INFLUENCE OF VALLEY-SPLITTING IN THE SPECIFIC HEAT OF Si:P

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We report a calculation of the electronic specific heat near 0 K for the Si:P system, taking into account the characteristic valley-splitting of the impurity levels near the conduction band minima. This effect is shown to describe properly the deviations from the free-electron model around the metal-to-nonmetal transition. This is a strong argument towards the picture of an Anderson-type (disorder-dominated) transition in indirect gap semiconductors. Our results account very well for the experimental findings.

IT IS WELL known that thermodynamic and electrical properties of doped semiconductors exhibit characteristic features due to electron correlation and disorder effects. The degree of interplay between them varies with the impurity concentration N_D [1, 2]. The influence of the host characteristics, such as the existence of many equivalent conduction band minima at $\mathbf{k} \neq 0$, is also believed to be of central importance in the behavior of the physical properties and has been the subject of many recent investigations [1, 3]. This inference applies to indirect-gap semiconductors (e.g. Si and Ge). However, the relative importance of all these effects is still not completely understood [1, 9]. Within the effective-mass approximation for shallow donor states in silicon, the $1s$ state is sixfold degenerate (excluding spin degeneracy) [10]. Infrared absorption experiments [11] indicate that this degeneracy is lifted, with the $1s(A_1)$ forming the ground-state and the $1s(E)$ lying slightly above the $1s(T_2)$. One then may speculate about the role of this splitting in Si:P in the way of Kohn–Luttinger (KL) scheme [10], i.e., considering the lowest energy level set at 44 meV separated by a 5 degenerated energy level at 32 meV, giving a split of $\Delta = 12$ meV. The impurity band being considered as formed from these levels will give the information we are looking for. Traces of such splitting remain in Si:P all the way up to metal–nonmetal (MNM) transition where they fade away [9]. Too little attention has been given to such effects in

connection with e.g., calculation of specific heat in n-doped Si. Kamimura [3] and Takemori and Kamimura [5] with a Gaussian model calculated the susceptibility and the specific heat reproducing fairly well the characteristic features observed in experiments in Si:P for 1.7×10^{18} cm^{-3}. For the specific heat they have taken into account the many-valley effects by multiplying by a factor of 6, in the final results, corresponding to the degeneracy. Franzèn and Berggren [6], with their calculations based on random cluster, account well for the observed susceptibility and specific heat in the low concentration region, well below the critical concentration N_C for MNM Transition in Si:P. They have used, for the exchange interaction, a many-valley KL wave function. Specific heat has been also calculated with a correlated electron–gas model by Berggren and Sernelius and Berggren [12]. This model is valid only in the metallic region, and gives a good agreement with experiment for $N_D > N_C$.

In d.c. conductivity one observes a dramatic drop at the MNM transition [23]. In the susceptibility there is neither a sharp jump nor even a sharp change at N_C [2]. That feature is also a characteristic of the specific heat. The thermodynamic density of states at the Fermi energy E_F suffers no dramatic change, whatsoever, and obviously continues finite for a large range of impurity concentration below N_C [14].

Searching for a mechanism which would enable us to take into account the disorder and the degeneracy

of the indirect-gap semiconductors and its influence on the impurity states in a large range of n-type doping regime, namely Si:P, we report here our recent calculation of the electronic specific heat γ based on the enhancement density of states, and compare it with the experimental data.

For doped semiconductors with monovalent impurities, the one-electron Hamiltonian for a given impurity configuration is expressed as

$$H = -\frac{\hbar^2}{2m}\nabla^2 + V_c(\mathbf{r}) + \sum_l V(\mathbf{r} - \mathbf{R}_l), \qquad (1)$$

where m is the electron mass, $V_c(\mathbf{r})$ is the potential to which an electron in the host conduction band is subjected and $V(\mathbf{r} - \mathbf{R}_l)$ is the attractive potential due to an impurity located in the position $\mathbf{R}_l$. The corresponding one-electron Green function is defined by

$$(E - H)G(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r}, \mathbf{r}'). \qquad (2)$$

