Thermodynamic properties of impurity band electrons

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The electronic specific heat $c_v(T)$ of a lightly doped compensated semiconductor is computed in a broad range of temperatures with the aid of the method of Monte Carlo computer simulation of the impurity band. The results of the simulation of the three-dimensional system confirm the existence in the function c_v/T of the low-temperature dip that was predicted earlier on the basis of a self-consistent equation for the density of dipole-excitation states. Somewhat unexpected is the discovery of a similar dip in the case of the two-dimensional system, for which the self-consistent-equation method does not reveal any low-energy anomalies in the density of states of the excitations determining the specific heat. New data pertaining to the properties of the ground state of the system in question are obtained incidentally.

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1. INTRODUCTION

We consider the so-called "classical" impurity band in a semiconductor, when the impurity concentration is so low that we can neglect the quantum overlap of the wave functions of neighboring impurities. The semiconductor is assumed to be compensated, i.e., to contain donor and acceptor impurities. For definiteness, we assume that the donor concentration N_D is higher than the acceptor concentration N_A. At low temperatures all the acceptors are negatively charged, some of the donors, with concentration N_D-N_A, are neutral, and the rest, with concentration N_A, are ionized and positively charged. The spread of the electron levels on the donors is established by the random Coulomb potentials of the charged impurities, the relative positions of the neutral and charged donors being found at low temperatures to be strongly correlated. It is this correlation that determines the low-temperature thermodynamic and kinetic properties of the system.

The energy of the system has the form

$$H=\frac{e^2}{\varkappa}\left[\frac{1}{2}\sum_{i\neq j}\frac{(1-n_i)(1-n_j)}{r_{ij}}-\sum_{i,\nu}\frac{1-n_i}{r_{i\nu}}+\frac{1}{2}\sum_{\nu\neq\mu}\frac{1}{r_{\nu\mu}}\right]. \tag{1}$$

The subscripts i and j label the donors, while the subscripts ν and μ label the acceptors; the $\mathbf{r}_i$ and $\mathbf{r}_\mu$ are the coordinates of the donors and acceptors, with $r_{ij}=|\mathbf{r}_i-\mathbf{r}_j|$; and the n_i are the occupation numbers for the donors: $n_i=1$ if the donor is neutral and $n_i=0$ if the donor is ionized. The electron charge is denoted by e; the permittivity, by $\varkappa$.

In its thermodynamic properties the impurity band resembles the Ising model with a random magnetic field. An important difference consists in the fact that in the case of the impurity band $\Sigma_i n_i$ is the total number of electrons in the band, and is a prescribed quantity, determined by the degree of compensation. In the Ising model this quantity is the system's total spin, which is uniquely determined by the temperature. Another important difference consists in the fact that the interaction of the charges in the impurity band has a Coulomb, and not a short-range, character.

As shown in Ref. 1, at low temperatures the dominant contribution to the thermodynamics of the system should be made by the electron transitions between pairs of donors located close to each other. If the temperature of the system is low, then these pairs are located far apart in space, and the interaction between them has a dipole-dipole character. This interaction leads to a situation in which the density $\Phi(\omega)$ of states of the pairs with low energy (i.e., of the soft pairs) has a logarithmic singularity at low excitation-energy values. (The same conclusion has been arrived at independently by Fisch.[2])

On the basis of this, it is concluded in Ref. 1 that there exists a logarithmic singularity in the specific heat of the impurity-band electrons. According to Ref. 1,

$$c_v\sim T/|\ln T|^{1/2}. \tag{2}$$

This result pertains only to a three-dimensional system. No singularity is predicted there for the two-dimensional system.

A number of criticisms can be leveled at the results obtained in Ref. 1.

1. The existence of a logarithmic singularity in the function $\Phi(\omega)$ was demonstrated only with the aid of a self-consistent equation, the applicability of which is not evident.

2. Strictly speaking, the existence of a singularity in the function $\Phi(\omega)$ does not say anything about the specific heat because the dipole excitations, which the soft pairs constitute, interact strongly with each other. The logarithmic singularity of the function $\Phi(\omega)$ is just the result of the fact that for each pair the energy of interaction with the other pairs is of the order of the excitation energy ω. In such a situation the contributions of the various pairs to the total energy of the system are not additive.

3. It can be assumed (although, in our opinion, there are no grounds for this) that there exist, besides the compact dipole excitations, which are investigated in Ref. 1, excitations that correspond to the simultaneous permutation of the electrons in the entire volume of the system, and are not

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additively made up of individual compact excitations. The classification proposed in Ref. 1 will not be applicable to such excitations.

