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Single-particle energy levels in doped semiconductors at densities below the metal-nonmetal transition

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The single-particle density of states is calculated for a random distribution of shallow donors in semiconductors at densities below the Mott density. The donors are described within the effective-mass approximation. Calculations of the energy bands to add an electron (D^- band) and to remove an electron (D^+ band) are presented in three parts: (i) At low densities, where the broadening of the D^+ and D^- levels arises primarily from donor pairs which are closer together than the average, we have employed the donor-pair approximation to calculate the energy bands. This leads only to a small broadening in single-valley semiconductors but in a many-valley semiconductor a D_2 complex can have an electron affinity as large as 0.4 Ry. (ii) Next, the band edges are presented for a simple cubic lattice of donors, which would be relevant in estimating mean band positions, mobility edge, etc., in the disordered case in the intermediate doping region. The D^- band is calculated using a potential derived by the method of polarized orbitals. The energy gap does not shrink appreciably until a factor of 4 below the Mott density. The energy gap is found to go to zero at a density very close to the Mott criterion ($n_D^{1/3}a_B = 0.25$) for single-valley semiconductors and at a lower density in many-valley semiconductors. (iii) Finally, to estimate the localized tail states in the many-valley case, the energies of small dense donor clusters are calculated using a local-density approximation. Because many electrons can be placed in the bonding orbitals of these clusters without violating the Pauli principle, they are found to have very large electron affinities. We find that clusters of four donors or more can attract an electron from an isolated donor. As a result there is no Mott-Hubbard gap due to correlation in many-valley semiconductors and their insulating property is due to Anderson localization. The very large fluctuations in the one-electron potential imply an Anderson transition to the metallic state.

I. INTRODUCTION

In a semiconductor lightly doped with shallow donors, the donors are essentially isolated and the system is simply a collection of noninteracting impurities with localized states below the conduction band that are described by an effective-mass theory. As the donor concentration (n_D) is increased, the average separation between donors decreases, and interactions among donors begin to play a role. One of the major effects of donor interactions is to delocalize the isolated donor wave function until finally, at large enough donor concentrations ($n_D = n_{MI}$), one undergoes a transition to a metallic state with a half-filled band of itinerant electrons. This transition has been the subject of considerable interest in recent years.[1-3] The subject of this paper is the behavior of the single-particle energy levels through this transition.

While the solution of the exact problem in doped semiconductors, with all the complications of many valleys, central-cell effects, disorder and electron correlation is extremely difficult, we can hope to make our approach reasonably realistic. For example, though we treat the donors within the effective-mass approximation with an isotropic mass tensor (so that central-cell and anisotropy effects are left out except for a qualitative discussion at the end), we do not make radical simplifying assumptions as are made, for example, in the Hubbard model with only on-site Coulomb interactions.[4]

We determine an average position of the one-electron energy bands by considering the problem for a lattice of donors at the same density. We choose a low-coordination lattice (simple cubic, $z = 6$) which is believed to be appropriate for lower density systems.[5] We use a potential for the neutral donor based on the method of polarized orbitals. This method gives a good description of low-energy phase shifts for electron-donor scattering and enables us to calculate the position and width of the energy bands accurately at low densities and approximately for densities $n_D \approx n_{MI}$. In this latter region Rose, Shore, and Sander[6] have recently reported calculations of the single-particle energy bands of a ferromagnetic donor lattice using a local density functional treatment of correlation and exchange. The agreement between these two different methods is only fair. At lower densities, the density functional method breaks down.[7] An important point of this paper is a discussion of the role of the extra degeneracy in Si or Ge due to the many electron valleys, i.e., equivalent conduction-band minima, and the differences between single- and many-valley semiconductors, which we shall cover at length later on.

It must be recognized, however, that a lattice model provides reasonable results only for a limited number of quantities—the mobility edge, an

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effective average band gap (though the true band gap, as we shall see, may be zero for these systems), and perhaps a qualitative form for the dielectric enhancement as the effective band gap closes. On the other hand, the true system consists of randomly distributed donors, with density fluctuations and statistically occurring dense donor clusters. The effects of these clusters are apparent in a number of experimentally accessible properties such as optical absorption[8-10] and magnetic susceptibility.[11,12] In fitting the absorption data at densities below 2×10^{17} cm^{-3} (~0.05 n_{MI}) in Si : P, it was shown[13] that randomly occurring donor pairs are the dominant effect on the isolated donor spectrum. At higher densities, calculations based on statistical cluster distributions fit the absorption data, including the tail, remarkably well.[8-10] Similarly, the susceptibility data in Si : P at donor concentrations below 10^{18} cm^{-3} (~0.25 n_{MI}) shows no spin ordering down to 5 mK (Ref. 12) (~10^{-5} Ry) when the coupling for an average lattice is $\approx$1 K, and clearly demonstrates the importance of randomness. In fact, the data are in good agreement with calculations of susceptibilities of spin clusters given by the random distribution.[11,12] Even at densities approaching n_{MI}, cluster effects can have a very important effect on the single-particle density of states (i.e., the density of states to add or remove an electron), particularly for donors in many-valley semiconductors such as Si or Ge. Our calculations show that in these cases, because of the multiplicity of valleys (which leads to not just 2, but 12 1s states in Si and 8 in Ge), dense random clusters of as few as four closely spaced donors can pull electrons off isolated donors. Thus there is no gap in the single-particle density of states, a statement which is equivalent to saying that doped many-valley semiconductors are never, in the strict sense, Mott insulators.[14]

We have divided our calculations into three natural sections. First, in Sec. II we discuss low densities where the pair approximation applies. For a single-valley semiconductor there is a complete analogy between the electron states in a pair of donors and in a pair of hydrogen atoms. We make use of the detailed calculations of the latter to obtain the single-particle density of states. In many-valley semiconductors the additional degeneracy introduced by the possibility of distributing the electrons among different valleys reduces the energy of a complex with three or more electrons and modifies considerably the energy of a D_2^- complex (3 electrons on 2 nearby donors). We report calculations showing a large affinity for the D_2 complex in the limit of zero separation.

We remark here that throughout the paper we have used the donor Bohr radius as the unit of length and the rydberg as the unit of energy. Because of the latter choice, i.e., of the rydberg instead of the hartree, motivated by the greater use of the former, many of our formulas differ from the form usually seen, by the presence of an additional factor of 2.

In Sec. III we consider the average energy bands to add an electron (D^- band) and to remove an electron (D^+ band) by considering a lattice array of donors. These band edges are calculated using a modification of the Wigner-Seitz method. First, for the D^- band, the potential for an electron scattering off a neutral donor is presented following the application of the method of polarized orbitals by Temkin and Lamkin[15] to the scattering of electrons from hydrogen atoms. This potential, which allows for the polarization of the 1s electron is $\sim -9/2r^4$ as the separation $r\rightarrow\infty$ and is $\sim -2/r$ as $r\rightarrow 0$. The band edge is calculated by solving for the lowest eigenvalue of this potential with the boundary condition of a flat wave function at the Wigner-Seitz sphere. The neighboring donors are assumed to be on a simple cubic lattice and their effect is also included through their polarization potentials. This is appropriate for the propagation of a down-spin electron in a ferromagnetic arrangement of up spins. It is also appropriate for an extra electron in a many-valley semiconductor with a large number of valleys since in this case the probability that the extra electron will encounter an electron with the same quantum numbers is very small. However, a lattice of donors in a single-valley semiconductor will have a ground state with an antiferromagnetic arrangement of spins. In this case there is a band narrowing due to spin-flip scattering which has been estimated in tight-binding theory[16] to be $\approx$25%. In the present case there is additional $\approx$20% band narrowing due to the fact that propagation requires the interchange of the loosely bound electron with a tightly bound 1s electron.

The D^+ band is calculated in a similar way with the difference that the electron sees a bare potential on the central atom. The top of the D^+ band is determined by the boundary condition of a node in the wave function at the Wigner-Seitz radius. The polarization correction raises the D^+ band since it reduces the energy of the final state after the electron is removed and a net positive charge remains on the ionized donor. The polarization forces and the broadening of the D^+ and D^- bands lead to a collapse of the energy gap at a density close to the Mott value in single-valley semiconductors but lower for many valleys. This is in qualitative agreement with experiments[17,18] on

Ge doped with Sb in which the number of valleys is changed by the application of uniaxial stress, though the difference in density is larger in the experiments than in our calculations. At higher densities, a description in terms of a metallic phase is more appropriate. The single-particle density of states in the metallic approximation is compared with the description in terms of a D^+ and D^- band.

