ZERO ANOMALIES IN THE RESISTANCE OF A TUNNEL JUNCTION CONTAINING METALLIC INCLUSIONS IN THE OXIDE LAYER

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A model is considered that describes the current state in granular media, and takes into account the threshold character of the charge transfer between granules due to the discreteness of the electric charge. In the case of tunnel junctions which contain metallic granules in the oxide layer, the law $\sigma \sim T$ is obtained for the tunnel conductivity. Oscillation effects related to the discreteness of the charge are considered.

1. CONDUCTIVITY OF GRANULAR SYSTEMS: CHOICE OF MODEL

THE flow of current in granular media is connected with tunnel transitions of electrons between metallic granules contained in a dielectric matrix. If the granule dimensions are sufficiently small, then the redistribution of charge between them, following the tunneling of the electrons, leads to a significant change in the electrostatic energy of the system. In particular, the increase in the energy of a single, initially neutral granule, which arises upon the removal or addition of a single electron, is equal to $e^2/2\epsilon r$ in order of magnitude (e is the electron charge, ϵ the dielectric permittivity, r the characteristic dimension of the granule) and amounts to several meV for $r \sim 100$ Å and $\epsilon \sim 10$. This means that, generally speaking, there exists an energy threshold for the mechanism of electron tunneling, one of the manifestations of which are the so-called "giant zero anomalies" of the tunnel characteristics of certain junctions. This type of anomaly, first observed by Rowell and Shen,[1] is a strong burst of differential resistance $R = dV/dI$ at $V = 0$. This burst is symmetric relative to the polarity of the voltage and does not depend on the magnetic field. A similar anomalous behavior was observed by Zeller and Giaever[2] on tunnel junctions, in the dielectric layer of which were placed metallic inclusions of small size. Another characteristic feature, also evidently connected with the activation character of the conductivity of granular systems, is the experimentally observed negative temperature coefficients of the resistance. In particular, in the experiment of Zeller and Giaever, $R(V = 0) \sim T^{-1}$.

The hypothesis advanced by a number of authors[2-4] concerning the role of electrostatic effects in the conductivity of granular systems lets us hope that the experimental data enumerated above can be explained in a model which takes into account the Coulomb energy of a system of conductors of small dimensions.

The problem of the calculation of the current in a granular system can be formulated in the following way. We consider a tunnel junction (Fig. 1) which is a granular system placed between two massive conductors (the junction edges). All the conductors are numbered by

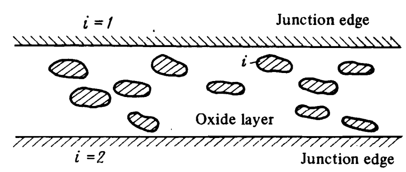

FIG. 1. Schematic form of tunnel junction containing metallic inclusions in the oxide layer.

the index i. For the junction edges, i = 1 and 2. If the tunnel coupling between conductors is weak, then the calculation of the current can be made by the method of the tunnel Hamiltonian.[5,6]

We write down the Hamiltonian of the system in the form

$$H = H_0 + H_e + \hat{T}, \qquad H_0 = \sum_i H_{0i}, \tag{1.1}$$

where H_0 is the Hamiltonian of the system of isolated uncharged conductors,

$$H_e = {}^1/_2 \sum_{i,j} \alpha_{ij} Q_i Q_j \tag{1.2}$$

is the electrostatic energy operator for a system of charged conductors, $Q_i = e(N_i - N_i^0)$ is the operator of uncompensated charge on the i-th conductor,

$$N_i = \sum_{p_i} a_{p_i}^+ a_{p_i},$$

α_{ij} is the matrix of reciprocal capacitances of the set of conductors;

$$\hat{T} = \sum_{i \neq j} \sum_{p_i, p_j} T_{p_i p_j} a_{p_i}^+ a_{p_j} + \text{h.c.} \tag{1.3}$$

is the tunnel contribution to the Hamiltonian.[5,6]

The space quantization of the energy of the electron on a conductor of small size was not taken into account in the formulation of the problem. The energy interval that is characteristic for space quantization (see, for example,[7]), $\Delta E_{sp} \sim \mu/N \sim \mu(a/r)^3$ (μ is the chemical potential and a is the interatomic distance), is much less than the electrostatic energy $E_e \sim {}^1\!/_2 e^2/\epsilon r \sim \mu a/\epsilon r$, if the size r of the conductor is greater than the interatomic distance: $\Delta E_{sp}/E_e \sim \epsilon(a/r)^2 \ll 1$ for $r/a > 3$, if $\epsilon \sim 10$. Under the condition

$$\Delta E_{sp} / kT \sim \mu / NkT \ll 1 \tag{1.4}$$

space quantization can generally be neglected. The condition (14) is satisfied for $T \gtrsim 1°K$ for granules with dimensions $r \sim 100$ Å.

The current $I_i = e\langle \dot{N}_i \rangle$ on the i-th conductor, to first order in the transmission, can be calculated in a manner similar to that used in[8]:

$$I_i = -4e\,\mathrm{Re}\sum_{j\neq i}\sum_{p_ip_j}|T_{p_ip_j}|^2\int_{-\infty}^{t}dt'\langle[a^+_{p_i}(t)a_{p_j}(t), a^+_{p_j}(t')a_{p_i}(t')]\rangle_0,$$
$$a_{p_i}(t) = \exp[i(H_0+H_e)t]a_{p_i}\exp[-i(H_0+H_e)t], \tag{1.5}$$
$$\langle\ldots\rangle_0 = \mathrm{Sp}\left\{\exp\beta\left(\Omega - H_0 - H_e + \sum_i \mu_i N_i\right)\ldots\right\}$$

is the mean over the grand canonical ensemble with the Hamiltonian $H_0 + H_e$, $\beta = (kT)^{-1}$; μ_i is the chemical potential of the i-th conductor;

$$\Omega = -\beta^{-1}\ln\left\{\mathrm{Sp}\left[\exp\beta\left(\sum_i \mu_i N_i - H_0 - H_e\right)\right]\right\}$$

is the thermodynamic potential of the system.