An answer to the first question is contained in Ref. 3, where the results of the simulation of a disordered system within the framework of the so-called lattice model are reported, and it is shown that the pair-excitation distribution function $\Phi(\omega)$ indeed possesses a logarithmic singularity at zero temperature. The remaining questions nevertheless remained unelucidated,and this stimulated us to carry out a simulation of the impurity band at a finite temperature with a view to computing the specific heat.

The main difficulty lay in the fact that, to detect a singularity in the specific heat, we had to carry out the simulation at temperatures that are very low compared to the interaction energy. The most informative temperature turned out to be the temperatures 0.025, 0.05, and 0.1 (in units of the energy of interaction over the average distance between the donors). As far as we know,this is the first time that thermodynamic properties have been simulated at such low temperatures. The results of the simulation confirm the existence of a low-temperature dip in the function c_v/T. New data pertaining to the properties of the ground state of this system were incidentally obtained.

2. THE SIMULATION PROGRAM

The simulation was carried out for both three- and two-dimensional systems. The corresponding programs are entirely similar, and below we shall, for definiteness, discuss the case of the three-dimensional system.

As the unit of length, we used the mean distance $N_D^{-1/3}$ between the donors; as the unit of energy and temperature, the quantity $e^2N_D^{1/3}/\varkappa$. We randomly located in a cube of linear dimension $N^{1/3}$ N donors and KN acceptors (which corresponded to unit donor concentration). The quantity N (the dimension of the block) ran through the values 200, 400, and 800. The degree K of compensation was, as a rule, equal to 0.5. Separate computations were also carried out for $K = 0.3$ and 0.7.

Further, $N(1-K)$ electrons were randomly distributed over the N donors. This meant that $N(1-K)$ randomly chosen donors were assigned the value $n_i = 1$; the remaining donors, the value $n_i = 0$. After this, using the algorithm proposed in Refs. 4 and 5, we carried out the minimization of the total energy (1), which amounted to the variation of the occupation numbers at a fixed value of $\Sigma_i n_i$. The result of such a minimization is sets $\{n_i\}$ of occupation numbers satisfying the conditions

$$\omega_i^j=\varepsilon_j-\varepsilon_i-1/r_{ij}>0 \tag{3}$$

for all pairs of donors with $n_i = 1$ and $n_j = 0$. Here

$$\varepsilon_i=\sum_\nu \frac{1}{r_{i\nu}}-\sum_{j\neq i}\frac{1-n_j}{r_{ij}} \tag{4}$$

is the potential produced on a donor by all the remaining charged impurities under the condition that the occupation of the donors is described by the set $\{n_i\}$. The quantity ω_i^j is the work that must be done in order to transfer an electron from an occupied donor i to an empty donor j under the condition that the population of the other donors does not change in the course of the transfer.

Thus, the state described by the set $\{n_i\}$ possesses the property that the transfer of any electron from an occupied to an empty donor increases the total energy of the system. The states described by such sets have been called pseudoground states. They differ from the ground state in that the simultaneous transposition of several electrons may result in a decrease in the energy of the system. There can be several pseudoground states for a given disposition of the donors and acceptors. They can be found within the framework of the same minimization program. The program gives, generally speaking, a different pseudoground state when the initial random set of occupation numbers is changed.

Let us now proceed to describe the simulation process at a finite temperature. It was performed by the standard Monte-Carlo method. To begin with, we chose donor pairs such that the separation inside a pair did not exceed some value R. This value was chosen to be so large that the probability of finding in the system a donor not participating in any pair was negligibly small. Each pair was assigned a number, and one and the same donor could figure in several pairs. As the initial set of occupation numbers, we always used the set corresponding to any of the pseudoground states. One Monte-Carlo step consisted in the following. One of the pairs was randomly chosen. If both donors of this pair had equal occupation numbers, then the step terminated there. If the occupation numbers were different, then the quantity ω_i^j, the work done in moving the electron from the occupied site of the pair to the empty site, was computed. If it turned out that $\omega_i^j<0$, then the transfer was certainly realized. If it turned out that $\omega_i^j>0$, then the transfer occurred only with probability $\exp\{-\omega_i^j/\tau\}$, where $\tau=kT\varkappa/e^2N_D^{1/3}$ is the temperature in dimensionless units. The transfer means that the occupation numbers for the donors of the pair in question change in the computer memory. After this, all the energies ε_i and the total energy H of the system are recomputed.

The main result of the computations was the specific heat

$$c=\frac{1}{\tau^2}\left[\frac{1}{M}\sum_{k=1}^{M}H_k^2-\left(\frac{1}{M}\sum_{k=1}^{M}H_k\right)^2\right]\frac{1}{N}, \tag{5}$$

where H_k is the value of the total energy after the step with number k and the summation is performed over all the steps, regardless of whether an electron transfer occurred in a given step or not; M is the number of steps made. The formula (5) gives the system's specific heat divided by the total number of donors and the Boltzmann constant k. It is precisely this quantity that is depicted below in the graphs.