The random positions of the donors cause large fluctuations in the local concentration and clusters with several donors close together. The electronic structure of such clusters is considered in Sec. IV. In the case of single-valley semiconductors, it can be qualitatively predicted from the electron affinity and ionization energy of atoms. The electron affinity never gets very large but the ionization energy of clusters of three close donors, which resemble an Li atom, is much reduced. Golka and co-workers[19] have calculated the electron affinity and ionization energy of clusters of three donors in a single-valley semiconductor and confirmed that the electron affinity remains small but the ionization energy is much reduced in magnitude when the donors are close. An energy gap remains, however, between the D^- and D^+ bands at low density. For a many-valley semiconductor such as Ge or Si, the energy levels of small clusters are greatly modified because of the freedom to place many electrons in bonding orbitals by distributing them among different valleys. We have made a series of calculations using the local density formalism to obtain the electron affinity and ionization of small clusters. The valley degeneracy enters through the exchange and correlation functional that is used and, more importantly, through the freedom to put all the electrons (up to a maximum of 8 in Ge and 12 in Si) in the lowest eigenstate of the cluster. (The overlap and scattering between electrons in different valleys is ignored.) Both the electron affinity and ionization energy increase in these clusters with large numbers of donors. We find that for clusters with more than three donors the electron affinity can actually be greater than 1 Ry, the binding energy of an isolated donor. This means that such clusters will be able to take up an electron from an isolated donor. As a result there will be no gap in the single-particle density of states. The effect of correlation is to reduce the density of states to a very small value at low densities but not actually to zero. The absence of conductivity other than by hopping is then to be attributed to Anderson localization of the single-particle states at the Fermi level rather than to an energy gap due to correlation. Estimates are presented of the amount of charge transfer and the density of states at the Fermi level. Finally in Sec. V some concluding remarks are made regarding the comparison of our calculations with experiment and their implication for the insulator-metal transition.

II. PAIR APPROXIMATION

At very low densities there will be a small number of donor pairs which are much closer together than the average. The number of close triples will be much smaller again. This can be seen by examining the nearest-neighbor distribution function

$$P_{nn}(R) = 4\pi n_D R^2 \exp(-4\pi n_D R^3/3) . \quad (2.1)$$

This is the probability density of finding a nearest neighbor between R and $R + dR$ for an uncorrelated distribution of donors of concentration n_D. The distribution of next nearest neighbors is given by

$$P_{nnn}(R) = \tfrac{16}{3} \pi^2 n_D^2 R^5 \exp(-4\pi n_D R^3/3) . \quad (2.2)$$

Since the electronic interactions between donors are short ranged, typically $\lesssim 5a_B$, pairs of nearest neighbors will be the dominant cluster for $n_D \lesssim 5\times 10^{-4} a_B^{-3}$, which is approximately a concentration thirty times smaller than the Mott concentration ($\frac{1}{64} a_B^{-3}$).

We consider first the case of single-valley semiconductors, ignoring central-cell corrections. In this case, we may simply scale the known energy levels of two hydrogen atoms.[20] The energy to add an electron to a pair of donors, of separation R, may be obtained by subtracting the energy of the initial state $[D_2(R)]$ from the energy of the final state $[D_2^-(R)]$. For large values of R the D_2^- complex will look like separate D and D^- centers and there will be an attractive polarization potential $\sim R^{-4}$. This is larger than the polarization potential between two neutral D centers which at large R goes like R^{-6}. As a result, the electron binding energy is increased at large R. However, at small R in the corresponding hydrogenic system there is an exchange repulsion between the electrons since two are in the same spin state and one electron is forced into an antibonding wave function. The binding energy has a shallow maximum ($\sim$0.06 Ry) at $R \approx 6\ a_B$ and drops quickly, passing through zero at $R \approx 3.5\ a_B$.[19] Fitting to a Morse form we obtain

$$E_2^-(R) = -0.0555 + 0.01(e^{-(R-6)} - 2e^{-0.5(R-6)}) . \quad (2.3)$$

(In the above equation the energy is measured in rydbergs and the length in Bohr radii.) The density of states in the pair approximation is obtained by convoluting with the pair distribution function

$$N(E) = \int P_{nn}(R)\delta(E - E_2^-(R))\, dR . \quad (2.4)$$

The result is shown in Fig. 1 at a density of $n_D = 0.002$ ($\sim\frac{1}{8}$ the Mott density). The shift in energy from an isolated D^- is very small.

However, in many-valley semiconductors such as Si or Ge there is another degree of freedom, namely that the electrons can be distributed among different valleys, thereby removing the exchange repulsion. Clearly this will have a drastic effect. If $R \lesssim a_B$ then the complexes are like atoms, but now the periodic table is changed since the first closed shell does not occur in Si until there are 12 electrons (8 for Ge). The electron affinity will clearly increase across a row in this new periodic table and will be largest for the last "element" before the closed shell—in Si that will be D_{11}^-. Thus our conclusion is that the binding energy of a D_2^- complex is a monotonically decreasing function of R. In Sec. IV we report calculations using a local density functional method for a variety of very small clusters in which all the positive charge is located at a point. In the case of D_2^- at zero separation, i.e., 3 electrons bound to a charge of $+2|e|$ at the origin, we find a binding energy for the last electron ≈ 0.4 Ry. This is a large binding energy, roughly 8 times larger than D^-. While we are unable to make a pair calculation in the absence of a complete curve for the R dependence of the binding energy, it is clear that the D_2^- is considerably more stable in a many-valley semiconductor.

Turning to the lower Hubbard band, we need the energy to remove an electron from a D_2 complex, leaving behind a D_2^+. Since only 2 electrons are involved, valley degeneracy does not play a role. The energies of the analogous hydrogenic states H_2 and H_2^+ are known accurately.[20] Again at large R the D_2^+ state has the larger binding energy because of the stronger polarization force. At small R the D_2 is more stable. Therefore, the ionization energy of the D_2 complex initially decreases in magnitude as R decreases, passes through a minimum value (≈ 0.957 Ry) at $R = 3.7a_B$, and then increases passing 1 Ry at $R = 2.5a_B$. As $R \to 0$, the complex is a He atom with an ionization energy of 1.81 Ry. We have parameterized the energy of the $D_2(R)$ and $D_2^+(R)$ complexes by a Morse form

$$(A\{\exp[-2B(R-C)] - 2\exp[-B(R-C)]\})$$

using the values listed in Table I. The energy difference is then convoluted with the pair distribution function to obtain the single-particle density of states. The results for a series of concentrations are shown in Fig. 1. There are two singularities in the density of states at -1 Ry corresponding to $R \to \infty$ and at -0.957 Ry which is a square root divergence arising from the minimum in the ionization energy at $R = 3.7a_B$. The relative weight of the two singularities depends on the concentration (see Fig. 1) and as the average nearest-neighbor separation drops, the weight at the upper edge of the D^+ band increases. (We note that there will be a smearing of the square root divergence in the actual system due to the presence of other neighboring donors, but this will be small at low concentrations.)

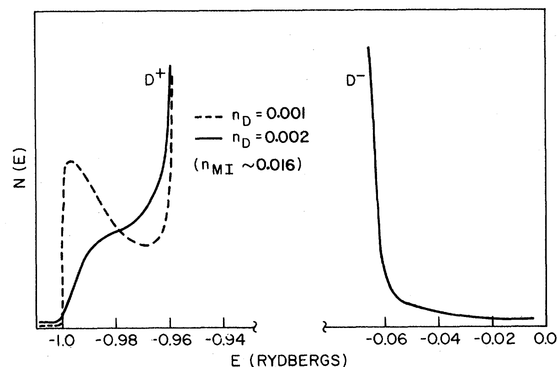

FIG. 1. The single-particle density of states to add an electron D^- and remove an electron D^+ at different concentrations (expressed in units of a_B^{-3}) at low densities where the broadening arises from donor pairs much closer than the average. The results are for single-valley semiconductors and the modifications in many-valley semiconductors are discussed in the text.

The energy in a many-valley semiconductor does not change so long as we ignore the valley-orbit coupling, since there are no more than two electrons involved in these states. In the presence of valley-orbit coupling, the bounds on the hole band remain the same but the weight at the band edge is much reduced. The ground state of the electron on each donor is a particular combination of the valleys (usually the symmetric combination relative to the donor site) and the overlap of the ground state on two neighboring donors is multiplied by a factor which is a rapidly oscillating function of the donor separation $[\frac{1}{3}\sum_{x,y,z}\cos(\vec{K}_x \cdot \vec{R})]$. As a result, the average overlap is much reduced and so is the broadening of the D^+ band.

