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Concentration-fluctuation model of a doped semiconductor in the nonmetallic regime: Pseudocluster investigation

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We have performed an improved unrestricted Hartree-Fock pseudocluster calculation with a correlated two-electron wave function for the D^- state to investigate the microscopic structure of impurity bands in doped semiconductors. Though the impurity density of states and the estimated specific heat support the Mott-Hubbard-Anderson model, in the nonmetallic regime the impurity states are cluster states and a doped semiconductor can be described as statistically distributed clusters of various sizes. The distribution function of the cluster states agrees with the recent conclusion obtained from analyzing the optical, magnetic, dielectric, and transport data. A new picture of thermally activated hopping is provided which is relevant to the observed non-Ohmic conductivity and large characteristic electronic length.

I. INTRODUCTION

It has been generally accepted that the Mott-Hubbard-Anderson (MHA) model describes properly the behavior of shallow impurity states in doped semiconductors in a wide range of impurity concentration N enclosing the critical concentration N_c for the metal-nonmetal (M-NM) transition.[1,2] The essential ingredient of this model is the interplay between the electron correlation and the disorder effects on the formation of an impurity band with increasing N. For an n-type semiconductor the donor band at low N has the structure of a split Hubbard band separated by a gap and all the states in the lower split band are localized. Owing to the random impurity potential, Anderson localization exists in the tails of the upper split band. As the impurity concentration increases, the split impurity bands broaden and eventually overlap with each other, as well as with the semiconductor conduction band. Although theoretical calculations with various versions of simplified MHA model can explain qualitatively and in some cases semiquantitatively the observed transport, magnetic, and thermodynamic properties,[1,2] the model itself has been questioned recently from the microscopic point of view.

A review[3] of such simplified MHA model calculations up to 1979 revealed some inconsistent assumptions and approximations used in different calculations. Each simplified model calculation is either valid in a limited range of impurity concentration or capable of explaining only very few experiments. This is a consequence of the fact that the MHA model was constructed macroscopically without precise specification of the parameters appearing in the model.

A microscopic insight of the impurity states was provided by numerical pseudocluster calculations in the Hartree approximation[4] and Hartree-Fock approximations with the spin-polarization potentials.[5,6] In the nonmetallic regime the impurity states are cluster states of various sizes, i.e., states localized on clusters consisting of different number of impurities. With N increasing toward N_c, cluster states grow in size due to the screening of electrons, most of which occupy the cluster states but a few of which occupy the donor-excitonic states (we should point out that these donor-excitonic states differ from those defined by Thomas *et al.*[7] in terms of the pair states). It was also found that as N increases the upper Hubbard band moves rapidly into the conduction band. Therefore, the nature of the D^- state and the D^- band, as well as the definitions of ϵ_2 and the Hubbard U should be examined very carefully.

It is very interesting to note that the recent development in the theory of impurity states, stimulated by the analyses of new experimental data in the nonmetallic regime, reaches a similar conclusion regarding cluster states. From the observed photoconductivity without[8] and with[9] magnetic field, as well as the far-infrared absorption spectra[10] of the impurity band, Narita and coworkers discovered cluster states localized on negatively charged small clusters of impurities. These experiments were studied theoretically by Kamimura[11] and by Natori and Kamimura[12] with a single D^- center, and by Golka[13] with a cluster model. The dominating role of cluster states in the nonmetallic regime also appears in other experiments such as the electron-spin-resonance spectrum,[14] the dielectric phenomena,[15] and the magnetic field dependence of the specific heat.[16] A recent calculation[17] based on the cluster states agrees well with the measured magnetic susceptibility and specific heat.

The clustering of the impurities prevails even in the metallic region near the M-NM transition. The optical absorption data on heavily doped Si:As and Si:B (Ref. 18) and the theoretical calculation of the electrical resistivity in heavily doped Ge:As and Si:P (Ref. 19) indicate the necessity of considering impurity concentration fluctuation when N reaches N_c from above within about one order of magnitude. By taking into account such concentration fluctuation, Serre *et al.*[20] calculated the interband absorption spectrum in satisfactory agreement with experiment.

The most systematic and thorough investigation of the cluster state has been done at the Bell Laboratories.[7,21–25] Clusters of as many as ten impurities were found to contribute to the far-infrared absorption coefficient[7,21] in nonmetallic samples with N near N_c. The measured low-temperature magnetic susceptibility has been fitted well with a calculation based on interacting small clusters.[22] In the vicinity of N_c the dielectric susceptibility derived from the optical absorption coefficient in the nonmetallic region,[23] and the DC conductivity can be fitted with a scaling form with a characteristic length that tends to diverge with the same exponent at both sides of N_c.[24] Furthermore, Bhatt and Rice[25] have shown that in many-valley semiconductors the localized tail state, if localized on a dense cluster of four impurities or more, can attract an electron from an isolated impurity. As a result of such self-compensation, there is no Mott-Hubbard gap due to correlation in many-valley semiconductors.

In view of all these new effects recently discovered, we will in this paper investigate with an improved numerical pseudocluster calculation the microscopic structure of the cluster states caused by the concentration fluctuation. In Sec. II we describe the calculation scheme and present some results in the framework of the MHA model. The characteristic feature of the cluster states is then demonstrated in Sec. III. We then discuss in Sec. IV the meaning of the thermoactivation energy ϵ_2 in accordance with the cluster states. A concluding remark follows in the last Sec. V.

II. PSEUDOCLUSTER CALCULATION

We can use a computer to generate $\mathcal{N}$ random sites $\{\vec{R}_i,\ i=1,\mathcal{N}\}$ in a volume Ω. If we imagine these random sites as the positions of $\mathcal{N}$ impurities, then a sample of a doped semiconductor with impurity concentration $n=\mathcal{N}/\Omega$ is simulated. We further generate $M=\xi\mathcal{N}$ more random sites outside Ω but within a volume $\xi\Omega$. On each of these M outer sites we attach one neutral impurity. Then the overall impurity concentration is unchanged. The effect of the M surrounding impurities on the $\mathcal{N}$ impurities in Ω will be approximated by an effective field, which has been explained in detail in an earlier paper.[4] The inner cluster of $\mathcal{N}$ impurities embedded in this effective field will be solved numerically using an improved Hartree-Fock scheme with spin-polarized potential. The value of $\mathcal{N}$ is limited by the computer capability; however, M can be as large as necessary. We call such a modified cluster the pseudocluster.