Furthermore, we computed the mean value of the thermal energy per donor:

$$E=\left[\frac{1}{M}\sum_{k=1}^{M}H_k-H_{min}\right]\frac{1}{N}. \tag{6}$$

Here $H_{\min}$ is minimum energy value, which is fixed for a given disposition of the donors and acceptors. At the beginning of the computations, as $H_{\min}$, we took the energy of the lowest of the pseudoground states obtained in the minimization. Further, in the course of the Monte-Carlo procedure, after each electron transfer that decreased the total energy (i.e., for which $\omega_i^j < 0$), the new value of the energy was compared with $H_{\min}$. If it turned out to be lower than $H_{\min}$, then it was thereafter taken as the $H_{\min}$. The final value of $H_{\min}$ was substituted into the formula (6).

For the group of 200 donors the value of $H_{\min}$ in the overwhelming majority of realizations coincided with the ground-state energy. We verified that, if we carry out 100 minimizations, then new pseudoground states with low energy scarcely appeared in the last 50 minimizations. This verification was carried out for 100 different realizations of the coordinates of a system consisting of 200 donors and 100 acceptors. It shows that the minimization procedure, repeated 100 times, yields practically all the pseudoground states, of which the one with the lowest energy is the ground state. An additional verification is the fact that, in the course of the Monte-Carlo procedure, the energy never dropped below the energy found in the above-indicated manner.

For groups consisting of 400 or more donors, the number of pseudoground states was so high that we could not fully sort them out and find the ground state. If we judge by the characteristic energy spread of the pseudoground states, then we can assert that the uncertainty in the ground-state energy is negligibly small as compared to the energy itself, but can be comparable to the thermal energy at low temperature ($\tau = 0.025$). Thus, in large groups the mean energy is known only up to a temperature-independent term, which is different for different realizations of the coordinates of the donors and acceptors. This circumstance does not prevent us from determining the specific heat with the aid of the mean energy by taking the difference between the values of E at different temperatures. For an infinitely large number M of steps this method should yield the same result as the formula (5), while for a finite number of steps there can be discrepancies, which will allow us to estimate the accuracy of the results obtained.

The main difficulty encountered in the simulation of the behavior of the system at very low temperatures lies in the choice of the optimal conditions under which the system goes over into the thermal equilibrium state within an acceptable period of time (of the order of an hour of computer time). In particular, it is very important to choose the optimal value for the maximum pair length R. According to the theory, the dominant contribution to the specific heat is made by the pairs with small lengths (i.e., with lengths smaller than unity). From this point of view, by increasing R, we force the computer to examine pairs with high energies and, thus, do unnecessary work. On the other hand, for small R values the mixing of the states separated from each other by energy barriers occurs very slowly. In Figs. 1(a) and 1(b) we show the mean energy and the specific heat computed respectively from the formulas (6) and (5) as functions of the number of steps for $\tau = 0.05$ and different values of R. We used only one realization of the coordinates of the donors and acceptors, carried out 50 minimizations, and obtained 18 pseudoground states. The continuous curves depict Monte-Carlo cycles that were started from the lowest pseudoground state (apparently, the ground state); the dashed curves, cycles that were started from the highest pseudoground state, which lay 0.0039 units (per donor) above the lowest state. It can be seen that, for small R values, the system cannot surmount the barriers separating the pseudoground states during the time of operation of the computer (of the order of several hours). But at higher R the system goes over into the equilibrium state, which leads to a sharp increase in the specific heat.

As the optimal value of R, we chose $R = 2$. To speed up the transition into the equilibrium state, we also introduce into the program steps of another type, in which transitions between any two donors are allowed, irrespective of the distance between them. The fraction of steps of the second type was varied with temperature. At $\tau = 0.025$ the fraction of steps of the second type was 1/4, at $\tau = 0.05$ and 0.1 it was 1/3, at $\tau = 0.2$ and 0.4 this fraction was equal to 1/2 of the total number of steps, and at temperatures of 0.8 and above only