In the pair approximation, the lower edge of the D^- band and the upper edge of the D^+ band do not overlap and the energy gap due to correlation, although reduced in magnitude, remains finite.

TABLE I. Morse parameters for the energy of the $D_2(R)$ and $D_2^+(R)$ (including internuclear repulsion).

	A (Ry)	B (a_B^{-1})	C (a_B)
$D_2(R)$	0.348 96	1.044 35	1.400 83
$D_2^+(R)$	0.205 44	0.719 35	2.003 13

III. SINGLE-PARTICLE DENSITY OF STATES FOR A CRYSTALLINE ARRAY

Before considering larger clusters it is interesting to examine a crystalline array of donors—we shall investigate a simple cubic lattice with varying lattice parameter R. In the large-R limit there is an energy gap, due to on-site correlation, between the D^+ and D^- bands while, at small R, the system is simply metallic. For the latter case, we can use the Wigner-Seitz approximation to describe the single-particle bands.

At large R an extra electron scatters off essentially isolated donors. The corresponding problem in atomic physics is the scattering of an electron off a neutral hydrogen atom. The method of polarized orbits developed by Temkin and Lamkin[15] which allows for the virtual excitation of the $1s$ electron on the hydrogen atom into a p state, gives a good description of the low-energy phase shifts of this problem. We will adapt this method to calculate the single-particle energy band.

In this method, the wave function is written in the product form which, for the present, we do not symmetrize:

$$\Psi(\vec{r},\vec{r}\,')=[\phi_{1s}(r')+\phi^1(\vec{r},\vec{r}\,')]F(r). \tag{3.1}$$

The coordinate $\vec{r}\,'$ denotes the position of the tightly bound electron and $\vec{r}$ the position of the scattering electron. The appropriate boundary conditions will be applied to F. The ϕ^1 term represents the change of the inner-electron wave function in the presence of the outer electron. If one ignores that change and sets $\phi^1\equiv 0$, then the variational principle on F

$$\frac{\delta}{\delta F}\langle\Psi|H|\Psi\rangle=0, \tag{3.2}$$

where the Hamiltonian is

$$H=-\nabla^2_{\vec{r}}-\nabla^2_{\vec{r}\,'}-\frac{2}{r}-\frac{2}{r'}+\frac{2}{|\vec{r}-\vec{r}\,'|}, \tag{3.3}$$

gives a Schrödinger equation for F

$$[-\nabla^2_{\vec{r}}+U_0(r)-E]F(r)=0 \tag{3.4}$$

and

$$U_0(r)=\int d^3r'\,\phi^2_{1s}(r')\left(\frac{2}{|\vec{r}-\vec{r}\,'|}-\frac{2}{r}\right) \tag{3.5}$$

$$=-\left(\frac{2}{r}+2\right)\exp(-2r). \tag{3.6}$$

The energy unit is the rydberg and the length unit the Bohr radius and $\phi_{1s}(r)=\pi^{-1/2}\exp(-r)$. The effective potential is the Hartree potential of the neutral donor. At large distances it falls off exponentially due to the screening of the ionic charge by the inner electron. As $r\to 0$ however, the screening is ineffective and the potential is a bare Coulomb potential. The defect of this potential is that it omits the polarization of the inner electron by the outer electron and as a result the outer electron is not bound in this approximation.

The inner electron sees a perturbing potential from the outer electron of the form

$$V(\vec{r}\,',\vec{r})=\frac{2}{|\vec{r}\,'-\vec{r}|}-\frac{2}{r}, \tag{3.7}$$

which for $r\gg r'$ can be expanded to give

$$V(\vec{r}\,',\vec{r})=\frac{2r'}{r^2}\cos\theta,\quad r>r' \tag{3.8}$$

in the dipole approximation where θ is the angle between $\vec{r}$ and $\vec{r}\,'$. Following Temkin and Lamkin[15] we solve for the change in energy of inner electron in second-order perturbation theory, ignoring all higher multipole terms in the expansion of Eq. (3.8). The calculation of the change in energy can be elegantly made by solving for the first-order change in the wave function ϕ^1:

$$\left(\nabla^2_{\vec{r}\,'}\frac{2}{r'}-1\right)\phi^1(\vec{r},\vec{r}\,')=\frac{2r'}{r^2}\cos\theta\,\phi_{1s}(r'). \tag{3.9}$$

Substituting

$$\phi^1(\vec{r},\vec{r}\,')=\frac{1}{\pi^{1/2}}\frac{\cos\theta}{r^2}\frac{\chi(r')}{r'} \tag{3.10}$$

gives a radial equation of the form

$$\left(\frac{d}{dr'^2}+\frac{2}{r'}-\frac{2}{r'^2}-1\right)\chi(r')=2r'^2e^{-r'}. \tag{3.11}$$

The solution of (3.11) is

$$\chi(r')=-(r'^2+\tfrac{1}{2}r'^3)e^{-r'}. \tag{3.12}$$

The change in energy to second order is obtained by integrating ϕ^1 with the perturbing potential and the unperturbed wave function, leading to

$$U_2(r)=-\int_{r'<r}d^3r'\frac{1}{\pi^{1/2}r^2}e^{-r'}(r'+\tfrac{1}{2}r'^2)\times\cos^2\theta\frac{2r'}{r^2}\frac{1}{\pi^{1/2}}e^{-r'} \tag{3.13}$$

$$=\frac{-1}{r^4}\left[\tfrac{9}{2}-e^{-2r}(\tfrac{9}{2}+9r+9r^2+6r^3+3r^4+\tfrac{2}{3}r^5)\right]. \tag{3.14}$$

The total potential $U(\equiv U_0+U_2)$ has the desired form; at large r it correctly describes the polarization-induced interaction between the outer electron and neutral donor, and at small r it has the form of a bare Coulomb potential with the ionic charge. The derivation given above could be modified to include the effects of an additional short-range central-cell potential or the change of the inner-electron wave function from a $1s$ form as

the lattice constant R decreases, but we shall restrict ourselves to using the forms (3.6) and (3.14) at all densities.

First we consider the large-R limit. In this case we can impose the boundary condition the $F(r)\to 0$ at $r\to\infty$. Using the form (3.1) without symmetrizing the wave function, we have made a variational calculation using a trial wave function of the form

$$F(r)=e^{-ar}+\frac{b}{r}\left(e^{-(1-\mu/2)r}-e^{-(1+\mu/2)r}\right). \qquad (3.15)$$

The second term is exact for a Hulthên potential and gives accurate results for a Coulomb potential with Thomas-Fermi screening.[21] We find a bound state with a minimum energy of −0.015 Ry with the parameters $a=0.34$, $b=7.3$, and $\mu=1.78$. However, in an isolated D^- the two electrons are in a spin singlet state and one must use a symmetrized wave function. In this case there are substantial exchange contributions to the energy. Using the value that Temkin and Lamkin[15] found for the low-energy scattering amplitude ($5.7a_B$), we can estimate from an effective-range expansion[22] the value of the bound-state energy of the symmetrized wave function as −0.046 Ry. This value is much closer to the exact value[23] (−0.0555 Ry) and shows that this method gives a reasonably accurate description of the bound state.

Our interest lies in the location and bandwidth of an extra electron propagating in a lattice of neutral donors. In this case, the extra electron does not correlate with each individual inner electron. The bandwidth depends on the spin arrangement of electrons on the neutral donors. This problem was investigated some years ago in the atomic limit of the Hubbard model by Brinkman and Rice.[16] They found that if the donors are ferromagnetically aligned there is no reduction in bandwidth and the extra electron propagates freely in the lattice of donors, but if the donor spins are randomly or antiferromagnetically aligned the extra electron can propagate only by reordering the spin arrangement and the bandwidth is reduced to ≈75% of the value for the ferromagnetic case due to spin scattering.

We start by calculating the bandwidth for the case of ferromagnetic spin alignment. We replace the cubic Wigner-Seitz cell by a sphere of the same volume, an approximation which seems justified in view of the randomness in the actual system we are interested in. The top and bottom of the band are determined by imposing the boundary condition $F=0$ and $\partial F/\partial r=0$ at the Wigner-Seitz radius $R_{WS}[=(3/4\pi)^{1/3}R]$ of a simple cubic lattice. The potential $U(r)$ is taken at the central site and also summed over all other lattice sites. The eigenvalues are determined variationally using a wave function of a constant added to the functional form of Eq. (3.15). The results for large values of R are shown in Fig. 2. The band broadens as R increases and the top of the band merges with the continuum at a value of $R\simeq 15$. This value corresponds to a density approximately $\frac{1}{50}$ of the Mott density. At this density there will remain a gap at the Brillouin zone due the donor potential but it is unlikely that there is a true energy gap at positive energies in the density of states for $R\leqslant 15$.

