

Conduction in multicomponent percolation

J. W. Halley

*Lyman Laboratory of Physics, Harvard University, Cambridge, Massachusetts 02138
and School of Physics and Astronomy,* University of Minnesota, Minneapolis, Minnesota 55455*

W. K. Holcomb

*Goddard Space Flight Center, † Greenbelt, Maryland 20771
and School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455*

K. Goetz

School of Physics and Astronomy, University of Minnesota, Minneapolis, Minnesota 55455

(Received 13 June 1979)

We present simulations and effective-medium theory calculations on conduction in a number of percolation models with up to four types of sites or bonds. We introduce the idea of chemical constraint in a multicomponent percolation system. The application of such models to the interpretation of recent experimental work on $\text{Na}_x(\text{NH}_3)_{1-x}$ mixtures and on charge-transfer salts is discussed.

I. INTRODUCTION

The idea of "polychromatic" percolation with more than two kinds of sites was recently introduced by Zallen.¹ Zallen systematically discussed the possible forms of site percolation but did not discuss conduction problems in either the site or the bond case. To characterize the models we let n be the number of different kinds of entities (sites or bonds) which can be placed on a lattice ($n=2$ for ordinary site or bond percolation). We denote by b the number of nearest-neighbor conductive parameters which are to be specified in a conduction problem corresponding to n , where for bond problems

$$b = n$$

and for site problems with isotropic sites

$$b = \frac{1}{2}n(n+1).$$

For example, for $n=2$ there are only two conductive parameters (say g_A and g_B) for the bond problem, but $b=3$ (g_{A-A} , g_{A-B} , and g_{B-B}) for the site problem. In this paper we will discuss the bond problem with $n=b=3$ and several site problems with $n=2$, 3, and 4.

The motives for these studies are, first, to begin a systematic study of polychromatic conductive percolation problems which can be expected ultimately to find a wide range of application in real multicomponent systems of scientific and technical interest. Second, we wish to explore the idea of chemical constraint in multicomponent percolation and to present results on several models which incorporate such constraints. The relevance of these models to recent experiments^{2,3} on $\text{Na}_x(\text{NH}_3)_{1-x}$ and charge-transfer salts will be dis-

cussed.

Section II reviews the theoretical methods which we use to compute the conduction in the various models. Section III presents results on some simple chemically unconstrained models. Section IV introduces the idea of chemical constraint and presents results on a number of models formulated in attempts to explore the possible origins of anomalies in the $\text{Na}_x(\text{NH}_3)_{1-x}$ experiment. Finally, we present a concluding discussion in Sec. V.

II. THEORETICAL METHODS

Here we describe the techniques used to calculate the conductivity of the various models. We used two main approaches. The first is a simple numerical simulation in which we solve Kirchoff's equations to an arbitrary accuracy on a finite lattice. The second approach is to use an effective-medium theory.

In the numerical simulations, we first choose a lattice and numbers P_α , giving the probability that any site is occupied by a species of type α ; α runs over the number of species in the particular model. We always consider quenched samples so that the probability for any site is independent of the occupancy of all other sites. We next choose a particular species for each lattice site using a pseudo-random number generator and the probabilities P_α . (The bond problem is set up in the same way, except that we occupy bonds rather than sites.) A unit potential difference is applied across the sample in one direction and periodic boundary conditions are applied in the other directions. Our sample then is effectively an infinite slab. There is a potential V_i at each site i . V_i is determined by solving Kirchoff's equations

$$\sum_j g_{ij}(V_i - V_j) = 0 \quad (2.1)$$

for all i subject to the boundary condition $V=0$ on one side and $V=1.0$ on the other. The sum on j is over nearest-neighbor sites only and g_{ij} is the conductance between sites i and j . g_{ij} is determined by the species which occupy sites i and j .

We solve Eq. (2.1) using a standard relaxation technique. We go through the sample sequentially replacing each V_i by

$$\sum_j g_{ij} V_j / \sum_j g_{ij}.$$

This is continued until the relative change in any V_i is smaller than a predetermined amount, typically 0.001. We also use overrelaxation and underrelaxation in some samples in order to improve convergence. The conductivity of the sample is then given by the current flowing into or out of the faces held at fixed potential (comparing these two numbers gives an added check for convergence).

The denominator $\sum_j g_{ij}$ vanishes if all the g_{ij} 's are zero, that is, if the site i is isolated. We avoid this problem by always keeping the g 's finite, but small, instead of zero. Typically we use values 10^{-2} – 10^{-3} times smaller than other "nonzero" conductions. We expect the main effect of this to be a slight rounding off of what would otherwise be a sharp resistive transition. Otherwise, we expect the effects to be very small.

Most calculations in this paper were done on samples of 1000 sites on simple cubic lattices. Some calculations were done on samples of 8000 sites in order to check the accuracy of using a 1000 site sample as an approximation to the thermodynamic limit. The calculations on 8000 site samples indicated that, except near critical points, the 1000 point simulations were excellent approximations to the thermodynamic limit.

The other approach that we have used is effective-medium theory.⁴ In this approach one replaces the random lattice by a uniform one where all the conductances have the same value g_m , which is determined by requiring that, on the average, the disturbance caused by replacing part of the effective medium by the real system is zero.

If the potential difference across each conductance in the direction of the applied potential gradient is V_m and one of the conductances is replaced by g_0 , then in bond problems there is an additional potential difference across it given by

$$V_0 = (g_0 - g_m) V_m / [(z-1)g_m - g_0], \quad (2.2)$$

where z is the number of nearest neighbors. The condition for determining g_m is that

$$\langle V_0 \rangle = 0$$

that is, for the two-bond problem,

$$p_A (g_A - g_m) / [(z-1)g_m - g_A] + p_B (g_B - g_m) / [(z-1)g_m - g_B] = 0.$$

Solving this equation then determines g_m as a function of p_A . It is well known⁴ that this approximation for the bond problem works well except near the critical point.

