

Mott transitions in Na:Ar and Cu:Ar mixtures

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(Received 30 October 1973)

The metal-to-nonmetal (MNM) transitions observed in Na:Ar and Cu:Ar mixtures at low temperatures have been studied by means of Mott's model for such transitions. Pseudopotential and *ab initio* type calculations predict critical densities which are in excellent agreement with experimental estimates. It is therefore argued that the observed MNM transitions are due to cooperative electron interaction effects, as in Mott's model. The MNM transition associated with the liquid-vapor transition of the pure metallic systems is also briefly discussed.

I. INTRODUCTION

Recent work^{1,2} has described a new type of experiment for investigating metal-to-nonmetal (MNM) transitions. In these experiments, films of a few thousand angstroms thickness are prepared by allowing a vapor-phase mixture of a metal, together with an inert gas, to impinge upon a substrate cooled to liquid-helium temperatures. It can be considered as an experiment on a metal of extremely low density at low temperatures, as the composition can be varied continuously.

This type of experiment is of interest, since it allows metals which normally have liquid-vapor critical points outside the regions of normal experimentation to be expanded by mixing in varying proportions of a nonreactive material. In the first experiment,¹ a very sharp MNM transition was observed in sodium-argon mixtures at 15-at. % Na, which corresponds to a sodium density comparable to the density at the liquid-vapor critical point. An extension of this early work has now been made to copper-argon mixtures (see Fig. 1). Also, in this case, a dramatic change in the electrical properties occurs at a certain critical concentration, namely 64% Cu. On the basis of a hard-sphere model, this composition corresponds to a density of ~ 2.7 g/cm³ for copper.² (Recently, Cusack³ has suggested a revised value of 58-at. % Cu corresponding to a density of ~ 2.3 g/cm³.) The density of normal copper is 8.9 g/cm³.

These experiments show some kind of transition in a system where the centers are not arranged in a crystalline lattice, and should therefore be compared with the transition in a doped semiconductor such as Si:P. On the other hand, there is a significant difference between the two types of transition. In Si:P, Ge:P, etc., the activation energy for conduction goes continuously to zero, so that at any finite temperature there is no sharp discontinuity in the conductivity. In Cu:Ar, as we have stated, the conductivity shows a very sharp transition.

There are several possibilities to explain the behavior of the metal-argon system.

(i) There may be phase separation, so that conducting channels form at a certain concentration. It would perhaps be unlikely that the results would be as repeatable as they are if this were the correct explanation, but it cannot be ruled out. Further experiments on this point seem most worthwhile.

(ii) Another possibility is that classical percolation theory can be applied to channels involving contacts between individual atoms. Many authors have favored this kind of explanation for noncrystalline metal-insulator systems. Mott⁴ argues against it, unless there are very-long-range fluctuations of composition too wide to allow tunneling; if he is right, this is unlikely.

(iii) Finally, we may consider that it is a transition of Mott-Hubbard type.⁵ We favor this explanation, but have to ask why the observed behavior is

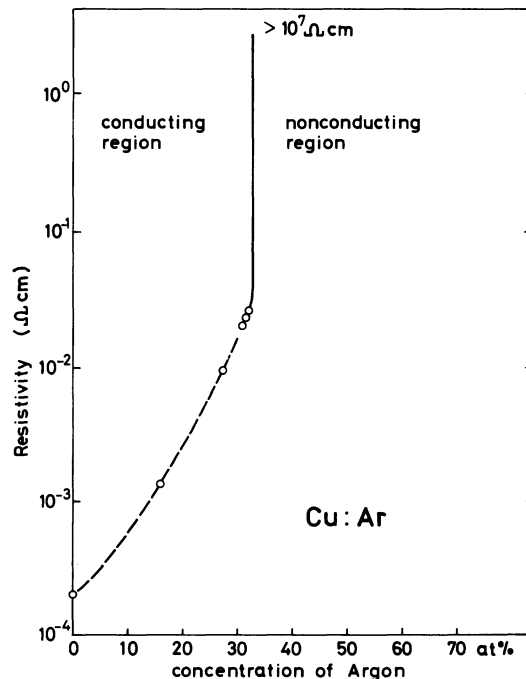


FIG. 1. Resistivity in copper-argon mixtures versus composition at ~ 4 K (Refs. 2 and 3).