The bottom of the band starts to drop once we reach values of $R\lesssim 10$. As R decreases further, the wave function at the bottom of the band becomes flatter and we switch for $R<10$ to the variational form

$$F(r)=1+\alpha e^{-ar}+\beta r e^{-br}. \qquad (3.16)$$

With this form we calculate the bottom of the band by solving the Schrödinger equation with the boundary condition, $|\partial F/\partial r|_{r=R_{WS}}=0$, using the potential $U(r)$ on the central site and on all the other sites as well. The results are shown in Fig. 3. The bottom of the band drops dramatically around $R=4$ from a combination of the polarizability of the surrounding donors and the band broadening. This result is appropriate for a single-valley semiconductor only if the donor spins are ferromagnetically aligned. It applies also to the many-valley semiconductor essentially independent of the alignment of spin and valley indices. This is because, with the large degeneracy, the extra electron rarely sees an exchange repulsion on a donor site and as a result it can propagate essentially freely through the lattice. Therefore, the simple band calculation applies to many-valley semiconductors such as Si or Ge and we will ignore the correction from exchange repulsion.

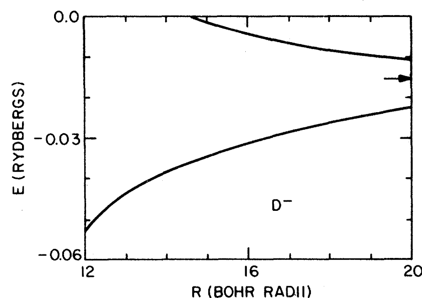

FIG. 2. The maximum and minimum of the D^- band for a simple cubic (sc) lattice (lattice parameter R) of donors in a many-valley semiconductor at low densities showing the merging of the D^- band with the continuum. The arrow illustrates the binding energy of an isolated bound state *using a wave function which is not symmetrized* (see text).

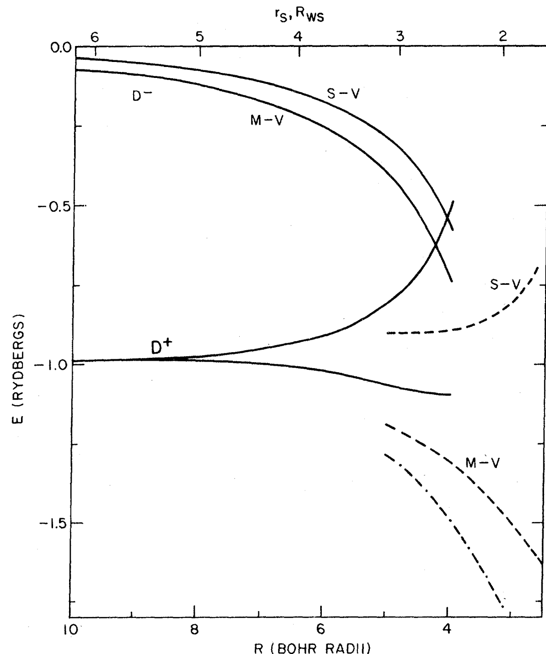

FIG. 3. The maximum and minimum energies of the D^+ band and the minimum energy of D^- band (solid lines) in single-valley (S-V) and many-valley (M-V) semiconductors for an sc lattice (lattice parameter R) of donors. At high densities the results of Wigner-Seitz calculations are shown for the bottom of band (chain lines) and the Fermi energy (dashed lines) assuming a metallic state. The upper scale is the average interdonor separation r_s or equivalent to the radius of the Wigner-Seitz sphere, R_{ws}.

In a single-valley semiconductor, however, the ground state will have an antiferromagnetic spin arrangement and this will affect the propagation of an extra electron in two ways. First, there is the reduction due to spin scattering that we mentioned earlier. This reduction has been estimated in the atomic limit of the Hubbard model by Brinkman and Rice.[16] They showed that the band narrows for this case by a factor ≈0.75 for a simple cubic lattice. We shall include this effect by calculating the bandwidth for a ferromagnetic spin arrangement by taking the center of the D^- band as

$$E_0 = \sum_j{}' U(\vec{R}_j), \tag{3.17}$$

where the prime denotes that the central site is omitted in the sum over all lattice sites. There is an additional narrowing factor which arises from the need to interchange an inner and an outer electron in the hopping process. This is illustrated in Fig. 4, which shows how an extra electron propagates along a line of spins with an antiferromagnetic spin arrangement. Each time it is the inner electron which hops. As a result, the hopping matrix element is reduced by a factor S which

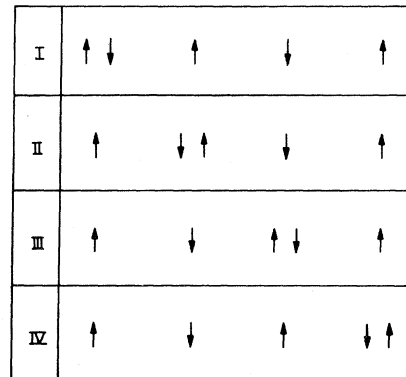

FIG. 4. The spin configurations that occur when an extra electron propagates in the D^- band of a single-valley semiconductor with an antiferromagnetic array of spins. Note that at each step it is a different electron which moves.

is the overlap of the inner and outer electrons. This factor varies from a value of $S = 0.68$ at $R = 10$, to a value $S = 0.86$ at $R = 4$. When this reduction of bandwidth of a factor of S is made as well as the reduction of 0.75 discussed earlier, the resulting band is shown in Fig. 3. In the single-valley case, the bottom of the band is ~0.1 Ry above the many-valley case, but it too drops dramatically at $R \sim 4$.

We turn now to the D^+ band. In this case, an electron is removed. The energy is calculated in two parts. First the bandwidth is calculated by solving the Schrödinger equation with appropriate boundary conditions for the top and bottom of the band and with an unscreened Coulomb potential on the central site and a potential $U(r)$ of neutral donors on all other sites. The bandwidth is then reduced by the factor of 0.75 due to the spin ordering in the case of a single-valley semiconductor. For the many-valley case, the same reduction applies. In the case of a hole in an occupied band the propagation of the hole requires a reordering of the arrangement of spin and valley indices in the ground states. As a result, only paths where the hole retraces itself are allowed in the path-counting method used by Brinkman and Rice.[16] There is, of course, no other reduction due to overlap for the holes. The polarization correction in this case will raise the hole or D^+ band in energy since it is the net positive charge of the hole which polarizes the lattice of neutral donors and reduces the energy to form a hole. We therefore calculate the shift in the center of the hole band as an upward shift equal in magnitude to Eq. (3.17) and then place the top and bottom of the D^+ band by using the reduced bandwidth. The results are shown in Fig. 3.

We see that again the rapid movement of the band around $R \approx 4$. The D^+ and D^- band cross at $R = 4.25$ for many-valleys and $R = 4.05$ for a single-valley semiconductor. These values are close to the Mott value ($R = 4$) and represent a shift at lower density of approximately a factor 0.86. In experiments on Sb-doped Ge, Cuevas and Fritsche[17,18] found a reduction factor of ≈ 0.5 in the Mott density in unstressed Ge (4 valleys) compared to uniaxially stressed Ge (1 valley). Our calculations predict an effect of the correct sign but the magnitude is too small. The comparison of our calculations for donors on a regular lattice with the experiments on randomly doped materials is clearly only qualitative at best. Further, as discussed below, the transition of an ordered array of donors will be first order since the long-range attraction between electron and holes causes a discontinuous onset in the number of electrons and holes.[24] The calculations presented above can only be regarded as giving an approximate value for the mobility edges of electrons and holes propagating in the random array of donors.

