states. Such a potential is appropriate *only* for systems in which there exists extensive overlap between the donor wave function and the electronic wave function of the surrounding matrix.[17] In addition, more recent work has shown that the *calculated* value of the constant in Eq. (1) is subject to the vagaries of choice[33] of the electronic wave function, as well as being sensitive to both the form of the itinerant-electron screening and nature of the host conduction band.[33-36]

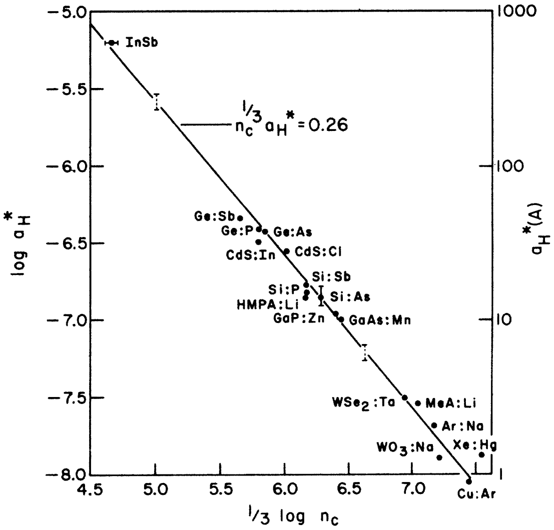

FIG. 1. Metal-nonmetal transition in condensed media. A plot of $\log a_H^*$ vs $\frac{1}{3}\log n_c$ (symbols defined in the text). The points represent experimental systems in which both a_H^* and n_c are known (Table I). Typical error estimates in n_c and a_H^* are shown (solid error bars) for the representative systems InSb and Si:As, respectively. A complete breakdown of error estimates (where available) in both n_c and a_H^* for all the experimental systems is contained in Fig. 2 and Table I. The vertical, broken-line, error bars represent the limits $n_c^{1/3}a_H^* = 0.23$ and 0.29.

Rather, we regard Eq. (6) as being representative of a realistic *experimental* correlation between critical concentrations and Bohr radii for matrix-bound systems in general. Accepting this, the Mott formulation [embodied in (1)] then represents a realistic model for only a certain class of these systems, namely, the high-dielectric materials. In an attempt to probe the origins of the apparent universality of Eq. (6), and to gain some insight into the role by a host matrix in a MNM transition, we have reexamined Berggren's formulation[40] of the Hubbard tight-binding model for the transition.

HUBBARD TIGHT-BINDING MODEL AS APPLIED TO METAL-NONMETAL TRANSITIONS IN CONDENSED MEDIA

Numerious interpretations of the Hubbard tight-binding Hamiltonian[9] now exist,[10,37-40] and it is generally recognized[13,14,37,38] that this formulation describes a transition from an insulating to a metallic state when the condition

$$W/U \sim 1 \tag{7}$$

is satisfied. Here W is the unperturbed bandwidth of an array of one-electron states and U is the intradonor Coulomb repulsion energy characteristic of electron correlation effects between a pair of electrons on the same donor.

Despite the fact that data are now available for a wide range of systems exhibiting a MNM transition (Table I), the Hubbard model has been applied *directly* to only a few systems.[32,40,50] This can probably be attributed to the complexities generally associated with transforming the tight-binding Hamiltonian into a working prescription for calculating transition densities. In this section, we demonstrate that a simple formulation of the Hubbard model is capable of predicting realistic critical densities for the onset of the MNM transition. The fundamental tenet underlying this approach is that the intradonor Coulomb repulsion U is the primary driving force in the transition from metallic to insulating states.

The original formulation of the model is that due to Berggren,[40] who studied the MNM transition in shallow donor states of germanium and silicon in terms of Hubbard's tight-binding model. In these particular systems, the ground-state wave function for the Wannier-like state is constructed from Bloch waves derived from the conduction band of the host material.[15,16] At this point we introduce our basic assumption: Namely, for materials in which the host conduction band is anisotropic, we may replace the ellipsoidal wave function by a spherical isotropic charge distribution. Obviously, this requirement is necessary only for large-radius states in which admixture of matrix orbitals into the donor ground-state wave function is appreciable. It is just these systems in which the assumption is generally accepted.[15] For tightly bound (Frenkel) impurity states, matrix orbital involvement in the ground-state wave function is negligible, and this assumption need not be invoked. In these cases, we require only that the isolated center be characterized by an isotropic Bohr radius.

