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Percolation in Heavily Doped Semiconductors*

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Determination of the detailed nature of the semiconductor-to-metal transition in doped semiconductors is obscured by the random placement of the impurities. We report the results of a Monte Carlo percolation calculation which show that the details of the Hall-coefficient data in Si:P and, less clearly, in Ge:Sb are consistent with the existence of a discontinuous transition from insulator to metal at $T=0°K$ as the impurity concentration is increased.

SINCE the original speculations and approximate theory of Mott,[1,2] there has been considerable interest in the basic question whether the electrical conductivity of a regular array of hydrogen atoms will increase discontinuously from zero at some particular value of the lattice constant as the lattice constant of the array is decreased, or whether the transition will be of a more gradual nature.[3] One can express the question by supposing that at a low concentration there is a full band of carriers separated from empty states by an energy gap ϵ. Figure 1 shows schematically several possible models for the manner in which that gap might vanish as a function of the concentration of hydrogen atoms, n_D.

Doped semiconductors form attractive systems for experimental investigation of the nature of this transition, but are flawed by the random placement of the pseudohydrogen atoms. We report here the results of a Monte Carlo computer calculation of "percolation" in such systems. Comparison of the results with the Hall-coefficient data in Si:P and Ge:Sb indicates that the experimental data, extrapolated to 0°K, are consistent with a model in which the electron of a given impurity is completely localized if no neighbor impurity atom is within $2r_0$ of that impurity, but can move freely to the other site if the nearest-neighbor separation is less than this distance. Here $2r_0$ is $4.4a_H$ for Si:P and $3.8a_H$ for Ge:Sb (a_H is the Bohr radius computed from the donor ionization energy). Implications of this comparison for making a choice among the models given in Fig. 1 will be discussed after a summary of the calculation and its results are given.

MODEL

Our percolation calculation is based on the following model system. Impurities are located at random on the lattice sites of a simple cubic lattice of lattice constant d. At each concentration, we ask whether a cluster of impurity atoms extends uninterruptedly from one side of the crystal to the other. The criterion for connectivity, starting from an arbitrary site, is that there be, *seriatim*, at least one other impurity within a distance $2r_0$ of the impurity in question. We expect r_0 to be of order a_H, the Bohr radius of the impurity, and hence many times the atomic spacing of the host lattice for the cases of Si and Ge, the materials to which we shall apply our results. For the model lattice, for reasons of economy in computer time, we choose d so that $2r_0=3d$. We have performed convergence tests which show that results of the calculation undergo only very minor changes for a finer grid in the model lattice. We note that our calculation differs from previous lattice percolation calculations[4] primarily in the fact that we permit the interpenetration of the impurity atoms, which is appropriate to the doped-semiconductor case.

The quantity of interest to us is P_∞, the probability that any randomly chosen impurity atom will find itself a member of those infinite clusters extending fully across the sample. We calculate values of P_∞ as a function of p, the probability that any single lattice site is occupied by an impurity. In comparing the results with the experimental data, we expect $P_\infty(p)$ to correspond to n/n_D, the ratio of the number of free electrons to the number of donors as measured by a dc transport

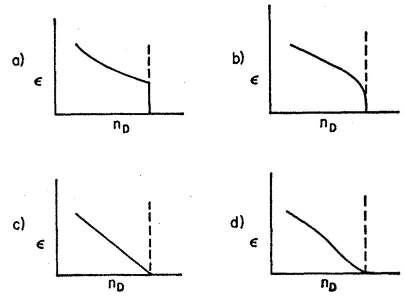

FIG. 1. Several possibilities for the qualitative behavior of ϵ, the energy gap between filled band and empty states, as a function of hydrogenlike atom density n_D. (a) Discontinuity in ϵ. (b) discontinuity in $d\epsilon/dn_D$, ϵ continuous. (c) Discontinuity in $d^2\epsilon/dn_D^2$, lower derivatives continuous. (d) Smooth transition, $d^2\epsilon/dn_D^2$ continuous.

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[3] See Rev. Mod. Phys. **40**, No. 4 (1968) for a status report on the subject.

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measurement such as the Hall coefficient or electrical conductivity.