so different from that of Si:P. It looks as if the discontinuous change in the number of carriers n , predicted by Mott in 1949,⁶ occurs for Cu:Ar and Na:Ar but not Si:P. The existence of this discontinuity has been given powerful theoretical support by the work of Brinkman and Rice⁷ on the formation of metallic droplets in illuminated Ge. Mott,⁸ in a recent review, suggests that the discontinuity should occur in all crystalline systems, but that in Si:P the random positions of the phosphorous atoms in space produce tails within the Hubbard bands where the electrons are localized in the Anderson sense^{9,10}; thus, the transition behaves like an Anderson transition, for which the activation energy goes to zero as $(C - C_0)^{1/8}$, where C is the concentration. Once an Anderson transition has taken place, so that the one-electron functions are localized, it is suggested that the discontinuous change in n , which depends on the Coulomb force e^2/r_{12} between free carriers, need not occur.

The Cu and Na atoms are more densely packed in the metal-argon systems than the P atoms in Si:P. At the critical density, the Cu atom, for example, is about the size of the Cu 4s wave function, whereas the P atom is quite small compared to the donor wave function. This implies that the density fluctuations are considerably smaller in Cu:Ar when the wave functions overlap, and we propose that a discontinuity *does* take place in the number of free carriers. If so, metallic behavior should appear suddenly at a value of the Cu concentration determined by Mott's original model,¹¹ namely the appearance of bound states in a dielectrically screened potential. Previous calculations on sodium-argon mixtures also indicate that this model may apply.^{12,13} These calculations were based on a dielectrically screened pseudopotential and variational techniques. Unfortunately, the use of pseudopotentials does not seem as straightforward for copper as for sodium. Furthermore, recent calculations have shown that the critical concentration determined in this way may be rather sensitive to the type of binding wave function used.¹⁴ In the present work we have therefore also proceeded to a more *ab initio* type of calculation, in which an effective potential is constructed from atomic wave functions, and the resulting Schrödinger equation is solved numerically for both Na:Ar and Cu:Ar. The calculations for copper are, however, also supplemented by rough estimates by means of pseudopotential theory. As mentioned above, the critical density of sodium in Na:Ar mixtures is comparable to the liquid-vapor critical density. Experimentally, this corresponds to the appearance of an activation energy in the conductivity for $T < T_C$. We have therefore also performed analogous calculations on pure alkali metals.