Treating the site problem is much more difficult.⁵ In the present work we will approximate the binary site problem with probabilities p_A and $p_B = 1 - p_A$ and conductivities g_{A-A} , g_{A-B} , and g_{B-B} by a three-bond problem with bond probabilities

$$p_{A-A} = p_A^2, \quad p_{B-B} = p_B^2, \quad p_{A-B} = 2p_A p_B \quad (2.3)$$

for the bond probabilities in the bond effective-medium theory. Of course, this neglects correlations between bonds. Nonetheless, we show in Sec. III that this simple theory works moderately well for the site problem.

III. SIMPLE CHEMICALLY UNCONSTRAINED MODELS

Here we present results on the simplest possible multicomponent systems whose behavior differs from that observed in simple percolation. The first model is the two-component site model ($n=2$) in which more than one of the three conductive parameters g_{A-A} , g_{A-B} , and g_{B-B} are nonzero. The case in which all three conductances are nonzero appears to be relatively uninteresting. When $g_{B-B} = 0$, however, interesting behavior results as a function of $y = g_{A-A}/g_{A-B}$. The case $y \rightarrow \infty$ corresponds to the ordinary site conduction problem, whereas the limit $y \rightarrow 0$ corresponds to a case in which there is conduction between unlike "atoms" but not between like "atoms." This second case may not be completely unphysical; there are compounds which are conducting, such as SN_x , though the elemental constituents are insulators. Nu-

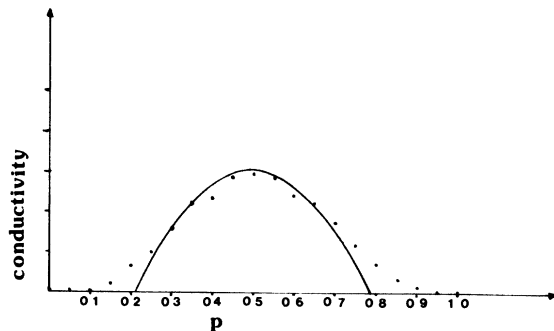


FIG. 1. Conductivity in the $n=2$, $b=3$ site problem with $g_{A-A} = g_{B-B} = 0$, $g_{A-B} = 1$. Dots are simulation with 1000 sites. Full line is crude effective-medium theory (EMT) described in the text.

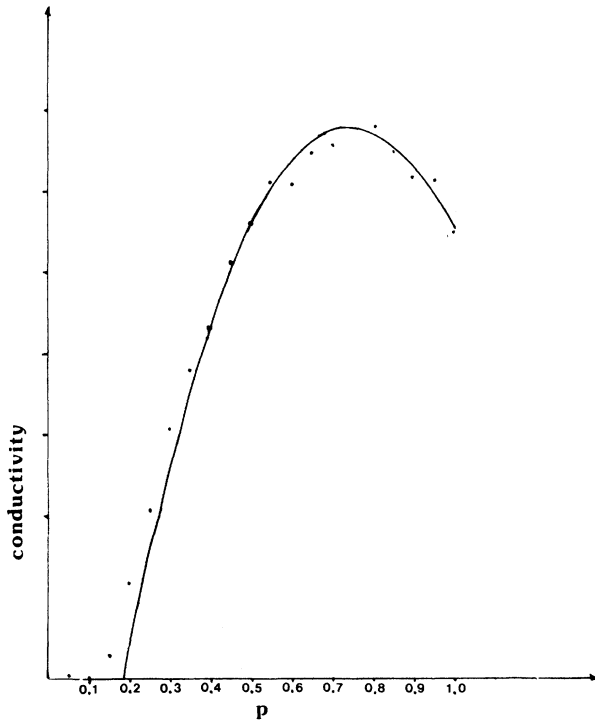
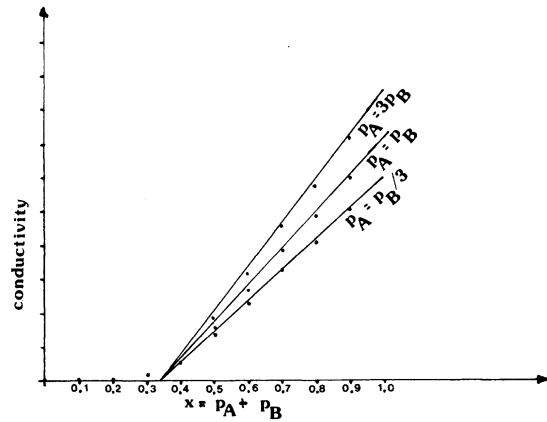
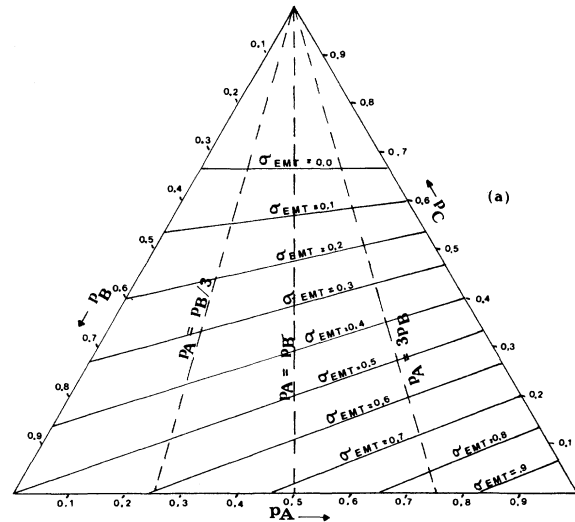


FIG. 2. Conductivity in the $n=2$, $b=3$ site problem with $g_{A-A}=1$, $g_{A-B}=2$, $g_{B-B}=0$. Symbols have same significance as in Fig. 1.