A. Improved unrestricted Hartree-Fock scheme

The Hamiltonian of the $\mathcal{N}$-impurity system is

$$H=\sum_i p_i^2/2m+\sum_i V^{\text{ion}}(\vec{r}_i)+\frac{1}{2}\sum_{i,j} V^{e\text{-}e}(\vec{r}_i-\vec{r}_j)\ , \tag{1}$$

where $V^{\text{ion}}(\vec{r}_i)$ is the impurity-ion potential acting on the ith electron. $V^{e\text{-}e}(\vec{r}_i-\vec{r}_j)$ is the Coulomb interaction between the ith and the jth electrons, and the summations are over all the $\mathcal{N}$ electrons. Let $\mathcal{N}(\sigma)$ be the number of σ-spin electrons in the system. In an unrestricted Hartree-Fock approximation, we solve two sets of coupled Schrödinger equations,

$$\{p^2/2m+V^{\text{ion}}(\vec{r})+V_{cx}^{\sigma}(i:\vec{r})\}\Psi_{i\sigma}(\vec{r})=E_{i\sigma}\Psi_{i\sigma}(\vec{r}) \tag{2}$$

for $\sigma=\uparrow,\downarrow$. Let $\Gamma(\sigma)$ be a set of indices which specifies the $\mathcal{N}(\sigma)$ single-particle wave functions occupied by σ-spin electrons. Then the Coulomb-exchange potential $V_{cx}^{\sigma}(i:\vec{r})$ can be expressed as

$$V_{cx}^{\sigma}(i:\vec{r})=\sum_{s}\sum_{j\in\Gamma(s)}\int|\Psi_{js}(\vec{r}\,')|^2V^{e\text{-}e}(\vec{r}\,'-\vec{r})\left[1-\frac{\Psi_{is}(\vec{r}\,')\Psi_{js}(\vec{r})}{\Psi_{is}(\vec{r})\Psi_{js}(\vec{r}\,')}\delta_{\sigma s}\right]d\vec{r}\,' \,. \tag{3}$$

We assume an impurity orbital $\phi_{i\sigma}(\vec{r})=\phi_{\sigma}(\vec{r}-\vec{R}_i)$ localized on each impurity. The form of these orbital will be specified later. From these orbitals we construct an orthonormal set of single-particle functions,

$$\psi_{i\sigma}(\vec{r})=\sum_{j}\phi_{j\sigma}(\vec{r})A_{\sigma ji} \,. \tag{4}$$

Then the eigenfunctions of (2) are assumed to be linear combinations,

$$\Psi_{i\sigma}(\vec{r})=\sum_{j}\psi_{j\sigma}(\vec{r})C_{\sigma ji}=\sum_{j}\phi_{j\sigma}(\vec{r})B_{\sigma ji} \,, \tag{5}$$

where $B_{\sigma ji}=\sum_k A_{\sigma jk}C_{\sigma ki}$. If we substitute this expansion for $\Psi_{i\sigma}(\vec{r})$ and $\Psi_{i\sigma}(\vec{r}\,')$ in Eqs. (2) and (3), then we obtain

$$\sum_{j}(H_{\sigma ij}-E_{l\sigma}\delta_{ij})C_{\sigma jl}=0 \,, \tag{6}$$

where

$$\begin{aligned}H_{\sigma ij}=&\int\psi_{i\sigma}^{*}(\vec{r})\{p^2/2m+V^{\text{ion}}(\vec{r})\}\psi_{j\sigma}(\vec{r})d\vec{r}\\&+\sum_{s}\sum_{l\in\Gamma(s)}\int\int\psi_{i\sigma}^{*}(\vec{r})\Psi_{ls}^{*}(\vec{r}\,')V^{e\text{-}e}(\vec{r}\,'-\vec{r})[\Psi_{ls}(\vec{r}\,')\psi_{j\sigma}(\vec{r})-\Psi_{ls}(\vec{r})\psi_{j\sigma}(\vec{r}\,')\delta_{s\sigma}]d\vec{r}\,d\vec{r}\,' \,.\end{aligned} \tag{7}$$

If we further use (4), (6) becomes

$$\sum_{i,j}B_{\sigma ik}^{*}H_{0\sigma ij}B_{\sigma jl}=E_{l\sigma}\delta_{kl} \,, \tag{8}$$

where

$$\begin{aligned}H_{0\sigma ij}=&\int\phi_{i\sigma}^{*}(\vec{r})\{p^2/2m+V^{\text{ion}}(\vec{r})\}\phi_{j\sigma}(\vec{r})d\vec{r}\\&+\sum_{s}\sum_{l\in\Gamma(s)}\int\int\phi_{i\sigma}^{*}(\vec{r})\Psi_{ls}^{*}(\vec{r}\,')V^{e\text{-}e}(\vec{r}\,'-\vec{r})[\Psi_{ls}(\vec{r}\,')\phi_{j\sigma}(\vec{r})-\Psi_{ls}(\vec{r})\phi_{j\sigma}(\vec{r}\,')\delta_{s\sigma}]d\vec{r}\,d\vec{r}\,' \,.\end{aligned} \tag{9}$$

We define the matrix $\widetilde{E}_{\sigma}$ with the element $E_{\sigma kl}=E_{l\sigma}\delta_{kl}$ to rewrite (8) as a matrix equation

$$\widetilde{B}_{\sigma}^{\dagger}\widetilde{H}_{0\sigma}\widetilde{B}_{\sigma}=\widetilde{E}_{\sigma} \,. \tag{10}$$

For a given input $\widetilde{H}_{0\sigma}$, we solve this eigenvalue equation to get the eigenenergies and the eigenfunctions. Using (5) again (9) can be expressed in the desired form for a numerical iteration process,

$$H_{0\sigma ij}=\int\phi_{i\sigma}^{*}(\vec{r})\{p^2/2m+V^{\text{ion}}(\vec{r})\}\phi_{j\sigma}(\vec{r})d\vec{r}+\sum_{s}\sum_{l\in\Gamma(s)}[B_{\sigma}^{\dagger}\widetilde{V}(\sigma s:ij)\widetilde{B}_{\sigma}]_{ll} \,, \tag{11}$$

where the electron-electron interaction matrix is defined as

$$V(\sigma s:ij)_{tq}=\int\int\phi_{i\sigma}^{*}(\vec{r})\phi_{ts}^{*}(\vec{r}\,')V^{e\text{-}e}(\vec{r}\,'-\vec{r})\,[\phi_{qs}(\vec{r}\,')\phi_{j\sigma}(\vec{r})-\phi_{qs}(\vec{r})\phi_{j\sigma}(\vec{r}\,')\delta_{s\sigma}]d\vec{r}\,d\vec{r}\,' \,. \tag{12}$$

To get the self-consistent solution of (10) and (11) we first neglect the exchange interaction in (2) to obtain the Hartree eigensolution $\widetilde{B}(HA)$. Then we use this $\widetilde{B}(HA)$ as the initial input to get $\widetilde{H}_{0\sigma}$. Knowing $\widetilde{H}_{0\sigma}$ we solve (10) for a new $\widetilde{B}_{\sigma}$ in order to construct a new $\widetilde{H}_{0\sigma}$ from (11). The iteration continues until we reach a self-consistent solution.

