# Coulomb gap and metal-insulator transition in disordered semiconductors with strongly localized states

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The low-temperature dependence of the electrical conductivity revealed a parabolic Coulomb gap in the spectrum of deep levels of Mn and Fe in amorphous silicon. The width of the gap  $\Delta$  was determined. The value of  $\Delta$  was an order of magnitude greater than the known values for semiconductors with shallow-level impurities. The dependence of the Coulomb gap width on the concentration N of the deep impurity was determined. The gap  $\Delta$  disappeared as a result of isothermal annealing at  $T_{\text{ann}} \ge 450$  °C. In the critical region of a metal-insulator transition the temperature corresponding to thermal "flooding" of the Coulomb gap coincided with the temperature at which the activation energy of hopping became comparable with  $\Delta$ . The critical exponents representing the behavior of the Coulomb gap, permittivity, and localization radius near the metal-insulator transition were determined for the first time in the case of disordered semiconductors with strongly localized states. The presence of a large-scale potential in amorphous silicon was found to increase the critical exponents compared with those, for example, of doped crystalline semiconductors.

#### **1. INTRODUCTION**

The Coulomb interaction between localized electrons creates a gap in the spectrum of states in a disordered semiconductor<sup>1</sup> and inside this gap the density of states vanishes in accordance with a power law:

$$g(E) = \alpha \frac{\varepsilon^3}{e^6} E^2, \qquad (1.1)$$

where E is the energy measured from the Fermi level;  $\varepsilon$  is the permittivity of the medium; e is the electron charge;  $\alpha$  is a numerical coefficient. In this case the low-temperature hopping conductivity is described by

$$\sigma(T) = \sigma_0 \exp\left[-(T_0/T)^{\frac{1}{2}}\right], \quad T_0 = \beta e^2/k\varepsilon a, \quad (1.2)$$

where k is the Boltzmann constant, a is the localization radius, and  $\beta$  is a numerical coefficient. The available experimental data on crystalline semiconductors containing shallow-level impurities confirm the law of Eq. (1.2). The width of the Coulomb gap exhibited by them is given by the expression

$$\Delta = (g_0 e^{\theta} / \alpha \varepsilon^3)^{\gamma_2}, \qquad (1.3)$$

where  $g_0$  is the localized-state density unperturbed by the Coulomb potential; the gap width calculated from the above expression does not exceed 1-2 meV.

Measurements of the low-temperature conductivity of amorphous semiconductors are difficult because cooling increases strongly the resistance of these materials and the experimental proof of the existence of a Coulomb gap has been lacking. The development of the physical principles of doping of amorphous silicon (a-Si) by ion implantation has made it possible to prepare amorphous materials with high values of  $\sigma$ . As a result, the low-temperature conductivity was measured and the Coulomb gap was discovered in a-Si (Ref. 2). The value of  $\Delta$  found for *a*-Si:P was of the same order of magnitude (1 meV) as for crystalline semiconductors.

It was demonstrated in Refs. 3 and 4 that amorphous

silicon can be doped effectively by atoms of transition metals belonging to the iron group (Mn, Fe, Cr). These metals are readily dissolved in the reticulate structure of a-Si and give rise to deep levels in the mobility gap. Studies of the lowtemperature dependence of the conductivity of a-Si:Mn with impurity concentrations N = 4 and 8 at. % enabled us to detect the Coulomb gap in the spectrum of deep impurity states.<sup>5</sup> We obtained an unusual value of  $\Delta$  for *a*-Si:Mn, 25 meV, which was an order of magnitude higher than the known values of  $\Delta$  for amorphous semiconductors (including a-Si) containing shallow-level impurities.

Our aim was to investigate the Coulomb gap in the spectrum of deep impurity levels in a-Si.