merical calculations of the conductivity for the values of $\gamma=0$ and $\gamma=0.5$ are shown for a simple cubic lattice in three dimensions in Figs. 1 and 2. The case $\gamma=0$ poses the following question: What is the behavior of g near the onset points p_c^{\pm} bounding the region $p_c^- < p < p_c^+$ of finite conductivity? This question does not appear to have a trivial answer because this conductivity problem does not scale simply to give the answer in terms of a known problem. Suppose we approximate the conductance of the $\gamma \rightarrow 0$ model with that of a bond problem with bond concentration $p^b = 2p^s(1-p^s)$. Then the points p_c^{\pm} would be $p_c^{\pm} = \frac{1}{2} \pm \frac{1}{2}(1-2p_c^b)^{1/2}$, where p_c^b is the ordinary bond percolation concentration. For the simple cubic lattice ($p_c^b = 0.247$), this gives $p_c^+ \approx 0.856(0.144)$. By numerical simulation, we find $p_c^+ \approx 0.95$ and $p_c^- \approx 0.05$. In view of the qualitative similarity of these results, we have worked out the effective-medium theory for the bond problem with three kinds of bonds as an approximation to the $n=2$, $b=3$ site problem. As discussed in Sec. II we must make some approximation in order to apply effective-medium theory to this site problem. We choose to approximate the site problem by a bond problem for the purpose of doing effective-medium theory taking



(b)

FIG. 3. (a) $n=3$, $b=3$ bond problem with $g_A=1.0$, $g_B=0.5$, $g_C=0$. Lines of constant conductivity in the EMT are shown with solid lines in the composition plane. Dashed lines show concentrations for which simulations are compared with EMT in (b). (b) EMT compared with simulations for the same model for concentrations along the dashed line in (a).

$$p_{A-A} = p_A^2, \quad p_{A-B} = 2p_A(1-p_A), \quad p_{B-B} = (1-p_A)^2. \quad (3.1)$$

Results are shown as dark lines on Figs. 1 and 2. Though the crude effective-medium theory is similar to the numerical results, the question cited earlier cannot be definitively answered by these techniques.

We next turn to the bond problem with $n=3$. This problem can be simply approximated by use of effective-medium theory. A straightforward extension of the technique of Ref. 4 gives the conductivity as the solution to the equation

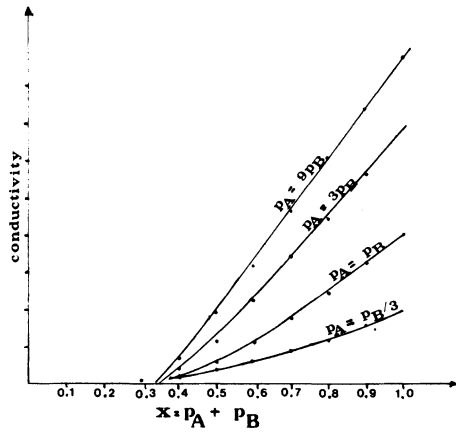
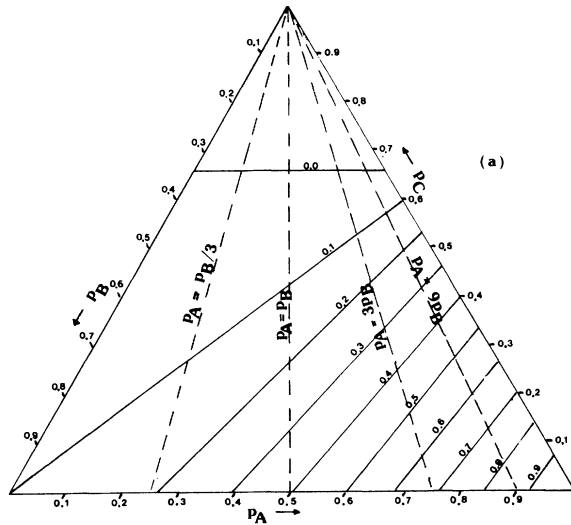


FIG. 4. (a) Same model as Fig. 3 with $g_A=1$, $g_B=0.1$, $g_C=0$. (b) Same as Fig. 3(b) but with $g_A=1$, $g_B=0.1$, $g_C=0$.

$$p_A(g_m - g_A) \left[g_m \left(\frac{z-2}{2} \right) + g_B \right] \\ \times \left[g_m \left(\frac{z-2}{2} \right) + g_C \right] + \dots = 0,$$

where the dots represent two cyclic permutations of A, B, C . This is cubic in g_m . Solutions are shown in Figs. 3 and 4 for $z=6$, appropriate for the simple cubic lattice. For comparison, we show results of numerical simulation for the simple cubic lattice. Figure 3(a) shows effective-medium lines of constant conductivity in a concentration diagram for $g_A=1.0$, $g_B=0.5$, with $g_C=0$. Figure 3(b) shows the conductivity along several lines in the concentration plane in Fig. 3(a), using both effective-medium theory (straight line)

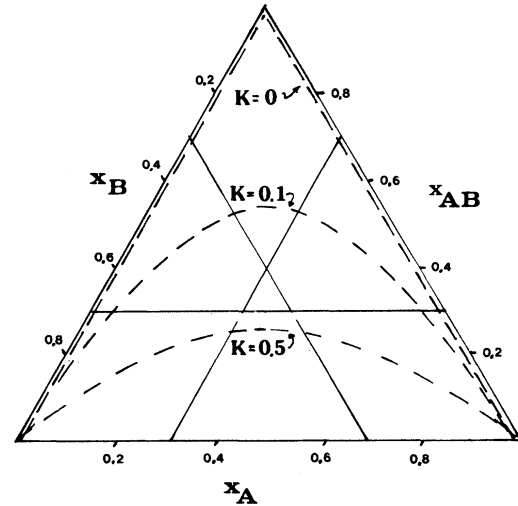


FIG. 5. Equation (4.4) for various values of K in the composition plane.

and numerical simulation (points). Figure 4 shows results for the three-bond model when $g_A=1$, $g_B=0.1$, and $g_C=0$. One sees that in this case the effective-medium theory gives reliable results except near the percolation concentration. The effective-medium theory works better for these models than it did for the $n=2$, $b=3$ site model because the additional approximation (3.1) is not necessary here. Critical properties of the unconstrained $n=b=3$ model have been studied by Straley and Kogut.⁶

IV. CHEMICALLY CONSTRAINED MULTICOMPONENT PERCOLATION

We now turn to chemically constrained models. The idea of chemical constraint³ is that the sites or bonds may be chemical entities and that some

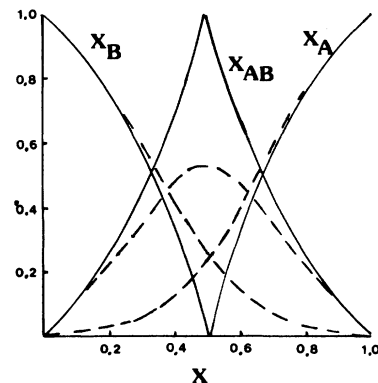


FIG. 6. Graph of Eqs. (4.3) and (4.4) for $K=0$ (solid lines) and $K=0.1$ (dashed lines).