For the isotropic-conduction-band case, the ground-state wave function has the form[15,16]

$$\psi(\vec{r})_{\mathrm{EM}} = \sum_{j=1}^{N} \alpha_j F_j(\vec{r})\phi_j(\vec{r}), \tag{8}$$

where N is the number of conduction band minima in $\vec{k}$ space, α_j are numerical coefficients of the appropriate linear combinations of $F_j(\vec{r})\phi_j(\vec{r})$, $\phi_j(\vec{r})$ is the Bloch wave at the jth minima and $F_j(\vec{r})$ represents the simple hydrogenic envelope function [cf. Eq. (3)]

$$F_j(\vec{r}) = (\pi a_{\mathrm{H}}^{*3})^{-1/2} \exp(-r/a_{\mathrm{H}}^*) \tag{9}$$

with a_{H}^* a realistic (isotropic) Bohr radius for the ground state. An important point to note is that although the electron described by Eq. (8) moves locally as if it were in a Bloch state, $\phi_j(\vec{r})$, over large distances (for example, distances of the order of several lattice sites) it is dominated by the hydrogenic function $F_j(\vec{r})$ which is characterized by a radius a_{H}^*.[15]

Berggren[40] utilized an approach somewhat similar to Slater's solution[41] for the H(1s) integrals in the hydrogen molecule, and obtained expressions for the hopping integral (T) and the intradonor repulsion energy for a regular array of centers,

$$T = \frac{e^2}{K_{\mathrm{st}} a_{\mathrm{H}}^*}\left[-\tfrac{1}{2}S - \left(\frac{R}{a_{\mathrm{H}}^*} + 1\right)\exp\left(\frac{-R}{a_{\mathrm{H}}^*}\right)\right] \Big/ \sqrt{N}, \tag{10}$$

$$U = \frac{5}{8}\left(\frac{e^2}{K_{\mathrm{st}} a_{\mathrm{H}}^*}\right), \tag{11}$$

and

$$S = \left[1 + \left(\frac{R}{a_{\mathrm{H}}^*}\right) + \frac{1}{3}\left(\frac{R}{a_{\mathrm{H}}^*}\right)^2\right]\exp\left(\frac{-R}{a_{\mathrm{H}}^*}\right), \tag{12}$$

and R is the separation between donor states.[42] T is related to the unperturbed bandwidth via

$$W = 2z\,|T|\,, \tag{13}$$

where z is the coordination number for a particular arrangement of centers.[43]

Calculated critical concentrations for the MNM transition in the group-IV semiconductors were in good agreement with the experimental values, provided a_{H}^* was obtained directly from the *experimental* ionization energy of the isolated donor.[40]

We point out two features of this particular formulation which are important in the present context:

(i) Although the expressions for T and U were derived[40] primarily for the large-radius Wannier-like states, they follow from simple hydrogenic arguments relating only to bandwidth and repulsion energies for a lattice of s-like states. As such the formulary[40] should be generally applicable to all manner of matrix-bound states (from Frenkel- to Wannier-like) whose ground-state wave functions can be reasonably approximated by an effective, isotropic, Bohr radius.

(ii) For a given value of a_{H}^*, both W [Eq. (13)] and U [Eq. (11)] are dependent upon the magnitude of the host dielectric constant. However, the Hubbard ratio (W/U), and therefore the transition concentration, is then insensitive to the particular value of the dielectric constant, *except insofar as the dielectric properties of the host material affect, or determine, the ground-state wave function of the matrix-bound state.*