Let us suppose that F^0 and F^1 respesent, respectively, the ground state and the first excited level of an isolated impurity atom. Then, in a tight binding scheme and neglecting the hibridization between the two levels, the matrix elements of the Green function obey the following equations

$$(E - E_0^0)G_{mn}^{00} = \delta_{mn} + \sum_l V_{ml}^{00} G_{ln}^{00} \qquad (3)$$

$$(E - E_0^1)G_{mn}^{11} = \delta_{mn} + \sum_l V_{ml}^{11} G_{ln}^{11} \qquad (4)$$

where E_0^0 is the energy of the ground state, E_0^1 is the energy of the excited level and

$$\begin{aligned} V_{ml}^{\gamma\gamma} &= V^{\gamma\gamma}(\mathbf{R}_{ml}) \\ &= \int F^\gamma(\mathbf{r} - \mathbf{R}_m)\, V(\mathbf{r} - \mathbf{R}_m)\, F^\gamma(\mathbf{r} - \mathbf{R}_l)\, d\mathbf{r}, \end{aligned}$$
$$\gamma = 0, 1 \qquad (5)$$

are the hopping matrix elements. In the derivation of the above equations we have neglected the three-centre integrals as well as the ionic terms. By applying the well-known Matsubara–Toyosawa diagrammatic method [8, 15] we obtain

$$E - E_0^0 - \frac{1}{\overline{G^0}} = \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{T_0(\mathbf{k})}{1 - N_D \overline{G^0}\, T_0(\mathbf{k})} - V^{00}(0), \qquad (6)$$

where $\overline{G^0}$ is the configurational average of the diagonal Green function matrix element G_{ii}^{00}, N_D is the number of impurity sites per unit volume and

$$T_0(\mathbf{k}) = \int V_{il}^{00}\, e^{-i\mathbf{k}\cdot\mathbf{R}_i}\, d_{\mathbf{R}_{il}} \qquad (7)$$

is the Fourier transform of the hopping matrix. Since the system is assumed to be statistically homogeneous $\overline{G_{ii}^{00}}$ is independent of i. Similar equations hold for $\overline{G^1}$.

For the representation of the two levels F^0 and F^1 we first examine the six KL wavefunctions given by [10]

$$F^{(i)}(\mathbf{r}) = \sum_\beta c_\beta^{(i)} \phi_\beta^{(i)}(\mathbf{r}) \psi_\beta(\mathbf{r}), \qquad (8)$$

where $\psi_\beta(\mathbf{r})$ is the Bloch function at the β-th conduction-band minimum, $\phi^{(i)}(\mathbf{r})$ is the envelope function which satisfies the effective-mass Schrodinger equation and the coefficients $C_\beta^{(i)}$ are given by

$$C^1: 1/\sqrt{6}\,(1, 1, 1, 1, 1, 1) \qquad (A_1) \qquad (9.1)$$

$$C^2: 1/2\;\;(1, 1, -1, -1, 0, 0) \qquad (9.2)$$

$$C^3: 1/\sqrt{2}\,(1, 1, 0, 0, -1, -1) \qquad (E)$$

$$C^4: 1/\sqrt{2}\,(1, -1, 0, 0, 0, 0) \qquad \cdot$$

$$C^5: 1/\sqrt{2}\,(0, 0, 1, -1, 0, 0) \qquad (T_1) \qquad \cdot$$

$$C^6: 1/\sqrt{2}\,(0, 0, 0, 0, 1, -1) \qquad (9.6)$$

The main effect of intervalley scattering is to lift the six-fold degeneracy of the above levels, so that the ground state (symmetry A_1) is non-degenerated at $E_0^0 = 44\,\text{meV}$ below the conduction-band (CB) unperturbed minimum and the excited level is very nearly five-fold degenerated, $\Delta = 12\,\text{meV}$ above E_0^0 ($E_0^1 = \Delta + E_0^0$). For the ground-state wavefunction we take, neglecting the anisotropy of the CB minima,

$$F^1(\mathbf{r}) = \sum_\beta C_\beta^1 \phi_\beta^1(\mathbf{r}) \psi_b(\mathbf{r}), \qquad (10)$$

with

$$\phi_\beta^1(\mathbf{r}) = (\alpha^3/\pi)^{1/2} \cdot \exp(-\alpha r). \qquad (11)$$

The excited level is handled in an approximative way: we consider the level E_0^1 as being described by only one eigenfunction, which is taken as a suitable linear combination of the five states (9.2) to (9.6), disregarding differences in the various envelope functions:

$$F^{(2)}(\mathbf{r}) = \sum_\beta \overline{C_\beta^2}\, \phi_\beta^2(\mathbf{r}) \psi_\beta(\mathbf{r}), \qquad (12)$$

$$\overline{C_\beta^2}: 1/\sqrt{6}\,(1, -1, 1, -1, 1, -1). \qquad (13)$$

The five-fold degeneracy of E_0^1 is taken into account a posteriori by simply multiplying the DOS obtained with (12), (13) by a factor of 5. The envelope function $\phi_\beta^2(\mathbf{r})$ is also taken to be the same as $\phi_\beta^1(\mathbf{r})$; in this manner, the impurity band originated from E_0^1 in the tight-binding model is exactly the same as the one originated from E_0^0, apart from a multiplicative factor (it is easy to see that the hopping matrix elements V_{ml}^{11} are equal to V_{ml}^{00} in this approximation). Further comments about these simplifications and the neglecting of hybridization terms will be done subsequently.