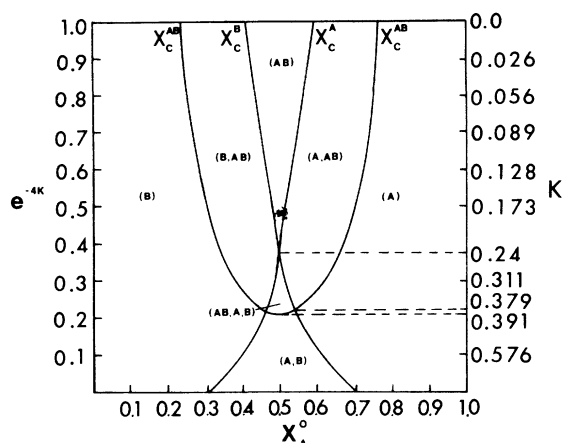


FIG. 7. "Phase diagram" for the $n=3$, $b=6$ chemically constrained site problem on a simple cubic lattice. Here K (or e^{-4K}) is plotted as a function of X_A^0 . The line labeled X_C^{AB} is the solution to the equations (4.3) and (4.4) when K and X_A^0 are regarded as independent variables with the additional constraint that $X_{AB}=0.307$ (the percolation concentration for the simple cubic lattice). The lines marked X_C^B , X_C^A are similarly the solutions with the constraints $X_B=0.307$ and $X_A=0.307$, respectively. Letters in parentheses indicate the species for which there is a finite probability of infinite clusters in the various regions of the X_A^0, K plane.

of the n species may be chemical combinations of some of the others. The law of mass action then establishes relations between the concentrations of these entities.

The simplest nontrivial model with chemical constraint is a bond model with $n=b=3$. Suppose that C is a chemical combination of A and B . We consider the reaction



characterized by equilibrium constant K . If the total concentration x_A^0 of A is fixed by experiment then the following equations fix the concentrations of x_A , x_B , and x_{AB} :

$$\begin{aligned} x_A x_B &= K x_{AB}, \\ x_A + x_B + x_{AB} &= 1, \\ x_A^0 &= (x_A + x_{AB}) / (1 + x_{AB}). \end{aligned} \quad (4.2)$$

These equations have solutions

$$x_B = [2(1 - x_A^0)]^{-1} \{ 1 - 2x_A^0 - K + [(1 - 2x_A^0 - K)^2 + 4K(1 - x_A^0)^2]^{1/2} \}, \quad (4.3)$$

$$x_A = K(1 - x_B) / (K + x_B). \quad (4.4)$$

Equation (4.4) is graphed as the dashed lines in Fig. 5. Other representations of Eqs. (4.3) and

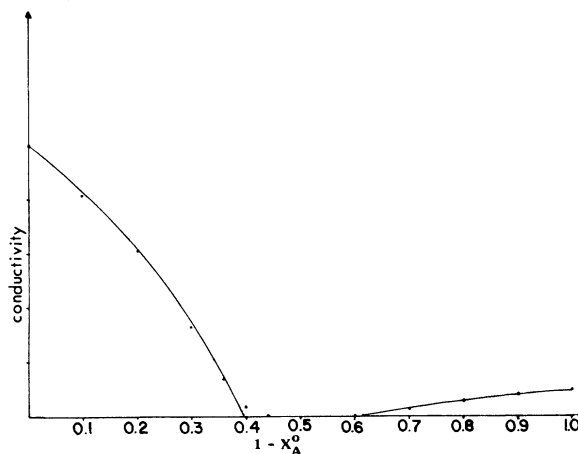
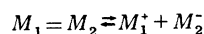


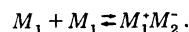
FIG. 8. Conductivity for the chemically constrained bond problem on a simple cubic lattice for $g_A=1$, $g_B=0.1$, $g_{AB}=0$ and $K=0$. Solid lines show EMT results and points are results of simulations on 1000 bond models.

(4.4) appear in Figs. 6 and 7. Using the solutions to the $n=b=3$ problem from Sec. III we find the conductivity for this model as a function of x_A^0 as shown in Fig. 8 for $K=0$ and for $g_A=1$, $g_B=0.1$, and $g_{AB}=0$. The conductivity is nonmonotonic as a function of x_A^0 . In Fig. 8, the effective-medium theory appears as a dark line while numerical simulation gives the points.

We suggest that this model may contain many of the qualitative features of the conductivity in charge-transfer salts. In such salts, a reaction of the form (M_1 and M_2 are metallic species)



takes place. One expects, however, that this reaction will not take place unless the two ions M_1^+ and M_2^- are near to one another in the lattice (to maintain local charge neutrality). Thus, we write the reaction as



M_1 and M_2 atoms, being metallic, are regarded as conducting bonds for electron transport while $M_1^+ M_2^-$ complexes are nonconducting or weakly conducting. We then have the $n=b=3$ model just discussed if we suppose that the $M_1^+ M_2^-$ complex goes on a single site. In Fig. 9 we show resistivity curves from this model which are qualitatively similar to data taken by Avci and Flynn⁷ on $\text{Cs}_{1-x}\text{Te}_x$, $\text{Cs}_{1-x}\text{Sb}_x$, $\text{Cs}_{1-x}\text{I}_x$, $\text{Cs}_{1-x}\text{Xe}_x$, $\text{Cs}_{1-x}\text{Sn}_x$, $\text{Na}_{1-x}\text{Sn}_x$, and $\text{Cs}_{1-x}\text{Au}_x$. In all of the curves which show the effective-medium theory for the constrained three-bond model, we have