The ordinary Hartree-Fock scheme with many-electron wave function represented by a single Slater determinant is inadequate for the strongly correlated problem considered here. If we take $\phi_{i\sigma}(\vec{r})$ as the single-particle ground-state wave function localized on the ith impurity as if the impurity is isolated (we call this the D^0 state), then the properly antisymmetrized $\phi_{i\uparrow}(\vec{r}_1)\phi_{i\downarrow}(\vec{r}_2)$ cannot correctly represent the two-electron wave function for two antiparallel spin electrons localized on the same impurity (we call this the D^- state). For example, in a single-valley semiconductor, the one-electron wave function $\phi_{i\sigma}(\vec{r})$ can be well approximated by a hydrogen 1s wave function with a properly scaled effective Bohr radius. However, the properly antisymmetrized $\phi_{i\uparrow}(\vec{r}_1)\phi_{i\downarrow}(\vec{r}_2)$ is not bound in contrast to the experimental result.

It is impossible to use the configuration interaction in the present problem because the numerical diagonalization of (10) is carried out on a computer and so is restricted by the computer capability. However, we can improve the Hartree-Fock scheme by introducing a correlated two-electron function $\Phi_i(\vec{r}_1,\vec{r}_2)$ for the D^- state localized on the ith impurity. Therefore, in (12) the $\phi^*_{i\sigma}(\vec{r})\phi^*_{ts}(\vec{r}\,')$ [or $\phi_{qs}(\vec{r}\,')\phi_{j\sigma}(\vec{r})$] should be replaced by $\Phi^*_i(\vec{r},\vec{r}\,')$ [or $\Phi_j(\vec{r},\vec{r}\,')$] if $i=t$ [or $j=q$] and $s=-\sigma$. For the special case $i=j=t=q$ the single-particle-operator part in (11) should also be modified by treating the negatively charged impur-with the two-impurity Hamiltonian:

$$(p_1^2+p_2^2)/2m+V_i^{\text{ion}}(\vec{r}_1)+V_i^{\text{ion}}(\vec{r}_2)+V^{e\text{-}e}(\vec{r}_1-\vec{r}_2)\ .$$

In Sec. VI A we will see that such improvement is essential for obtaining the correct D^- band.

B. Impurity band and MHA specific heat

For a many-valley semiconductor the wave function of an electron localized on a single isolated impurity is very complicated when the anisotropic effective mass and the central-cell correction are taken into account. The purpose of the present work is to demonstrate via a large pseudocluster calculation the characteristic feature of the impurity states and its impact on the physical properties of doped semiconductors. At the end of the paper it will be clear that in order to perform a first-principles calculation for a microscopic investigation on the thermodynamic properties of doped semiconductors in insulating regime, one must study small clusters consisting of up to ten impurities and then take a statistical average. Then it is necessary to use such complicated impurity orbitals. Even though the isotropic effective mass is assumed and the central-cell correction is ignored in this paper, extremely tedious computation is required to derive the self-consistent solutions. We will return to this point for further discussion.

The single-particle orbital $\phi_{i\sigma}(\vec{r})$ is then approximated by a hydrogenic 1s wave function with an effective Bohr radius a_0. For the D^- orbital $\Phi_i(\vec{r}_1,\vec{r}_2)$ we use the variational wave function proposed by Chandrasekhar[26]

$$\Phi_i(\vec{r}_1,\vec{r}_2)=\eta[\exp(-\alpha|\vec{r}_1-\vec{R}_i|-\beta|\vec{r}_2-\vec{R}_i|)+\exp(-\alpha|\vec{r}_2-\vec{R}_i|-\beta|\vec{r}_1-\vec{R}_i|)][1-\gamma(|\vec{r}_1-\vec{r}_2|)]\ , \tag{13}$$

with $\alpha=1.074\,78$, $\beta=0.477\,58$, and $\gamma=0.312\,14$. η is the normalization constant. The Chandrasekhar wave function yields a rather accurate binding energy 0.0259 hartree for a free H^- ion as compared to the measured value 0.0275 hartree. The charge density at the nucleus given by (13) is in error by only 2% relative to Pekeris's calculation.[27] The angular correlation $1-\gamma(|\vec{r}_1-\vec{r}_2|)$ in (13) is very important because it reduces the screening of the outer electron from 0.72 to 0.52.

Since the eigenfunctions (5) are linear combinations of impurity orbitals only, the present calculation is valid only in the insulating regime. For low-impurity concentration it is reasonable to neglect the three- and four-center integrals in (12). From our previous work[5] we found it necessary to have clusters of $\mathcal{N}=40$ impurities. The number M of outer impurities which provide a mean field for the inner $\mathcal{N}=40$ impurities is taken to be 960. The final results are obtained with a configuration average over 50 sample pseudoclusters.

We have chosen the effective hartree as our energy unit, and set the zero reference energy at the bottom of the conduction band. It is convenient to define a dimensionless impurity concentration as $P=32\pi\mathcal{N}a_0^3/\Omega$. For most doped semiconductors the critical concentration P_c is around 0.8 to 0.9. The density of states for a single spin $\rho(E)$ is normalized to