Now equation (7) yields

$$\frac{\alpha^3 T_0(\mathbf{k})}{2E_0^0} = -\frac{32\pi}{6} \sum_l \frac{1}{\left(1 + \left(\frac{\mathbf{k} - \mathbf{k}_l}{\alpha}\right)^2\right)^3} \qquad (14)$$

where $\mathbf{k}_l$ is the wave-vector associated to minimum l. Taking into account equation (14), equation (6) can be approximated to [8]

$$E - E_0^0 - \frac{1}{\overline{G^0}} = 6 \int \frac{d\mathbf{k}}{(2\pi)^3} \frac{T_0^*(\mathbf{k})}{1 - N_D \overline{G^0} T_0^*(\mathbf{k})} - V^{00}(0), \qquad (15)$$

where

$$T_0^*(\mathbf{k}) = -\frac{32\pi}{6} \frac{1}{(1 + k^2)^3}. \qquad (16)$$

Solving equation (15) for $\overline{G^0}$ and the corresponding one for $\overline{G^1}$ we obtain the configuration averaged density of states per particle as

$$D(E) = -\frac{1}{\pi} I_m(\overline{G^0} + \lambda \overline{G^1}). \qquad (17)$$

The factor $\lambda = 5$ in the above equation is due to the fivefold degeneracy of level 1.

Using the Sommerfeld expansion the specific heat at low temperatures can be shown to be expressed by
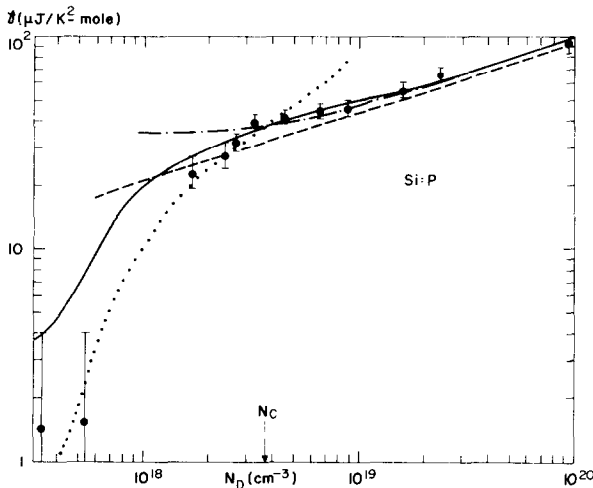
$$C_V = \gamma T \qquad (18)$$

where

$$\gamma = \frac{\pi^2}{3} k_B^2 N_D D(E_F), \qquad (19)$$

k_B is the Boltzmann constant and E_F is the Fermi energy, defined by

$$\int_{-\infty}^{E_F} 2D(E) = 1, \qquad (20)$$

where the factor 2 is due to spin degeneracy.

The experimental data, full circles with error bars, for Si : P by Sasaki and co-workers [14], are shown in Fig. 1 with our results (solid line). It is seen that γ gradually decreases with decreasing phosphorus concentration N_D from the metallic region somewhere around $N_c = 3.7 \times 10^{18}\,\text{cm}^{-3}$ [13]. Below N_c it drops rapidly, remaining finite down to $N_D = 4 \times 10^{17}\,\text{cm}^{-3}$ where E_F lies in a continuum of localized states. At concentrations somewhat around N_c the experimental values as well as our results lie around 10–30 percent higher than the dashed line; this line represents the values for the undisturbed conduction band (free electron model) with the effective-mass density of states and the valley degeneracy of pure Si. For comparison, we also show in Fig. 1 the results obtained by the correlated electron-gas model [12] and the calculations we did with valley-splitting neglected at all ($\Delta = 0$).

The relative small enhancement of γ above the dashed line suggests, furthermore, the influence of the energy-splitting in the impurity states. In Fig. 2 we can see clearly the behaviour of the impurity density of states $D(E)$ due to such splitting, for various values of N_D.

It is to be noted that the good experimental agreement obtained by the present model indicates that intervalley scattering effects are important up to high concentrations, but disorder effects can give rise to impurity bands which dictate the behaviour of E_F (the Fermi energy) versus N (the impurity concentration). In fact, intervalley terms are essential to maintain the level splitting at such high concentrations; at the same time, these terms have minor influence on the diagonal elements of the Matsubara–Toyozawa's Green function when Kohn–Luttinger wavefunctions are considered [8]. These facts are in perfect accordance with the apparent contradictory findings of Selloni and Pantelides [16] and Berggren and Sernelius [17].