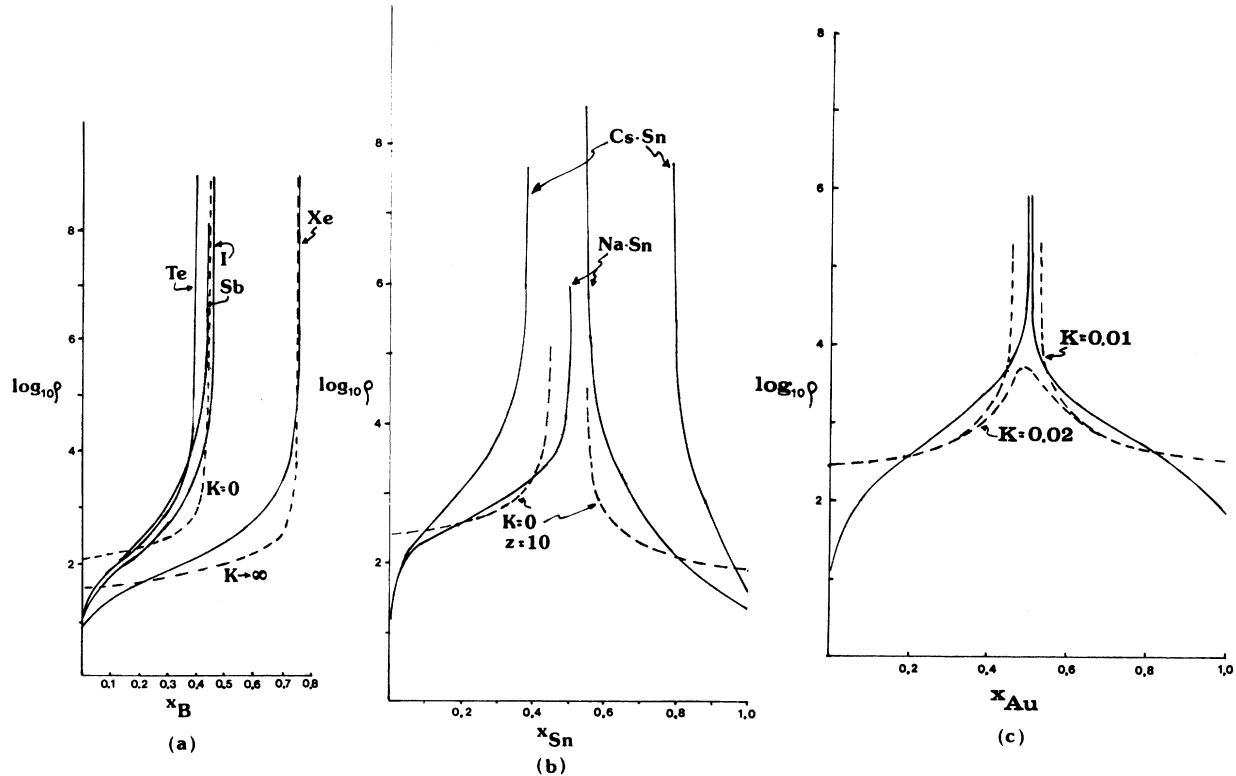


FIG. 9. Comparison of experimental resistivity of alloys (solid lines) compared with fits to the chemically constrained $n=b=3$ bond model as described in the text. In all cases, the dashed lines show the effective-medium theory with $z=10$ and $g_{AB}=0$. (a) $Cs_{1-x_B}B_{x_B}$ with $B=Te, I, Sb, Xe$. (b) $M_{1-x_B}Sn_{x_B}$ with $M=Cs, Na$. (c) $Cs_{1-x_B}Au_{x_B}$.

taken the values $z=10$ and $g_{AB}=0$. K was fixed by requiring that the observed critical points be as close as possible to the predicted ones. The resulting values of K and g_B seem very reasonable: $g_{BB}=0$ and $K \rightarrow \infty$ for $Cs_{1-x_B}Xe_{x_B}$, and $g_{BB}=0$ and $K=0$ for $Cs_{1-x_B}Te_{x_B}$, $Cs_{1-x_B}I_{x_B}$, and $Cs_{1-x_B}Sb_{x_B}$, with intermediate values of K and g_{BB} for the other systems. The shapes of the resistivity curves are, on the other hand, only qualitatively reproduced and the predicted symmetry of the critical points is not observed in $Na_{1-x_B}Sn_{x_B}$. The observed critical points for $Cs_{1-x_B}Sn_{x_B}$ cannot be obtained with reasonable values of z in this model and the asymmetry is very marked. Correlation effects and the different Cs and Sn crystal structures probably play a role in $Cs_{1-x_B}Sn_{x_B}$.

We have also explored several chemically constrained site models. The simplest of these is a three-component model for which the constraint equations are again (4.2). (In the case of $\frac{1}{2}$ molecule per site, $X_A + X_B + X_{AB} = 1$ is changed to $X_A + X_B + 2X_{AB} = 1$.) If the molecule is taken to be isotropic, then there are six conductivity parameters in these models with one molecule per site:

$$\bar{g} = \begin{pmatrix} g_{A-A} & g_{A-B} & g_{A-AB} \\ g_{B-A} & g_{B-B} & g_{B-AB} \\ g_{AB-A} & g_{AB-B} & g_{AB-AB} \end{pmatrix}.$$

We have to the present only considered models for which \bar{g} is of the form

$$g = \begin{pmatrix} 1 & 0 & y \\ 0 & 0 & 0 \\ y & 0 & x \end{pmatrix}.$$

Figure 10 shows simulation results for a simple cubic lattice with $y=0$, $x=1$, and $K=0$. This result, which was presented earlier,³ is intended as a preliminary model for experiments on sodium ammonia mixtures,² which show a similar non-monotonicity in the resistivity as a function of concentration (Fig. 11). This model has two major deficiencies as a description of the experiments: First, the dip in the resistivity as a function of concentration is less than that observed in the ex-

