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Roles of the lower and the upper Hubbard bands and the donor-excitonic states in the theory of shallow-impurity states in doped semiconductors

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A self-consistent unrestricted Hartree-Fock pseudocluster calculation has been performed to investigate the roles of various bands in doped semiconductors. While the lower and the upper Hubbard bands of the Mott-Hubbard-Anderson (MHA) model are well defined at low concentration, the donor-excitonic states are important at higher concentration where the upper Hubbard band is pushed into the conduction band. The so modified MHA model can still explain almost all the experimental results.

The Mott-Hubbard-Anderson (MHA) model[1] which explicitly emphasizes the electron correlation and the Anderson localization has been generally accepted as a proper description of the novel behavior of the shallow impurity band in doped semiconductors. The MHA model consists of three bands, namely, the lower Hubbard band (LHB), the upper Hubbard band (UHB), and the semiconductor conduction band (SCB). It can account qualitatively for almost all the existing experimental data associated with the metal-nonmetal transition.

On the other hand, different authors have emphasized various parts of the MHA model in their own simplified model approaches to investigate certain special aspects of the shallow impurity band. Berggren,[2] Sernelius,[3] and Ghazali and Leroux Hugon[4] have ignored the UHB, and Berggren and Sernelius even approximated the LHB by a single impurity level. Aoki and Kamimura,[5] Kikuchi,[6] Yonezawa *et al.*,[7] and Chao and Berggren[8] have concentrated their efforts on the LHB and the UHB with fixed centers of gravity of the bands. Finally, Matsubara and Toyozawa,[9] Ishida and Yonezawa,[10] and Chao and co-workers[11] have calculated various physical quantities as weighted averages over the contributions from the LHB and the UHB. Although such specific approaches are valid in a limited impurity-concentration (IC) regime,[12] it is difficult to generalize them to a wider range of the IC.

Although the MHA model contains almost all the characteristic features derived from experimental data, certain points remain to be clarified. First we need to know the IC dependences of the positions of the centers of gravity of the LHB and the UHB, as well as the modification of the SCB states near the SCB minima. With decreasing effective Hubbard U at higher IC due to the screening effect, whether one can still identify the LHB and the UHB is a serious question. Furthermore, recent experiments on D^- states in a magnetic field by Narita[13] and far-infrared transmission measurements[14] have shown the existence of negatively charged impurity clusters and bound D^+D^- pairs. The lack of sufficient information on the above-mentioned phenomena must be the reason why a general analytical approach for quantitative investigation of the shallow impurity states in a wide range of IC has so far not emerged. The purpose of this paper is to clarify the above listed ambiguities with the exact numerical solution of a self-consistent unrestricted Hartree-Fock pseudocluster calculation where a spin-polarized nonlocal potential is used.

For a given IC we generate a cluster of N random sites $\{\vec{R}_i;\ i=1,N\}$ in a volume Ω as the locations of N substitutional impurities with a hard-core impurity-pair-correlation function of radius R_0. At each site is attached an impurity orbital $\phi(\vec{r}-\vec{R}_i)$ which is approximated by a hydrogenlike wave function with an effective Bohr radius a_0. a_0 is determined empirically from the measured binding energy of a single isolated impurity. It will be helpful for the calculation if we first obtain an orthonormal set

$\{\psi_i(\vec{r})=\sum_j \phi(\vec{r}-\vec{R}_j)A_{ji};\ i=1,N\}$ and then introduce the spin-wave function to express the orthonormal set as $\{\psi_{i\sigma}(\vec{r});\ i=1,N \text{ and } \sigma=\uparrow,\downarrow\}$.

The Hamiltonian of this finite system is simply

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

where $V^{\text{ion}}(\vec{r}_i)$ is the impurity-ion potential acting on the ith electron, $V^{\text{el-el}}(\vec{r}_i-\vec{r}_j)$ is the Coulomb interaction between the ith and the jth electrons, and the summations are over all the N electrons. In Hartree-Fock approximation, we have to solve the Schrödinger equation

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

self-consistently, where V_{cx} is the Coulomb and the exchange interaction potential derived from $V^{\text{el-el}}$ via the Hartree-Fock approximation and $n_{j\sigma}$ is the occupation probability for $\psi_{j\sigma}(\vec{r}\,')$. At zero temperature we have $n_{j\sigma}=0$ or 1.