$$\int\rho(E)dE=P/32\pi=(\mathcal{N}/\Omega)a_0^3\ .$$

Two series of density of states are given in Figs. 1

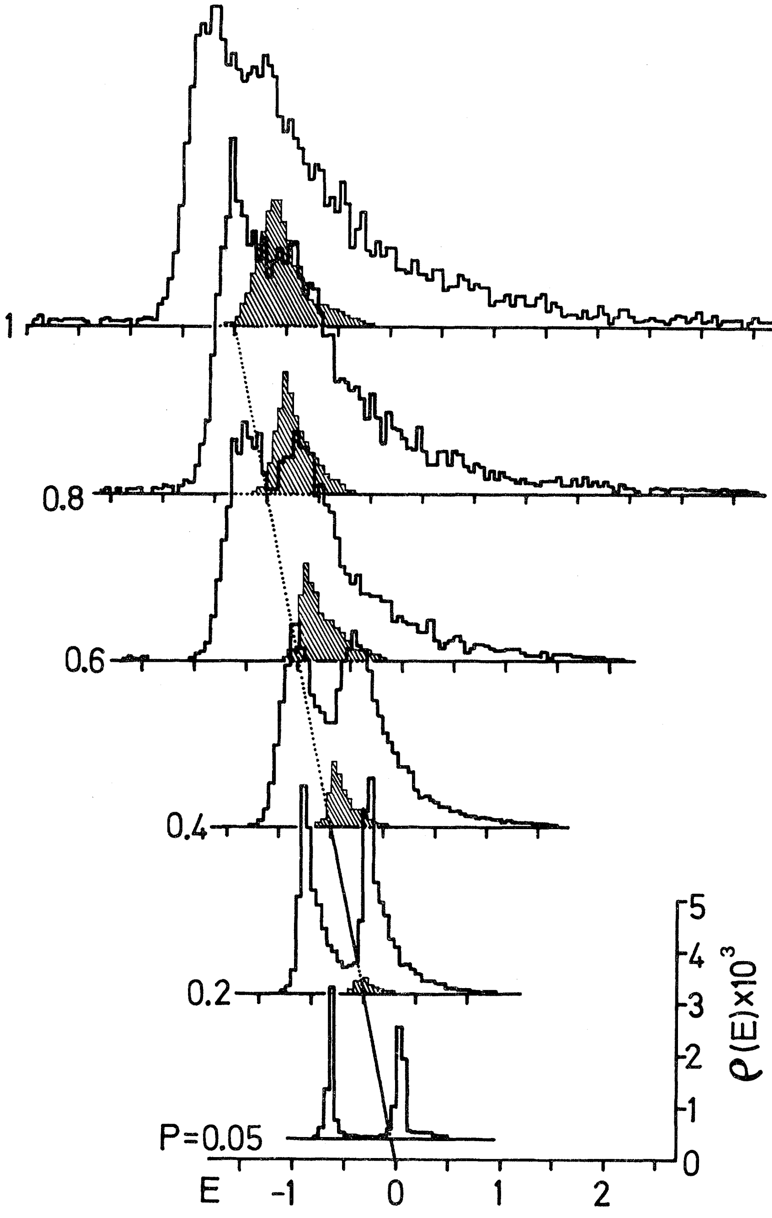

FIG. 1. Impurity-band density of states based on only hydrogenic 1*s* orbitals. Shaded region represents the overlap of split bands.

and 2. Figure 1 is obtained by neglecting the intra-impurity correlation effect and assuming

$$\Phi_i(\vec{r}_1,\vec{r}_2)\simeq\phi_{i\uparrow}(\vec{r}_1)\phi_{i\downarrow}(\vec{r}_2)\ ,$$

while the Chandrasekhar wave function is used in Fig. 2. Without using the correct D^- orbital, we see in Fig. 1 that the upper split band does not converge to the correct binding energy of D^- as the impurity concentration P approaches zero. The bandwidths in Fig. 1 are substantially wider than those in Fig. 2. Excepting these differences, the discussion in Ref. 5 concerning the qualitative properties of the impurity band applies here (Fig. 2) also. However, for Fig. 2 the Fermi energy moves into the conduction band at $P\simeq 0.78$, which is very close to the critical concentration for the

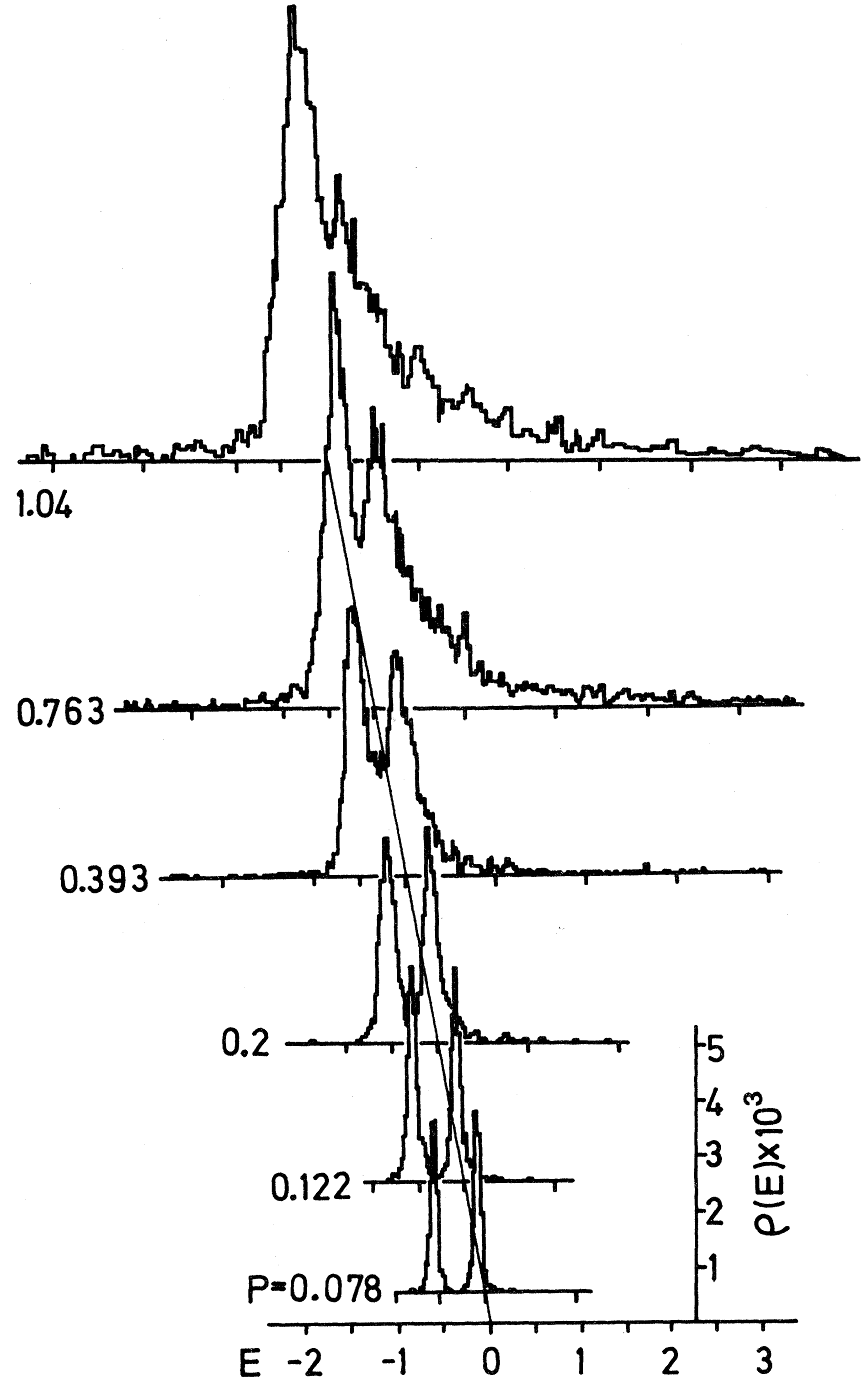

FIG. 2. Impurity density of states with Chandrasekhar wave function for D^- state.

M-NM transition, but for Fig. 1 the Fermi energy crosses the bottom of the conduction band at $P \simeq 0.57$.