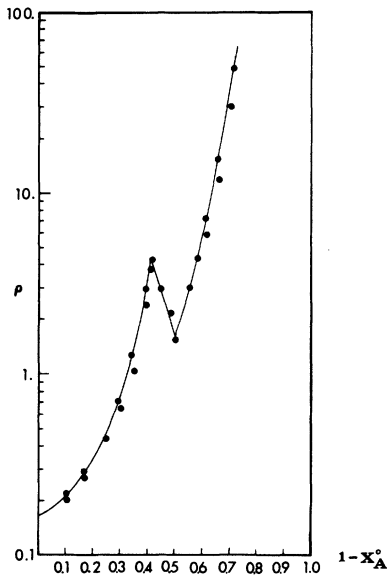


FIG. 10. Resistivity in the $n=3$, $b=6$ chemically constrained site model with $g_{A-A}=1$, $g_{AB-AB}=0.1$, $K=0$. The solid line is obtained by scaling numerical results of Kirkpatrick.

periments. Second, the model of Fig. 10 takes $y=g_{A-AB}=0$, which is unrealistic. If one takes $y \neq 0$, then the nonmonotonicity rapidly disappears as y grows. This is indicated in Fig. 12 where $y=0.01$ and 0.001 , and $x=0.1$. Further, it is

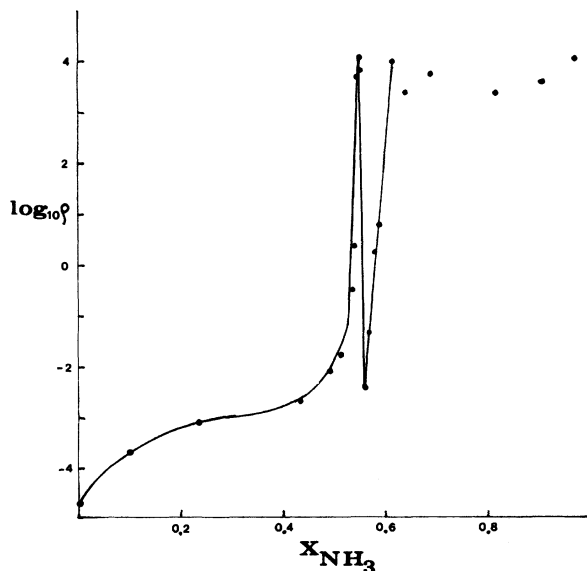


FIG. 11. Experimental results on $\text{Na}_x(\text{NH}_3)_{1-x}$ by McNeal and Goldman. The solid line is a guide to the eye.

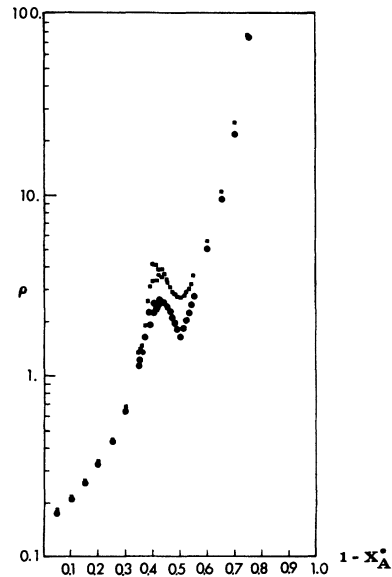


FIG. 12. Resistivity in the $n=3$, $b=6$ chemically constrained site model with $g_{A-A}=1$, $g_{AB-A}=0.001$, $g_{AB-AB}=0.1$, $K=0.01$ (squares) and with $g_{A-A}=1$, $g_{AB-A}=0.01$, $g_{AB-AB}=0.1$, $K=0.0$ (dots).

possible to show⁸ that with the plausible inequality $1 > y > x$ (which we have violated in taking $y=0$ and $x \neq 0$) one has a monotonic resistivity as a function of concentration. (Figure 12 also shows a similar rounding effect when $K \neq 0$.) Here we briefly discuss several possible solutions to these problems. The sharpness of the secondary peak in the resistivity seems to be strongly dependent on the effective coordination number of the lattice. The peak becomes sharper as the effective coordination number decreases. This effect is illustrated in a model containing one *anisotropic* molecule per site. In such a model, there are in principle seventeen possible conductive parameters as indicated in Fig. 13. One decreases the effective coordination number by choosing a limited number of the seven possible *AB-AB* conductive parameters to be nonzero. In Fig. 14 we show the resistivity found by simulation when the three boxed parameters in Fig. 13 are made nonzero. Here, as in Figs. 10 and 12, we have taken all conductivities *AB-A* equal to zero and have chosen to keep only those *AB-AB* conductivities nonzero in which the largest number of atoms within the molecules are adjacent. The calculation is intended only to illustrate the qualitative effect of anisotropy. ($g_{A-A}=1$ and the two nonzero g_{AB-A} are both equal to 0.1.) The peak is seen to be sharpened. A somewhat similar effect is seen in Fig. 15, which shows the resistivity for one isotropic molecule per site in a diamond lattice. These results suggest that the sharp

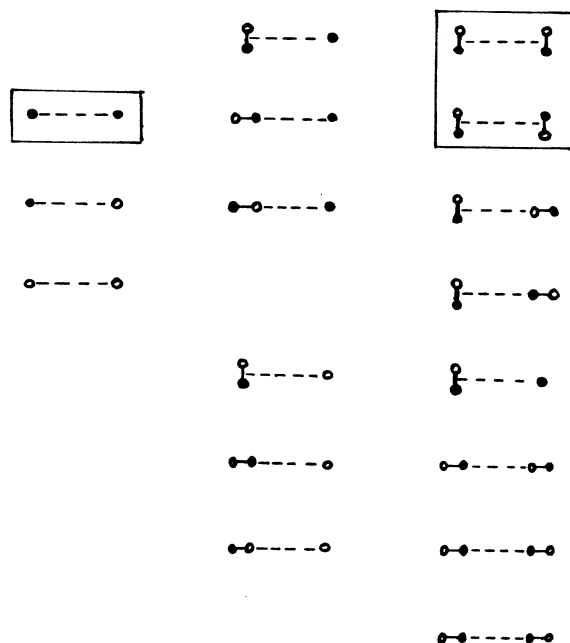


FIG. 13. Possible conductive parameters in the $n = 3$ chemically constrained site model with one anisotropic molecule per site. There are $b = 17$ possible conductive parameters. The boxes indicate the parameters which were taken to be finite in the simulation of which the results are shown in Fig. 14.

peak in resistivity may arise in part from an effectively low coordination number in the sodium ammonia mixtures.