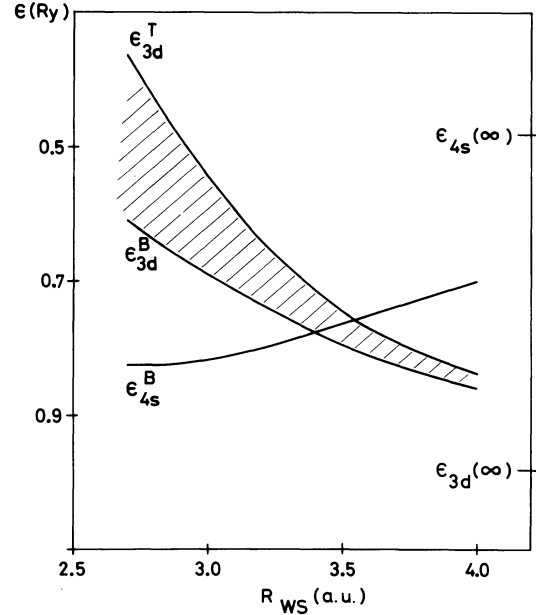


FIG. 2. Position of the 3d band relative to the bottom of the 4s band in pure copper as a function of the Wigner-Seitz radius R_{WS} (Ref. 15). The top of the 3d band, ϵ_{3d}^T , is obtained from $\phi_{3d}(r=R_{WS})=0$, where ϕ is the radial wave function. The quantities ϵ_{3d}^B and ϵ_{4s}^B , the bottom of the 3d and 4s bands respectively, are determined by the condition $\phi'(r=R_{WS})=0$. The energy levels of the free atom are denoted $\epsilon_{3d}(\infty)$ and $\epsilon_{4s}(\infty)$.

Before proceeding, it is instructive to consider the conventional band picture for expanded states of pure copper. Figure 2 shows the width and position of the 3d band relative to the bottom of the 4s band as a function of the Wigner-Seitz radius R_{WS} . These results were obtained from a spherical Wigner-Seitz model, with the usual boundary conditions determining the bottom and top of the bands.¹⁵ The figure illustrates that at densities less than $\sim 3.6 \text{ g/cm}^3$ (corresponding to $R_{WS} \sim 3.6$ a.u.), the bands become well separated. Thus, at the critical density, hybridization effects will not complicate our model. To a good approximation, we may also treat the 3d states as core states.

In Sec. II we describe the estimates of the critical densities obtained from pseudopotential theory. In Sec. III our *ab initio* type calculations are described, and results are reported. Finally, Sec. IV contains concluding remarks.

II. BOUND STATES IN A SCREENED PSEUDOPOTENTIAL

According to Mott, the MNM transition takes place when the potential from an ion, dielectrically screened by the free gas of valence electrons, is strong enough to capture an electron.^{14,16} Mott's original model, however, was developed with particular reference to doped semiconductors like

Si:P. Here we shall therefore make a slight extension of his model. Because of the large background dielectric constant in doped semiconductors, the radius associated with an impurity wave function is large (of the order 20–40 Å). This means that the electron spends most of its time far away from the core region. For this reason, a simple screened Coulomb potential was sufficient to describe the electron-donor interaction. The background dielectric constant in metal-argon systems is, however, roughly ten times smaller than in doped Ge and Si, which increases the importance of treating the core region more carefully. To include the effects of the core we therefore assume, as in Refs. 12 and 13, that the bare ion potential can be represented by Ashcroft's¹⁷ model potential

$$V(r) = 0, \quad r < r_0 \\ = -e^2/r, \quad r > r_0, \quad (1)$$

where r_0 is a parameter determined from independent measurements. A valence electron then interacts with the ion core through a screened potential, which is determined by its Fourier transform

$$V(q) = -\frac{4\pi e^2 \cos qr_0}{q^2 \kappa \epsilon(q)}, \quad (2)$$

where κ is the dielectric constant from the argon background. In the metallic phase, $\epsilon(q)$ is the dielectric screening function of the free gas of valence electrons (but with e^2 replaced by e^2/κ because of the argon background). The presence of the argon matrix is thus simulated only by the inclusion of κ in Eq. (2).

In Ref. 12, the sodium-argon critical density was determined by using a Hubbard-Sham¹⁸ dielectric screening function (see Sec. III) and a 1s hydrogenic variational wave function

$$\psi(r) = (1/\sqrt{\pi}) (\alpha/a_H^*)^{3/2} e^{-\alpha r/a_H^*}, \quad (3)$$

where α is the variational parameter and a_H^* is the Bohr radius of the material,

$$a_H^* = \hbar^2 \kappa / m e^2. \quad (4)$$

The corresponding energy is

$$E = \frac{e^2}{\kappa a_H^*} \left(\frac{\alpha^2}{2} - \frac{32\alpha^4}{\pi} \int_0^\infty dk \frac{\cos(kr_0/a_H^*)}{\epsilon(k/a_H^*)} \frac{1}{(4\alpha^2 + k^2)^2} \right), \quad (5)$$

which is to be minimized with respect to α . The critical density follows from the condition that $E=0$ when $\partial E/\partial \alpha = 0$.