## 2. EXPERIMENTAL METHOD. MONITORING OF THE STRUCTURE

We determined the temperature dependence of the conductivity of amorphous silicon films doped by ion implantation of manganese and iron. Films of a-Si were prepared by electron-beam evaporation of crystalline Si in 10<sup>-5</sup> Pa vacuum. This evaporation process resulted in deposition of a film on a quartz substrate at a rate of 3-5 Å/s. Samples of *a*-Si were doped with transition elements by implantation of ion doses of  $10^{16}$ – $10^{17}$  cm<sup>-2</sup> in an accelerator. The density of the ion current was  $0.5-2.0 \,\mu$ A/cm<sup>2</sup>. A homogeneous distribution of the impurity across the film thickness ( $d = 0.25 \,\mu$ m) was ensured by varying the ion energy within the range 30-280 keV. The impurity concentration distribution was calculated on a computer. The maximum deviation of the calculated concentration from the real one was 9.7%. Our a-Si films contained Mn in concentrations of 0.8-14 at. %. In the case of *a*-Si:Fe the concentration of Fe was 2-4 at. %.

The conductivity measurements were carried out under dc conditions corresponding to the ohmic parts of the current-voltage characteristic. The temperature was measured in the range 4.2-77 K by a semiconductor thermistor of the KG 35E-11 type, whereas in the range 77-500 K we used a copper-constantan thermocouple. The structure of the re-



FIG. 1. Mössbauer spectra of conversion electrons of the <sup>57</sup>Fe isotope implanted in *a*-Si, recorded after annealing at various temperatures  $T_{ann}$  (°C): 1) 25; 2) 200; 3) 510; 4) 660; 5) 710.

sultant *a*-Si:Mn:Fe films was monitored by electron diffraction in the reflection configuration, by x-ray structure analysis, and by Mössbauer spectroscopy. The diffraction spectrum of the original undoped *a*-Si film was in the form of a halo indicating the absence of a crystalline phase in this sample.

Mossbauer resonance absorption spectra were recorded by detection of low-energy conversion electrons. We used the transition in the 57Fe nucleus characterized by an energy of 14.4 keV. We investigated a-Si:<sup>57</sup>Fe films with iron concentrations 0.4 and 4 at. %. There was no difference between the Mössbauer spectra obtained for these two concentrations. The Mössbauer spectrum of a-Si:<sup>57</sup>Fe consisted of two wide lines (Fig. 1) which, according to the published data,<sup>6</sup> clearly corresponded to the quadrupole splitting of the excited state of the iron nucleus caused by an electric field gradient near the Fe atom in a-Si. The existence of such splitting indicated that the implanted ions occupied low-symmetry positions in the unit cell. Broadening of the Mössbauer doublet showed that the environment of the <sup>57</sup>Fe nuclei was disordered. Isothermal annealing at  $T_{ann} > 400$  °C reduced the widths of the lines. This clearly corresponded to the lattice ordering processes and at  $T_{ann} > 600$  °C there were reflections associated with the formation of the silicide FeSi<sub>2</sub>. An x-ray structure analysis<sup>7</sup> of a-Si:Mn films indicated formation of silicides and of pure manganese only after annealing at  $T_{ann} > 350$  °C.

Our analysis of the investigated structures thus led us to the conclusion that homogeneous amorphous silicon films were formed and they were doped with transition metals but free of silicides and metal inclusions.

## 3. RESULTS OF MEASUREMENTS

The electrical conductivity  $\sigma$  of *a*-Si:Mn and *a*-Si:Fe films with different impurity concentrations was measured

at temperatures 4.2–500 K and an activation  $\sigma(T)$  dependence was found for films with impurity concentrations below 12 at. %. At temperatures T < 300 K the activation energy was not constant, but decreased continuously as a result of cooling. This type of conduction indicated migration of carriers between localized states within a narrow band of energies near the Fermi level.<sup>8</sup> In general, the hopping conductivity with a variable activation energy can be described by

$$\sigma(T) = \sigma_0 \exp\left[-(T_0/T)^x\right], \quad 0 \le x \le 1.$$
(3.1)

The parameters  $\sigma_0$ ,  $T_0$ , and x which describe, with the aid of the functional dependence (3.1), the experimentally observed values of the conductivity and temperature  $(\sigma_i, T_i)$ , where i = 1,...,M can be found by least squares. The whole numerical analysis of the experimental data was carried out on a computer in accordance with the following procedure. We selected an arbitrary value of the parameter x and then reduced the dependence (3.1) to the form

$$Z = AY + B,$$
  

$$Z = \ln \sigma, \quad Y = T^{x}, \quad A = -T_{0}^{x}, \quad B = \ln \sigma_{0}.$$