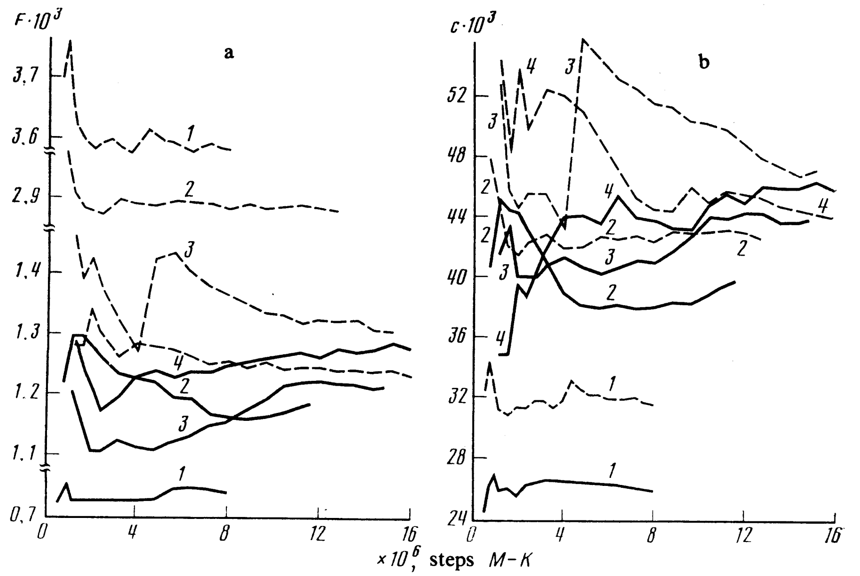

FIG. 1. The thermal energy (a) and the specific heat (b) as functions of the number of steps in the Monte-Carlo cycle for different values of the maximum pair length R: 1) 1.0; 2) 1.45; 3) 2.0; and 4) 3.0. The continuous curves correspond to cycles that were started from the lowest pseudoground state; the dashed curves, to cycles that were started from the highest pseudoground state; $N = 200$.

steps of the second type were made. In the course of a Monte-Carlo cycle the computer recorded the number of steps that resulted in the transposition of electrons.

The operating program with the aid of which the results presented below were obtained was organized as follows. The Monte-Carlo cycle was started from one of the pseudoground states. In order that that section of the cycle on which the system was still in the nonequilibrium state did not contribute to the energy and the specific heat, the averaging was started after a specific number of dummy steps. This number was varied with temperature, and was chosen such that several hundred electron transpositions were effected during the idling. During the subsequent operation of the program three energy and specific-heat values, obtained after 4000, 8000, and 12 000 electron transpositions, were printed out. At $\tau = 0.025$, when the establishment of the equilibrium state occurred especially slowly, the entire first stage of the calculation, which involved 4000 electron transpositions, was regarded as an "idle operation," and the averaging was performed over only the results of the next two stages, which together involved 8000 transpositions. The intermediate results enabled us to check the convergence of the process. We verified the absence of a significant difference between the results of the averaging over the various stages of the cycle at $\tau \geqslant 0.05$. There was a difference at $\tau = 0.025$, but it did not have a systematic character.

The average number of steps per transposition depended on the temperature, the chosen R, and the ratio of the number of steps of the first type to the number of steps of the second type. For $R = 2$ and the above-indicated fractions of the steps of the second type the average number of steps per electron transfer was of the order of 1700 at $\tau = 0.025$, 600 at $\tau = 0.05$, 170 at $\tau = 0.1$, and 60 at $\tau = 0.2$. It is clear that at infinite temperature and for the degree of compensation $K = 0.5$ this number should be equal to two, since every second pair will be singly occupied, and the transition probability will be equal to unity in this case. For example, this number was equal to 2.018 at $\tau = 200$.

The computer spent 160 μsec on a step in which an electron transfer did not occur; the time spent on a transfer was significantly longer,and depended on the dimension of the block under investigation, since it was necessary in this case to recalculate the energies of all the donors. For example, in a block with $N = 800$ the time spent on a transfer was 143 msec; in a block with $N = 400$, 73 msec. In the case of the block with $N = 200$ we were able to put all the interdonor distances in the computer memory, as a result of which this time was only 10 msec. The values obtained for the mean energy and the specific heat were averaged over the various realizations of the coordinates of the donors and acceptors. The simulation was performed at $\tau = 0.025$; 0.05; 0.1; 0.2; 0.4; 0.8; 1.6; 3.2; 6.4; 12.8; 25; 50; 100; and 200.

The molar specific heat $c_v(T)$ can be obtained, using the function $c(\tau)$ computed by us, from the formula

$$c_v(T) = N_D v k c(kT\varkappa/e^2 N_D^{1/3}),$$

where v is the volume of a gram-mole of the material.

3. PROPERTIES OF THE GROUND AND PSEUDOGROUND STATES OF THE THREE-DIMENSIONAL SYSTEM

In the present section we discuss the results obtained at the first stage of the operation of the program before the incorporation of the Monte-Carlo temperature cycle. As has already been indicated, we could determine the ground-state energy with a sufficiently high degree of accuracy in all the blocks that were studied. For $K = 0.5$ the ground-state energy per donor was equal to -0.910 ± 0.005 in a block with $N = 200$, -0.92 ± 0.01 in a block with $N = 400$, and -0.93 ± 0.03 in a block with $N = 800$. Besides the $K = 0.5$ case, we further studied the cases $K = 0.3$ and 0.7, but only in a block with $N = 200$. For $K = 0.3$ the ground-state energy per donor was equal to -0.600 ± 0.003; for $K = 0.7$, -1.10 ± 0.04.