Because of the low concentration of sodium at the MNM transition in Na:Ar, namely 15 at.%, the background dielectric constant κ could be chosen in Ref. 12 as 1.6, which is approximately the value for liquid argon. For two different choices of the parameter r_0 , namely 1.66¹⁷ and

1.85 a. u.,^{19,20} the critical densities were found to be 0.20 and 0.16 g/cm³, respectively. This is in good agreement with the experimental value¹ ~ 0.14 g/cm³, and the calculations do indeed support the hypothesis that the transition observed in sodium-argon mixtures is of a Mott-Hubbard type. The variational calculations in Ref. 13 also give similar results.

As mentioned in the Introduction, it is less obvious that the same approach could be used for copper-argon mixtures. Despite the difficulties with the pseudopotential model for metals with a d band within the conduction band, Ashcroft and Langreth²¹ have estimated the parameter r_0 from the transport properties of liquid copper. They obtained in this way 0.81 a. u. for r_0 . In the present work we have adjusted this value slightly to 0.78 a. u., which gives the correct ionization energy for an isolated copper atom. Because the MNM transition in copper-argon mixtures occurs at 58-at. % Cu, the value for κ must be reduced with respect to liquid argon. Using the Clausius-Mossotti relation and densities for argon, as estimated in Refs. 2 and 3, we then find that $\kappa \approx 1.35$ should be an appropriate value at the critical composition. Proceeding in the same way as for sodium-argon mixtures, we obtain a critical density $\rho = 2.65$ g/cm³. (Ashcroft's value of r_0 would also give a value close to this.) The experimental value^{2,3} is estimated to be between ~ 2.3 and ~ 2.7 g/cm³. In spite of the great uncertainties in the pseudopotential model for copper, we have thus obtained an excellent agreement with experiments.

This agreement would seem to depend more on the fact that our model suggests intimate association between critical densities and ionization energies, rather than on any particular parametrization of the pseudopotential. The essential physics of the model is the stripping of an electron from an atom; thus whatever potential is chosen, it must correctly predict the ionization energy of the free atom. For example, Solt and Kollár^{22,23} have recently used Ashcroft's empty-core model to produce the equation of state of copper and have found $r_0 = 1.28$ a. u. This value is remarkably close to that obtained by fitting Ashcroft's potential to the first node in Moriarty's²⁴ elaborate pseudopotential, namely $r_0 \approx 1.25$ a. u. Solt and Kollár's calculations also suggest that the effective charge seen by the 4s electrons should be greater than 1, because the 4s wave function penetrates the d shell. In order to check for potential dependence in our results, we have therefore included an effective charge Z_{eff} in Eq. (1). A correct ionization energy is then obtained if $Z_{\text{eff}} = 1.235$ with $r_0 = 1.25$ a. u. Using these values, we obtain a critical density of 2.45 g/cm³, which is encouragingly close to our previous result of 2.65 g/cm³ and the ex-

perimental value of ~ 2.3 – 2.7 g/cm³. A closer examination of our two pseudopotentials shows that Ashcroft's parametrization may be more appropriate in the present application. The integrand in Eq. (5) is sharply peaked in a region of small k , and in this region Ashcroft's parametrization produces a pseudopotential closer to Moriarty's.

The above results are strongly suggestive of the association between critical densities and ionization energies. This association is further suggested by Fig. 3, which shows the correlation between ionization energies and the critical densities at the liquid-vapor transition in alkali metals.

III. AB INITIO TYPE CALCULATIONS

In Sec. II we have reported on calculations of the critical densities at which MNM transitions occur in metal-argon mixtures. In general, excellent results were obtained. We have, however, expressed doubts about the applicability of our pseudopotential model to such systems as metallic copper, in spite of its numerical success.