The values of the parameters A and B minimizing the rms deviations of the experimental points from the curve of Eq. (3.1), which was defined by these parameters, were calculated using familiar expressions employed in the linear variant of the least-squares method.<sup>9</sup> The value of x was varied within the range 0 < x < 1. We found x that ensured the minimum rms deviation S:

$$S = \left[\frac{1}{M} \sum_{i=1}^{M} \left(\frac{100}{\sigma_i} \left\{\sigma_0 \exp\left[-\left(\frac{T_0}{T_i}\right)^{\star}\right] - \sigma_i\right\}\right)^2\right]^{\gamma_i}.$$
 (3.2)

Figure 2a shows the dependence of the rms deviation S on x for a-Si:Mn with an impurity concentration N = 6 at. % based on the data obtained at  $T \le 65$  K. It is clear from this figure that S had its minimum value (about 7%) at x = 0.5. Similar values of the parameters x were obtained for the lf conductivity of other a:SiMn films (N = 0.8-11 at. %), as well as for a-Si:Fe films (N = 2 and 4 at. %).

The Coulomb gap could be estimated [see Eq. (4.1)



FIG. 2. Results of a numerical analysis (by the least-squares method) of the experimental data for a film of *a*-Si:Mn (N = 6 at. %):a) dependence of the rms deviation *S* on the variable parameter *x* at  $T^{-}$  65 K; b) dependence of *x* on the upper limit of the temperature range  $T^{+}$ . The arrow identifies the temperature  $T_{c}$  below which the conductivity obeys the law of Eq. (1.2).



FIG. 3. Temperature dependences of the conductivity of films of a-Si:Mn (a) and a-Si:Fe (b). The numbers alongside the dependences give the concentration of the transition metal (%).

below] provided we knew the limiting or critical temperature  $T_c$  below which the conductivity began to follow the Shklovskii-Efros law described by Eq. (1.2). We found  $T_c$ by the above procedure of numerical analysis of the experimental results between 4.2 K and some temperature  $T^+$ , which we varied in the range 10-300 K. Determination of  $T_c$ is illustrated in Fig. 2b, which gives the dependence of x minimizing S on the value of  $T^+$  for a-Si:Mn (N = 6 at. %).

As in Refs. 10–12, the exponential temperature dependence of the conductivity given by Eq. (1.2) and observed at temperatures  $T \leqslant T_c$  (Fig. 3) was interpreted by us postulating hopping charge transport between states in a parabolic Coulomb gap. We demonstrated that the dependence (1.2) exhibited by *a*-Si:Mn:Fe was due to the electron–electron interaction of localized charges and not due to the tunnel transitions between metal granules in *a*-Si. This was done by investigating the temperature dependence of the conductivity of *a*-Si:Mn (N = 7 at. %) and *a*-Si:Fe (N = 4 at. %) samples after isothermal annealing at various temperatures. Our structure analysis indicated that annealing at  $T_{ann} > 400$  °C caused precipitation of the solid solution of transition-element atoms in *a*-Si producing precipitates and silicides.

Annealing of *a*-Si:Mn:Fe reduced the fraction of the electrically active component of the metal. At the same time there was a reduction in the density of the impurity states  $g_0$  and, according to Eq. (1.3), narrowing of the Coulomb gap. In the process of reduction of the gap the dependence  $\sigma(T)$  should evolve in such a way that the temperature  $T_c$  corresponding to the lower limit of validity of the law (1.2) would shift toward lower temperatures. When  $g_0$  decreased suffi-



FIG. 4. Temperature dependences of the conductivity of a film of *a*-Si:Fe (N = 4 at. %) before (1) and after (2, 3) annealing. Annealing temperature  $T_{ann}$  (°C): 2) 450; 3) 540.

ciently so that the optimal (from the point of view of hopping) difference between the energy levels exceeded  $\Delta$ , the presence of the gap in the energy spectrum should not be manifested in the low-temperature hopping conductivity. Therefore, if the law (1.2) was due to jumps between states in a parabolic Coulomb gap, then annealing should shift this law toward lower temperatures and then the law in question should no longer be obeyed. We found experimentally that annealing of *a*:Si:Mn (N = 7 at. %) at  $T_{ann} = 300$  °C reduced threefold the temperature  $T_c$ .

