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Hubbard model for disordered systems: Application to the specific heat of the phosphorus-doped silicon

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A self-consistent many-body theory of disordered systems, described by the Hubbard Hamiltonian with random transfer integrals, is developed. The random nature of the system is taken into account by the Matsubara-Toyozawa theory of impurities in semiconductors. By considering the hydrogenlike impurity states, the electronic specific heat of uncompensated phosphorus-doped silicon is calculated and compared with experimental results. It is found that it agrees well with experiment in the entire semiconductor–to–dilute-metallic region.

I. INTRODUCTION

Recently, considerable attention has been given to the study of doped semiconductors because they provide a good model system where both disorder and electron correlations play a role.[1] Theremodynamic and electrical properties of these systems show that the degree of interplay of electron correlations and disorder varies with the concentration of the impurities. However, the relative importance of these effects is still not fully understood.

At present, experimental results are reasonably well understood only for impurity concentrations very much smaller or very much larger than the critical concentration N_C where a semiconductor-to-metal (SM) transition occurs. For example, in the concentration region very much smaller than N_C, quantitative interpretation is possible in terms of electrons localized at the randomly distributed donor impurities. Here electron correlation plays the essential role. It is believed that it produces an antiferromagnetic exchange to make the system a prototype of an amorphous antiferromagnet. However, no evidence of antiferromagnetic ordering has been found.[2] On the other hand, at concentrations much larger than N_C, the properties of the metallic sample can be understood in terms of the rigid-band model, which assumes that the electrons occupy a slightly modified conduction band of the host.[2] However, in the case of both amorphous antiferromagnetic and metallic samples, the above-mentioned models become unsatisfactory as the concentration approaches N_C.

At intermediate concentrations, Mott[1] describes the SM transition as follows. For concentrations very much smaller than N_C, there are two separated Hubbard bands[3]: a lower band, consisting of D^0 states (related to singly occupied impurities), and an upper band, consisting of D^- states (doubly occupied impurities). The energy gap between the two bands corresponds to the intra-atomic Coulomb interaction of two electrons at the same impurity site, and the system behaves as a semiconductor. As the concentration increases, the Hubbard bands are broadened and eventually start overlapping. If the disorder due to random distribution of impurities is not sufficient to produce localized states at the bottom of the upper Hubbard band, an SM transition takes place at the concentration at which the two bands just start overlapping. On the other hand, for sufficiently strong disorder which produces localized states in the bottom of the upper Hubbard band up to a mobility edge E_C, the SM transition takes place when the Fermi energy enters the region of extended states above E_C. With further increase of concentration, the Fermi level enters the conduction band of the host and the properties of the system can be described by assuming that the electrons move in the slightly modified host conduction band. According to this picture one should expect a Friedman anomaly in the Hall coefficient, p-type thermopower on the semiconductor side of the transition, activation energy and N_C sensitive to the compensation, and very strong enhancement of the specific heat. So far, the first three effects have not been observed, and the enhancement of specific heat is observed to be quite weak. To avoid these difficulties, Mott[1] suggested that the transition is purely Anderson type[4] due to the localization of electronic states caused by disorder at the Fermi energy as N_C is approached from above. However, Economou and Antoniou[5] found that random off-diagonal disorder cannot produce localization in the middle of the band and thus raised doubts about a completely disorder-dominated transition. Thus, at least for uncompensated samples, the electron correlation and not the disorder plays a major role near the SM transition; for any theory of doped semiconductors to be valid in the whole range of concentration of impurities, both dis-

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order and electron correlation should be taken into account.

We, in this paper, present such a theory by considering that the disordered systems are described by the Hubbard Hamiltonian[3] with random transfer integral. In the past,[6] this Hamiltonian has been studied to calculate densities of states and the critical concentration using Hubbard's approximation[7] which, as shown by Edwards and Hewson,[8] suffers from the difficulty that no sharp Fermi surface exists in the metallic region of a translationally invariant system.

Fedro and Wilson[9] developed a self-consistent many-body theory for the single-particle Green's function. Here we use the generalization proposed by Kishore[10] for the many-particle Green's function to obtain the equation of motion for the single-particle Green's function. Also, we use an approximation which, in the case of translationally invariant systems, is equivalent to that of Ikeda *et al.*[11] and is free from the defects of Hubbard's approximation.[7] The configuration average of these equations is performed according to the method of Matsubara and Toyozawa.[12] By considering the hydrogenlike impurities, we calculate the specific heat of the uncompensated phosphorus-doped silicon and compare it with the experimental results of Sasaki and co-workers[13] and Marko *et al.*[2] and the theoretical calculations based on the highly correlated electron-gas (HCEG) model[14] and the alternant-molecular-orbital method in the Matsubara-Toyozawa scheme[15](AMO-MT).