To ensure that our results are not fortuitous, we have found it necessary to go beyond the pseudopotential model. We have therefore considered a model in which the potential for the valence electron and the ion core interaction is constructed from the orbitals of the free atom. This can be done as follows. If $\rho(r)$ is the electronic density of a metal ion and $\rho(q)$ its Fourier transform, the bare Hartree potential due to the core is

$$V(r) = 4\pi e^2 \int \frac{d\vec{q}}{(2\pi)^3} \frac{Z - \rho(q)}{q^2} e^{i\vec{q}\cdot\vec{r}}, \quad (6)$$

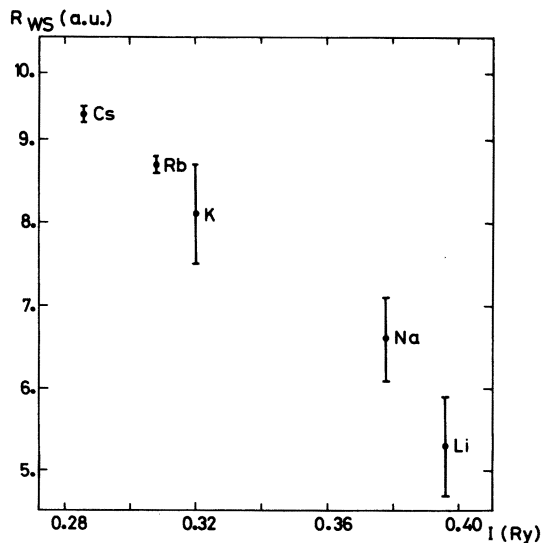


FIG. 3. Wigner-Seitz radius of the alkali metals at the critical point versus the experimental ionization energies. Values for the critical densities were obtained from Ref. 25.

where Ze is the nuclear charge. The screened Hartree potential is then

$$V(r) = 4\pi e^2 \int \frac{d\vec{q}}{(2\pi)^3} \frac{Z - \rho(q)}{q^2 \epsilon(q)} e^{i\vec{q}\cdot\vec{r}}, \quad (7)$$

where $\epsilon(q)$ contains the q -dependent contributions from both the free gas of valence electrons and the argon background, as described below. In constructing a potential in this way, it is important also to include the q dependence in the screening from the argon atoms, to ensure that the core region of the metal ions is unaffected by the argon background. In Sec. II, a constant κ could be used only because the screened potential is very weak in the core region.

The screened Hartree potential in Eq. (7) is to be supplemented by an exchange potential V_x , for which we use the Slater²⁶ exchange multiplied by an adjustable parameter η ,

$$V_x(r) = -3e^2 [(3/8\pi)\rho(r)]^{1/3} \eta. \quad (8)$$

The value 0.45 was obtained for the factor η by numerically integrating the Schrödinger equation for the unscreened ionic potential [$V(r)$ of Eq. (6)] plus the exchange V_x . The parameter η was adjusted so that the nodes of the resulting atomic wave function, with an energy equal to the experimentally observed ionization energy, coincided with the nodes of the corresponding Hartree-Fock wave function. The same value was found acceptable for both copper and sodium. Our value for η is smaller than the commonly used values of $\frac{2}{3}$ to 1. Our procedure is not self-consistent, however, and as stressed in Sec. II, the important point is that the potential yields the correct ionization energy. The dielectric screening from the argon background is not included in V_x , since the exchange potential operates essentially only within the core region of the metal ions.

The total potential, as described above, tends to zero for increasing arguments, and may therefore be put equal to zero outside a certain radius R . The Schrödinger equation is then conveniently solved by numerical integration for $r \leq R$, and the solution is matched to the outer exact solution at $r = R$ through the continuity condition. In particular, the appearance of a bound state is determined by the logarithmic derivative

$$R \left[\frac{d \ln \phi(r)}{dr} \right]_{r=R} = -1, \quad (9)$$

where $\phi(r)$ is the radial wave function.