If we use the density of states at the Fermi energy and the ordinary band theory to estimate the linear electronic specific heat C_e, the $\gamma = C_e/T$ so obtained seems to agree reasonably well with experimental data[28] as shown in Fig. 3. Furthermore, from Fig. 2 one can still identify the peak position of the upper split band lying below the conduction band for $P < P_c$. Hence, the thermoactivation energy ϵ_2 can be well defined as conventional. Never-

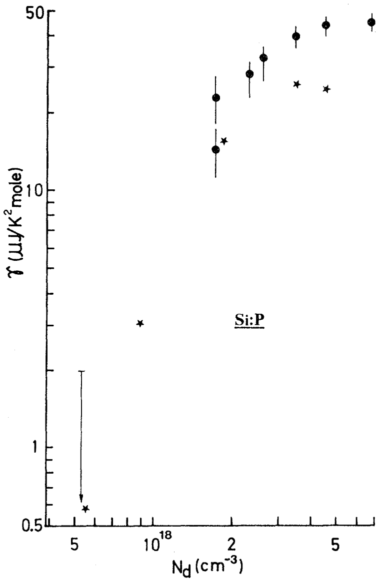

FIG. 3. Linear specific heat coefficient vs the donor concentration N_d. Dots are experimental data and stars are present calculations.

theless, such success of the MHA model should not be overemphasized for the following reasons. In the next section we will see that the eigenstates are cluster states and so the Koopmans's theorem may not be valid. In the picture of cluster states no sharp mobility edge can be defined and the thermoactivation energy needs a more careful treatment.

III. CLUSTER STATES

To study the localization of the eigenstates we calculate the inverse participation ratio (IPR) originally defined by Bell *et al.*[29] For the present problem it is more suitable to use the version of Visscher[30] for the IPR of the ith eigenstate,

$$L_{\sigma i}=\left[\sum_j |B_{\sigma ji}|^4\right] \Big/ \left[\sum_j |B_{\sigma ji}|^2\right]^2 . \qquad (14)$$

If the orbitals $\phi_{i\sigma}(\vec{r})$ are orthogonal to each other, then $L_{\sigma i}$ has the value from zero for the extended limit to one for the localized limit, provided the system under consideration is infinite. Although in our case the system is finite and the basis functions are not orthogonal to each other, we can still use (14) to estimate the localization of the electronic wave functions.

The IPR as functions of the eigenenergy are shown in Figs. 4(a)–4(f) for various impurity concentrations. For $P<P_c/3$ most of the states in the lower split band (which are occupied by electrons) have their IPR values greater than or equal to 0.5, indicating that most of the occupied eigenstates are either isolated impurity states or pair states. This agrees with the finding of Thomas *et al.*[7] from analyzing the optical data. In the regime $P>P_c/2$ (corresponding to the intermediate doping regime defined in Ref. 7) larger clusters appear with increasing weights and the whole system (in the insulating regime) should be considered as statistically distributed clusters of various sizes. It is worthwhile to point out that even in the metallic regime there is still a non-negligible fraction of the occupied states exhibiting localized properties. Although our model is not reliable in the metallic regime, we believe that this last conclusion is correct as it agrees with other authors results both experimentally[18] and theoretically.[19]

The mean value of IPR of each sample pseudocluster with fixed impurity concentration is given in Fig. 5 as a function of P. The solid curve is the configuration average of IPR over all the sample clusters. This figure shows clearly that for low concentration the system is dominated by isolated impurities or pairs of impurities. Andres *et al.*[22] have used the modified pair approximation to calculate the magnetic susceptibility and the result agrees well with the experimental data for impurity concentration up to $P\simeq 0.25$. We notice from Fig. 5 that for $P<0.25$ the mean value of IPR is greater than 0.5.

IV. THERMAL ACTIVATED HOPPING

To get the microscopic insight of the cluster states we single out seven eigenstates from an arbitrary sample pseudocluster with fixed concentration. These seven states are labeled as 1,2, . . . , 7 with increasing eigenenergies. States 1–4 are just below and states 5–7 are just above Fermi energy. Figure 6 shows the positions of the impurities in a sample pseudocluster with $P=0.078$. Referring to these positions the localizations of the seven eigenstates of each spin are shown in Fig. 7. We say that the ith eigenstate covers the jth impurity if $|B_{\sigma ji}|\geq 0.1$, and the localization is demonstrated in Fig. 7 in terms of such coverage. For example, state 1 with down spin is a pair state covering impurities 2 and 8. At such low concentration the