In Sec. II, we describe the Hubbard Hamiltonian for the disordered systems. After giving a brief outline of the self-consistent many-body theory, equations of motion of the single-particle Green's functions are obtained and then Matsubara-Toyozawa theory is used to obtain the configurationally averaged Green's function. In Sec. III, the energy of the system and, from that, the low-temperature electronic specific heat is calculated. In Sec. IV, we discuss our numerical results for the specific heat of phosphorus-doped silicon and give concluding remarks.

II. GREEN'S-FUNCTION FORMULATION

We consider a disordered system described by the Hubbard Hamiltonian[3]

$$H=\sum_{ij\sigma} V_{ij}a^{\dagger}_{i\sigma}a_{j\sigma}+\tfrac{1}{2}U\sum_{i\sigma} n_{i\sigma}n_{i-\sigma}\,, \tag{1}$$

where $a^{\dagger}_{i\sigma}$ and $a_{i\sigma}$ are the creation and the annihilation operators of an electron of spin σ at site i, V_{ij} is the random transfer integral associated with sites i and j, U represents the intra-atomic Coulomb interaction (or correlation) energy, and $n_{i\sigma}=a^{\dagger}_{i\sigma}a_{i\sigma}$ is the number operator corresponding to site i and spin σ. We shall apply the above Hamiltonian to an n-type doped semiconductor with randomly distributed donor impurities. In this case, the summation over sites in (1) should be considered as a summation over the impurity sites. Also, we shall restrict ourselves to uncompensated samples in which V_{ii} can be considered a constant independent of the site i.[16] We shall define the energy scale such that $V_{ii}=0$. The transfer integral V_{ij} and intra-atomic interaction U will be calculated from hydrogen 1s wave functions.

The single-particle Green's function is calculated by using the self-consistent many-body theory developed by Fedro and Wilson[9] and Kishore.[10] A brief outline of the theory is given as follows. An equation of motion for the Green's function[17]

$$G_{ij}(t)=i\Theta(t)\langle[A_i,B_j(t)]_\eta\rangle\,,\quad \eta=\pm \tag{2}$$

for any two sets of Heisenberg operators A_i and B_j, obeying the condition

$$\langle[A_i,B_j]_\eta\rangle=\langle[A_i,B_j]_\eta\rangle\delta_{ij}\,, \tag{3}$$

is given as

$$-i\frac{\partial}{\partial t}G_{ij}(t)=\langle[A_i,B_i]_\eta\rangle\delta_{ij}\delta(t)+i\Theta(t)\langle[A_i,LB_j(t)]_\eta\rangle\,, \tag{4}$$

where for the Hamiltonian H and any operator χ, the Liouville operator L is defined as

$$L\chi\equiv[H,\chi]_-\,, \tag{5}$$

and the angular brackets $\langle\;\rangle$ denote the grand canonical ensemble average. Now, the operator $B_j(t)$ is broken into two parts:

$$B_j(t)\equiv PB_j(t)+(1-P)B_j(t)\,. \tag{6}$$

The projection operator P is chosen such that

$$P\equiv\sum_j P_j \tag{7}$$

and

$$P_j\chi=\frac{B_j\langle[A_j,\chi]_\eta\rangle}{\langle[A_j,B_j]_\eta\rangle}\,. \tag{8}$$

By substituting identity (6) in Eq. (4) and using the relation $\langle[\chi,LY]_\eta\rangle=-\langle[L\chi,Y]_\eta\rangle$, obtained from the cyclic invariance of the trace implied in the ensemble average, we get

$$-i\frac{\partial}{\partial t}G_{ij}(t)=\langle[A_i,B_i]_\eta\rangle\delta_{ij}\delta(t)+\sum_l\Omega_{il}G_{lj}(t)-i\Theta(t)\langle[LA_i,(1-P)B_j(t)]_\eta\rangle\,, \tag{9}$$

where

$$\Omega_{il}=\frac{\langle[A_i,LB_l]_\eta\rangle}{\langle[A_l,B_l]_\eta\rangle}\,. \tag{10}$$

From the solution of the equation of motion of the operator $(1-P)\Theta(t)B_j(t)$, it can be shown that[9,10]

$$(1-P)\Theta(t)B_j(t)=\sum_l\int_0^\infty dt\, e^{i\tau(1-P)L}(1-P)L \times\frac{B_l}{\langle[A_l,B_l]_\eta\rangle}G_{lj}(t-\tau)\,. \quad (11)$$

The substitution of Eq. (11) in Eq. (9) gives a closed equation for the Green's function,

$$-i\frac{\partial}{\partial t}G_{ij}(t)=\langle[A_i,B_i]_\eta\rangle\delta_{ij}\delta(t)+\sum_l\Omega_{il}G_{lj}(t) +\sum_l\int_{-\infty}^{\infty}dt\,\gamma_{il}(\tau)G_{lj}(t-\tau)\,, \quad (12)$$

where

$$\gamma_{il}(\tau)=\frac{-i\Theta(\tau)\langle[LA_i,e^{i\tau(1-P)L}(1-P)LB_l]_\eta\rangle}{\langle[A_l,B_l]_\eta\rangle} \quad (13)$$