Some comments about the approximations here employed are in order. The first remark concerns the neglecting of hybridization terms in equation (3); this is likely to imply some quantitative corrections in the position of the Fermi energy E_F and therefore in the value of γ around N_c. We see no serious reason to

Fig. 1. Electronic specific-heat coefficient γ for Si : P as a function of the impurity concentration N_D. Full circles with error bars are the experimental data measured by Sasaki and co-workers [14]. Solid line is the present calculation. Dashed line (– – –) is the undisturbed conduction-band of Si. Dotted line ($\cdots$) is the calculation neglecting valley-splitting ($\Delta = 0$). Dot-dashed line (–·–·–·–) is the result of the correlated electron–gas model [12], valid for $N > N_c$. N_c is the critical concentration.
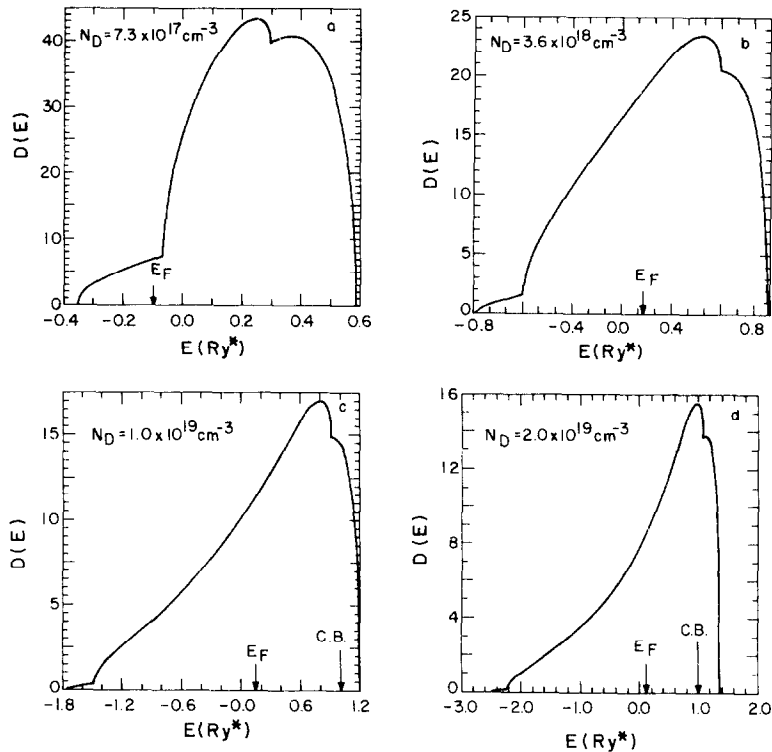
Fig. 2. (a) Impurity density of states $D(E)$, of Si : P for $N_D = 7.3 \times 10^{17}$ cm^{-3}. E_F is the Fermi energy. The bottom of the conduction band is set at $1R_\Gamma^* = 44$ meV. The lowest energy state is set at the origin. (b) Impurity density of states for $N_D = 3.6 \times 10^{18}$ cm^{-3}. (c) Impurity density of states for $N_D = 1.0 \times 10^{19}$ cm^{-3}. C.B. is the conduction band. (d) Impurity density of states for $N_D = 2.0 \times 10^{19}$ cm^{-3}.

believe in any qualitative change this approximation might cause in the behaviour of $\gamma \times N$; the state of affairs is such that the same imprecision is caused by the lack of an exact value for a_0^*, the effective Bohr radius to be used at N_c. Some details of the DOS are of course sensible to such simplification: for example, the singular (non-differenciable) points seen in Fig. 2 should disappear in a more precise calculation. Overlap corrections in the matrix elements, equation (3), were also neglected. There are a lot of reasons to suspect that overlap corrections to the 1s basis (equation (10)), when applied to the simple one-electron Hamiltonian (equation (1)), does not give physical meaningful results [18]; but here it suffices to mention that such corrections are small when applied to the Kohn–Luttinger basis [8].

Our assumption of an impurity band without electron correlation fits the data equally well in a large range of concentration, suggesting the central role of the energy splitting due to the valley degeneracy in the investigation of the thermodynamic and transport properties of indirect-gap doped semiconductors.

It is to be noted that a very distinct picture is expected for the behaviour $\gamma \times N_D$ when the host is a direct-gap semiconductor. In this case, one should rather expect a true Mott transition around N_c, the Fermi energy lying in a Coulomb gap for $N_D < N_c$. Measurements of C_v at low temperatures for heavily doped n-type direct-gap semiconductors (such as CdS : Cl) would elucidate this point.

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