CALCULATION

Our computer calculation follows the strategy laid down by Frisch *et al.*[5] The computer is programmed to construct clusters of n impurity atoms for $n=1, 2, \cdots, N$ for suitably large N. For each n the computer data yield an estimate of $P_n(p)$, the probability that a randomly chosen atom lies in a cluster containing n or more impurities. The desired relation is the limit

$$P_\infty(p)=\lim_{n\to\infty} P_n(p). \tag{1}$$

During the calculation, random numbers c (actually pseudorandom numbers of nine digits) rectangularly distributed between 0 and 1 are assigned to all the lattice sites $\mathbf{x}$ in the crystal except for the origin, which is assigned the value 1. Clusters are formed by adding impurities one at a time, using the following procedure: Suppose a cluster of size n has already been formed with its n impurities located at the lattice points $\mathbf{I}_1, \mathbf{I}_2, \cdots, \mathbf{I}_n$. Let $c(\mathbf{I}_i)$ be the random number assigned to the ith impurity and set g_n equal to the smallest of these n numbers. Define S_n as the set of lattice sites which are not occupied by impurities but are within $2r_0$ of some impurity.

$$g_n=\min c(\mathbf{I}_i), \quad 1\leq i\leq n$$
$$S_n=(\mathbf{x}\,|\,\mathbf{x}\neq\mathbf{I}_i, \text{ for any } i, \text{ and } |\mathbf{x}-\mathbf{I}_i|\leq 2r_0 \text{ for some } i, \quad 1\leq i\leq n). \tag{2}$$

The next impurity atom is placed at the site in S_n with the largest assigned random number:

$$c(\mathbf{I}_{n+1})=\max c(\mathbf{x}) \text{ for } \mathbf{x} \text{ in } S_n. \tag{3}$$

Now $n+1$ impurities are in the cluster, and g_{n+1} and S_{n+1} are defined as before by Eq. (2). The procedure starts with the first impurity located at the origin $\mathbf{I}_1=\mathbf{0}$ and is repeated until the cluster contains N impurities.

Hammersley and Handscomb[6] have proved that $P_n(p)$ is the cumulative distribution function of $1-g_n$; i.e.,

$$P_n(p)=\text{probability that } 1-g_n\leq p. \tag{4}$$

Accordingly, an empirical estimate of $P_n(p)$ is obtained from the construction of K clusters:

$$P_n(p)\cong\text{fraction of all clusters with } g_n\geq 1-p. \tag{5}$$

The calculations were performed on an IBM 360/65 computer. In order to obtain the general form of $P_n(p)$, 200 clusters of $N=200$ and $2r_0=3d$ were constructed. The computer time required amounted to 7.5 sec/cluster. An additional 800 clusters of $N=50$ and $2r_0=3d$ were constructed to define more accurately the portion of the curve for P_n near 1 [we take advantage of the fact that the shape of the curve for $P_n\cong 1$ becomes independent of n for rather small values of n, as is evident from Fig. 2(a)]. For convergence tests, 25 clusters of $N=200$ were constructed for each of the following values of $2r_0$: d, $2d$, $4d$, and $5d$.

As a check, the computer output for $n=2$ was compared with the theoretical formula

$$\begin{aligned} P_2(p)&=1-(1-p)^{M(2r_0)-1} \\ &\cong 1-e^{-Mp}, \quad (p\ll 1) \end{aligned} \tag{6}$$

where $M(2r_0)$ is the number of lattice sites in a sphere of radius $2r_0$. (For $2r_0=3d$, $M=123$.) The close agreement of the calculation with Eq. (6) can be seen in the two curves farthest to the left in Fig. 2(a).

RESULTS

Figure 2(a) shows the results of the calculation. P_n for $n=2$, 3, 10, 50, 100, and 200 are shown, as well as P_∞. The P_∞ curve was obtained as an extrapolation of calculations of P_n at $n=50$, 67, 100, 133, 167, and 200. The value of p_c obtained from the extrapolated curve, where p_c is the critical probability for the onset of percolation, is estimated to be correct to within 10%. Values of p along the abscissa are normalized values. They express the probability that an impurity atom is located somewhere in an arbitrary volume $\frac{4}{3}\pi r_0^3$, not the probability that an individual lattice site is occupied. The critical radius r_0 is eventually to be determined by comparison with experimental data.