Equation (12) can be easily solved by introducing the Fourier transform

$$F(t)=\frac{1}{2\pi}\int_{-\infty}^{\infty}d\omega\, e^{i\omega t}F(\omega)\,, \quad (14)$$

where F represents either G or γ. We now take the Fourier transform of (12) to find

$$\omega G_{ij}(\omega)=\langle[A_i,B_i]_\eta\rangle\delta_{ij}+\sum_l\Omega_{il}G_{lj}(\omega) +\sum_l\gamma_{il}(\omega)G_{lj}(\omega)\,, \quad (15)$$

which is the starting point of our present work. By choosing $A_i\equiv a_{i\sigma}n^{\pm}_{i-\sigma}$, where $n^{+}_{i-\sigma}\equiv n_{i-\sigma}$ and $n^{-}_{i-\sigma}\equiv 1-n_{i-\sigma}$, $B_i\equiv a^{\dagger}_{i\sigma}$, and $\eta=+$, Eq. (15) becomes

$$\omega G^{\pm}_{ij\sigma}(\omega)=n^{\pm}_{-\sigma}\delta_{ij}+\sum_l\Omega^{\pm}_{il\sigma}G_{lj\sigma}(\omega)+\sum_l\gamma^{\pm}_{il}(\omega)G_{lj\sigma}(\omega)\,, \quad (16)$$

where, for simplicity, $n^{\pm}_{-\sigma}\equiv\langle n^{\pm}_{i-\sigma}\rangle$ is assumed to be independent of the site index in spite of the randomness of the system. The functions $G^{\pm}_{ij\sigma}(\omega)$ and $\gamma^{\pm}_{ij\sigma}(\omega)$ are the Fourier transforms of

$$G^{\pm}_{ij\sigma}(t)=i\Theta(t)\langle[a_{i\sigma}n^{\pm}_{i-\sigma},a_{j\sigma}]_+\rangle \quad (17)$$

and

$$\gamma_{ij\sigma}(t)=\frac{-i\Theta(t)\langle[La_{i\sigma}n^{\pm}_{i-\sigma},e^{it(1-P^{\pm}_\sigma)L}(1-P^{\pm}_\sigma)La^{\dagger}_{j\sigma}]_+\rangle}{n^{\pm}_{-\sigma}}\,, \quad (18)$$

respectively. Also,

$$\Omega^{\pm}_{ij}=\frac{\langle[a_in^{\pm}_{i-\sigma},La^{\dagger}_{j\sigma}]_+\rangle}{n^{\pm}_{-\sigma}}\,, \quad (19)$$

and the projection operators $P^{\pm}_\sigma$ are defined as

$$P^{\pm}_\sigma\equiv\sum_j P^{\pm}_{j\sigma} \quad (20)$$

with

$$P^{\pm}_{j\sigma}\chi=\frac{a^{\dagger}_{j\sigma}\langle[a_{j\sigma}n^{\pm}_{j-\sigma},\chi]\rangle}{n^{\pm}_{-\sigma}}\,. \quad (21)$$

We are interested in the Fourier transform $G_{ij\sigma}(\omega)$ of the single-particle Green's function

$$G_{ij\sigma}(t)=i\Theta(t)\langle[a_{i\sigma},a^{\dagger}_{j\sigma}]\rangle\,, \quad (22)$$

which is the sum of the Green's functions $G^{+}_{ij\sigma}(t)$ and $G^{-}_{ij\sigma}(t)$. The Green's function $G_{ij\sigma}(\omega)=G^{+}_{ij\sigma}(\omega)+G^{-}_{ij\sigma}(\omega)$ can be calculated from the solution of the equations of motion (16). In case of a translationally invariant system, (16) can be solved by taking the Fourier transform in momentum space. This case has been considered by Kishore *et al.*[18] In disordered systems, Eq. (16) should be averaged for all the random configurations before taking the Fourier transform in momentum space. For configurational averaging, we shall use the method of Matsubara and Toyozawa.[12] Before applying their method of configurational averaging, we shall assume that $\gamma^{\pm}_{il\sigma}(\omega)=0$. Within this approximation, by substituting

$$\Omega^{\pm}_{il\sigma}=V_{il}+\tfrac{1}{2}U(1\pm1)\delta_{il} \quad (23)$$

obtained from Eq. (19) for the Hubbard Hamiltonian (1) in Eq, (16), we get

$$(\omega-\epsilon^{\pm})G^{\pm}_{ij\sigma}(\omega)=n^{\pm}_{-\sigma}\delta_{ij}=\sum_l V_{il}G^{\pm}_{lj\sigma}(\omega)\,, \quad (24)$$

where $\epsilon^{+}=U$ and $\epsilon^{-}=0$. In the case of translationally invariant systems, Eq. (24) gives the result of Ikeda *et al.*,[11] which is exact in, both atomic and band limits, and which for small U/Δ (where Δ is the bandwidth) differs from Hartree-Fock theory only by an exponentially small quantity. Also it has a sharp Fermi surface in the metallic region ($U/\Delta<1$) and thus removes the difficulties of the Hubbard approximation.[7,8] For $U/\Delta>1$, it gives two separated Hubbard bands with local moment formation. The effects of $\gamma_{ij\sigma}(\omega)$ have been considered by Kishore *et al.*[18] It was found that for $U/\Delta>1$, $\gamma^{\pm}_{ij\sigma}(\omega)$ gives spin-dependent shifting and narrowing of the bands. These effects make the ferromagnetic state more stable compared to the paramagnetic state. We hope that for our paramagnetic system these effects will not alter the results very much.