Figure 4 shows the results of a determination of  $\sigma$  before (curve 1) and after (curves 2 and 3) annealing at  $T_{ann} = 450$ and 540 °C of a sample of *a*-Si:Fe (N = 4 at. %). Clearly, curves 2 and 3 became rectified when plotted as the dependence of log  $\sigma$  on  $T^{-1/4}$  at temperatures 240–10 K. The results of a numerical analysis of the experimental data by the method of least squares also confirmed that annealing at  $T_{ann} > 400$  °C changed the Shklovskii–Efros law for the hopping conductivity to a law described by Eq. (3.1) with x = 0.25, which was first derived by Mott<sup>8</sup> for noninteracting electrons. The experimentally observed Mott temperature dependence of the conductivity was clearly due to a reduction in the width of the Coulomb gap to such an extent that electrons tunneled between states outside the gap where g(E) depended weakly on the energy.

## 4. COULOMB GAP IN a-Si:Mn

The width of the Coulomb gap was determined by equating it to the activation energy of tunnel jumps at the temperature  $T = T_c$ :

$$\Delta = \frac{1}{2}k(T_0T_c)^{\frac{1}{2}} . \tag{4.1}$$

The dependences of  $T_c$  and  $T_0^{1/2}$  on the implanted impurity concentration in *a*-Si:Mn, determined using the above procedure of numerical analysis of the experimental data, are plotted in Fig. 5. The nature of the  $\Delta(N)$  curves for *a*-Si:Mn and *a*-Si:Fe can be judged on the basis of Fig. 6. We can see that at concentrations of Mn less than 4 at. % the width of the gap increased on increase in the impurity concentration. Excitation of an electron from an occupied state *i* 



FIG. 5. Dependences of the parameters representing the conduction process involving levels in the Coulomb gap on the concentration of Mn implanted in *a*-Si:  $\triangle$ )  $T_0^{1/2}$ ; •)  $T_q$ ; •)  $T_c$ . Extrapolation of the linear dependence  $T_0^{1/2}(N)$  to zero made it possible to find the impurity concentration  $N_c$  corresponding to a metal-insulator transition.

to an empty state *j* should be accompanied by an increase in the energy of the system described by

$$\delta E = E_j - E_i - e^2 / \varepsilon r_{ij}, \tag{4.2}$$

where  $E_i$  and  $E_j$  are the one-electron energies of the levels *i* and *j*, and  $r_{ij}$  is the distance between these levels. The value of  $\delta E$  was positive when the spectrum became modified and a Coulomb gap appeared at the Fermi level.<sup>1</sup>

The width of a band of localized states in an amorphous semiconductor is governed by a fluctuation potential due to the absence of a long-range order in the system and it is independent of the impurity concentration. Therefore, an increase in N increases the density of the impurity states. This means that for fixed values of  $E_i$  and  $E_i$  the spatial separation of the levels decreases. Consequently, when the impurity concentration is increased, the condition  $\delta E > 0$ ceases to be satisfied in an increasing range of energies, i.e., the Coulomb gap increases. A further increase in the impurity concentration results in an overlap of the wave functions of localized electrons. This gives rise to macroscopic regions where carriers are delocalized and able to screen the Coulomb interaction. The effective permittivity of such a medium increases on increase in the impurity concentration and the width of the gap described by Eq. (1.3) decreases and vanishes at the point of transition of the system to a metallic



FIG. 6. Dependences of the Coulomb gap  $\Delta$  and of the position of the Fermi level relative to the percolation edge  $E_P - E_F$  on the impurity concentration in *a*-Si:Mn. The black dots represent the value of  $\Delta$  for *a*-Si:Fe. The finite nature of the value of  $E_P - E_F$  on the metal side (N > 12.8 at. %) indicated that a metal-insulator transition occurred in an impurity energy band. The residual activation energy ( $\sim 30 \text{ meV}$ ) represents the thermal transfer of carriers from the impurity to the conduction band.

