PHYSICAL REVIEW B VOLUME 23, NUMBER 2 15 JANUARY 1981

Metal-insulator transition in dilute alkali-metal systems

J. H. Rose
Department of Physics, University of Michigan, Ann Arbor, Michigan 48109

(Received 7 July 1980)

The metal-insulator transition is studied for dilute systems of alkali metals. Using a spin-split self-consistent band-structure approach, we find the transition density, a strikingly enhanced magnetic susceptibility, and the electron effective mass. The critical density n_c is found to be given by the simple relation $r_s^c = r_0 + 2.8$. Here $r_s^c = [3/(4\pi n_c)]^{1/3}$ and r_0 is the model potential radius which is roughly the radius of the neutral atom. The Mott criterion of $n_c^{1/3} a_B \simeq 0.25$ (where a_B is the appropriate Bohr orbit) is found to be inadequate for describing these systems. The predicted effective mass and magnetic susceptibility enhancements are largest for Li and become systematically smaller for the heavier alkalis. We compare our results for the transition density with two sets of experiments, namely the gas-liquid critical density and the metal-insulator transition for codeposited thick films of alkali-metal and rare-gas atoms. Good agreement is found in both cases.

I. INTRODUCTION

The metal-insulator (MI) transition in real three-dimensional solids is of considerable interest.[1,2] One of its principal fascinations is the large number of mechanisms which plays some role in the transition. Examples of such mechanisms are Anderson localization[3] and percolation (due to randomness), and the Mott transition[1] (due to electron correlation effects). It does not appear possible to make calculations which incorporate all of these features and which at the same time make realistic connections with a physically realizable system. In this paper we will concentrate on presenting a realistic calculation of the properties of a simple, physically reasonable model where the metal-insulator transition is driven by electronic correlations. Our model is a rigid monatomic lattice of alkali-metal ions with a compensating number of electrons. Using a self-consistent band-structure approach we determine the enhancement of the electron effective mass and the uniform ($q = 0$) magnetic susceptibility as a function of density. A large enhancement of the magnetic susceptibility at the transition is a signature of the presence of electron correlation effects. The enhancement arises because of the spontaneous breaking of the s-band spin degeneracy due to the magnetic ordering which is caused by the electronic correlations.[4] In addition to the enhancement of the electron effective mass and the paramagnetic susceptibility, we also calculate the MI transition density for the entire alkali-metal series.

There are two sets of experiments to which we will compare our results. First, we consider codeposited thick films of alkali-metal and rare-gas atoms (e.g., Xe-Rb).[5-7] As the concentration of the metal atoms is varied there is a relatively sharp MI transition. Experimental transition densities are known for several metal–rare-gas systems. A second set of experiments involves the gas-liquid critical densities of the alkali metals. By going to high temperatures and pressures dilute systems of liquid alkali metals can be obtained. In such systems the metal-insulator transition is found experimentally to be associated with the gas-liquid critical density.[2,8] Such a connection was apparently first introduced on theoretical grounds by Krumhansl.[9] At the critical density the system changes continuously from a liquid to a gas. The liquid's binding energy is due to the metallic electrons. In the gas phase the electrons are bound to the atoms and an insulating state results. (The actual gaseous state may be made in part of dimers as suggested by the recent results of Freyland[8] for Cs.) Thus at the critical density we pass from the metallic liquid state to the nonmetallic gaseous state. One possible conjecture is that the energetics of the gas-liquid critical point is determined by the metal-insulator transition. If this conjecture were true we would expect to find a strong correlation between our calculated results for the metal-insulator transition at zero temperature and the experimentally observed values of the critical density for the alkali metals. Such a strong correlation will indeed be shown to exist.

We emphasize the role of electron correlations in determining metallization. In doing so we neglect several other effects. First, we neglect the Anderson localization mechanism, which is due to the randomness of the electron's potential, or the percolation of electrons between metal-rich regions in the sample.[1,2] Similarly, we neglect MI transitions due to lattice distortions. Our emphasis on electron correlations stems from a recently proposed theory which employs the spin-density functional formalism.[10,11] From it one obtains first-principles estimates of the metal-insulator transition density, the magnetic susceptibility, and the static electron-ion coherent scattering contribution to the electron's effective mass. Basically, the technique consists of determining the ground-state energy as a function of the average density and average spin moment from a self-consistent band-structure calculation. By examining the total energy as a function of the density and spin moment one can determine the various phase transitions.

The spin-density functional approach described above is suited to problems involving periodic structures. It was first applied to a model problem suggested by Mott. There one has a simple, rigid lattice of protons and an equal number of electrons. The metal-insulator transition was studied by varying the average interproton spacing. Although it is not, in principle, so restricted, our present development of the theory emphasizes cases such as Mott's model problem, where there is a simple transition between a doubly occupied s-like band at high densities, and a spin-split singly occupied s band at low densities.