Now we expand the Green's function $G^{\pm}_{ij\sigma}(\omega)$ in Eq. (24) in powers of $1/(\omega-\epsilon)$ by making use of an iteration procedure and get

$$G^{\pm}_{ij\sigma}(\omega)=\frac{n^{\pm}_{-\sigma}}{\omega-\epsilon^{\pm}}\left(\delta_{ij}+\frac{V_{ij}}{\omega-\epsilon^{\pm}}+\frac{\sum_l V_{il}V_{lj}}{(\omega-\epsilon^{\pm})^2}+\cdots\right)\,. \quad (25)$$

The configurationally averaged Green's function $\langle G^{\pm}_{ij\sigma}(\omega)\rangle_{\rm av}$ can be obtained by just taking the configurational average of the right-hand side of

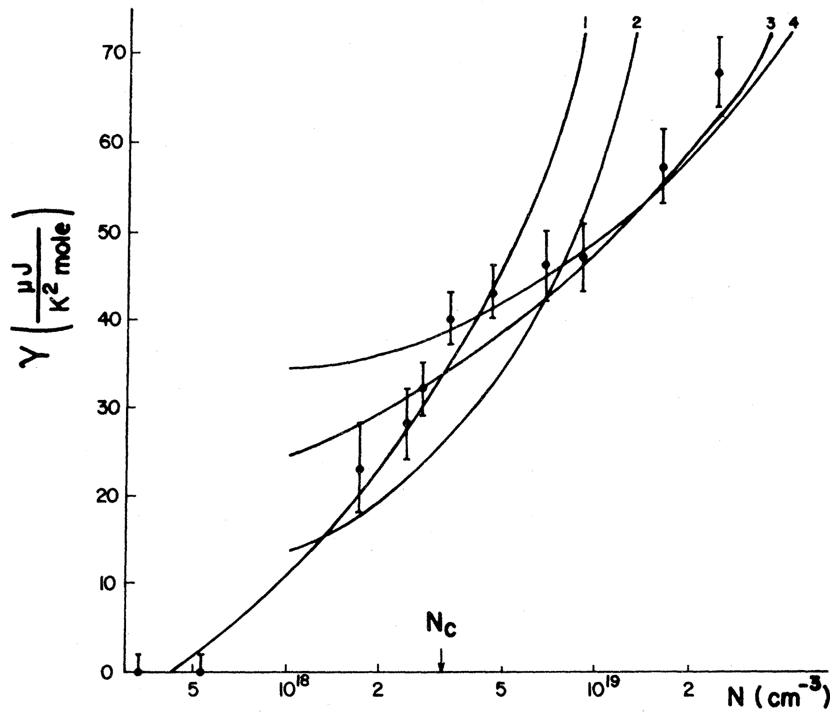

FIG. 1. Electronic specific-heat coefficient γ for Si:P as a function of the impurity concentration N. Curve 1 is the present calculation. Curve 2 (Ref. 15) is the AMO-MT calculation. Curves 3 and 4 (Ref. 14) are the results from the highly correlated electron-gas model. The dots with error bars are the experimental data measured by Sasaki and co-workers (Ref. 13). N_c indicates the impurity critical concentration.