Our value for p_c, 0.29, is not in agreement with the value of 0.372 obtained by Roberts and Storey[7] for the case of a homogeneous background medium. (The quantity which Roberts actually calculates, t_c, is related to our p_c by the expression $p=\frac{4}{3}\pi t$.) On the basis of our tests for convergence with increasing $2r_0$ (increasing $2r_0$ implies a lattice of finer grain), we would expect the results to be in close agreement. We are, at the moment, unable to point with certainty to the reason for the discrepancy. The Roberts-Storey value is based on a different method of attack, which yields t_c, but not the probability curve $P_\infty(p)$. We have confidence in our calculation, but will not discuss here possible reasons for the discrepancy with Roberts and Storey, since the value of the comparison with the experimental semiconductor data depends primarily upon the shape of the $P_\infty(p)$ curve rather than upon the specific value of p_c.

In Fig. 2(b) we compare the calculated curve for $P_\infty(p)$ with values of n_H/n_D calculated on the basis of the available Hall-coefficient data for Si:P, that of

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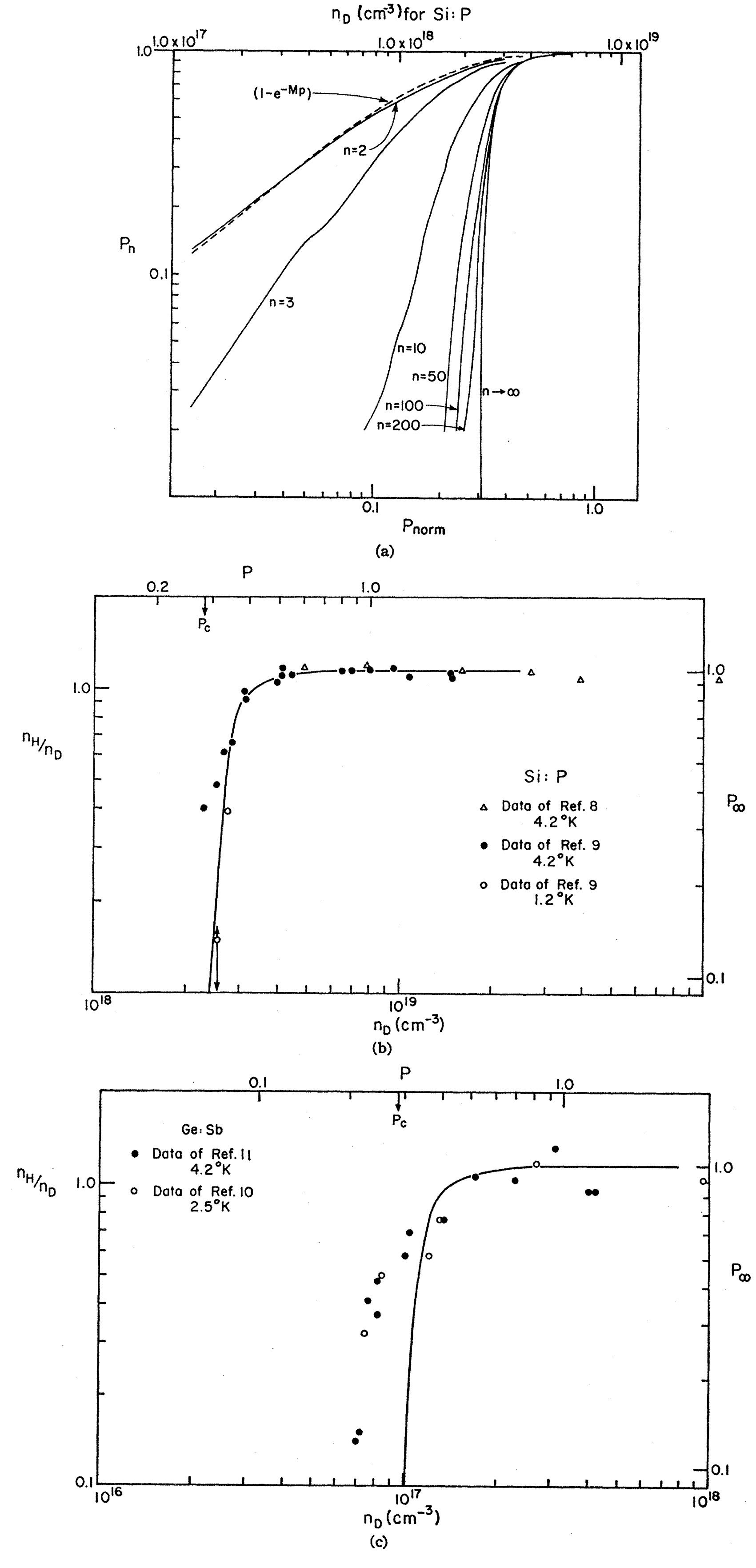