The idea of using a band-structure calculation with spin-split bands to calculate the metal-insulator transition was originally suggested by Slater.[12] Since that time a few calculations have been reported for the low-density expanded lattice of Li.[13, 14] These calculations were performed at the time when the band-structure calculations were being enlarged from the spin-restricted Hartree-Fock to a more general spin-split formalism. The low-density limit served as an important check on the new formalism. These results are suggestive of the path our calculations took. However, they did not examine exhaustively the metal-insulator transition itself nor did they attempt to relate their results to experiment.

Berggren and Lindell[15] have studied the metal-insulator transition for both of the experimental systems mentioned above. They also start from the point of view that the transition is driven by the electronic correlations. It was, in fact, the relatively successful outcome of their investigation which led us to extend the spin-density functional calculations to these systems. However, their work differs from ours in two important ways. First, rather than solving a system which directly exhibits a metal-insulator transition, they used an approximate criterion suggested by Mott.[16] They start by using an Ashcroft pseudopotential to represent a single alkali-ion core, which they considered to be immersed in a paramagnetic electron gas. The metal-insulator density is estimated to be that density at which the potential first binds a conduction electron. This criterion is useful for establishing trends but cannot be expected to yield quantitative results. For example, within density functional theory the proton in the uniform electron gas forms a bound state at $r_s = 1.96 a_B$.[17,18] The metal insulator transition takes place at $r_s = 2.84 a_B$.[11] Hence, the criterion given above would lead to a factor-of-3 error in the transition density. The second departure of our work from Berggren and Lindell's involves the codeposited rare-gas–alkali-metal films. They screened the entire pseudopotential, including the core region, with the static dielectric constant of the rare-gas solid. We, on the other hand, completely ignore any electronic role for the rare-gas atoms and consider them only as spacers which keep the alkali atoms apart. Thus we neglect the possibility that the conduction electrons are strongly scattered by the rare-gas atoms. This limitation of the theory should be kept in mind, given the good agreement with experiment which will be shown to exist.

Aside from the effects of randomness, the alkali-metal experiments mentioned above admirably satisfy the requirements of the theory. The conduction electrons in the alkali metals are of an s-like nature. Further, the cores can be easily modeled by simple pseudopotentials, which considerably eases the computational effort. The spin-ordered state is assumed to be ferromagnetic for purposes of computational ease since this choice of spin symmetry preserves the monatomic symmetry. The implications of this choice of the magnetic symmetry on the magnetic susceptibility will be discussed in Sec. V.

Neglecting randomness in a liquid or random mixture is of course a rather major approximation. However, it seems possible that the gross structure of the MI transition is determined by the electron correlations, while randomness only affects the physics near the transition density. In any case, we proceed with our correlation-based approach and obtain definite results for the transition density which compare well with experiment. Additionally, we make predictions for the enhancement of the electron effective mass and for the magnetic susceptibility of the metallic phase.

The structure of the rest of this paper is as follows. The second section presents certain general considerations of the alkali metals and the role of the pseudopotential. The calculational technique is described in the third section. The fourth section describes the use of the model potential for some normal metal properties of the alkali metals. Section V gives our general results for the expanded alkali systems. Sections VI and VII compare our results with the experiments. Finally, we conclude the paper with a discussion of the results.

II. GENERAL CONSIDERATIONS

Here we write down explicitly our model and discuss some of its general features. Consider a rigid close-packed lattice made of the nuclei of an alkali metal such as sodium. Then introduce enough electrons to satisfy charged neutrality. The question we wish to answer is this: Are any of the electrons insulating (i.e., unable to contribute to the current)? The answer will depend on the average density of the system. At sufficiently high densities all of the electrons will be metallic since this allows the electrons to lower their kinetic energy. However, for zero pressure and temperature only the outermost valence electrons of the alkali metals are metallic. If we imagine pulling the lattice further apart the valence electrons will eventually have a phase transition to the insulating state. It is this latter transition of the valence electrons which we wish to study.

There are two interesting features which are associated with metallization in this system. First, at high densities the system is metallic and paramagnetic. At low densities the system is insulating and spin-ordered, presumably antiferromagnetic. Thus the system must become spin ordered at some intermediate density. Also, at some density the system must switch from being conducting to being insulating. We find for our model that both these transitions occur as a single first-order phase transition, in contrast to the situation for a lattice of protons.[11]

The essence of our calculation is to compute the ground-state energy of the system using spin-density functional theory. The result is a self-consistent band structure which yields directly the ground-state energy and spin density. By examining the single-particle bands we have a direct criterion for the occurrence of metallization, namely, whether there are any available states just above the Fermi energy. This use of the single-particle eigenspectrum is not justified formally. However, this criterion is very plausible and widely used and we adopt it for the purposes of our calculations. The nature of the spin-density functional calculation and our approximations in performing it are discussed in the next section. The rest of this section describes our treatment of the alkali cores.