Calculations of the appearance of bound states, and thereby the critical densities for the onset of a MNM transition, have been performed for the sodium- and copper-argon systems as outlined above. In these calculations the dielectric function in Eq. (7) was chosen in the following way.

TABLE I. Critical quantities for Na:Ar.

Quantity	Pseudopotential calc.		<i>Ab initio</i> calc.	Empirical ^c
	$r_0=1.66$ a. u. ^b	$r_0=1.854$ a. u. ^b		
R_{WS}^0 (a. u.) ^a	6.6	7.1	7.7	~7.6
ρ (g/cm ³)	0.20	0.16	0.13	~0.14

^aThe Wigner-Seitz radius at the critical composition.

^bReference 12.

^cReference 1.

On the metallic side of the transition, the screening function may be written as

$$\epsilon(q) \approx 1 + \alpha_{\text{val}}(q) + \alpha_{\text{Ar}}(q), \quad (10)$$

where $\alpha_{\text{val}}(q)$ reflects the screening properties of the free gas of valence electrons, and $\alpha_{\text{Ar}}(q)$ similarly for the argon matrix. Polarization effects from the Cu d states are not included in Eq. (10) because these must in some sense be included in our fitting procedure for η in Eq. (8). In the Hubbard-Sham approximation¹⁸ we then have

$$\alpha_{\text{val}}(q) = \frac{\gamma^2}{q^2} \left(1 - \frac{1}{2} \frac{q^2}{q^2 + k_F^2 + \gamma^2} \right) g(q/k_F), \quad (11)$$

where k_F is the Fermi momentum, and

$$\gamma^2 = \frac{4(3n/\pi)^{1/3}}{a_H}, \quad (12)$$

with n for the density of valence electrons, and a_H for the Bohr radius. The function $g(x)$ is as usually defined by

$$g(x) = \frac{1}{2} - \frac{1}{2x} \left(1 - \frac{x^2}{4} \right) \ln \left| \frac{2-x}{2+x} \right|. \quad (13)$$

From Penn's²⁷ model for the dielectric properties of an insulating material, we further have

$$\alpha_{\text{Ar}}(q) = \left(\frac{\hbar\omega_p}{E_g} \right)^2 F \left[1 + \frac{E_F}{E_g} \left(\frac{q}{k_F} \right)^2 F^{1/2} \right]^{-2} \quad (14)$$

where ω_p is the plasma frequency, E_g the bandgap, k_F the Fermi momentum, and E_F the Fermi energy of the model insulator. The quantity F is given by

$$F = 1 - E_g/4E_F + \frac{1}{3}(E_g/4E_F)^2. \quad (15)$$

The particular form in Eq. (14) has been given by

Fry.²⁸ Because Eq. (11) reduces to $\kappa - 1$ in the limit $q \rightarrow 0$, all the parameters in the expression may be determined from the Clausius-Mossotti relation for any given density of argon. As mentioned in Sec. II, the variation of the background dielectric screening with composition should be included in the case of copper-argon mixtures.

Using Clementi's²⁹ analytical Hartree-Fock orbitals to evaluate ρ in Eqs. (6)–(8), we have obtained the results listed in Tables I–III. Considering the type of calculations we have performed here, we find the agreement with experiments quite satisfactory. We note that, as usual, a relatively moderate deviation from experiment in the computed Wigner-Seitz radius appears as a much larger deviation in terms of densities.

It is indeed quite a delicate problem to calculate with high precision at which critical screening an electron may be stripped off an ion to which it is bound. If, for example, the potential used gives too small an ionization energy for the free atom, the computed critical density for the delocalization of the valence electron is also likely to come out too small, and *vice versa*. Thus, as a check of the dependency of the critical density on the exchange factor η in Eq. (8), we have repeated the calculations for a range of η values. We find that over a wide range of values ($\eta=1.0-0.2$) the calculated critical Wigner-Seitz radii bracket the experimental values reasonably well. For Na:Ar, the range is 4.2–10.3 a. u.; for Cu:Ar, 2.8–5.6 a. u.. Given the extreme sensitivity of the calculated densities to variations in the potential, we find this bracketing to be, perhaps, the result most highly suggestive of the correctness of the Mott model.