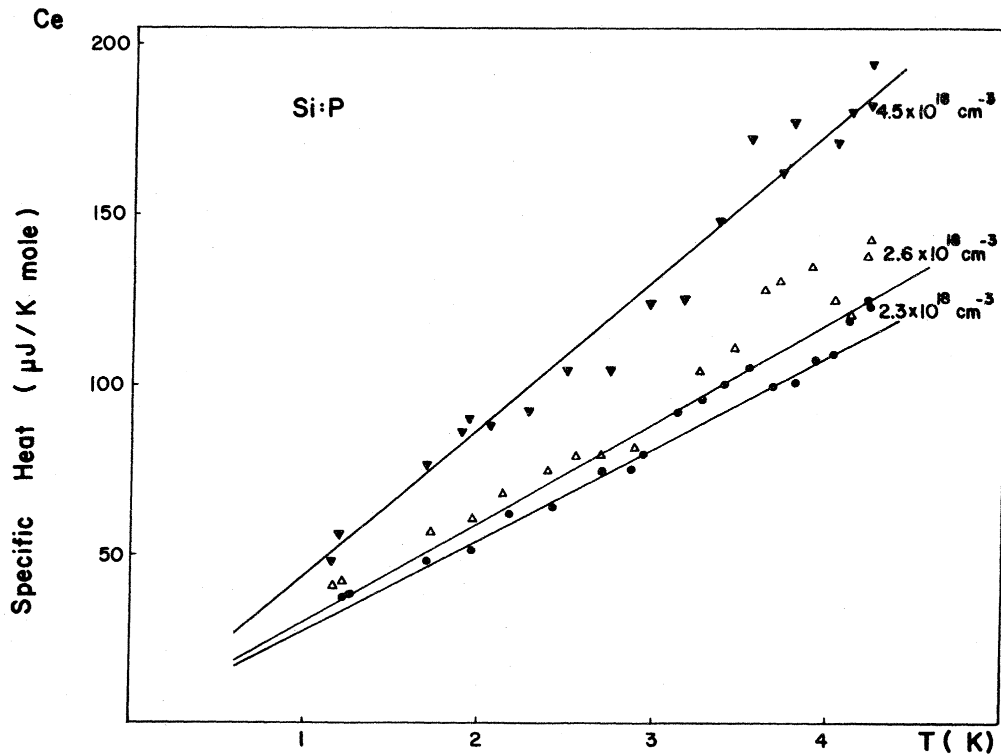

FIG. 2. Electronic specific heat of Si:P in units of μJ/K mole as a function of temperature for various impurity concentration indicated by the numbers. Solid curves refer to the present calculation. Open triangles, solid triangles, and solid circles are the experimental data of W. Sasaki and co-workers (Ref. 13).

(25) over the random distribution of the transfer integral. For this, we use the diagramatic summation method of Matsubara and Toyozawa[12] and obtain the configurationally averaged diagonal Green's functions (here, $\langle\,\rangle_{av}$ denotes configurational average)

$$\langle G^{\pm}_{ii\sigma}(\omega)\rangle_{av} = \frac{n^{\pm}_{-\sigma}}{\omega - \epsilon^{\pm}}\zeta(\omega - \epsilon^{\pm}), \tag{26}$$

where

$$\zeta(\omega) = \frac{1}{1-\eta(\omega)}, \tag{27}$$

and

$$\eta(\omega) = \frac{N\zeta(\omega)}{8\pi^3\omega^2}\int \frac{V^2(\vec{k})d\vec{k}}{1-[N\zeta(\omega)/\omega^2]V(\vec{k})}. \tag{28}$$

N is the number of the impurity sites per unit volume and

$$V(\vec{k}) = \int V(\vec{R})e^{i\vec{k}\cdot\vec{R}}d\vec{R} \tag{29}$$

is the Fourier transform of

$$V_{ij} = -V_0(1+\alpha|\vec{R}_i - \vec{R}_j|)e^{-\alpha|\vec{R}_i-\vec{R}_j|} = V(|\vec{R}_i - \vec{R}_j|). \tag{30}$$

Equation (30) is obtained from the hydrogenlike $1s$ wave functions. Here, V_0 is equal to twice the ionization energy of the $1s$ state and α^{-1} the radius of the $1s$ orbit. The Matsubara-Toyozawa method[12] can also be applied to calculate the configurational average of the off-diagonal elements of the Green's functions. However, for our purpose, we shall require only the diagonal element.

III. SPECIFIC HEAT

The calculation of the specific heat requires the energy of the system, which can be expressed in terms of the single-particle Green's function for the system described by the Hubbard Hamiltonian (1). The energy of the system is given as[19]

$$E = \langle H\rangle = -\frac{1}{2\pi}\lim_{\epsilon\to 0^+}\sum_{ij\sigma}\int_{-\infty}^{\infty}(\omega\delta_{ij}+V_{ij}) \times\{\mathrm{Im}[G_{ji\sigma}(\omega+i\epsilon)]\}f(\omega)d\omega \tag{31}$$

where $f(\omega)$ is the Fermi distribution function

$$f(\omega) = \frac{1}{e^{\beta(\omega-\epsilon_F)}+1}, \tag{32}$$

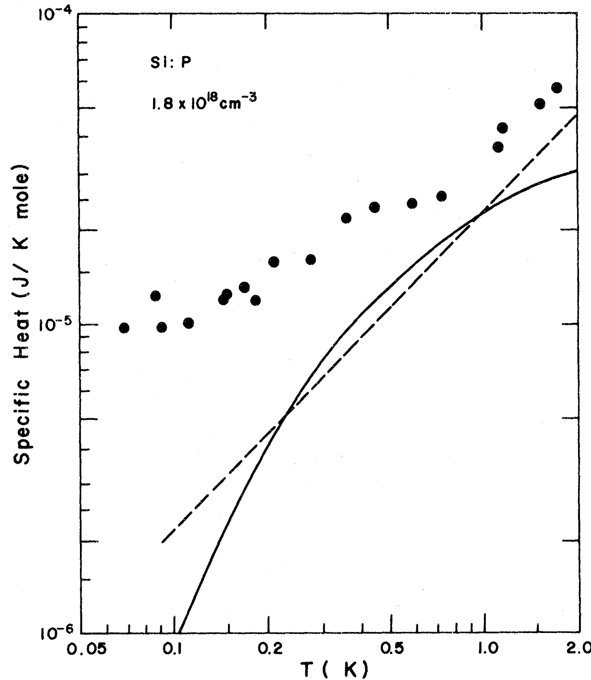

FIG. 3. Electronic specific heat of Si:P in units of J/K mole as a function of temperature for impurity concentration 1.8×10^{18} cm^{-3}. Dashed line refers to the present calculation. Solid line refers to the inhomogeneity model by Marko *et al.* (Ref. 2). Solid circles correspond to the experimental data by Marko *et al.* (Ref. 2).