An alkali atom can be considered to be an ion of charge one (with a tightly bound rare-gas core) and a single weakly bound *s* electron. For a wide range of metal properties it has proven possible to remove the ion cores from the problem and to model their effect on the outer electron by means of a model potential. The model potential is Coulombic outside the core region and is modified in the core region to account for the inner electrons. A general feature of such model potentials is to provide a realistic electron wave function outside the core region. Since the effects we are interested in involve the overlap of the valence wave functions in neighboring cells, we expect that the model potential approximation may provide a good basis for our calculation.

A particularly simple one-parameter form for the model potential is $v=-2e^2/r$ for $r>r_0$ and $v=-2e^2/r_0$ for $r<r_0$ (see the inset to Fig. 1). The core radius was chosen by requiring that the bulk solid have the correct equilibrium density. This choice of r_0 is also found to give the electron binding energy rather accurately. A particularly nice feature of this potential is that it depends only on a single parameter which is fixed by the bulk properties of the equilibrium metal. This simplicity of form greatly aids in the analysis of the calculated results.

The chosen form for the model potential was suggested by the work of Shaw.[19] He developed a model potential of the same form except that the cutoff radius $R_l(E)$ depended on the angular momentum and energy. In order to reduce his result to our simpler form, we chose $l=0$ and E equal to the Fermi energy E_F. These values were then used for all electrons. This approximation seems reasonable for the alkali metal and in Sec. IV we will show that Shaw's radius for $l=0$ and $E=E_F$, $R_0(E_F)$, is very similar to the value which we determine empirically for r_0.

III. SPIN-DENSITY FUNCTIONAL THEORY

The total energy of an inhomogeneous electron system in a fixed external potential can be written as a unique functional of the density $[n(r)=n^{\uparrow}(r)+n^{\downarrow}(r)]$ and the spin density $[m(r)=n^{\uparrow}(r)-n^{\downarrow}(r)]$.[20] This functional can be expressed as

$$E[n^{\uparrow},n^{\downarrow}]=T_s[n^{\uparrow}]+T_s[n^{\downarrow}]+\tfrac{1}{2}\int\frac{n(r)n(r')}{|\vec{r}-\vec{r}'|}d^3r\,d^3r'+\int v_{\mathrm{ext}}(r)n(r)\,d^3r+E_{\mathrm{xc}}[n^{\uparrow},n^{\downarrow}]\,. \quad (1)$$

Hence $T^s[n^{\uparrow}]$ is kinetic energy of a noninteracting collection of electrons with density $n^{\uparrow}$ (and similarly for $n^{\downarrow}$). The second term is the electrostatic energy. The third term represents the interaction of the valence electron with the model potential. The final term E_{xc} represents the exchange-correlation energy of the inhomogeneous electronic system. Equation (1) is formally exact. In practice, however, several approximations are necessary. First, E_{xc} is an unknown functional of $n^{\uparrow}$ and $n^{\downarrow}$ and must be approximated. We will use the local approximation in this paper, namely,

$$E_{\mathrm{xc}} = \int d^3r\, n(r)\epsilon_{\mathrm{xc}}[n^{\uparrow}(r), n^{\downarrow}(r)] \,. \tag{2}$$

Here ϵ_{xc} is the energy per particle for a uniform electron gas with densities $n^{\uparrow}$ and $n^{\downarrow}$. We use the interpolation formula of Gunnarson and Lundquist for ϵ_{xc}.[21]

To proceed with the calculation, we note that due to periodicity the energy calculation can be reduced to a unit cell. We then minimize the energy with respect to the variation of the class of single-particle wave functions which satisfy periodic boundary conditions on the unit cell. The result of this procedure is a self-consistent band-structure calculation. The form of the self-consistent equations is determined by the first variation of the total energy[22] and is

$$-\frac{\hbar^2}{2m}\nabla^2\psi_{\vec{k}}^{\uparrow} + v_{\mathrm{eff}}^{\uparrow}(\vec{r}; n(r))\psi_{\vec{k}}^{\uparrow} = \epsilon_{\vec{k}}\psi_{\vec{k}} \,, \tag{3}$$

$$v_{\mathrm{eff}}^{\uparrow}(\vec{r}) = v_{\mathrm{ext}}(\vec{r}) + \phi(\vec{r}) + \frac{d}{dn^{\uparrow}}(n\epsilon_{\mathrm{xc}}) \,, \tag{4}$$

$$n^{\uparrow}(\vec{r}) = \sum_{\vec{k}}^{k_F} |\psi_{\vec{k}}^{\uparrow}(\vec{r})|^2 \,. \tag{5}$$

Here $\psi_{\vec{k}}^{\uparrow}$ represents the wave function and $\epsilon_{\vec{k}}$ the eigenvalue. The spin-up density is denoted by $n^{\uparrow}$ and $v_{\mathrm{eff}}^{\uparrow}$ is an effective potential as given by Eq. (4). The electrostatic potential is denoted by $\phi(r)$, k_F is the Fermi energy, and V_{ext} is the pseudopotential. Similar equations obtain for the spin-down component.