TABLE II. Critical quantities for Cu:Ar.

Quantity	Pseudopotential calc.		<i>Ab initio</i> calc.	Empirical ^b
	$r_0=0.78$ a. u.	$r_0=1.25$ a. u.		
R_{WS}^0 (a. u.) ^a	4.0	4.1	4.6	~4.2–4.0
ρ (g/cm ³)	2.65	2.45	1.73	~2.3–2.7

^aThe Wigner-Seitz radius at the critical composition.

^bReferences 2 and 3.

TABLE III. The Wigner-Seitz radius in a. u. at the critical density of pure alkali metals.

	<i>Ab initio</i> calculations	Empirical ^a
Li	6.3	5.3 ± 0.6
Na	6.8	6.6 ± 0.5
K	9.5	8.1 ± 0.6

^aValues corresponding to the density at the critical point (Ref. 25).

IV. CONCLUDING REMARKS

The purpose of this work has been to propose a particular model for the MNM transition in metal-argon systems, and to test the implications of this model with numerical calculations. Both the pseudopotential and *ab initio* type calculations stress the central role of the ionization energy implicit in the Mott model. All our numerical results strongly suggest that these MNM transitions are indeed of the Mott-Hubbard type.

We have also performed calculations on expanded states of pure alkali metals. Ross and Greenwood³⁰ have discussed the possibility of a MNM transition at the liquid-vapor transition. At present, it would be exceedingly hard to give a full quantum statistical treatment of these phenomena, but their comments make it tempting to look for the appearance of bound states in the expanded metallic state at $T=0$ K. The degeneracy temperature of the electron gas is much higher than T_c ; i.e., the electron gas is not too far from degeneracy at temperatures of interest. We therefore expect that our calculations at 0 K should give a correct order of magnitude for the densities at the critical points. Table III shows that this is indeed the case.³¹

Although we find our case for the Mott model to be rather convincing, it is clearly not completely conclusive. Our treatment has been quite elementary; for example, it does not include orthogonality to the Fermi sea.⁷ Therefore, further

elaboration of the Mott model and consideration of other formulations of the MNM transition seem necessary. For example, the Hubbard³² tight-binding formulation might prove useful in this context, as it has in the treatment of the MNM transition in doped semiconductors.³³ Another possibility is the type of finite cluster calculations applied by Cyrot-Lackmann and Gaspard to impurity bands in disordered systems.³⁴

If the present model is correct, then the MNM transition in metal-argon systems is the only existing experimental evidence for a pure Mott transition, i.e. without complications of disorder effects as in doped semiconductors. It therefore seems to us most worthwhile to pursue further experimental work on alkali-metal- and noble-metal-inert-gas mixtures.

Note added in proof. Recently F. Yonezawa and M. Watabe [Phys. Rev. B **8**, 4540 (1973)] have discussed the metal-insulator transition in a substitutionally disordered *n*-component system on the basis of the Hubbard model and of the localization-delocalization concept in the Anderson sense. A possible extension of the method to amorphous systems with topological disorder is mentioned in relation to the MNM transition in metal-rare-gas solids. The MNM transition in Na:Ar has also been investigated recently by K.-F. Berggren [J. Chem. Phys. (to be published)] by means of Herzfeld's semiclassical model. These investigations support the conclusions in the present paper that the transition is indeed driven by the dielectric properties of the medium.

ACKNOWLEDGMENTS

We are greatly indebted to Professor Sir Nevill Mott for valuable discussions and encouragement. His suggestions for preparation of the manuscript, furthermore, have been very helpful. We are also indebted to Ulf von Barth for performing the copper band-structure calculations, and to Professor Norman Cusack for correspondence.

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