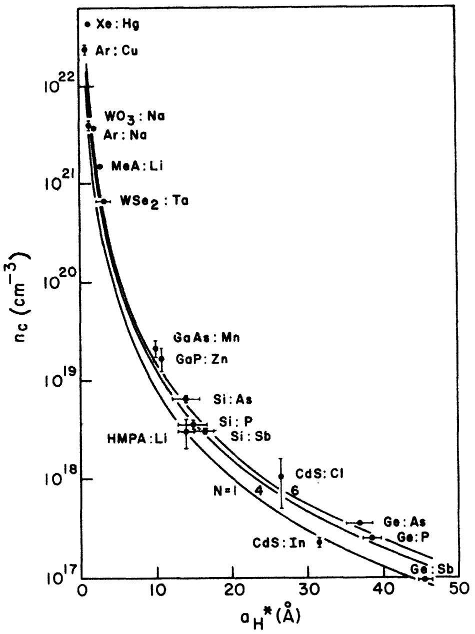

FIG. 2. Metal–nonmetal transition is condensed media. The solid lines represent the predicted (universal) variation of n_c with a_H^* based on the interpretation of the Hubbard Hamiltonian outlined in the text. Curves are presented for (matrix) conduction bands with 1, 4, and 6 equivalent minima is $\vec{k}$ space. The points, and associated error bands, are experimental values, and a detailed breakdown of the data is contained in Table I.

Therefore, the phenomenon of the MNM transition at finite donor concentrations reduces to a simple one-electron problem[39] of competing potential- and kinetic-energy effects, but with the concentration grid suitably displaced by an amount dependent upon the dielectric properties of the host.[44]

These arguments suggest a certain universality in this particular formulation of the Hubbard model, and we would expect Eqs. (10)–(13) to be directly applicable to all systems in which the MNM transition is triggered primarily by electron-correlation effects. Utilizing Hubbard's estimate[9,45] of 1.15 for the critical value of W/U at the MNM transition, we have computed transition densities as a function of a_H^*, the isotropic Bohr radius of the isolated donor states. Since our approach implies that the MNM transition in condensed media can be viewed primarily as a simple overlap-correlation problem, we require in a_H^* a *realistic* (experimental) estimate of the Bohr radius (as in the variational form of the Mott criterion, see Table I).

In Fig. 2,[46] we compare our numerical calculations with results for both donor and acceptor states in various host matrices. We find good agreement for systems differing widely in dielectric properties and critical concentrations. Calculated values of $n_c^{1/3}a_H^*$ from this Hubbard tight-binding approach are 0.20, 0.24, and 0.25 for $N = 1$, 4, and 6, respectively, which agree well both with the universal relation $n_c^{1/3}a_H^* = 0.26 \pm 0.05$, obtained from our analysis of experimental data, and with earlier estimates by Berggren[40] for the transition in the group-IV semiconductors.

SUMMARY

In this work we have analyzed experimental data from a wide variety of systems which exhibit a MNM transition. We have shown that the simple criterion $n_c^{1/3}a_H^* = 0.26 \pm 0.05$ has almost universal application. The possible origins of this universality have been formulated from an analysis of the Hubbard model for the MNM transition as applied to condensed systems. In essence, we have suggested that the role of the host matrix in the phenomenon of the MNM transition is important primarily in the sense that it serves to determine the form of the radial distribution of the impurity center in the low-electron-density regime. Once these perturbations to the isolated (free) atom eigenstates of the donor are taken into account, the ensuing transition to the metallic state is essentially invariant to the particular nature of the host matrix; being primarily a one-electron problem in a suitably scaled concentration grid.

Obviously, our approach has completely neglected the role of unimodal disorder in the various systems.[47] The fundamental tenet underlying our approach has been that electron-electron correlation effects are primarily responsible for the transition from metallic to insulating states in systems devoid of possible large scale (bimodal) inhomogeneities.[49] This viewpoint, shared by several other authors,[14,37,40,48,50] appears to be vindicated by the success of the simple Hubbard formulation outlined here.

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[46] Figure 2 shows results for states with Bohr radii up to approximately 50 Å and critical concentrations down to $\sim 10^{17}$ cm^{-3}. For InSb ($a_H^* \simeq 620$ Å) we find n_c(calc) $= 3.2\times10^{13}$, 4.6×10^{23}, and 5.8×10^{13} cm^{-3} (for $N=1$, 4, and 6, respectively) compared to the experimental spread in values of $(7\text{–}12.5)\times10^{13}$ cm^{-3}.

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