Even with the above cautions, it is of interest to compare the positions of the single-particle bands calculated above and those given in the metallic approximation which is applicable at higher densities. Although several methods have been applied to describe metallic hydrogen with a fixed lattice of protons, the differences with the original calculations of Wigner and Huntington[25] are not great. We calculate the position of the bottom of the band and the Fermi energy using the Wigner-Seitz method. (Note that we do not include the effect of the surface dipole layer since we are interested in comparing to the calculations in the insulating state described above. The potential of the dipole layer varies smoothly with density and does not affect the energy gap between the D^- and D^+ bands, but rather rigidly shift them with respect to the energy level in an undoped crystal.) The bottom of the band, E_{BB}, is determined first by calculating the eigenvalue, E_W, of the Schrödinger equation with a bare Coulomb potential subject to the Wigner-Seitz boundary condition at $r = R_{WS}$. The correction to E_W arises from the interaction of the electron with the negative charge in the Wigner-Seitz sphere and from exchange and correlation corrections. These two corrections largely cancel each other and the net correction is small. Adding these two terms gives

$$E_{BB} = E_0 + \frac{1.2}{r_s} + \epsilon_{xc}(r_s) - \frac{r_s}{3}\frac{d}{dr_s}\epsilon_{xc}(r_s)\,, \qquad (3.18)$$

where r_s is the interparticle spacing in units of $a_B\,(r_s = R_{WS})$ and ϵ_{xc} the exchange and correlation correction to the ground-state energy per electron. For a single-valley semiconductor we use the Wigner form for ϵ_{xc}:

$$\epsilon_{xc} = -\frac{0.916}{r_s} - \frac{0.88}{r_s + 7.8}\,. \qquad (3.19)$$

The results are shown in Fig. 3 and also the chemical potential determined by adding the Fermi energy

$$\mu = E_{BB} + \frac{3.683}{r_s^2}\,. \qquad (3.20)$$

For a many-valley semiconductor the Fermi, exchange, and correlation energy all change depending on the number of valleys. For Si, Rose *et al.*[26] calculated the exchange and correlation energy. We have fit their results for the correlation energy to a Wigner form giving

$$\epsilon_{xc} = -\frac{0.48}{r_s} - \frac{1.31}{r_s + 2.15}\,. \qquad (3.21)$$

Substituting in Eq. (3.18) gives a value for the bottom of the band E_{BB} somewhat below the single-valley semiconductor value. It is also shown in Fig. 3 and also the chemical potential for the parameters appropriate to Si:

$$\mu = E_{BB} + 1.115/r_s^2\,. \qquad (3.22)$$

There is a substantial difference in the position of the bottom of the band and also the chemical potential between the two sets of calculations. This reflects in part the different treatments of correlation in the two approximations. In one, the polarization corrections are treated statically and no attempt is made to achieve self-consistency by allowing for change of the inner electron with a decreasing energy gap. In the metallic approximation the short-range intracell correlations are described inadequately. As a result, it is hard to assess the reliability of the energy differences shown in Fig. 3.

To conclude this section, we compare our calculations to those made by others. The closest in spirit are those recently reported by Mott and Davies[27] who used the Hartree potential U_0 [see Eq. (3.7)] in a Wigner-Seitz calculation. The D^- band in their calculations broadened considerably less than in Fig. 3, presumably due to the absence of polarization corrections on the central site and on the neighbors. The D^+ band also broadens upward less—again there are no polarization corrections. As a result, they did not obtain a crossing until $R_{WS} = 2$ or $R = 3.2$.

The density-functional method has been applied to this problem by two groups. Ghazali and Leroux-Hugon[28] have reported a narrow energy band (presumably D^+) and a broad energy band

(D^-) which overlap at $R \approx 5$ and even coexist at smaller R. Their results do not have much in common with ours. Recently Rose, Shore, and Sander[6] have reported calculations for a ferromagnetic lattice of donors in a single-valley semiconductor at $R \approx 4.6$. They use the density-functional method also and study the ground-state energy through the Mott transition. Single-particle energy bands are also obtained. However, the mean energy of the occupied (D^+) band at $R = 4.6$ lies at ≈ -0.5 Ry, substantially above the position of the D^+ band in Fig. 3. This discrepancy shows the inadequacy of the single-particle bands obtained by the density-functional method and it will be discussed in detail elsewhere.[29]

Rose, Shore, and Sander[6] obtain a first-order transition to the metallic state with a discontinuous jump in number of electrons in the D^- band and holes in the D^+ band to a value of $(n_{e,h}/n_D)^{1/3} \approx 0.45$. As we mentioned previously, such a discontinuous transition has been predicted by Brinkman and Rice[24] as a consequence of the stability of a finite density of electrons and holes which form the electron-hole liquid. We can use the latter calculations to estimate the value of $n_{e,h}$. First we need to know the electron and hole masses (m_e, m_h). From the D^- and D^+ bandwidths calculated above, we estimate $m_e \approx 0.6$ and $m_h \approx 1.2$. Next, the dielectric constant can be estimated by assuming it scales inversely with the square of the direct band gap. This band gap, unlike the indirect one, is not varying rapidly near the Mott density, and therefore we may use the value at $R = 4.5$ from Fig. 3 where the gap between the bottom of each band ≈ 0.6 Ry. This gives

$$\epsilon = 1 + 18\pi n_D (1/0.6)^2 \simeq 2.7 . \tag{3.23}$$

The exciton rydberg and Bohr radius are then ≈ 0.055 Ry and 6.75, respectively. At the transition, the stable density of electrons and holes is given by $r_s = 1.7$ in exciton Bohr radii leading to a value

$$(n_{e,h}/n_D)^{1/3} = (3/4\pi)^{1/3} R / r_s a_B^{ex} \approx 0.25 . \tag{3.24}$$

This value is somewhat different from their value, which is not surprising in view of the reasons discussed below and the differences in approach. The approximation of a spherically symmetric D^+ band used by Rose *et al.*, leads to a one-dimensional van Hove singularity at the top of the D^+ band rather than the three-dimensional singularity given by tight-binding theory of the simple cubic lattice. The use of a one-dimensional van Hove singularity leads to a very large effective-hole mass and a larger first-order transition. Another point of difference between the two calculations is the energy dependence on $n_{e,h}$ (the density of electrons in the minority spin band or holes in the majority spin band). In the density functional method a term proportional to $n_e^{4/3}$ is included from exchange and correlation among the electrons but the corresponding term is not present for the holes, whereas in the electron-hole-liquid theory they are treated symmetrically, as they should be. Furthermore, both calculations show that only a few percent of the electrons are involved in the transition, which is at the limits of where a local-density-functional (LDF) method would be expected to yield a reasonable description.

IV. DENSITY FUNCTIONAL CALCULATIONS OF CLUSTER STATES

The D^- and D^+ bands calculated in the previous section for a lattice arrangement of donors gives a reasonable description of the average position of the single-particle energy bands. However, as emphasized in the introduction, band tailing occurs due to the presence of large-density fluctuations, which can lead to localized states. Of particular importance is the nature of the overlapping band states, i.e., the low-energy tail of the D^- band and the high-energy tail of the D^+ band. As pointed out earlier, the situation is different for the case of single-valley and many-valley semiconductors. In the former case, the tail states of the D^- and D^+ bands due to dense clusters of a few donors follow the trends of the electron affinities and ionization potentials of the atomic periodic table. There is not much increase in electron affinity, so the tailing of the D^- band to lower energies is not large. There is a substantial decrease in the ionization potential of three close donors, which behave as a Li atom, and this causes the D^+ band to rise upward to meet the D^- band as Golka and co-workers[19] have shown. This is a direct consequence of the Pauli exclusion principle which limits the number of electrons in any orbital state of the cluster to two. The electron affinity of the most electronegative case (for a reasonable number of donors, $N < 15$), the D_9 corresponding to fluorine, is only 0.25 Ry. The ionization potential in the most favorable cases, D_3 and D_{11}, corresponding to lithium and sodium are 0.40 and 0.38 Ry, respectively. For other values of N, and sparser clusters, the affinities would be lower and the ionization potentials higher. Thus, at low enough concentrations there is a Mott-Hubbard gap due to electron-electron repulsion in the single-particle density of states in the single-valley semiconductor system.

In a many-valley semiconductor, the situation is quite different: Because the exclusion principle is inoperative till 12 electrons in Si (8 in Ge),

the electron affinities (and ionization potentials) of the small clusters [$n< 11$ (12)] keep on rising as the cluster volume gets reduced. Thus tailing of the D^- and D^+ states due to these small dense clusters is toward low energy, and the picture is one of the D^- band coming down to meet the D^+ band, the exact opposite of the single-valley case. (This result may seem a bit contradictory to Fig. 3 for the lattice, where there is upward motion of the D^+ band. This is because of two effects. Firstly, the clusters for which this downward trend is sizable have densities beyond n_{MI}, but because of the relatively small numbers N and consequent large relative fluctuations, they are present in fair numbers below n_{MI}. These are absent in the lattice calculation and thus the lattice model does not have such tail states. Secondly, there is a polarization correction on the bands due to the charged state present in the calculation of Sec. III which has not been included in the above argument; this will tend to lower the ionization potentials and push the D^+ states up somewhat.)