We can expand the eigenfunctions of a finite cluster as

$$\Psi_{i\sigma}(\vec{r})=\sum_j \psi_{j\sigma}(\vec{r})B_{ji}^{\sigma}\ . \tag{3}$$

Substituting this expansion into Eq. (2), the eigenequation problem reduces to the diagonalization of the effective one-particle Hamiltonian matrix $\underline{H}_\sigma(\{n_{js}\})$ with the elements defined as

$$H_\sigma(\{n_{ks}\})_{ij}=\int \psi_{i\sigma}^*(\vec{r})\left[\frac{p^2}{2m}+V^{\text{ion}}(\vec{r})+V_{\text{cx}}(\{n_{ks}\})\right]\psi_{j\sigma}(\vec{r})\,d\vec{r}\ . \tag{4}$$

Using Eq. (3) and the definition $\psi_{i\sigma}(\vec{r})=\sum_j \phi_\sigma(\vec{r}-\vec{R}_j)A_{ji}$, it is easy to see that to calculate Eq. (4) we have to compute such integrals as

$$\int \phi_{\sigma_1}^*(\vec{r}-\vec{R}_i)\phi_{\sigma_2}^*(\vec{r}\,'-\vec{R}_j)Q\phi_{\sigma_3}(\vec{r}-\vec{R}_k)\phi_{\sigma_4}(\vec{r}\,'-\vec{R}_l)\,d\vec{r}\,d\vec{r}\,'\ ,$$

where Q can be either a one-particle or a two-particle operator. The one- and the two-center integrals can be calculated analytically. In this paper we are interested in the IC regime which is lower than or around the critical IC, and so the three- and the four-center integrals are less important and can be neglected.

The diagonalization of $\underline{H}_\sigma(\{n_{js}\})$ can be performed self-consistently by iteration. We first randomly choose half of the N impurity orbitals and let them being occupied by up-spin electrons and the rest half occupied by down-spin electrons. We can then construct the initial V_{cx} from such occupations and calculate Eq. (4). The $\underline{H}_\sigma(\{n_{js}\})$ is diagonalized to obtain N eigensolutions for the σ-spin electrons. At zero temperature, only the eigenstates corresponding to the lower half of the eigenenergies will be occupied. Using these new occupied eigenstates for σ-spin electrons and the old occupied states for $(-\sigma)$-spin electrons, we can construct a new V_{cx} and calculate Eq. (4). Then we diagonalize $\underline{H}_{-\sigma}(\{n_{js}\})$ to get the N eigenstates for $(-\sigma)$-spin electrons. We continue this process for the σ and $(-\sigma)$ spin alternately until we get a self-consistent solution.

To take care of the surface effect, we surround the N impurities in Ω by M random impurities but keep the IC unchanged. The effect of the M surrounding impurities on the N impurities in Ω will be approximated by an effective field, which has been explained in detail in an earlier paper.[15] We call such modified cluster the pseudocluster.

We will use a dimensionless IC defined as $P=32\pi \times(N/\Omega)a_0^3$, which has been used by many authors.[5-7,9-12] For most doped semiconductors the critical concentration P_c is around 0.8 to 0.9, for example, $P_c=0.81$ for Si:P and $P_c=0.80$ for Ge:Sb. We have set the hard-core radius $R_0=a_0$ and $M=900$, but we found that for the IC regime considered in this paper the value of R_0 is not important. In Fig. 1 we show the density of states for $P=0.6$ from two pseudocluster calculations. For histogram A we use $N=40$ and average over 50 samples, while for histogram B we use $N=50$ and average over 40

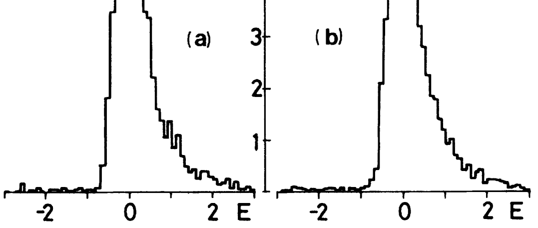

FIG. 1. Two pseudocluster results of density of states for $P=0.6$.

samples. Except for the small difference around the peaks, the two density of states curves have the same gross features. Since the computer time for B histogram is twice as much as that for A histogram, in our calculation we have chosen $N=40$ and average over 50 samples.