The ground-state energy of the system can be estimated with the aid of the "dipole model" proposed in Ref. 6 for electric-field calculations. In this model it is assumed that all the charges of the system form dipoles consisting of an acceptor and the nearest donor, which is assumed to be charged. The intradipole interaction energy is equal to $-1/r$, where r is the distance between the donor and the acceptor, and the interdipole interaction energy is assumed to be small. Using the nearest-neighbor distribution function, we find that the mean energy per acceptor is equal to

$$-4\pi \int_0^\infty \frac{1}{r} r^2 \exp\left(-\frac{4}{3}\pi r^3\right) dr = -2.18$$

(the length r is measured in units of $N_D^{-1/3}$!). Correspondingly, the energy per donor is equal to -2.18 K (in units of $e^2 N_D^{1/3}/\varkappa$). The dipole model should work well in the limit of small K. But for $K = 0.3$ and even for $K = 0.5$ it yields results in surprisingly good agreement with the results of the simulation. For $K = 0.7$ the difference turns out to be significant. As pointed out in Ref. 6, the electric-field calculations can also be carried out with the aid of the dipole model for $K \lesssim 0.5$.

Another important characteristic of the system at zero temperature is the pseudoground-state spectrum. This spectrum was obtained in full in a block with $N = 200$. We studied 100 different realizations of the donor and acceptor coordinates, carrying out 100 minimizations in each realization. We found on the average 11.32 pseudoground states per realization. Figure 2 shows the energy distribution function of the pseudoground states. As the energy reference point in each realization, we took the ground-state energy (which varied from realization to realization). It can be seen that the distribution function in the region of energies higher than 0.1 decreases rapidly with increasing energy. Let us emphasize that it is the total energy that figures in this graph, and not the energy per donor. The mean ground-state energy is equal to -182, so that the pseudoground-state energies differ very little from the ground-state energy.

In the simplest case the pseudoground state differs from the ground state in the occupation numbers of four donors, two of which are occupied by electrons and the remaining two are empty. The potentials on the donors are such that a donor-to-donor transition of one electron is disadvanta-

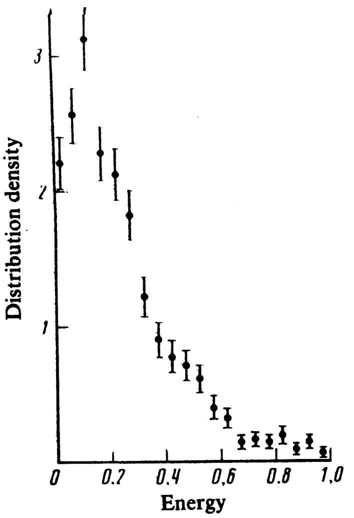

FIG. 2. The pseudoground-state-energy distribution function for $N = 200$. Plotted along the abscissa axis is the system's total energy, measured from the ground-state energy (which is equal, on the average, to -182). The averaging was performed over 100 coordinate realizations. The vertical short lines indicate the limits of the confidence interval.

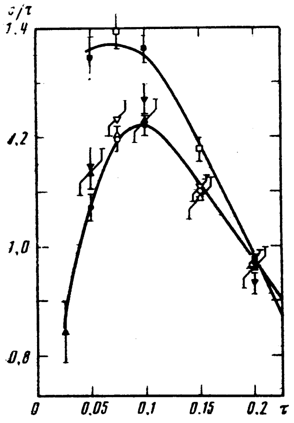

FIG. 3. The quantity c/τ for a three-dimensional system as a function of the temperature: ● and ○) $N = 200$; ▼ and ▽) $N = 400$; ▲ and △) $N = 800$; ■ and □) for $N = 200$ and a screened potential. The dark symbols correspond to the results obtained with the aid of the formula (5); the open symbols, to the results of the differentiation of the thermal energy with respect to τ.

geous, whereas the simultaneous transition of the two electrons decreases the total energy of the system. This type of "lock" can also be realized by a large number of donors. Unfortunately, we were not able to carry out a detailed investigation of the spatial structure of the pseudoground states. But the obtained spectrum of the pseudoground states allows us to compute their contribution to the thermodynamics of the system with the aid of the Gibbs distribution. (In this case we cannot, strictly speaking, use the averaged distribution function shown in Fig. 2: we must compute the specific heat for each realization of the donor and acceptor coordinates, and then perform the averaging.) Calculations of this kind lead to an important conclusion: the contribution of the pseudoground states is roughly an order of magnitude smaller than the specific-heat value obtained by the Monte-Carlo method, and given below. This confirms the viewpoint, expressed in Ref. 1, that the low-energy excitations are primarily "soft pairs," and not quadruplets or more complicated objects.