state. The manganese concentration  $N_c$  corresponding to this transition can be found from

$$\lim T_0(N) = 0, \tag{4.3}$$

which—according to Eq. (1.2)—corresponds to an infinite value of the product  $\varepsilon a$ . It is found that  $N_c = 12.8$  at. % (Fig. 5). This value of  $N_c$  is in agreement with the results of measurements of  $\sigma(T)$  carried out on *a*-Si:Mn samples with N = 13 and 14 at. %, reported in Refs. 5 and 13 where it was found that the activated nature of the conduction process in the case  $N \le 12$  at. % changed to "metallic" in the range  $N \ge 13$  at. %.

As pointed out already, the width of the Coulomb gap in *a*-Si:Mn:Fe was an order of magnitude greater than the values of  $\Delta$  reported earlier for semiconductors containing a shallow-level impurity. According to Ref. 1, the value of  $\Delta$ was governed by the density of localized states  $g_0$  near the Fermi level and by the permittivity of the system  $\varepsilon$  [see Eq. (1.3)]. The high solubility of transition metals in *a*-Si made it possible to achieve a high concentration of an electrically active impurity in the investigated material ( $\geq 10^{21}$ cm<sup>-3</sup>).<sup>13</sup> However, an increase in N caused the system to approach the metallic state and near this transition the permittivity showed a divergence. According to Mott,<sup>14</sup> a metal-insulator transition occurs when

$$N_c a^3 = \text{const.}$$
 (4.4)

Consequently, in the case of a deep impurity a metal-insulator transition can be expected at higher impurity concentrations than in the case of a shallow impurity. It follows that the high solubility of Mn and Fe in a-Si and a strong localization of electrons at impurity atoms enabled us to prepare a material with a high density of localized states even outside the critical region corresponding to a metal-insulator transition so that the divergence of  $\varepsilon$  was still unimportant and this ensured a large Coulomb gap.

The arguments predicting the vanishing of g(E) at the Fermi level as a result of the electron-electron interaction are strictly speaking valid only if T = 0. A recent computer experiment<sup>15</sup> demonstrated that in the three-dimensional case we can expect thermal excitations to "flood" the gap at  $T \neq 0$ , so that it disappears at a "quenching temperature"

$$T_q = \Delta / \sqrt[4]{11}k. \tag{4.5}$$

We checked this result bearing in mind that the following condition should be satisfied:

$$T_q \geqslant T_c . \tag{4.6}$$

The black dots in Fig. 5 represent the  $T_q(N)$  dependence; the values of  $T_q$  were determined from Eq. (4.5). Within the limits of the experimental error we found that the condition (4.6) was indeed satisfied and that in the critical region of a metal-insulator transition we had  $T_q = T_c$ . This circumstance was not self-evident and we have yet to find a convincing explanation.

## 5. CRITICAL BEHAVIOR OF THE PROPERTIES OF *a*-Si:Mn NEAR A METAL-INSULATOR TRANSITION

The critical behavior of an experimental characteristic  $\Phi$  of a disordered system near a metal-insulator transition is frequently described by analogy with second-order phase

transitions and this is done using power-law functions of the critical parameter<sup>16-18</sup> expressing the proximity of the system to a transition:

$$\Phi = \Phi^* (p - p_c)^{\nu_{\Phi}}. \tag{5.1}$$

The critical exponents  $v_{\Phi}$  are usually found by solving model problems of percolation in a conducting lattice with complete and broken bonds<sup>1</sup> assuming *a priori* that  $v_{\Phi}$  are universal, i.e., that their values are independent of the actual disordered system. In our opinion, this general theory is not always correct when applied to real semiconductors undergoing a metal-insulator transition. The presence of a fluctuating large-scale potential in such a semiconductor (for a number of reasons such a potential is present in amorphous and crystalline compensated semiconductors) should increase the critical exponents compared with the values expected in the case of, for example, doped uncompensated crystals.<sup>1</sup> We shall give below qualitative arguments and, moreover, we shall support our view with experimental results.