Since the D^- band tails down toward the D^+, the nature and extent of these D^- tail states is crucial to the understanding of the transition from the insulating to the metallic phase. We have therefore carried out calculations of electron affinities, ionization potentials, and total energies of donor clusters. Our calculations show that in the limit of zero separation, as few as four donors are required to exceed an electron affinity of 1 Ry. This implies that in many-valley semiconductors there is, strictly speaking, no Mott-Hubbard gap at any density. Because dense clusters of more than four donors can in fact attract electrons off isolated donors, the ground state will in fact involve charge transfer on a microscopic scale.

We have carried out two sets of calculations using the LDF formalism developed by Kohn, Sham, and Hohenberg.[30,31] The LDF method has been applied successfully to calculate the ground-state energies of many atoms, molecules, ions, etc.[32] The method is now well known and we will only outline the steps here.

In the first set of calculations, we calculate total energies $E(N,N_D;R)$ of clusters with N_D donors in a sphere of radius R with N electrons (we consider only $N=N_D-1,N_D,N_D+1$). Initially we replace the donor ion charges with a uniformly distributed spherical "jellium" charge density ($\rho_D\equiv 3N_D/4\pi R^3$) over a cluster radius R and then correct approximately for the effects of the point donor ions. Our calculations are for clusters with donor concentration exceeding n_{MI} ($r_s< 2.5$), so that the electronic wave functions within the cluster are pretty well delocalized and are well classified in terms of the cluster orbitals.

We work in reduced units, and for the case of donors in silicon with no central-cell correction they are $m^*=0.32m$ for mass, a rydberg of 33.7 meV, and a Bohr radius of 18.9 Å as given by Rose, Shore, and Zaremba.[26] (We remind readers that because of the use of rydberg instead of Hartree as an energy unit, many formulas differ from the usual by the presence of the additional factor 2.) We solve a set of self-consistent equations

$$[-\nabla^2+\phi(\vec{r})+v_{xc}(\vec{r})]\psi_i(\vec{r})=\epsilon_i\psi_i(\vec{r}) , \tag{4.1}$$

with an electrostatic potential assuming the donor ion charge ρ_D is uniformly distributed over a radius R,

$$\phi(\vec{r})=-2\int_{r'<R}\frac{\rho_D d^3r'}{|\vec{r}-\vec{r}'|}+2\int\frac{n(\vec{r}')d^3r'}{|\vec{r}-\vec{r}'|} , \tag{4.2}$$

and the electronic density

$$n(\vec{r})=\sum_{j=1}^{N}|\psi_j(\vec{r})|^2 . \tag{4.3}$$

The exchange and correlation potential

$$v_{xc}(\vec{r})=\epsilon_{xc}(n(\vec{r}))-\frac{r_s}{3}\frac{\partial\epsilon_{xc}(n(\vec{r}))}{\partial r_s} \tag{4.4}$$

is obtained by parametrizing the exchange and correlation energy[26] in a Wigner form:

$$\epsilon_{xc}(n(\vec{r}))=-\frac{0.478}{r_s}-\frac{1.31}{r_s+2.15} , \tag{4.5}$$

where $n^{-1}=4\pi r_s{}^3 a_B^3/3$. The total energy for a cluster with N_D donor ions in a radius R and N electrons is given by

$$E(N,N_D;R)=\sum_{j=1}^{N}\epsilon_i-\int\int\frac{n(\vec{r})n(\vec{r}),d^3r d^3r'}{|\vec{r}-\vec{r}'|}+\int n(\vec{r})[\epsilon_{xc}(n(\vec{r}))-v_{xc}(n(\vec{r}))]d^3r+E_D . \tag{4.6}$$

The last term E_D is a correction to represent the energy difference between the discrete ion-charge distribution and the uniformly distributed charge. The ion-ion electrostatic repulsion should be added to Eq. (4.6) to compare our results for energy per electron donor pair with those of Rose *et al.*, for a uniform lattice of Li donors in Si using a spherical Wigner-Seitz cell approximation (like that used by us in Sec. III). However, it is not relevant for the energy differences of interest to us here. As noted by Rose *et al.*, the last term in Eq. (4.6) is important in stabilizing donor clusters in Li-doped Si, and we find it necessary to include it in order to achieve agreement (for the larger clusters) with their results. We find, in addition, that it is a non-negligible correction in the calcu-

lation of the electron affinity of clusters.

A first estimate of this difference in electron-ion electrostatic attraction may be obtained by imagining a roughly uniform electronic charge of magnitude (N/N_D) in a spherical Wigner-Seitz cell of radius $r_{\rm WS}=R N_D^{-1/3}$ around each ion. In such a case, the net effect of each Wigner-Seitz sphere on the other is zero, and the net difference of the electrostatic interaction between the point ion and the uniformly distributed donor charge turns out to be

$$E_D=-3N/5r_{\rm WS} . \tag{4.7}$$

In calculations of energies per electron-donor pair, the above approximation is adequate. However, it does not take into account the effect of the expansion (contraction) of the electronic charge when an electron is added to (subtracted from) a cluster. In order to include this effect, which is important in calculating electron affinities and ionization potentials, we replace in Eq. (4.7) the Wigner-Seitz radius $r_{\rm WS}$ characteristic of the donor density by an electronic Wigner-Seitz radius $r_{\rm WS}^{\rm elec}$ determined by the radius of the electronic charge distribution:

$$r_W \to r_{\rm WS}^{\rm elec}=r_{\rm WS}\frac{\langle R\rangle_{\rm elec}}{R} , \tag{4.8}$$

where

$$\langle R\rangle_{\rm elec}=\frac{\int n(\vec{r})r\,d^3r}{\int n(\vec{r})d^3r} . \tag{4.9}$$

We have used two- and three-parameter variational wave functions for the 1s cluster levels and iterated to self-consistency within the parameter space used. We find the final results are not very sensitive on the level of accuracy (10–20%) that we feel is inherent in the approximations that have been made, especially of E_D. We present results using a Fermi-function form for the electronic wave function:

$$\psi(r)=\frac{C}{1+e^{\alpha(r-r_0)}} , \tag{4.10}$$

with α and r_0 as variational parameters and C as a normalization constant.

To obtain the single-particle density of states, we need to calculate the energy to add and subtract an electron. The negatives of these are the electron affinity and ionization potential of the neutral cluster of N_D donors given, respectively, by

$$E_{N_D^-}(R)=E(N,N_D;R)-E(N+1,N_D;R) \tag{4.11a}$$

$$E_{N_D^+}(R)=E(N-1,N_D;R)-E(N,N_D;R) . \tag{4.11b}$$

The energy per electron-ion pair for the same cluster is given by

$$E_{N_D0}(R)=E(N_D,N_D;R)/N_D , \tag{4.11c}$$

Calculations of $E_{N_D\sigma}(\sigma=+,0,-)$ were performed for twenty clusters of sizes $2\leq R\leq 5$ and $3\leq N_D \leq 11$, and the results fitted to the empirical form ($r_{\rm WS}\equiv RN_D^{-1/3}$):

$$E_{N_D\sigma}=\frac{A_1}{r_{\rm WS}}\left(1+\frac{R_1}{R}\right)+\frac{A_2}{r_{\rm WS}^2}\left(1+\frac{R_2}{R}\right), \tag{4.12}$$

where A_1, A_2, R_1, and R_2 are fitting parameters. Using the empirical fit above, we construct curves of constant E_{N_D0} on an N_D vs R plot, and these are displayed in Figs. 5(a)–(c). The large negative values of E_{N_D0} are in agreement with the stability trends found by Wang and Kittel[33] and also reflect the large binding energy of the metallic state in the calculations of Rose *et al.*[26] Of particular interest are the large values of electron affinity (compared to that of the isolated donor value of 0.055 Ry), some of which even exceed the isolated donor binding energy of 1 Ry.

The second set of calculations have been done for the extreme limit of zero donor separation. We use existing programs developed[34] for calculating atomic energy levels self-consistently in LDF formation, modified to include up to 12 electrons in the 1s shell and using the exchange and correlation potential of Eqs. (4.4) and (4.5). The calculation is done by numerical integration of the radial Schrödinger equation both outward from the origin and inward from infinity, and using perturbation theory on the mismatch in the logarithmic derivative at the matching point, to generate a new guess for the eigenvalue. Self-consistency is achieved within ten to twelve iterations.