4. SPECIFIC HEAT OF A THREE-DIMENSIONAL IMPURITY BAND

Figure 3 shows c/τ versus τ curves obtained in the low-temperature region with the aid of simulation. The results were averaged over the various realizations of the donor and acceptor coordinates. For $N = 200$ we used 75 realizations; for $N = 400$, 22 realizations; and for $N = 800$, 10 realizations. The dark symbols indicate the c/τ values obtained with the aid of the formula (5); the open symbols, the results of the differentiation of the thermal energy computed from the formula (6).

Figure 4 shows data for the reduced specific heat in a broader temperature range.

As can be seen from Fig. 3, the quantity c/τ attains a maximum at $\tau \approx 0.1$, and then falls off in the low-temperature region. We interpret this decrease as the theoretically predicted manifestation of the interaction of the soft pairs. The dependence given by Eq. (2) is asymptotic, and we cannot establish the accuracy with which it is satisfied. But the decrease of c/τ with decreasing temperature does appear to us to be a reliable result. An alternative explanation could be that there exist at low temperatures regions of phase space separated by so high barriers that the system does not have time to "cross" into these regions during the simulation. This would imply the "kinetic freezing" of a definite number of degrees of freedom and a false reduction in the specific heat. Speaking against such an explanation are the following facts:

1. The barriers should have different heights, so that a definite fraction of them would be surmounted upon the in-

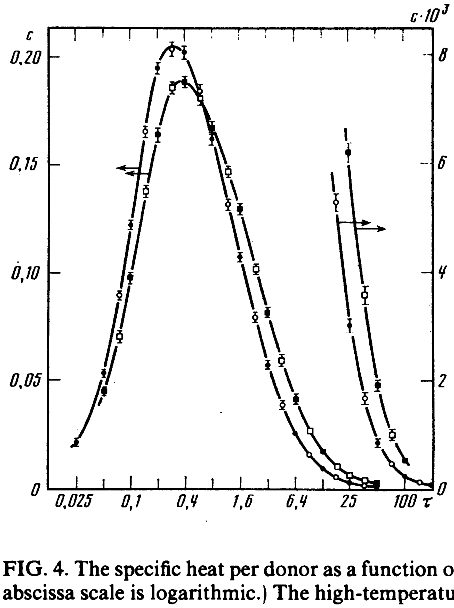

FIG. 4. The specific heat per donor as a function of the temperature. (The abscissa scale is logarithmic.) The high-temperature section is shown separately on an enlarged scale (the right-hand scale). The circles represent the results obtained for the three-dimensional system; the squares, for the two-dimensional system. The dark circles and squares correspond to the results obtained with the aid of the formula (5); the open symbols, to the results of the differentiation of the formula (6).

crease of the number of steps in the Monte-Carlo cycle. This would have led to a monotonic increase of the specific heat with increasing number of steps, which was not observed.

2. As can be seen from Fig. 3, the data obtained through the differentiation of the thermal energy with respect to temperature agree with the data obtained with the aid of the formula (5). This indicates that the Monte-Carlo process "converges."

3. Using the curve shown in Fig. 4, we can compute the integral

$$A=N\int_0^\infty (c/\tau)\,d\tau=N\int_{-\infty}^{\infty} c(\ln\tau)\,d\ln\tau. \tag{7}$$

By definition of specific heat, $A=S(\infty)-S(0)$, where $S(\tau)$ is the entropy of the system at the temperature τ.

Contrary to the prediction of some spin-glass models, the ground state of a system with randomly disposed charged acceptors cannot, it seems to us, be degenerate. Therefore, the Nernst theorem is valid, and $S(0)=0$. The entropy at infinite temperature is easy to compute. It is equal to the logarithm of the number of combinations of N donors taken KN (ionized donors) at a time:

$$S(\infty)=\ln\,[N!/(KN)!\,(N-KN)!]. \tag{8}$$

For $K=0.5$ and $N=200$ we obtain, according to (8), $S(\infty)=135.75$. If the area enclosed in Fig. 4 by the curve corresponding to the three-dimensional system agrees with this value, then this shows conclusively that this curve describes the equilibrium specific heat, and should not change when the time of observation of the system is increased. We can thus show that there indeed exists a dip in the quantity c/τ in the low-temperature region. In fact, if we assume that the quantity c/τ coincides with the computed values at $\tau\geqslant 0.1$, and is equal to a constant at all lower temperatures, i.e., if we assume that the dip does not occur at all, then we find that $A=139.0\pm0.8$, which is significantly greater than $S(\infty)$. But if we assume that c/τ coincides with the computed values in the region $\tau\geqslant0.025$ and is equal to a constant in the region of lower temperatures, then we obtain $A=135.4\pm0.8$, which agrees with $S(\infty)$. We obtain almost the same result (135.0) when we assume that the quantity c/τ decreases according to a linear law in the region $\tau<0.025$. Such an extrapolation yields $c/\tau\approx0.6$ at $\tau=0$, which is, as will be seen below, in good agreement with the theoretical predictions. In our opinion, this is the most reliable proof of the certainty of a dip in the quantity c/τ.