The effective Hartree is chosen as our energy unit measured from the bottom of the SCB. The density of states (DOS) is normalized to $\int \rho(E)\,dE = P/32\pi = (N/\Omega)a_0^3$. In Fig. 2 we show a series of DOS with increasing IC. The heavy (or thin) lined histograms correspond to the ensemble averages over the lower (or upper) halves of the energy spectra. Since there is no preferable direction for the spin, the ensemble averaged DOS curves are identical for both spins. Hence, $\rho(E)$ is defined for a single spin.

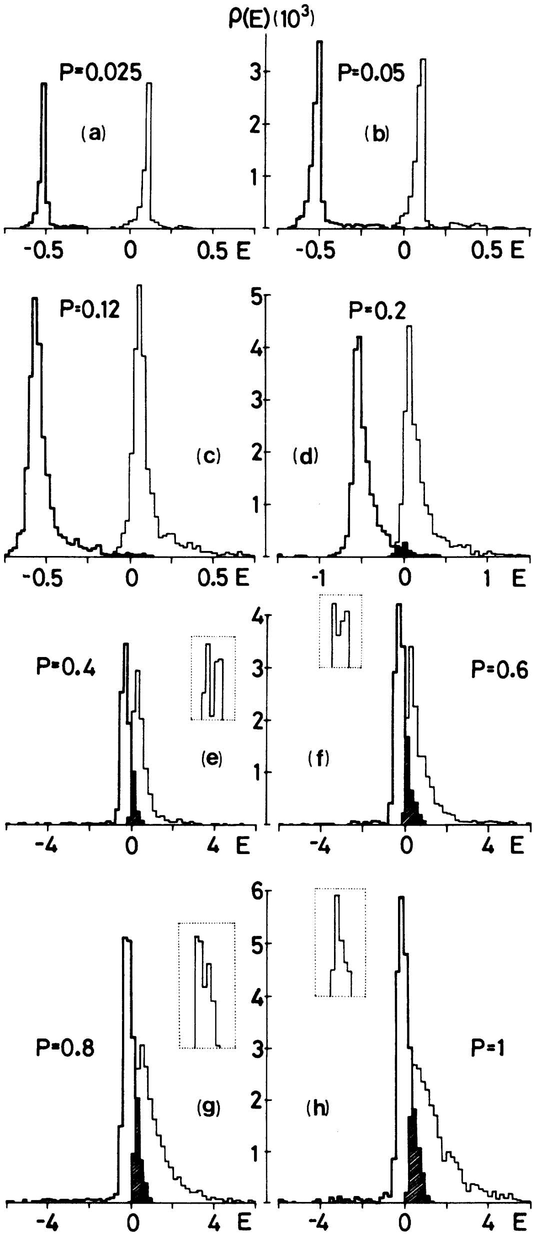

FIG. 2. Systematic change of the density of states from $P=0.025$ to 1.

At very low-impurity concentration $P=0.025$, the lower half of the energy spectrum (LHES) is completely separated from the upper half of the energy spectrum (UHES). In this case we can check the eigenfunctions. We found that the states around the center of the LHES are D^0-type localized on different impurity ions. Most of the states around the tails of the LHES are molecular-orbital type localized on close neutral impurity pairs or neutral aggregates of small number of impurities, as a result of the density fluctuation. On the other hand, the states in the UHES are either the D^- states or the molecular-orbital-type states localized on small but singly negatively charged clusters of close impurities. Consequently, we can identify the LHES as the LHB and the UHES as the UHB in the MHA model. For the ground state, up spins keep away from down spins.