Once the self-consistent band structure has been determined,[11] we use Eqs. (1) and (2) to find the ground-state energy E. By varying the lattice spacing and the relative occupation of the spin-up and spin-down bands we obtain the energy as a function of the density n and the magnetic moment m. By studying the properties of E as a function of these variables, we determine various physical properties of the system, including the transition density.

We have one final comment. We simplify our calculation by replacing the true Wigner-Seitz cell by a Wigner-Seitz sphere. This approximation has two effects. First, the ground-state energy is changed by an amount typical of the structural energy which is negligible on the energy scale driving the metal-insulator transition. Secondly, modifying the Wigner-Seitz cell leads to changes in the electron density of states, particularly for states near the boundary of the zone. However, the metal-insulator transition takes place abruptly in our model from half-filled (paramagnetically ordered) bands to a completely filled (ferromagnetically ordered) band and we do not expect the details of the Brillouin zone to be important.

IV. NORMAL METAL PROPERTIES

The determination of the metal-insulator transition relies on calculating the energy differences between the paramagnetic and the spin-ordered phase. If our calculation of these energy differences is to be reasonable it is necessary that the same procedure yield good values for the normal (zero pressure and temperature) equilibrium properties of the alkali metals. We have calculated the equilibrium density and electronic binding energy of the alkali metals and we will report our results below. The values of the model potential radius $R_0(E_F)$ given by Shaw[19] are found to give a good account of the alkali equilibrium properties, except for Li, for which it is too large. We adjust the value of the model potential radii r_0 so that the metals have exactly the correct equilibrium density.

Our calculation proceeds as follows. For each value of r_0 there is a value of r_s which minimizes the total energy E. In Fig. 1 we show this value of r_s as a function of r_0. Similarly, in Fig. 2 we show the minimized value of E as a function of r_0. Using Fig. 1 we determine that value of r_0 which yields the observed bulk density for each of the alkalis. These values of r_0 are given in Table I, where they are compared with Shaw's $R_0(E_F)$. To test the reasonableness of this choice

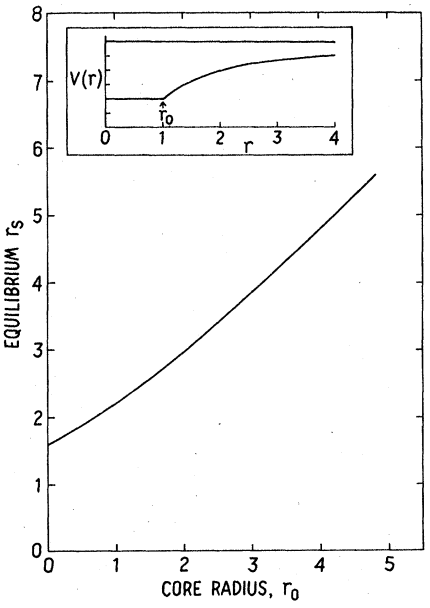

FIG. 1. The equilibrium r_s is shown as a function of the pseudopotential core radius r_0. The inset shows the form of the model potential used in this paper.

TABLE I. The table gives two estimates for the radius of the Shaw pseudopotential radius. The second column gives the values obtained by Shaw. The third column gives our values obtained by fitting to the observed bulk density for the metal.

	$R_0(E_F)$	r_0
Li	3.02	2.34
Na	3.26	3.11
K	4.20	4.15
Rb	4.46	4.44
Cs		4.88

of r_0 we then plot the experimental value of the equilibrium binding energy[23] on Fig. 2. The comparison shows quite good agreement for all of the alkalis. Our values of the core radius agree with the values published by Shaw for Na, K, and Rb to within 4%. Shaw did not give a value for Cs. For Li we found $r_0 = 2.34a_B$. It should be noted that Shaw's criterion for determining $R_0(E_F)$ did not rely on fitting the bulk cohesive properties. Rather, he determined $R_0(E_F)$ by a "smoothness" condition in joining the nodeless interior solution ($r < r_0$) to the realistic external solution ($r > r_0$) for the model wave function. Since our procedure has given quite good answers for the bulk properties, we will proceed with the metal-insulator calculation.

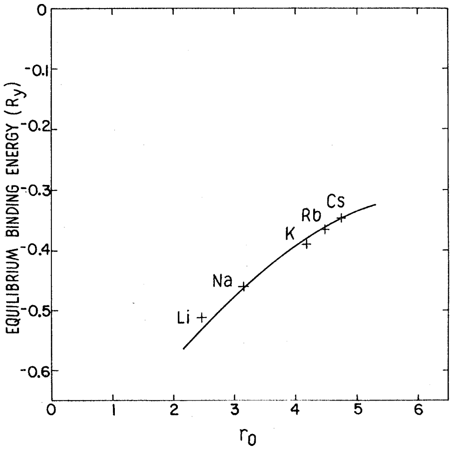

FIG. 2. Having chosen r_0 to give the correct equilibrium density, we plot the calculated binding energy as a solid curve. The crosses are the experimental values for the alkali metals.