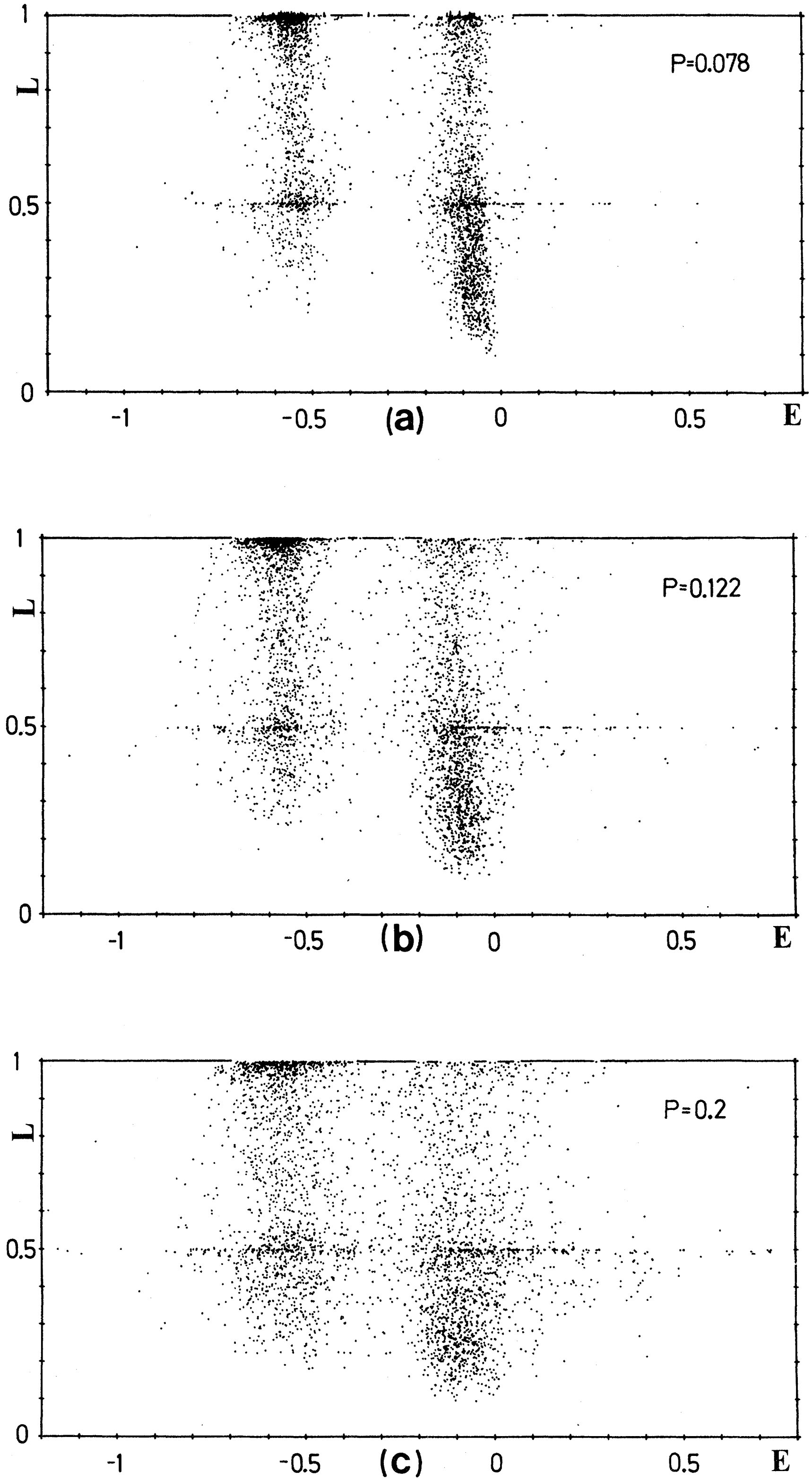

FIG. 4. Inverse participation ratio for (a) $P=0.078$, (b) $P=0.122$, (c) $P=0.2$. Inverse participation ratio for (d) $P=0.393$, (e) $P=0.763$, (f) $P=1.04$.

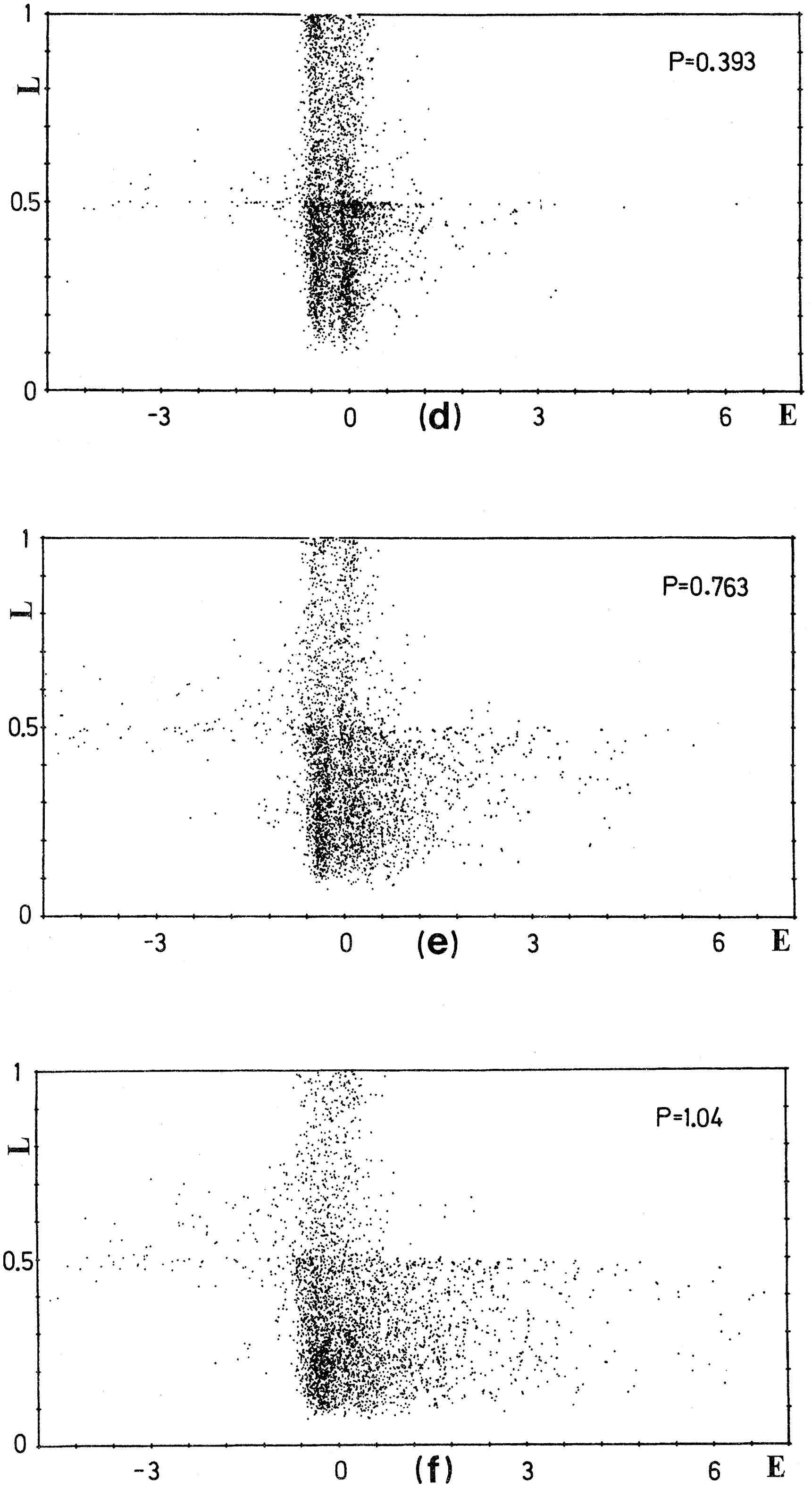

FIG. 4. (*Continued.*)