This feature of localization persists with increasing IC up to $P=0.2$. In each sample there is no overlap between the LHES and the UHES, but the LHES of one sample may overlap the UHES of the other sample. If we treat each sample as a small part of a bulk material, the overlap of the band tails suggests a slight further delocalization of the states with energies in the overlap region of the LHES and the UHES. From Figs. 2(a)–2(d), we can say that the LHB and the UHB as well as the Hubbard parameter can be well defined up to $P=0.2$. Around $P=0.2$, a pseudogap begins to develop. The insets in Figs. 2(e)–2(h) are the resultant density of states near the peak region. From $P=0.2$ to 0.8, the g ratio defined by Mott[1] as a measure of the strength of the pseudogap should gradually diminish.

Suppose one state in the LHES of Fig. 2(a) is localized around $\vec{R}_i$ and is occupied by an up-spin electron. We can always find a D^- state in the UHES of Fig. 2(a) which is also localized around $\vec{R}_i$. But the possibility for such identification becomes less and less when P increases from $P=0.4$. Therefore, the definitions of the LHB and the UHB as well as the Hubbard U become more ambiguous for larger P.

Since the total number of states in the long tails of the LHES is rather small, the location of the Fermi energy does not provide much information. Let us instead define N_l (and N_u) as the total number of states in the LHES (and UHES) with positive (and negative) energies. To calculate N_u, we should note that the center of gravity of the UHES approaches 0.125 as $P \rightarrow 0$. This is because in our calculation we have used the rigid impurity orbital which is valid for neutral impurities but not for D^- configuration. The proper wave function for D^- state can be constructed with LCAO and the binding energy of D^- can be calculated as 0.0278 effective Hartree. For the IC we consider here such wave-function correction gives almost a rigid shift of the UHES by an amount of energy 0.152 to the low-energy side. With this correction we have calculated N_l and N_u, and the results are shown in Fig. 3.

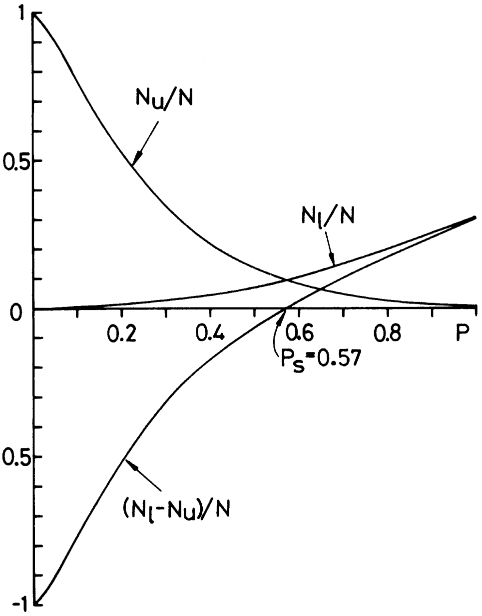

FIG. 3. Measure of the shift of density of states with P. See text for detail.

With increasing P, N_u/N drops very fast while N_l/N increases very slowly, suggesting a slow shift of the LHES to the high-energy side and a rapid moving of the UHES entirely into the SCB. For $P > P_s = 0.57$, $(N_l - N_u)/N$ increases to positive value; the SCB will then be populated and holes appear in the high-energy tail of the LHES. Since the holes in the LHES are relatively localized, they attract the electrons in the SCB to form donor excitons. With increasing P, the donor excitons will form a band and eventually merge with the SCB. In this case, the eigensolutions should be recalculated with the potential including the contribution from the donor-excitonic states. Consequently, our solution is self-consistent for $P < P_s$, and in this concentration regime it is reasonable to neglect the three- and the four-center integrals.

To summarize, we have shown that the original MHA model is valid for $P \lesssim P_s$. For $P_s \lesssim P < P_c$, the role of the UHB is taken over by the donor-excitonic states. Of course, such transformation is gradual around P_s. The so modified MHA model can still explain almost all the experimental results. Calculations of the thermodynamic properties with the pseudocluster model will be reported in the future.

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