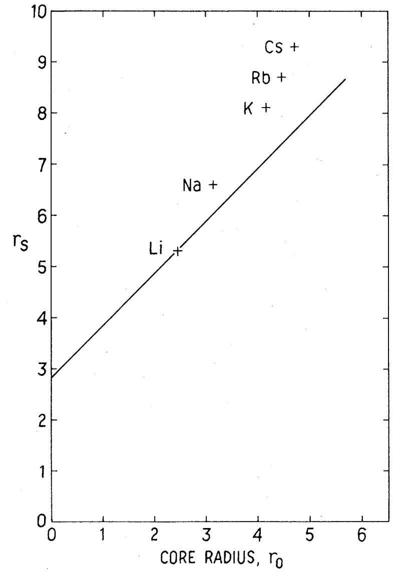

FIG. 3. The solid line shows our calculated results for the transition density. The crosses are the experimental results for the gas-liquid critical density of the alkalis.

V. RESULTS FOR EXPANDED ALKALI SYSTEM

We find a single first-order metal-insulator transition from the paramagnetic metal to the spin-ordered insulator for all the alkalis. The critical density for the metal-insulator transition is shown as a function of the core radius r_0 in Fig. 3. A striking feature of this curve is that the calculated transition density, for all alkalis, is given to within 2% by $r_s^c = 1.04r_0 + 2.8$. The appearance of such an apparently simple relationship suggests an underlying simple explanation of the physics. Up until now such an explanation has not been forthcoming. However, it is interesting to note that r_0 correlates roughly with the radius of the neutral atom.[24] Thus, we restate the relationship for r_s^c in words: the critical r_s is given by the atomic radius plus 2.8.

Electrons in a *rigid* periodic lattice have a change in their effective mass due to their coherent scattering by the ions. We calculate the effective mass at the Fermi surface by

$$m^* = k_F \left(\frac{\partial \epsilon_k}{\partial k}\right)^{-1}\Bigg|_{k_F}, \qquad (6)$$

where k_F is the Fermi wave vector. The change of the effective mass is shown in Fig. 4. As expected, the effective mass is largest for the most strongly scattering potential. The enhancement of the effective mass reflects itself in several material properties, e.g., the electronic specific heat. However, there are other effects which significantly influence the density of states at the Fermi surface, such as the electron-phonon coupling. These other effects may also vary rapidly near the phase transition. Hence it might be difficult to clearly observe the relatively small mass enhancement which is predicted by our

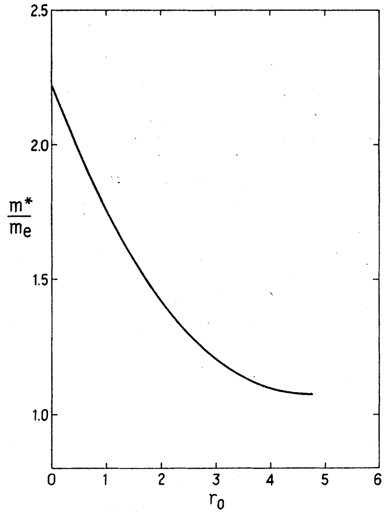

FIG. 4. The enhancement of the electron effective mass due to the presence of the static lattice of ion cores.

theory.

On the contrary, the enhancement of the static magnetic susceptibility is much larger and should provide an easily observed experimental effect. The magnetic susceptibility can be determined by a calculation of the total energy E as a function of the magnetic moment m. Then χ is given by

$$\chi = \left(\frac{\partial^2 E}{\partial m^2}\right)^{-1}\Bigg|_{m=0} . \qquad (7)$$

The total energy as a function of m is determined numerically and then expanded to obtain χ.

For the case of sodium we present results for the magnetic susceptibility in a little more detail than for the other metals. First, for the normal metal $\chi/\chi_f = 1.8$ for Na. Here χ_f is the magnetic susceptibility for the noninteracting electron gas evaluated at the same r_s as χ. The value for χ/χ_f at the normal metal is in relatively good agreement with both theory and experiment,[25,26] being perhaps 5–10% too large. This discrepancy is accounted for by the neglect of the core electrons, which is implicit in our calculations. Figure 5 shows the magnetic susceptibility of Na for densities which range from the normal metal density to the metal-insulator transition density. As can be seen, the magnetic susceptibility is very greatly enhanced at the transition. Figure 6 shows the enhancement of the susceptibility at the transition density for all of the alkali metals. We note that core effects become more important for the heavier alkalis. Our estimate for χ/χ_f is approximately 25% too large for bulk Cs.[27] We expect similar errors in the value of χ/χ_f at the metal-insulator transition density for Cs.