Let us consider a semiconductor with an impurity energy band modulated by a large-scale potential. An increase in the concentration of the main impurity shifts the Fermi level  $E_F$  toward the percolation level  $E_P$ , which is in the appropriate tail of the density of impurity states. As soon as the difference  $E_P - E_F$  becomes comparable with the amplitude  $\Omega$  of fluctuations of the potential, the behavior of electrophysical properties of such a system becomes critical: electrons collect to form metallic drops and the size of these drops (and, consequently, the carrier localization radius and the effective permittivity of the medium) increases as  $E_F$  and  $E_P$ approach each other. Obviously, the size of the critical region is governed by the value of  $\Omega$ . The larger  $\Omega$  in a disordered semiconductor, the more extended is a metal-insulator transition and we can easily show that this corresponds to large values of the critical exponents.

In the case of doped amorphous semiconductors a large-scale potential is primarily due to a topological disorder and its amplitude can reach  $\Omega = 0.1-0.3$  eV (Ref. 21). The contribution of the electrostatic potential of a randomly distributed charged impurity is small and in the case of *a*-Si:Mn it can be found from<sup>1</sup>

$$\gamma = 0.26 (e^2/\epsilon) ({}^4/_3 \pi N) {}^{1/3} K^{1/4},$$

where K is the degree of compensation of the impurity. If we assume that  $N = 10^{21}$  cm<sup>-3</sup> and K = 0.1, we find that  $\gamma \approx 0.01$  eV. Therefore, an increase in the degree of compensation of a doped crystalline semiconductor should increase the critical exponents which should reach their maximum

| TABLE | I. |
|-------|----|
|-------|----|

| TABLE I.                    |  |  |  |  |  |
|-----------------------------|--|--|--|--|--|
| Degree of com-<br>pensation | v۵   | <sup>∿</sup> T₀  | v <sub>a</sub>   | Ref.   |  |
| uncompens.                  | _  | _  | $-0.55\pm0.1$  | [22]   |  |
| »                           |  | -  | $-0.48 \pm 0.07$                                       | [24]   |  |
| 0.03                        | -  | -  | $-0.60\pm0.04$   | [25]   |  |
| 0.05                        |  | _  | $-0.70\pm0.20$   | 231  |  |
| 0.20-0.35                   | -  | -  | $-1.0\pm0.1$   | [23]   |  |
| _                           | $1.4 \pm 0.2$  | $2.0 \pm 0.1$  | -1.1   | 191  |  |
| 0.3-0.5                     | $1.9 \pm 0.2$  | $2.1 \pm 0.1$  | $-0.8\pm0.2$   | [ [10]   |  |
| -                           | $2.6 \pm 0.2$  | $2,9{\pm}0.2$  | -1.2   | our results  |  |
|                             | Degree of com-<br>pensation<br>uncompens.<br>0.03<br>0.05<br>0.20-0.35<br>0.3-0.5<br>- | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ | $\begin{array}{c c c c c c c c c c c c c c c c c c c $ |  |

\*Here, pyro-PAN denotes pyrolytic polyacrylonitrile.



FIG. 7. Critical behavior of  $\Delta$  and  $T_0$ .

values for amorphous material and also for a heavily doped strongly compensated semiconductor.

The critical parameter p in Eq. (5.1) is usually the density n of uncompensated carriers. In our case there is no guarantee that the whole implanted impurity is electrically active (we only know that the doping efficiency exceeds 1/ 3—see Ref. 13). However, in the critical region of a metalinsulator transition, defined by the condition

$$(E_P - E_F)/\Omega < 1, \tag{5.2}$$

the proximity of the investigated system to this transition can be described satisfactorily by the position of the Fermi level relative to the percolation level:

$$\Phi = \Phi^* (E_P - E_F)^{\nu} \Phi, \qquad (5.3)$$

and the experimentally determined values  $v_{\Phi}$  are then independent of whether the critical parameter is  $(n_c - n)/n_c$  or  $(E_P - E_F)/\Omega$ , because as long as the condition (5.2) is satisfied, we have

$$(n_c - n)/n_c \approx (E_P - E_F)/\Omega.$$
(5.4)