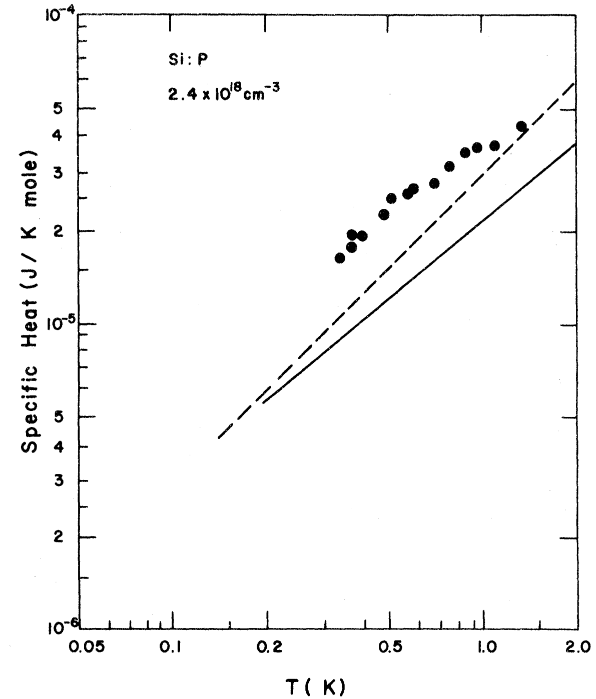

FIG. 4. Electronic specific heat of Si:P as a function of temperature for impurity concentration 2.4×10^{18} cm^{-3}. Dashed line is the present calculation. Solid line is the inhomogeneity model and solid circles are experimental data from Marko *et al.* (Ref. 2).

ϵ_F denotes the Fermi energy, and $\beta = 1/kT$. Equation (31) can be expressed solely in terms of the diagonal Green's function by using Eq. (24), which gives

$$(\omega - \epsilon^{\pm}) \,\mathrm{Im}[G^{\pm}_{ii\sigma}(\omega + i\epsilon)] = \sum_j V_{ij} \,\mathrm{Im}[G^{\pm}_{ji\sigma}(\omega + i\epsilon)] . \quad (33)$$

By substituting Eq. (33) in Eq. (31), we get

$$E = -\frac{1}{2\pi} \lim_{\epsilon \to 0+} \sum_{i\sigma} \int_{-\infty}^{\infty} (2\omega - \epsilon^{\pm}) \{\mathrm{Im}[G^{\pm}_{ii\sigma}(\omega + i\epsilon)]\} f(\omega) d\omega \quad (34)$$

Since we are dealing with a disordered system, Eq. (34) must be averaged over all the random configurations. The configurational average of (34) gives us

$$\overline{E} = -\frac{N}{\pi} \lim_{\epsilon \to 0+} \sum_{p\sigma} \int_{-\infty}^{\infty} (\omega - \tfrac{1}{2}\epsilon^{p}) [\mathrm{Im}\,\langle G^{p}_{ii\sigma}(\omega + i\epsilon)\rangle_{\mathrm{av}}] f(\omega) d\omega , \quad (35)$$

where $p = \pm$. Equation (35) can be rewritten in terms of the density of states defined as

$$D(\omega) = \sum_p D^p(\omega) , \quad (36)$$

with

$$D^p(\omega) = -\frac{N}{\pi} \lim_{\epsilon \to 0+} \sum_{\sigma} \mathrm{Im}\,\langle G^{p}_{ii\sigma}(\omega + \epsilon i)\rangle_{\mathrm{av}} , \quad (37)$$

and $D^{+}(\omega)$ and $D^{-}(\omega)$ correspond to the density of states of the upper and the lower Hubbard bands,