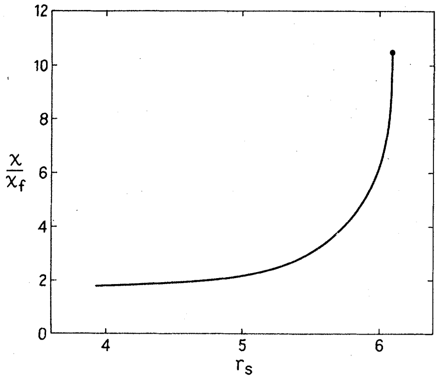

FIG. 5. The enhancement of the magnetic susceptibility is shown for Na. Note that χ_f is the magnetic susceptibility of a noninteracting electron gas calculated at the given r_s.

In our calculation we only allow states which have paramagnetic or ferromagnetic symmetry. The choice of a ferromagnetic ground state was made to simplify the numerical calculations. In fact, we expect the ground state of the insulating phase to be antiferromagnetic. It is reasonable to ask whether our choice of ferromagnetic symmetry for the insulating state will affect the magnetic susceptibility enhancement which we are predicting. There are two mechanisms which might be expected to influence the susceptibility enhancement. First, there are low-lying excited states of antiferromagnetic symmetry. Secondly, taking the antiferromagnetic symmetry into account might lower the transition density and hence decrease the enhancement (see Fig. 5).

As discussed briefly earlier in this section, the magnetic susceptibility is determined by calculating the change in energy when electrons are transferred from the spin-down band to the spin-up band. The existence of low-lying antiferro-

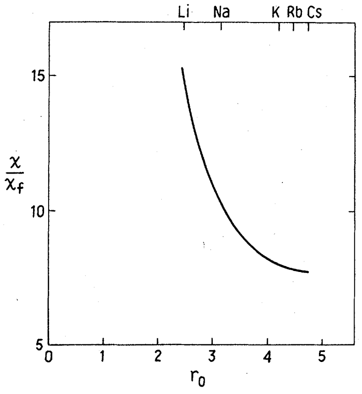

FIG. 6. The enhancement of the magnetic susceptibility at the metal insulator transition is shown for the alkali metals.

magnetic excited states does not influence this transfer and hence does not affect the determination of the $q=0$ magnetic susceptibility which we have been discussing. The low-lying antiferromagnetic excited states will, however, induce, in addition, a large q-dependent magnetic susceptibility, where q is the wave vector of the antiferromagnetic state.

The second way that taking the antiferromagnetic symmetry into account could affect the enhancement of the $q=0$ susceptibility would be to substantially shift the transition density. This is not expected to occur for the following reason. The energy difference between the antiferromagnetic and the ferromagnetic state at the transition density is expected to be on the order of a Curie temperature, i.e., 0.005 Ry. This is a small energy compared to the changes in the total energy near the transition density. Thus the transition density is not expected to be substantially changed by the difference in magnetic symmetry. Consequently, the $q=0$ magnetic susceptibility will not be greatly changed.

VI. COMPARISON: GAS-LIQUID CRITICAL PROPERTIES

As mentioned in the Introduction, it has been suggested that the gas-liquid critical point for the alkali metals is determined by the MI transition for the valence electrons. In Fig. 3 we have plotted the experimental values of the alkalis' gas-liquid critical density.[15] This allows a comparison with our estimate for the metal-insulator transition density, which is also plotted on the same figure. The agreement between experiment and theory is good. The agreement improves systematically for higher electron-density (smaller r_s) alkali metals.

The theoretical results are obtained for zero temperature while the experiments were performed at the critical temperatures of the alkalis. If the picture of the gas-liquid critical density being driven by the MI transition is true, we would expect that deviations from our predictions for the transition density would depend on the ratio of the critical temperature to the Fermi temperature. Qualitatively, this is observed. The ratio T_c/T_F increases systematically as we go from the dense alkalis to the less dense alkalis. For example, $T_c/T_F=0.17$ for Na and the agreement with theory is good. On the other hand, $T_c/T_F=0.28$ for Cs and the disagreement is systematically larger.

These deviations suggest that our theory should be extended to finite temperatures. This work is in progress. However, one preliminary comment may be in order. The preferred phase is determined by comparing the free energies of the paramagnetic and spin-ordered phase. If we continue to focus only on the electronic degrees of freedom, the effects of finite temperature on the free energy F show up through the electronic entropy and contribute a term $\Delta F=-TS$, where T is the temperature and S is the electron entropy. The metallic phase has a large density of states at the Fermi level, while the insulating state has a zero density of states at the Fermi surface. We would thus expect this change in the free energy to make the paramagnetic state more preferred at a given density as the temperature is raised. The result would be a larger critical r_s, as is, in fact, observed. This encourages us to consider for the future a more systematic calculation of temperature effect using the finite temperature generalization of density functional theory suggested by Mermin.[28]

Recently, experimental results have become available for the magnetic susceptibility of liquid Cs for densities ranging from that of the bulk metal to nearly the critical density. These results show a large enhancement of the paramagnetic susceptibility. However, unlike our model, the experimental susceptibility reaches a peak before the critical density and then decreases as one approaches the critical point. The maximum value observed for the enhancement of the susceptibility, χ/χ_f, is about three. Our theory predicts a value of seven. However, the enhancement of the susceptibility increases rapidly as $r_s \rightarrow r_s^c$ (see Fig. 5). Hence we would expect that the effects of randomness would be to smear and hence substantially reduce the predicted enhancement. It is encouraging that the experiment shows a large increase in the paramagnetic susceptibility. The discrepancies between the experiment and our model results are not too surprising, considering our restriction to zero temperature and a perfect lattice. A realistic comparison with these experiments will require a detailed calculation of the system at finite temperatures, with some account taken for the random nature of the liquid.