FIG. 2. (a) Results of the percolation calculation for various cluster sizes. P_n is the probability that any randomly chosen impurity will find itself a member of a cluster of size n or larger. p is the normalized occupation probability (see the text). The theoretical function for P_2 is also shown. (b) Comparison of values of n_H/n_D extracted from published measurements of R_H for Si:P with the calculation of $P_\infty(p)$. (n_H is the density of Hall carriers defined by the relation $R_H = 1/n_H ec$ and n_D is the donor concentration.) The technique for fitting is described in the text. The 1.2°K value for n_H/n_D at $n_D = 2.55 \times 10^{18}$ cm^{-3} is a rough estimate obtained by extrapolating the curve published by Yamanouchi *et al.* for that sample at higher temperatures. (c) Comparison of experimental data for n_H/n_D for Ge:Sb with the calculation of $P_\infty(p)$. The technique for fitting differs from that of (b) and is described in the text.

Chapman *et al.*,[8] and that of Yamanouchi *et al.*[9] Proper horizontal placement of the calculated curve was determined by fitting to the experimental data for values of n_H/n_D above 0.7. Note that the experimental curve levels off at $n_H/n_D=1.13$ rather than at $n_H/n_D=1.0$. That fact no doubt represents a failure of the simple parabolic-band relation which we have used, $R_H=1/n_Hec$. Since we are only interested in *changes* in the ratio n_H/n_D, we do not concern ourselves with this departure from unity.

The effects of thermal excitation on the number of Hall carriers, even at 4.2°K, is evident in Fig. 2(b) in the differences of the fragmentary 1.2°K data from that obtained at 4.2°K.

Figure 2(c) shows the same comparison with the Ge:Sb data of Fritzsche[10] and of Yamanouchi.[11] In this case, we have fitted the computed curve to place p_c at $n_D=0.96\times10^{17}$ cm^{-3}, the value estimated by Fritzsche[12] for the vanishing of ϵ_2. (Fritzsche's quantity ϵ_2 is the average value of ϵ at the donor concentration in question.) We attribute the much greater width of the transition in Ge to the substantial thermal activation of carriers at 2.5 and 4.2°K at values of p substantially below the point at which $p=p_c$. This conclusion is consistent with the average values for ϵ determined at the concentrations in question.

CONCLUSIONS

We draw the following conclusions.

(1) The Hall-coefficient data for Si at 1.2°K are consistent with our model calculation. Thus, for Si:P, the nonzero width of the transition in dc transport properties can be ascribed entirely to the effects of random impurity placement. Hence, the experimental data near $T=0$°K are consistent with any theoretical model which includes the feature of a sudden change from localized to delocalized carriers at a particular value of n_D. For Ge:Sb, it appears that very-low-temperature data would be required in order to make a satisfactory test of the model.

(2) There is little evidence of a temperature dependence in the value of n_D at which the transition occurs. We draw this conclusion from the fact that there is no temperature dependence discernible for either Si:P or Ge:Sb in the data for values of n_H/n_D above 0.6.

(3) The fact that the temperature dependence in the data appears only below a rather well-defined value of n_D, particularly for Si:P, seems to us to militate against a theoretical model in which $d^2\epsilon/dn_D{}^2$ is continuous at the transition [e.g., Fig. 1(d)], a model which appears to be suggested implicitly by Mott and Davis.[13]

(4) However, the data shown in Fig. 2 do not permit a choice to be made among models of the types in Figs. 1(a)–1(c). More extensive data as a function of temperature, below 4.2°K, would be required before any realistic attempt at such a choice could be made. Fritzsche's[12] curve for ϵ_2, the average value of ϵ, favors a curve of the type shown in Fig. 1(c).

As an aside, we note that comparison of the P_2, P_3, P_{10}, and P_∞ curves in Fig. 2(a) with ESR data[14] confirms earlier speculation[15] that the ESR "delocalization" transition occurs at substantially lower concentration than that at which actual charge transport is possible. The curves permit estimates of the relative intensities of the different constituent line shapes which go to make up the total ESR absorption. Each constituent line arises from clusters of a particular size. Comparison of such estimates with the ESR data suggests a delocalization concentration of about 8×10^{17} for ESR exchange in Si:P.

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