According to the theory, the logarithmic singularity described by the formula (2) is due to the long-range interaction. In order to verify whether the dip in c/τ at low temperature has such a character, we replaced the Coulomb potential in the expression (1) for the total energy by the screened potential: $r^{-1}\rightarrow r^{-1}\exp\{-r/r_0\}$. Figure 3 shows the results of the calculation with $r_0=1.5$. It can be seen that the dip at low temperatures is, in conformity with the theory, significantly smaller. We believe this is an important demonstration of the fact that the phenomenon discovered is connected with the interaction of the soft pairs.

Each pair is a two-level system, and its specific heat is equal to:

$$c'(\omega)=\omega^2/4\tau^2\,\mathrm{ch}^2\,(\omega/2\tau), \tag{9}$$

where ω is the pair-excitation energy. According to the theory developed in Ref. 1, the number of pairs excited at a temperature τ is such that the energy of their dipole-dipole interaction over the mean distance between them is of the order of τ. Therefore, the contributions of the individual pairs to the specific heat cannot, strictly speaking, be considered to be independent. Nevertheless, it is useful to make as estimate with the aid of the formula

$$c=\int \Phi(\omega)\,c'(\omega)\,d\omega, \tag{10}$$

where $\Phi(\omega)$ is the pair distribution function computed for one donor in the ground state of the system.

As shown in Ref. 1, the existence of the function $\Phi(\omega)$, which does not depend on the block dimension, is itself a consequence of the Coulomb interaction. (It should not be forgotten that the total number of different pairs in the system is proportional to N^2, and not N.) We should, in computing $\Phi(\omega)$, take into account only the pairs with length R significantly smaller than $1/\omega$. Then, as shown in Ref. 1, the number of pairs will be proportional to N, and will not, in the first approximation, depend on R. We computed the function $\Phi(\omega)$ for an $N=200$, $K=0.5$ block with no limitation placed on the pair length. The length of the block in this case is roughly equal to 5.85, and there cannot be pairs of length greater than $5.85\sqrt{3}$ in it. Therefore, we should obtain, at least for $\omega\ll0.1$, a reasonable approximation for $\Phi(\omega)$. The results of the $\Phi(\omega)$ calculation are shown in Fig. 5. We obtained them through averaging over 200 donor- and acceptor-coordinate realizations, computing in each realization the pair density for the ground state. The calculations with the formula (10) yield for $\tau=0.025$ the value $c/\tau=0.80$ (per donor), which satisfactorily agrees with the value 0.84 given in Fig. 3. This again shows that the specific heat is largely determined by the donor pairs.

It should be borne in mind that the quantity c/τ in a finite block should not tend to zero as $\tau\rightarrow0$. According to theory (see Ref. 1),

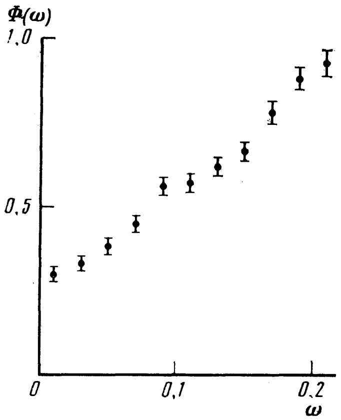

FIG. 5. The pair distribution function per donor, computed in the ground state for a block with $N=200$.

$\Phi(0)\approx(\ln N)^{-1/2}$, while $(c/\tau)_{\tau=0}\approx\Phi(0)\pi^2/6$.

For $N=800$ we obtain $(c/\tau)_{\tau=0}\approx 0.64$, which, as has already been indicated, is in good agreement with the result shown in Fig. 3.

All the results presented above pertain to the case $K=0.5$. In order to investigate the dependence of the low-temperature specific heat on the degree of compensation, we also computed the values of c for $\tau=0.1$ and two other values of K. For $K=0.3$ we found that $c=0.12\pm 0.01$; for $K=0.7$, $c=0.091\pm 0.003$. In the $K=0.3$ case the averaging was performed over 5 realizations; in the $K=0.7$ case, over 20 realizations of a block with $N=200$. As can be seen from Fig. 4, for $K=0.5$ and $\tau=0.1$, $c=0.122\pm 0.002$. Naturally, the specific heat should be smaller at very high and very low values of the degree of compensation, at which the degrees of freedom in the impurity band are few. It is natural to conclude on the basis of the above-presented data that, for $\tau=0.1$, the specific heat has a maximum at $K\approx 0.4$.