On the other hand, the effective coordination number can be increased by suitable modeling. For example, in the case of $\frac{1}{2}$ molecule per site (one "atom" of the A - B pair on each site) one has, in the simple cubic lattice, a total of 92 ways of placing one A - B pair next to another so that at least one member of each pair is in nearest-neighbor coordination with one element of the other pair (see Fig. 16). Fifteen of these possibilities are distinguishable (not reducible to one another by translations, rotations or reflections of the lattice) so that the model has a total of 15 nearest-neighbor conductive AB - AB parameters. In addition, there are 20 ways to place a single A or B in nearest-neighbor coordination with AB and 8 conductive AB - A and AB - B parameters. Finally, one has the three parameters for A - A , A - B , and B - B so that $b = 26$ for this model. Such a model is clearly not useful phenomenologically, but can illustrate the effects of increasing coordination number. In Fig. 17 we show a simulation result in which we have taken $g_{A-A} = 1$ and have set five of the g_{AB-AB} parameters equal to 0.1 while the other conductances are 0 as indicated in Fig. 16.

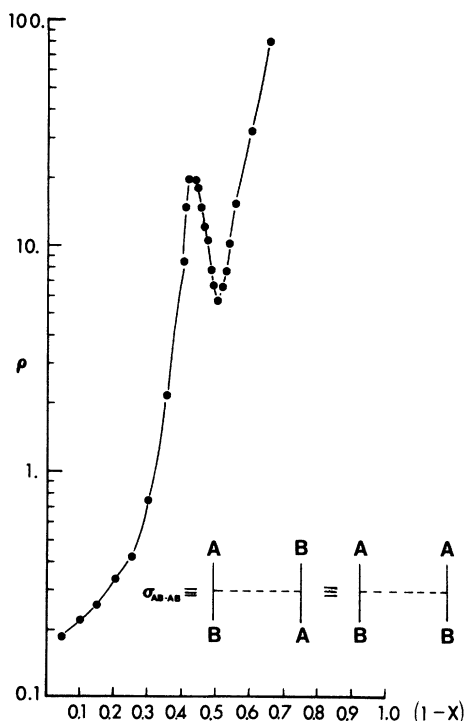
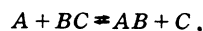


FIG. 14. Resistivity for the $n = 3$, $b = 17$ site model with one anisotropic molecule per site. The conductive parameters shown in Fig. 13 were all zero except for $g_{A-A} = 1$, $g_{AB-AB} = 0.1$, $K = 0$.

With this constraint, there are still 24 ways for a given AB molecule to be connected by a conductance to another AB and the peak in the resultant resistivity is very broad. (Note that this effective coordination number of 24 for the AB molecules is not directly related to the number $b = 26$ of independent conductive parameters.)

A physically more realistic model which reduces the effective coordination number is a four-component model in which the species A , B , and C react as follows:



with equilibrium constant K . We assume that there is one molecule per site. This reaction has the form of the reaction forming sodium amide from sodium and ammonia with $A = \text{Na}$, $B = \text{NH}_2$, and $C = \frac{1}{2}\text{H}_2$. If we suppose that, as in this realization, the species C occupies $\frac{1}{2}$ a site, then the constraint equations include

$$x_A + x_{AB} + x_{BC} + \frac{1}{2}x_C = 1,$$

$$X_A^0 = \frac{x_A + x_{AB}}{x_A + x_{BC} + x_{AB} + x_C} = \frac{x_A + x_{AB}}{1 - \frac{1}{2}x_C},$$

$$X_A^0 = \frac{x_{BC} + x_{AB}}{x_A + x_{BC} + x_{AB} + x_C} = \frac{x_{BC} + x_{AB}}{1 - \frac{1}{2}x_C}.$$

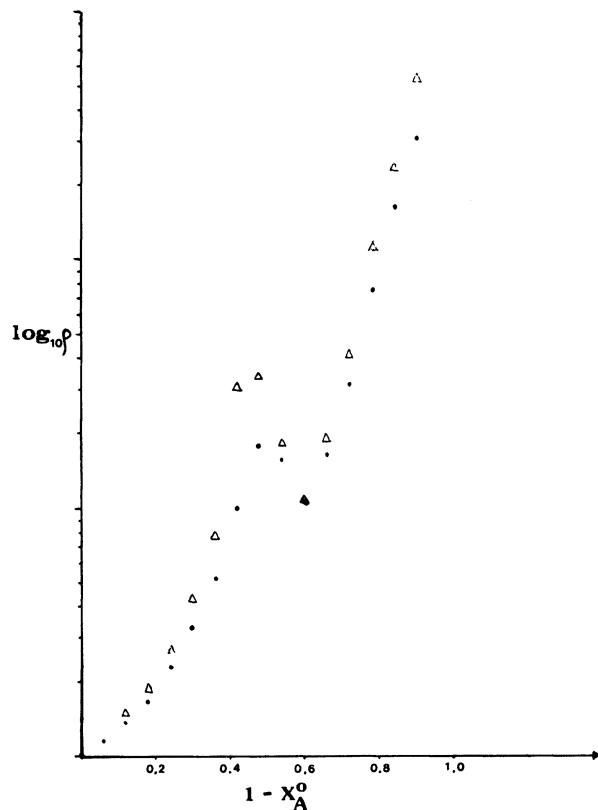


FIG. 15. Comparison of the $n=3$, $b=6$ chemically constrained models' resistivity for simulations on the diamond (triangles) and simple cubic (dots) lattices. $g_{A-A}=1$, $g_{AB-AB}=0.1$, $K=0$.