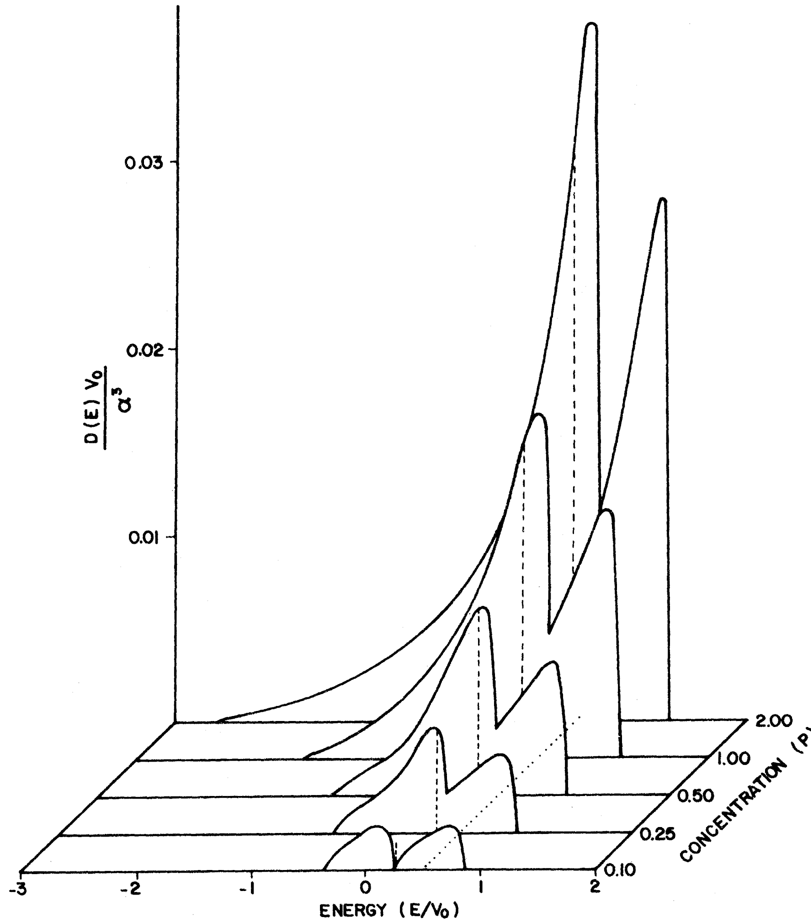

FIG. 5. Density of states of impurity Hubbard bands for various values of the normalized impurity concentration $P = 32\pi N a_0^3$. N is the true impurity concentration and a_0 (α^{-1}) is the Bohr radius of the impurity. The position of the Fermi energy is indicated by dashed lines and the bottom of the host conduction band by a dotted line.

respectively. From Eqs. (36) and (37), Eq. (35) becomes

$$\overline{E}=\int_{-\infty}^{\infty}[\omega D(\omega)-\tfrac{1}{2}U D^{+}(\omega)]f(\omega)d\omega . \quad (38)$$

Because of the Fermi distribution function $f(\omega)$ in (38), the energy of the system E is a temperature-dependent quantity. At low temperatures, we can express it in powers of temperature. This is done by using the low-temperature expansion, for any arbitrary function $F(\omega)$,[20]

$$\int_{-\infty}^{\infty}F(\omega)f(\omega)d\omega=\int_{-\infty}^{\epsilon_F}F(\omega)d\omega+\tfrac{1}{6}(\pi kT)^2\left(F'(\epsilon_F)-F(\epsilon_F)\frac{D'(\epsilon_F)}{D(\epsilon_F)}\right)+\cdots . \quad (39)$$

Here, ϵ_F is the Fermi energy at $T=0$, and

$$F'(\epsilon_F)=\frac{dF(\omega)}{d\omega}\bigg|_{\omega=\epsilon_F}, \quad (40)$$

and

$$D'(\epsilon_F)=\frac{dD(\omega)}{d\omega}\bigg|_{\omega=\epsilon_F}.$$

By taking $F(\omega)=\omega D(\omega)-\frac{1}{2}UD^{+}(\omega)$, Eq. (39) gives

$$\overline{E}=\int_{-\infty}^{\epsilon}[\omega D(\omega)-\tfrac{1}{2}UD^{+}(\omega)]d\omega+\tfrac{1}{6}(\pi kT)^2\left[D(\epsilon_F)-\tfrac{1}{2}U\left(D^{+}(\epsilon_F)-\frac{D^{+}(\epsilon_F)D'(\epsilon_F)}{D(\epsilon_F)}\right)\right], \quad (41)$$

which on differentiating with respect to T gives the low-temperature specific heat

$$C_v=\frac{d\overline{E}}{dT}=\gamma T \quad (42)$$

with

$$\gamma=\tfrac{1}{3}\pi^2k^2\left[D(\epsilon_F)-\tfrac{1}{2}U\left(D^{+}(\epsilon_F)-\frac{D^{+}(\epsilon_F)D'(\epsilon_F)}{D(\epsilon_F)}\right)\right]. \quad (43)$$

Thus, the calculation of the specific heat requires the total and the upper Hubbard band densities of states and their derivatives at the Fermi energy ϵ_F, which can be calculated from the formula

$$nN=\int_{-\infty}^{\epsilon_F}D(\omega)d\omega , \quad (44)$$

where $n=\sum_{p\sigma}n_\sigma^p$ is the total number of electrons per impurity. In the next section we shall discuss the results of numerical calculation of specific heat of uncompensated phosphorus-doped silicon using Eq. (42) together with Eqs. (43), (37), (36), and (26)–(30).