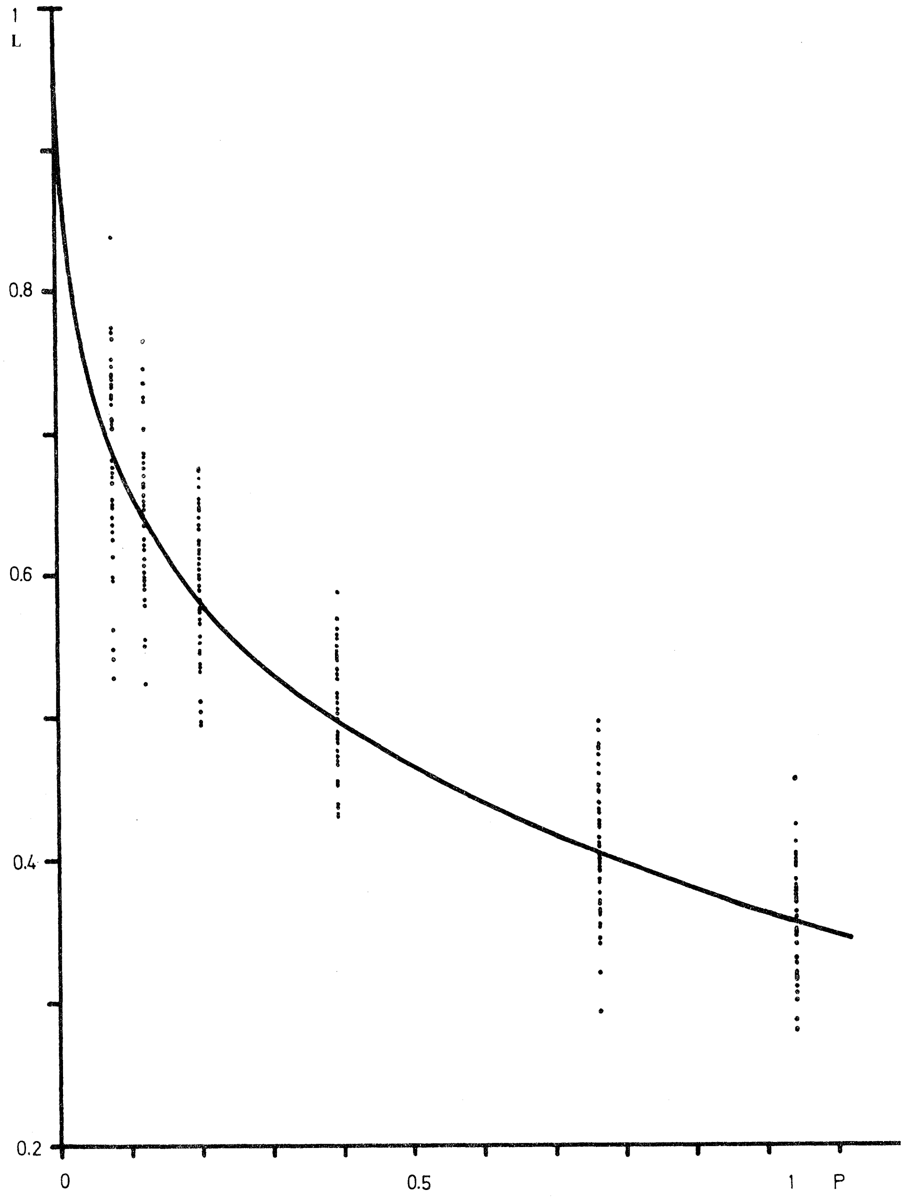

FIG. 5. Average inverse participation ratio vs impurity concentration P.

occupied states are really either isolated impurity states or pair states.

Figure 8 is for the seven states of up spin with $P=0.393$. Impurities covered by the same eigenstate are connected by one type of lines. For example, states 3 and 1 are indicated by solid lines, states 2, 5, 6, and 7 by dotted lines, and state 4 by dashed line. Although all the states near the Fermi energy are localized, we see states of different energies such as states 1 and 5 overlapping with each other spatially at one impurity. State 4 does not overlap spatially with states 1 and 5, but in a certain region they are spatially very close to each other. Similar eigenstates are plotted for $P=0.763$ in Fig. 9 where more delocalization and stronger spatial overlap between states with different eigenenergies are seen.

The states below and above the Fermi energy are separated by small energies. However, many states above the Fermi energy are spatially either overlapping with or very close to many states below the Fermi energy. Hence, thermal activated hopping is largely enhanced in contrast to the conventional picture that localized states are widely separated in

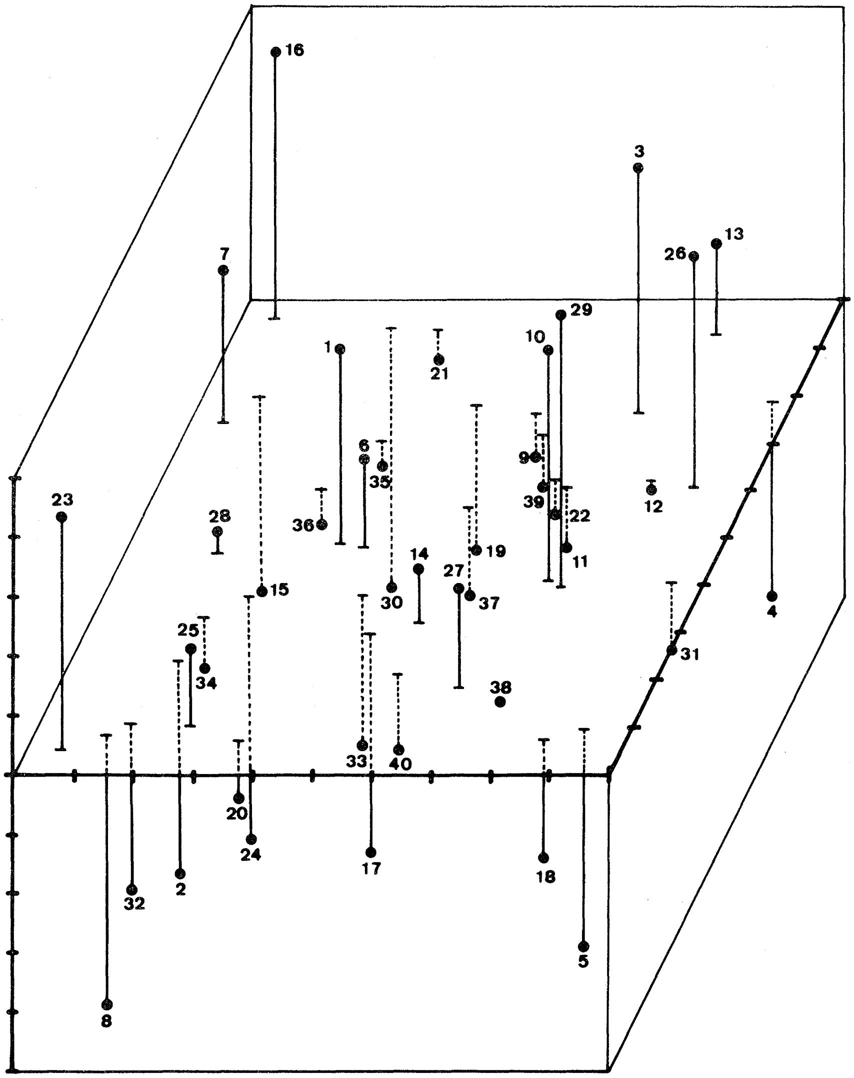

FIG. 6. Spatial distribution of impurities in a sample pseudocluster with $P = 0.078$.

space. The thermoactivated conductivity is then dependent on the concentration, the temperature, and the applied electric field. If one measures the thermoactivated conductivity in such system, and then uses the formula derived from the percolation theory[31] to evaluate the characteristic electronic length, the so obtained characteristic length must be an order of magnitude larger than the true characteristic length. We believe that such a feature is relevant to the recently discovered non-Ohmic conductivity and large characteristic electronic length in Si:P.[32]

It is impossible to have a mobility edge separating one group of cluster states from the other, if we consider the impurity states below the bottom of the conduction band, judging from the IPR shown in Figs. 4(a)—4(f). Consequently, one cannot define a single thermoactivation energy ϵ_2 of order of Hubbard U. On the contrary ϵ_2 must be reexamined very carefully in terms of the cluster states as a function of the concentration and temperature.