VII. COMPARISON: CODEPOSITED FILMS

Our theory makes a prediction for the r_s of the metal-insulator transition in codeposited thick films of rare-gas atoms and alkali atoms. We plot our results in Fig. 7. For comparison, we include experimental results for the systems Xe-Cs, Rb-Kr, and Na-Ar. The agreement is very encouraging. However, the experimental results are difficult to obtain and should probably be considered somewhat uncertain. Further, the theory regards the rare-gas atoms only as spaces. A

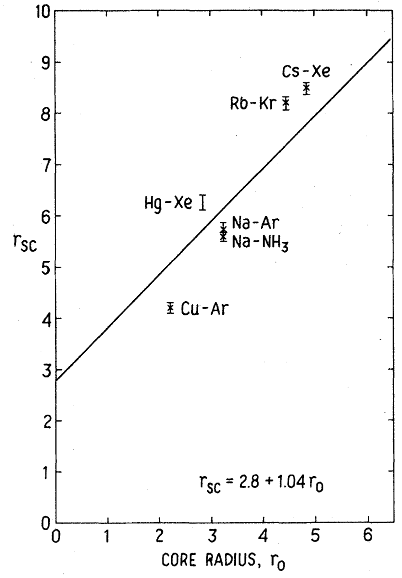

FIG. 7. The solid line shows our calculated results for the transition density. The x's show the experimental results. The error bars are based only on uncertainties in the packing fraction.

more realistic comparison would require one to take into account the scattering of the conduction electrons by the rare-gas atoms. For purposes of comparison we have included three systems which do not satisfy the conditions under which the theory was developed. There are Hg-Xe,[29] Cu-Ar,[30] and Na-NH$_3$.[7] The sodium-ammonium system was treated just as the rare-gas–alkali mixtures above. For the copper and mercury mixtures we used the approximate relationship that the transition r_s is given by the metal atom's atomic radius plus 2.8. Overall, the theory is consistent with the experimental results.

VIII. DISCUSSION AND CONCLUSIONS

Several competing theories have been used to describe the metal-insulator transition of dilute systems of alkalis. Mechanisms proposed to describe the transition include the effects of electron correlation, Anderson localization due to randomness, and percolation models. We have focused entirely on the effects of electron correlations. We have found that our approach yields good estimates for the transition densities for two types of experiments. However, our theory indicates that the metal-insulator transition for codeposited thick film should be first order. In fact, the experimental result is a continuous transition. We suggest the following picture. The electronic correlations determine the rough value of the transition density n_c and some other physical properties when $|n-n_c|/n_c$ is large. On the other hand, in the region of the transition $|n-n_c|/n_c \ll 1$, the effects of randomness and the percolation process are expected to be very important.

Large enhancements of the $q=0$ magnetic susceptibility are expected near the MI transition density.[4] Within our model we make detailed predictions for the enhancement as a function of density. There are two major approximations which limit our ability to directly compare our results with experiment. These are the effects of randomness and temperature. For the codeposited thick films the measurements are made at temperatures which are very small compared to the Fermi energy, and for these systems the restriction to zero temperature is not expected to be important. Hence it would be of considerable interest to obtain experimental results for these systems. Such experiments and their comparison to theory might give some indication of the relative importance of the effects of randomness and electron correlation near the transition.

Mott[16] has proposed a criterion for the metal-insulator transition in simple s-band materials, namely,

$$n_c^{1/3} a_B^* \cong 0.25 . \qquad (8)$$

Here n_c is the critical density and a_B^* is the radius of an orbit chosen to represent the outer electron. We find this criterion adequately describes the case when there are no cores, such as a lattice of protons or an array of donor centers in a semiconductor. However, we find that it is inadequate for describing the metal-insulator transition of the alkalis which have large ion cores. Figure 8 shows the electronic density of an isolated Cs atom using the Shaw pseudopotential. Choosing that value of r for which the density is e^{-2} of the density at the origin to define the Bohr orbit a_B^*,

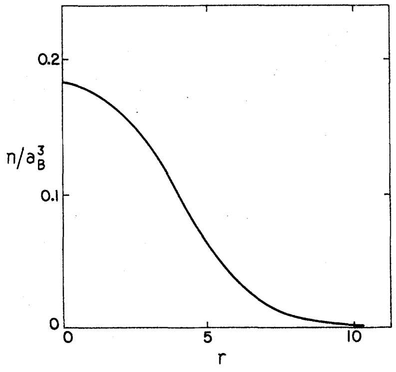

FIG. 8. The density for an isolated Cs atom using the Shaw pseudopotential.

we find

$$n_c^{1/3}a_B^* \cong 0.52\,, \qquad (9)$$

in clear disagreement with Mott's estimate. For the alkali metals we suggest, instead, our result that $r_{sc} = 2.8 + 1.04 r_0$.