The law of mass action would have the form

$$X_A^2 X_{BC}^2 = K X_{AB}^2 X_C,$$

but here, for simplicity, we used the relation

$$X_A X_{BC} = K X_{AB} X_C.$$

We have performed simulations for this model. The results show a resistivity peak at $x_A^0 = 0.5$ which is sharper than that of the three-component models but which again disappears before the condition $g_{AA} > g_{A-AB} > g_{AB-AB}$ is satisfied.

Finally, we note that a correlated model⁹ in which some segregation of the species AB and A takes place during sample formation is expected to reduce the appearance of $AB-A$ bonds and thus make a sharper peak possible in the presence of more realistic values of g_{AB-A} . We have not yet explored such a model in any detail.

V. CONCLUSIONS AND DISCUSSION

In this work we have begun to explore the conductive properties of multicomponent percolation mod-

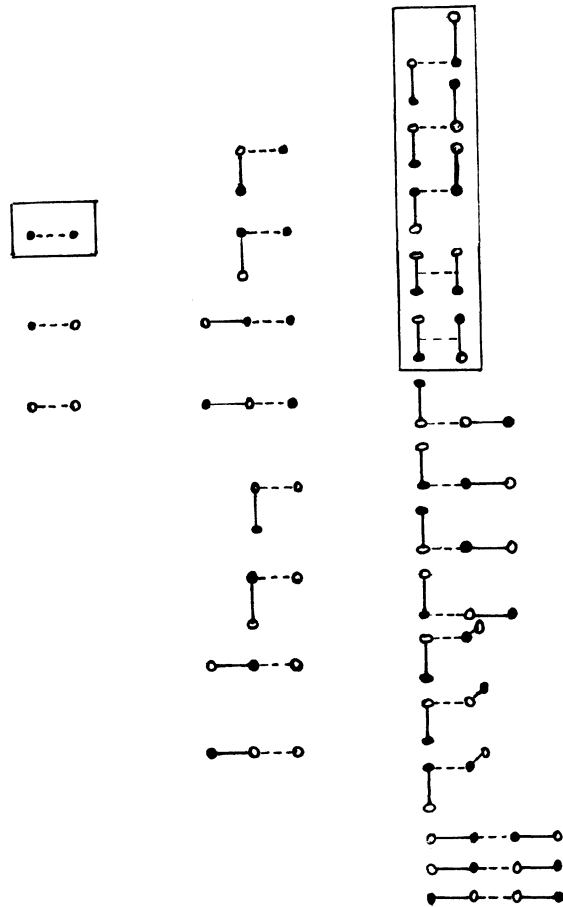


FIG. 16. Conductive parameters in a site model with $n=3$, $b=26$. Here each "molecule" fills 2 sites. In the simulation for which results are shown in Fig. 17, we have taken only the boxed parameters to be finite.

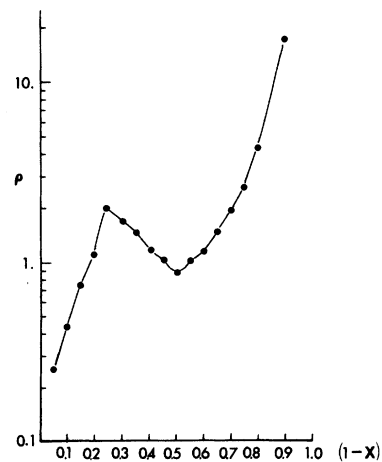


FIG. 17. Simulation result for the $n=3$, $b=26$ model with one molecule filling two sites $g_{A-A}=1$. The five conductive $AB-AB$ parameters which are boxed in Fig. 16 are set equal to $g_{AB-AB}=0.1$ in this simulation. All other conductive parameters are set equal to 0.001.

els both with and without chemical constraint, using the most direct technique of simulation and the theoretically simple approximation scheme of effective-medium theory. We have found that even the simplest unconstrained models have intriguing properties. For example, the site problem with $n=2$, $b=3$ has interesting structure of possible physical relevance with $g_{A-B} \neq 0$, $g_{A-A} = g_{B-B} = 0$. In chemically constrained systems we found that a nonmonotonic resistivity versus concentration curve is generated by the $n=b=3$ bond problem in the case that the reaction $A+B \rightleftharpoons AB$ is considered when $g_{AB}=0$. This model appears capable of modeling charge-transfer systems in a plausible qualitative way with just three parameters (g_A , g_B , and K). In multicomponent site percolation we have discussed a number of models which give a secondary resistivity peak such as that seen in $\text{Na}_x(\text{NH}_3)_{1-x}$ in the $n=3$, $b=6$ model and in related

models with anisotropic molecules and two-site molecules. None of the models considered quantitatively describes the conductivity of the $\text{Na}_x(\text{NH}_3)_{1-x}$ system. The most promising avenue for further narrowing the gap between theory and experiment in the sodium ammonia system appears to us to be the introduction of clustering correlations in a chemically constrained three-component model.

ACKNOWLEDGMENTS

This work was supported in part by the National Science Foundation and the University of Minnesota Graduate School. We are grateful to A. Goldman and N. McNeal for discussion of their experiments, to R. Zallen for a letter concerning some of this work, and to C. P. Flynn and co-workers for a discussion of their experiments.

*Permanent address.

† Present address.

¹R. Zallen, *Phys. Rev. B* **16**, 1426 (1977).

²N. A. McNeal and A. M. Goldman, *Phys. Rev. Lett.* **38**, 445 (1977).

³J. W. Halley and W. Holcomb, *Phys. Rev. Lett.* **40**, 1670 (1978).

⁴S. Kirkpatrick, *Phys. Rev. Lett.* **27**, 1722 (1971).

⁵B. P. Watson and P. L. Leath, *Phys. Rev. B* **9**, 4893

(1974).

⁶P. M. Kogut and J. Straley, *A. I. P. Conf. Proc.* **40**, 383 (1978); and (unpublished).

⁷R. Avci and C. P. Flynn, *Phys. Rev. Lett.* **41**, 428 (1978); and (unpublished).

⁸P. Visscher (private communication).

⁹M. H. Cohen, J. Jortner, and I. Webman, *Phys. Rev. B* **17**, 4555 (1978).