V. DISCUSSION

The present self-consistent calculation suggests a new picture for doped semiconductors in a nonmetallic regime as statistically distributed clusters of various sizes. This new picture is originated from the concentration fluctuation. If we use the same description as for the eigenstates shown in Figs.

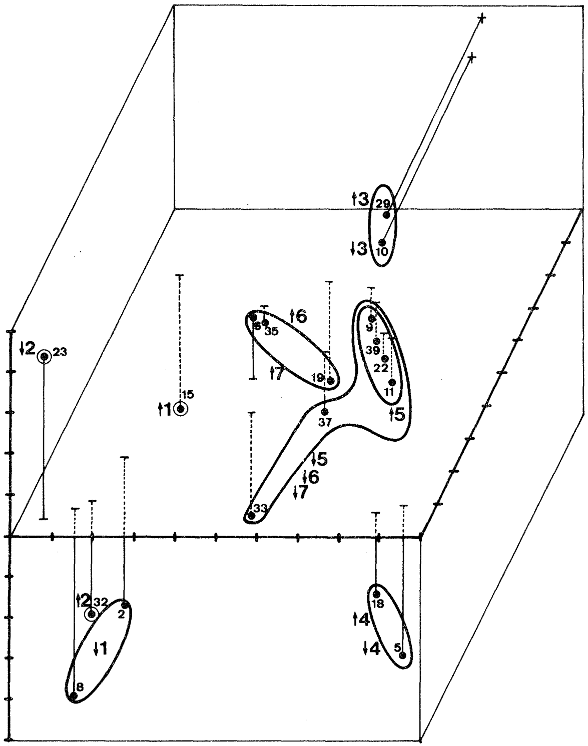

FIG. 7. Seven cluster states near Fermi energy with $P=0.078$.

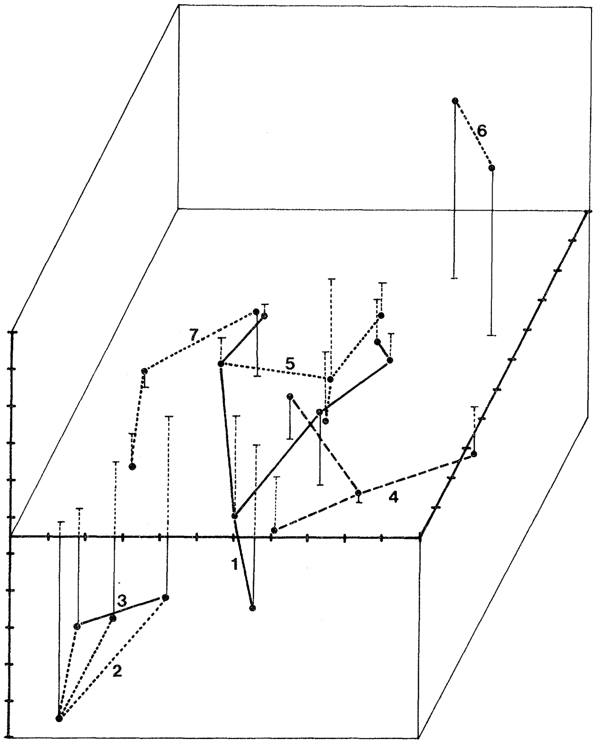

FIG. 8. Seven cluster states near Fermi energy with $P=0.393$.

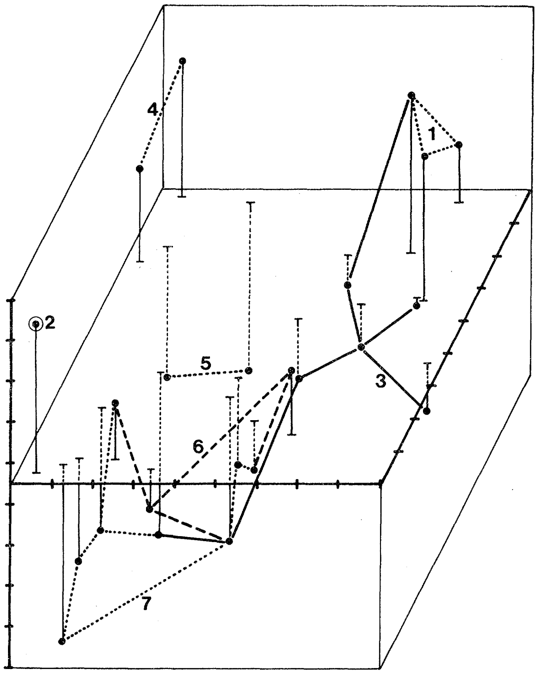

FIG. 9. Seven cluster states near Fermi energy with $P=0.763$.

7−9, then the probability $\Pi(\eta)$ to have cluster states covering η impurities can be calculated. Figure 10 illustrates these probabilities for various impurity concentrations. Since the states in the long tails are in the upper split band and are with energies above the bottom of the conduction band,

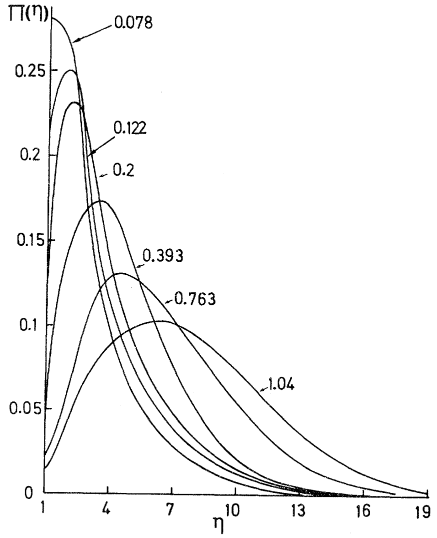

FIG. 10. Probability distribution of cluster states vs the number of impurities covered by the cluster states. Impurity concentrations are marked by numbers next to the curves.

they can be ignored if we are interested in a nonmetallic regime. One can find certain correspondences between Fig. 10 and the information derived from the optical data (Fig. 14 of Ref. 7).

A better understanding of the impurity states in doped semiconductors can be achieved via a first-principles calculation of the cluster states in clusters of as many as ten impurities, using an accurate many-valley impurity orbital with anisotropic effective mass and central-cell correction. Such work is being carried out and will be reported in the future.

ACKNOWLEDGMENT

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[1] For a review, see N. F. Mott, *Metal-Insulator Transition* (Taylor and Francis, London, 1974); in *The Metal-Insulator Transition in Disordered Systems,* edited by L. R. Friedman and D. P. Tunstall (SUSSP, Edinburgh, 1978).

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