In conclusion, we have studied the metal-insulator transition for a dilute system of alkali atoms on a lattice. We obtain estimates for the critical density which are consistent with two sets of experiments. Finally, we predict the enhancement of the electron effective mass and the magnetic susceptibility at the transition.

ACKNOWLEDGMENTS

I would like to thank Len Sander, Herb Shore, Eugene Zaremba, John Dobson, and John Perdew for useful and interesting discussions. Further, I would like to thank Len Sander for a critical reading of the manuscript. This work was supported in part by the National Science Foundation under Grant No. DM8-78-25012.

---

[1] N. F. Mott, *Metal-Insulator Transitions* (Taylor and Francis, London, 1974).

[2] *The Metal Non-Metal Transition in Disordered Systems*, Proceedings of the 19th Scottish Summer School in Physics, edited by L. R. Friedman and D. P. Tunstall (Scottish Summer School in Physics, St. Andrews, 1978).

[3] P. W. Anderson, Phys. Rev. 109, 1492 (1958).

[4] The enhancement of the paramagnetic susceptibility due to electron correlations at the MI transition has been pointed out by other authors. For example, Brinkman and Rice [Phys. Rev. B 2, 4302 (1970)] have estimated the enhancement for the nearly antiferromagnetic electron gas.

[5] D. J. Phelps and C. P. Flynn, Phys. Rev. B 14, 5279 (1976).

[6] R. C. Cate, J. G. Wright, and N. E. Cusack, Phys. Lett. 32A, 467 (1970).

[7] N. A. McNeal and A. M. Goldman, Phys. Lett. 61A, 268 (1977).

[8] W. Freyland, Phys. Rev. B 20, 5104 (1979).

[9] J. A. Krumhansl, in *Proceedings of the First International Conference on Physics of Solids at High Pressure*, edited by C. T. Tomizuka and R. M. Emrick (Academic, New York, 1965).

[10] A. Ghazali and P. Leroux-Hugon, Phys. Rev. Lett. 41, 1569 (1978).

[11] J. H. Rose, H. B. Shore, and L. M. Sander, Phys. Rev. B 21, 3037 (1980).

[12] J. C. Slater, Phys. Rev. 82, 538 (1951).

[13] J. L. Calais and G. Sperber, Int. J. Quantum Chem. 7, 501 (1973).

[14] W. A. Goddard and P. M. O'Keefe, in *Computational Methods in Band Theory*, edited by P. M. Marcus, J. F. Janak, and A. R. Williams (Plenum, New York, 1971).

[15] K.-F. Berggren and G. Lindell, Solid State Commun. 13, 1589 (1973).

[16] N. F. Mott, Philos. Mag. 6, 287 (1971); Proc. Phys. Soc. London Sect. A 62, 416 (1949).

[17] E. Zaremba, L. M. Sander, H. B. Shore, and J. H. Rose, J. Phys. F 7, 1763 (1977).

[18] C. O. Ambladh, U. von Barth, Z. D. Popović, and M. J. Stott, Phys. Rev. B 14, 2250 (1976).

[19] R. W. Shaw, Phys. Rev. 163, 604 (1967); Ph.D. thesis, Stanford University, 1968 (unpublished).

[20] P. Hohenberg and W. Kohn, Phys. Rev. 136, B864, (1964).

[21] O. Gunnarson and B. I. Lundquist, Phys. Rev. B 13, 4274 (1976).

[22] W. Kohn and L. J. Sham, Phys. Rev. 140, A1133 (1965).

[23] N. W. Ashcroft and D. C. Langreth, Phys. Rev. 155, 682 (1967).

[24] N. A. McNeal, thesis, University of Minnesota, 1977 (unpublished).

[25] A. H. MacDonald, J. P. Perdew, and S. H. Vosko, Solid State Commun. 18, 85 (1976).

[26] J. F. Janak, Phys. Rev. B 16, 255 (1977).

[27] S. H. Vosko, J. P. Perdew, and A. H. MacDonald, Phys. Rev. Lett. 35, 1725 (1975).

[28] N. D. Mermin, Phys. Rev. 137, A1441 (1965).

[29] B. Raz. A. Gadanken, U. Even, and J. Jortner, Phys. Rev. Lett. 28, 1643 (1972).

[30] H. Endo, A. I. Eatah, J. G. Wright, and N. E. Cusack, J. Phys. Soc. Jpn. 34, 666 (1973).