IV. RESULTS AND DISCUSSIONS

In Fig. 1 we have plotted our numerical result for γ, curve 1, as a function of donor impurity concentration N for uncompensated phosphorus-

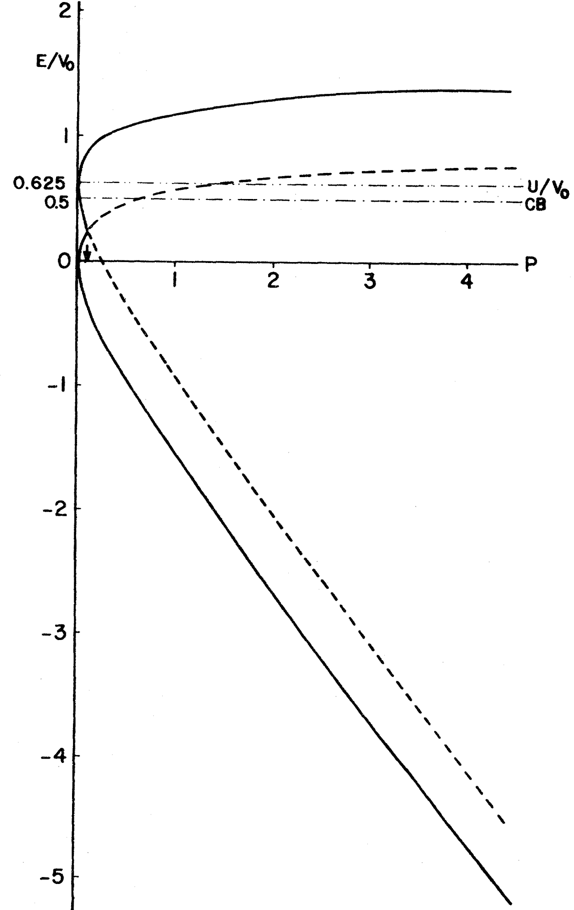

FIG. 6. Top and bottom edges of the impurity Hubbard band as a function of the impurity concentration P. CB is the bottom of the conduction band at $E/V_0=0.5$. U/V_0 is the intra-atomic correlation energy equal to 0.625. The arrow indicates the concentration where the bands start overlapping.

doped silicon. The experimental critical concentration N_c, at which SM transition occurs, is also shown. The experimental results of Sasaki and co-workers[13] are shown as dots with error bars. We see very good agreement between our calculation and experiment over the entire semiconductor–to–dilute-metallic region ($N < 5 \times 10^{18}$ cm^{-3}). We have also shown the results of calculation based on the HCEG model of Berggren and Sernelius[14] as curves 3 and 4 and the AMO-MT method of Chao and Ferreira da Silva[15] as curve 2. Although the HCEG model, based on the electron-hole droplet model[21] with immobile impurity ions playing the role of the mobile holes, gives good agreement with experiment in the metallic region $N > N_c$, it fails completely in the semiconductor region $N < N_c$. On the other hand, the AMO-MT method, which takes into account the correlation effects in Matsubara-Toyozawa[12] theory, gives only rough agreement in the intermediate region ($N \sim N_c$). In Figs. 2–4 we have plotted the specific heat C_v as a function of temperature for various concentrations of donor impurity along with the experimental results of Sasaki and co-workers[13] and Marko *et al.*[2] and calculations based on the inhomogeneous model.[2] It should be noted that our results agree fairly well with experiment and are better than those of inhomogeneous model.[2]

The shape of the density of states and the position of the Fermi level are shown in Fig. 5 for various concentrations of donor impurities. In Fig. 6 the behavior of the top and the bottom edges of the Hubbard bands is shown. These figures show that the Hubbard bands start overlapping at a concentration much less than the critical concentration N_c. This shows that the electronic states near the bottom of the upper Hubbard band should be localized so that the SM transition can occur when the Fermi level crosses the mobility edge, separating the regions of localized and extended states. The localization of the electronic states near the bottom of the upper Hubbard band has been shown by Aoki and Kamimura.[6] Thus, our theory supports Mott's description of SM transition in doped semiconductors as described in Sec. I. It should be noted that the density of states in both Hubbard bands is tailed on the low-energy side. It has been shown by Aoki and Kamimura[6] that the consideration of resonance broadening (dynamical motion of the electrons with spin), neglected by us, can give tailing in both low- and high-energy sides of the Hubbard bands. Recently, Ferreira da Silva *et al.*[22] have shown that impurity-impurity correlations can also produce this high-energy tailing.

In our theory, we have not taken into account the presence of the host conduction band which, we think, is necessary to get agreement with experiment in the metallic region ($N > 5 \times 10^{18}$ cm^{-3}). Nonorthogonality corrections, resulting from the nonorthogonal nature of the 1s wave functions, should also be incorporated in the theory. At present, we are studying these effects. To give further support to our theory, we shall also calculate the conductivity and the susceptibility. The present theory can be improved by considering also resonance-broadening corrections and impurity-impurity correlation.

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