A theory of the specific heat of impurity-band electrons is constructed for $\tau\gg 1$ in Ref. 7. Unfortunately, a satisfactory comparison of the results of Ref. 7 with the results of the present paper is impossible, since the screening distance is large in the $\tau\gg 1$ case, and we need, for the comparison, a theory that takes account of the finiteness of the system's dimensions.

5. THE TWO-DIMENSIONAL IMPURITY BAND

We also considered the case in which the donors and acceptors are located in the same plane, and their energy is, as before, given by the formula (1), i.e., the interaction has the Coulomb form. This model bears a direct relation to the impurity band formed by atoms located on the surface of a semiconductor.[8]

We performed for the two-dimensional system essentially the same calculations that we performed for the three-dimensional system, but the number of calculations was smaller. Only the $K=0.5$ case was investigated. The ground-state energy per donor was found to be equal to -1.12 ± 0.03 for a block with $N=200$, -1.23 ± 0.02 for a block with $N=400$, and -1.29 ± 0.03 for a block with $N=800$. The dipole model yields for this case the value -1.57. The dimensional effect, which is much stronger than in the three-dimensional case, is a surprising fact.

The main purpose of the simulation was to investigate the low-temperature specific heat. As has already been indicated, theory[1] does not predict in this case a logarithmic singularity of the type (2). In Fig. 6 we present the results obtained for c/τ by means of the simulation in the two-dimensional case. We have also carried over here the results for the three-dimensional case.

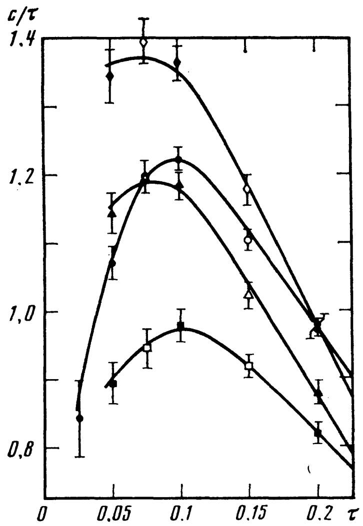

FIG. 6. The quantity c/τ for two- and three-dimensional systems as a function of the temperature. The results are for a block with $N=200$ and, in the case of the three-dimensional system, a block with $N=800$ and $\tau=0.025$. ■ and □ represent the results for a two-dimensional system with the Coulomb potential. The averaging was performed over 40 realizations. ▲ and △ indicate the results for a two-dimensional system with a screened potential with $r_0=1.5$. The averaging was performed over 30 realizations. The points corresponding to the two other curves pertain to a three-dimensional system, and were transferred from Fig. 3. The dark symbols correspond to the results obtained with the aid of the formula (5); the open symbols, to the results of the differentiation of the thermal energy with respect to τ.

As can be seen from Fig. 6, a dip occurs in the low-temperature region in the two-dimensional case also, although it is less pronounced. Unfortunately, we were not able to obtain here reliable results for $\tau=0.025$, which, possibly, would have clarified the situation. As in the three-dimensional case, we computed the entropy. The quantity A defined by the formula (7) is equal in this case to 135.9 ± 1. In computing it, we assume that when the temperature is lowered in the region $\tau<0.05$ the quantity c/τ decreases linearly with slope equal to the slope at $\tau=0.05$. As in the three-dimensional case, $S(\infty)=135.75$.

If we compute A under the assumption that c/τ does not decrease in the region $\tau<0.1$, i.e., that no dip occurs, we obtain $A=137.7\pm 1$, which is greater than $S(\infty)$. Thus, a low-temperature dip evidently occurs in the two-dimensional case as well, although it is less pronounced than in the three-dimensional case.

As in the three-dimensional case, we performed an experiment with a screened potential. As can be seen from Fig. 6, the shape of the c/τ-versus-τ curve reacts more weakly to the screening than the shape of the corresponding curve in the three-dimensional case. We cannot give the cause of the low-temperature dip in the two-dimensional case, but this effect seems to us to be genuine.

Unfortunately, thus far measurements of the low-temperature electronic specific heat of lightly doped semiconductors have been performed only on uncompensated samples of phosphorus-doped silicon.[9] The measurement of the specific heat of compensated samples could play an important role in the solution of the problem, discussed in Refs. 1 and 2 and in the present paper, of the interaction of the dipole excitations.

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