In fact, at T = 0, we have

$$n_c - n = \int_{E_p}^{B_p} g(E) dE.$$
(5.5)

If the integral on the right-hand side is a function of  $E_F$ , we can expand it near the point  $E_F = E_F$ :

$$\int_{E_{F}}^{E_{P}} g(E) dE = g(E_{P}) (E_{P} - E_{P}) + \frac{1}{2} \frac{dg(E_{P})}{dE_{F}} \Big|_{E_{F} - E_{P}} (E_{P} - E_{P})^{2} + \dots \quad (5.6)$$

Since the scatter of levels in an impurity energy band is of the order of  $\Omega$  and the function g(E) has no singularities with the exception of the Coulomb gap of width  $\Delta \ll \Omega$ , we can write down

$$g(E_P) = \frac{n_e}{\Omega}, \quad \frac{dg(E_P)}{dE_F}\Big|_{E_F = E_P} = \frac{n_e}{\Omega^2},$$

when

$$n_c - n = \frac{n_c}{\Omega} (E_F - E_F) + \frac{1}{2} n_c \left(\frac{E_F - E_F}{\Omega}\right)^3 + \dots \qquad (5.7)$$

Retaining only the linear term of the above expansion, we obtain Eq. (5.4).

We shall now turn to the experimental results. The difference  $E_P - E_F$  was determined experimentally by assuming that it was equal to the constant activation energy of the conduction process which at temperatures T > 300 K obeyed the equation

$$\sigma = \sigma_0' \exp[-(E_P - E_F)/kT].$$
(5.8)

A weak concentration dependence of the preexponential factor indicated that the law of Eq. (5.8) was not due to hopping conduction between the nearest impurity atoms.<sup>1</sup> The dependence of  $E_P - E_F$  on the concentration of the impurity implanted in a-Si:Mn is shown in Fig. 6. It is clear from this figure that the behavior of the Coulomb gap became critical in the range N > 4 at. % and the activation energy corresponding to this manganese concentration of 4 at. % was 0.1 eV, i.e., it was of the order of  $\Omega$  for an amorphous semiconductor. Figure 7 shows that the behavior of the  $\Delta(E_P - E_F)$ and  $T_0(E_P - E_F)$  curves can be described by Eq. (5.3). The slopes of the straight lines in this figure give  $v_{\Delta}$  and  $v_{T_{\alpha}}$ (Table I). It is of considerable interest to estimate also the critical exponents of the divergence of the permittivity and of the carrier localization radius. We find from Eq. (1.3)that

$$v_{\varepsilon} = -\frac{2}{3} v_{\Delta}, \tag{5.9}$$

whereas the exponent  $v_a$  deduced from Eq. (1.2) is

$$v_a = -v_{T_0} - v_e. \tag{5.10}$$

The values of  $v_{\Phi}$  found in this way for *a*-Si:Mn are listed in Table I together with the published experimental data for other systems. An analysis of these data leads to the conclusion that the large-scale potential influences the critical exponents of a disordered semiconductor.

## 6. CONCLUSIONS

The relationships describing the behavior of the Coulomb gap obtained by us were not a characteristic feature of a-Si:Mn:Fe compounds, but were probably a property of all disordered semiconductors. Amorphous silicon doped with 3d elements is only a convenient material object in which correlations between localized electrons are manifested clearly (because of the high density of the impurity states in the mobility gap) in charge transport processes at relatively high temperatures (up to the temperature of liquid nitrogen). We are of the opinion that this should make it possible to investigate in future the influence of the Coulomb gap in the spectrum of energy states on electronic properties of disordered semiconductors, such as the specific heat, nature of the screening, tunnel and hopping conductivities in moderate and strong electric fields, and magnetoresistance without recourse to ultralow temperatures (as is necessary at present for semiconductors containing shallow-level impurities) and this would simplify greatly the experimental techniques.

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<sup>&</sup>lt;sup>1)</sup> The influence of disorder of the system on the critical exponents was first pointed out in Ref. 20 in the case of GeSb. Subsequently, the attention to this point was drawn in Refs. 10 and 19.

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