We caution the reader that these calculations have been done in the context of shallow donors and the effective-mass theory. The zero-separation results are indicative of results for clusters which are on the scale of the Bohr radius or smaller, so long as the energies (electron affinities, ionization potentials) remain on the scale of the effective-mass rydberg, i.e., much smaller than the band gap. Some of the larger clusters in the limit of zero separation (i.e., nearest-neighbor donors in the host lattice) may well turn out to be deep traps not described by the shallow-donor effective-mass theory. However, our interest is in using these "atomic" calculations for interpolating between them and our earlier results to determine clusters with affinities $\approx$1 Ry, where effective-mass theory should certainly be accurate.

We obtain the electron affinities and ionization potentials using the Slater transition-state calculations. Since in LDF formalism the eigenvalue is

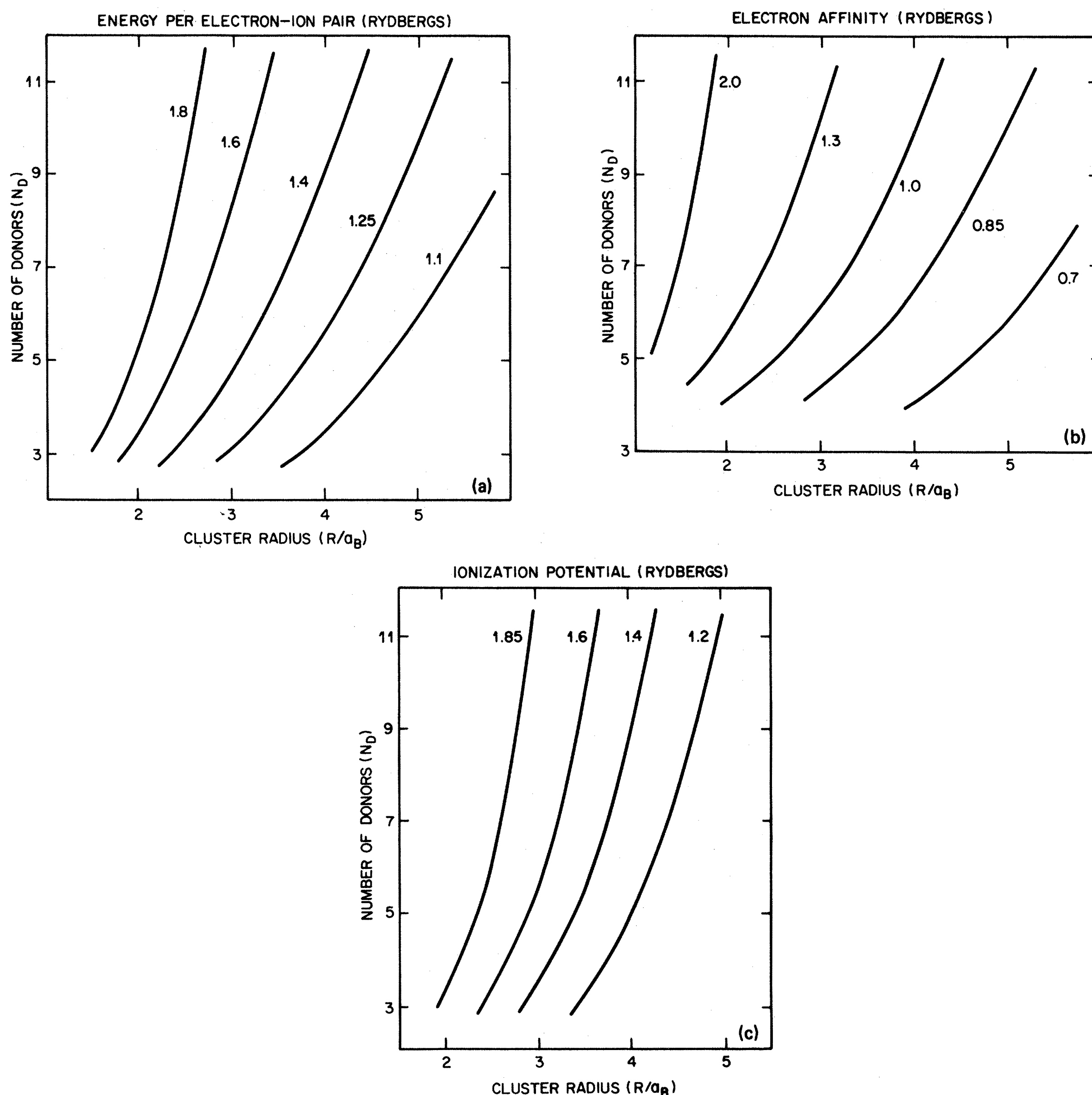

FIG. 5. Lines of constant energy per electron-ion pair (a), electron affinity (b), and ionization potential (c), for effective-mass donor clusters in many-valley semiconductors. The numbers next to the curves are the value of the constant quantity in rydbergs.

the derivative of the total energy with respect to the number of electrons:

$$\epsilon(N,N_D)=\left(\frac{dE(N',N_D)}{dN'}\right)_{N'=N}, \qquad (4.13)$$

the electron affinities and ionization potential of clusters are equal (except for third and higher derivatives) to the LDF energy eigenvalues with one-half electron added or removed from the neutral cluster, respectively. Using this scheme, we obtain the electron affinity and ionization potential curves plotted in Fig. 6, where the result for D^- is taken from known results, as the D^- is not bound in simple LDF schemes. As can be seen, the electron affinity is close to 1 Ry for $N_D=3$, and increases rapidly for larger N_D. Of course, so does the ionization potential.

To calculate the magnitude of the charge transfer, we note that a donor is essentially isolated if it has no neighbors within $\sim 5a_B$. Since the probability of no neighbors in a volume v is $e^{-n_D v}$ and the metal-insulator transition density $n_{MI}\approx \frac{1}{64}a_B^{-3}$, the

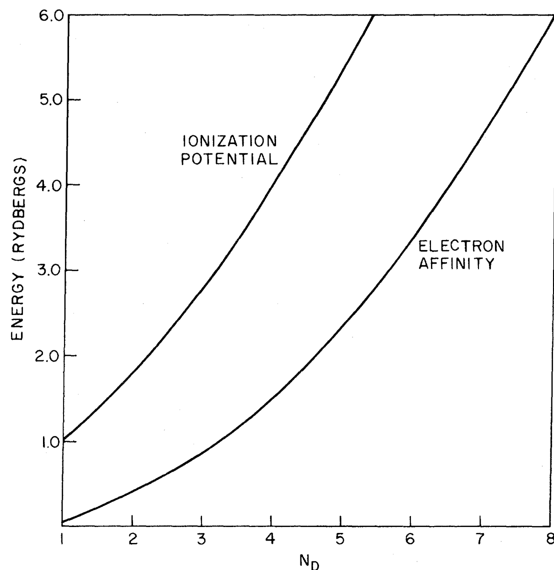

FIG. 6. Plot of electron affinity and ionization potential of "point" clusters as a function of number of effective-mass donors in many-valley semiconductors.

number of isolated donors at density $n_D \approx n_{MI}/3$ and $n_D \approx n_{MI}/2$ is approximately 7% and 2%, respectively. On the other hand, the number of clusters with affinities greater than 1 Ry is given by adding clusters with N_D varying from 4 to 11 with volumes such that they lie above the 1 Ry affinity line in Fig. 5(b) (extrapolated to the 1 Ry point from Fig. 6 for $R = 0$). In principle one should correct for multiple counting, e.g., the possibility of a dense 8-atom cluster already having once been counted as a 4-atom cluster, and also allow for higher electron affinity levels, i.e., the possibility of more than one electron being attracted by a really dense cluster. However, clusters with affinities greater than 1 Ry are rare, and both these corrections (which have opposite signs) are still smaller effects. We have therefore neglected them, and arrive at the result of 0.15% and 1.2% of donors in the highly affinitive clusters at $n_D \approx n_{MI}/3$ and $n_D \approx n_{MI}/2$. Thus our calculations predict a non-negligible amount of charge transfer (a sort of self-compensation) in the ground state of the insulating phase, which is a rapid function of the donor density.

Our estimate does not include the Madelung energy, i.e., the Coulomb attraction between the negatively charged cluster and the positively charged donor; this will be an important effect in stabilizing charge transfer. The central-cell potential which removes the degeneracy of the ground state, on the other hand, will tend to reduce the charge transfer.

We know of no reason why there should not be excited states with different amounts and location of charge transfer to the ground state arbitrarily close to the ground state in energy. Such states will contribute a finite density of states at the Fermi level. The charge transfer, as indicated by our estimates, is controlled by the availability of affinitive clusters and thus can be expected to increase as the Mott transition is approached. These results imply that the fluctuations in the one-electron potential are large and as a result the metal-nonmetal transition will be an Anderson transition, as Mott[1] has proposed.

V. DISCUSSION AND CONCLUSIONS

Though the single-particle density of states which has been the focus of this work is not directly accessible to experiment, several comparisons with experiment can be made using our results.

In the more dilute regime a clear demonstration that the interactions between close pairs of donors are the first change from isolated donors has been demonstrated by a study of donor optical spectra.[13] In this regime, a measure of the distribution of D^- states was obtained by the photoconductivity studies of Norton,[35,36] Aleksandrov *et al.*,[37,38] and Taniguchi *et al.*[39] These experiments measure the photoconductivity at long wavelengths in the presence of a background of room-temperature radiation which excites some electrons into negatively charged donor states. The long-wavelength spectrum then measures the distribution of energies to excite an electron from the band of D^- states to the mobility edge. At very low concentrations $n_D^{1/3} a_B \lesssim 0.03$ there is a sharp threshold for photoconductivity at an energy $E_i = 1.8$ meV in Si:P and 0.625 meV for Ge:Sb. These energies agree well with the values expected for the binding energy of isolated D^- levels and the overall shape of the photoconductivity spectrum also agrees with this interpretation.

At higher densities the threshold is observed to shift to higher energies by all three groups in Si:P, Ge:Sb, and other systems; however, their interpretations are all different. Norton[35] originally attributed the shift to the formation of a D^- (or upper Hubbard) band at these densities. This is clearly in disagreement with our calculations shown in Fig. 3 which puts the onset of a significant broadening due to interactions at the average separation a factor of 30 higher in density at least. Aleksandrov *et al.*,[37,38] propose the formation of D^+-D^- centers in which the D^- electron is more tightly bound by the attraction of a nearby D^+ center as the explanation. However, in their experiments the density of D^- centers (and conse-

quently of D^+ centers), n_{D^-}, is very low, $n_{D^-} \ll n_D$, perhaps as low as $n_D \sim 10^{10}$ cm^{-3} as Norton[35] estimates. Therefore, for samples which show deviations from the isolated donor result, there is a much larger probability of finding a neutral donor, D^0, around a D^- center than a charged D^+ center. To be specific, to account for the $\approx$6-meV threshold seen in a sample of Si : P with concentration 9×10^{16} cm^{-3} ($n_D^{1/3}a_B \simeq 0.1$), requires a shift $\approx$4 meV; in other words, a D^+ within a radius of 300 Å assuming a simple Coulomb attraction. This is very unlikely; if $n_D^+ \approx 10^{10}$ cm^{-3} it has a probability $\sim 10^{-6}$. On the other hand, we have shown above that this shift ($\approx$0.13 Ry) can easily be obtained in a many-valley semiconductor by a reasonably close D^0 neighbor, and since there are so many more of them, it is not unreasonable to ascribe the shift to the D_2^- complexes. This is the explanation that Taniguchi, Narita, Hasegawa, and Kobayashi[39] have put forward. They have performed an elegant series of experiments which strongly support the D_2^- explanation. They took a sample of Ge : Sb concentration 9×10^{14} cm^{-3} ($n_D^{1/3}a_B \approx 0.04$) in which a threshold energy of $\approx$1.5 meV (0.15 Ry) was measured, and applied a uniaxial stress and observed the threshold energy drop to a value $\approx$0.6 meV (0.06 Ry). Under a [111] uniaxial compression, the four degenerate valleys are split and a single valley drops down. This drop in threshold energy they interpreted as arising from the large reduction of the binding energy D_2^- when one passes from a many-valley to a single-valley semiconductor. Our calculations, reported above show the stability of a D_2^- in a many-valley semiconductor when all 3 electrons can be placed in bonding or s states. Our calculated value for a D_2^- complex at zero separation ($\approx$0.4 Ry) is larger than the threshold value quoted above. Though we cannot make a direct comparison of our results with the experimental line shapes in the absence of detailed calculations at intermediate separations, they are qualitatively in agreement with the D_2^- interpretation.

Another point of comparison we can make at the higher densities is the energy gap between the mobility edges of the D^+ and D^- bands. Various measurements of this energy gap have been made and are displayed in Fig. 7. The solid curve in Fig. 7 is the energy gap between the D^+ and D^- bands in the lattice calculations of Sec. III. At low densities the energy gap shown is the activation energy of the dc conductivity[40] and the energy gap measured in photoconductivity.[41] At higher densities, it is ϵ_2, i.e., activation energy of dc conductivity[42,43] at intermediate temperatures, which is plotted. This latter is clearly much smaller than theoretical values. In making this comparison one must

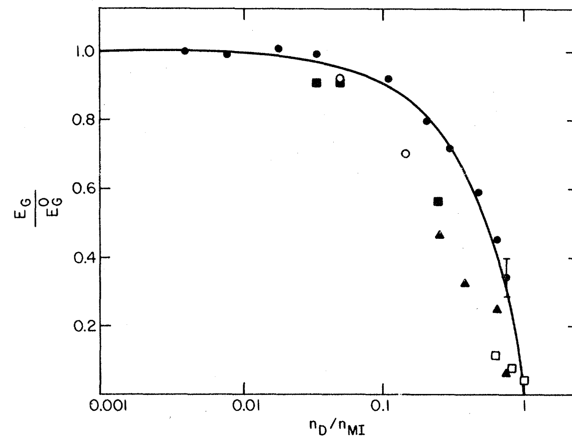

FIG. 7. A comparison of the theoretical energy gap in a lattice of donors between the top of the D^+ band and the bottom of the D^- band in a many-valley semiconductor (from Fig. 3) to various experimental measures in Si:P. The activation energies of the dc conductivity at low densities (ϵ_1) from the data of Penin (Ref. 40) (open circles); at intermediate densities (ϵ_2) from the data of Yamanouchi (Ref. 42) (open squares) and Toyotomi (Ref. 43) (triangles). Also shown is the photoconductivity edge from the data of Guichar *et al.* (Ref. 41) (solid squares) and the characteristic energy determined by scaling the polarizability (Ref. 44) (solid circles) (see text). We are grateful to G. A. Thomas for the compilation of the experimental data.

consider the location of the Fermi energy. At low densities because of large downward broadening of the D^- band and small upward broadening of the D^+ band, the Fermi energy should lie at the top of the D^+ band and the conductivity activation energy equals the photoconductivity threshold as in Fig. 7. At larger concentrations, there may be some upward movement of the D^+ band edge due to polarization effects and the Fermi energy may lie between the D^- and D^+ edges in Fig. 3. In this latter case, it is more appropriate to compare $2\epsilon_2$ with the calculated energy gap in Fig. 7. Clearly this would improve the agreement between theory and experiment. The best agreement in Fig. 7, however, is with the characteristic energy which enters the enhancement of the electric polarizability χ per donor. This energy E_c is obtained[44] by scaling $\chi/\chi_0 = (E_g^0/E_c)^2$, where χ_0 and E_g^0 are the polarizability and energy gap in the isolated donor regime. This energy agrees remarkably well (in fact, better than expected) with the calculations. (Note in making this comparison we assume that the $\vec{k}$-selection rule for optical transitions has broken down due to the random positions of the donors and that it is the lowest energy gap of the lattice calculation that is relevant.) In general, the theoretical values of the energy gap of the lattice are in reasonable agreement with $2\epsilon_2$ and other

experimental values.

The major result of this work is the large-scale fluctuations in the one-electron potential, especially for many-valley semiconductors. The combination of the complete randomness of donor positions with the large binding energy of small dense clusters is such that correlation does not impose an energy gap in the one-electron density of states at any density. Direct experimental proof of this result is difficult because of the small amount of charge transfer which can easily be masked by a small number of acceptors. Perhaps the best way to measure the charge transfer is to look in the very far infrared for evidence of additional absorption due to hopping as discussed by Miller and Abrahams[45] and Blinowski and Mycielski.[46] As the density increases towards the insulator-metal transition density, the potential fluctuations become prominent and there is little doubt the transition is an Anderson transition; that is to say, it is governed by the large fluctuations in the one-electron potential rather than by correlation effects.

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