As is seen from (1.5), the currents on the conductors are functions of the chemical potentials μ_i. What is actually known in the experiment, however is the voltage V applied to the junction. To eliminate the chemical potentials of the individual granules, we use the conditions of dynamic equilibrium:

$$I_i = e\frac{d}{dt}\langle N_i\rangle = 0, \quad i\neq 1,2, \tag{1.6}$$

which means that the charge on the granule does not change with time. In this case, the current through the junction is $I_1 = -I_2$ and, with account of (1.6), can be expressed in the form of a function of the chemical potentials for the junction edges, the difference between which is determined by the voltage applied to the junction: $\mu_1 - \mu_2 = eV$.

Although the spectrum and the states of the system of conductors with account of the electrostatic interaction in the form (1.2) are found automatically (inasmuch as $[H_0, H_e] = 0$), the calculation of the thermodynamic averages is a very complex problem, even for such a simple system. The principal difficulty lies in the summation over the fluctuations of the numbers of particles on the conductors, which is impossible to carry out independently for each conductor. Therefore, in what follows, we shall analyze a simpler situation, similar to that described in[2].

We consider a tunnel junction in which the shortest distance between the metallic droplets is much greater than their characteristic dimensions or the distances between the junction edges. In this case, because of the strong screening effect of the junction edges, the electrostatic effect of the droplets on one another is greatly reduced. This indicates a great decrease in the nondiagonal elements of the matrix α_{ij}. Analysis shows that if $\beta e^2 \sum_{j\neq i}\alpha_{ij} \ll 1$, then one can neglect the electrostatic effect of the droplet on one another in the calculation of the currents. Moreover, in this limit of small concentration of droplets, we can neglect the tunnel coupling between the droplets. Then the solution of the problem can be carried out in two steps. We calculate first the current through a junction containing a single metallic droplet. Then this result is averaged over the parameters of the inclusions and multiplied by their concentration to obtain the total current.

2. TEMPERATURE DEPENDENCE OF THE TUNNEL CURRENT

In the calculation of the current from Eq. (1.5), we must recognize that since the dimensions of the junction edges are sufficiently large, the conditions

$$\beta e^2\alpha_{1i} \sim \beta e^2\alpha_{2i} \sim \beta e^2/\varepsilon L \ll 1 \tag{2.1}$$

are easily satisfied in the real situation. Here L is the characteristic dimension of the junction edges (for example, if $L \sim 1$ cm, $T \sim 1°K$, and $\epsilon \sim 10$, then $\beta e^2/\epsilon L \sim 10^{-5}$). In this approximation, and also for the condition (1.4), we can calculate the current in the metallic droplet:

$$I_i = -\frac{2\beta^{-1}}{e}\sum_{j=1,2}\frac{\mathrm{sh}[{}^1/{}_2\beta(\mu_i-\mu_j)]}{R_{ij}}P(\varkappa, \alpha_{ii}, \mu_i-\mu_j), \tag{2.2}$$

$$P(\varkappa,\alpha_{ii},\mu_j) = e^{\gamma/4}\left(\sum_{m=-\infty}^{+\infty}\exp[-\gamma(m-\varkappa)^2]\right)^{-1}$$
$$\times\sum_{m=-\infty}^{+\infty}\exp[-\gamma(m-\varkappa-{}^1/{}_2)^2]\frac{\gamma(m-\varkappa-{}^1/{}_2)+{}^1/{}_2\beta(\mu_i-\mu_j)}{\mathrm{sh}\{\gamma(m-\varkappa-{}^1/{}_2)+{}^1/{}_2\beta(\mu_i-\mu_j)\}}, \tag{2.3}$$

where the resistances R_{ij} of the tunnel junctions between conductors have been introduced;[8]

$$\gamma = {}^1/{}_2\beta e^2\alpha_{ii}; \tag{2.4}$$

m is the integer closest to $N_i - N_{ie}$:

$$m = N_i - N_{ie} + \varkappa, \quad -{}^1/{}_2 < \varkappa \leqslant {}^1/{}_2. \tag{2.5}$$

The quantity N_{ie} is determined by the given chemical potential of the drop:

$$\mu_i = \mu_{i0}(N_{ie}) + e^2\sum_{j=1,2}\alpha_{ij}(N_{ie} - N_i^0), \tag{2.6}$$

where $\mu_{i0}(N_{ie})$ is the chemical potential of the uncharged drop as a function of the density $(\sim N_{ie}/r^3)$ of the electron gas on the drop. It is seen from (2.2) and (2.3) that, in the case in which the characteristic Coulomb energy is small in comparison with the temperature $(\gamma^{1/2} \ll 1)$, the expression for the current in the drop has the usual form (Ohm's law is valid over the entire range of voltages) and the conductivity does not depend on the temperature. The most interesting is the opposite limiting case, when

$$\gamma \gg 1, \tag{2.7}$$

which holds for not too high temperatures (if $r \sim 100$ Å, $\epsilon \sim 10$, then $\gamma \sim 100/T$ [°K]). In this case, the volt-ampere characteristic of the junction is linear only for sufficiently small voltages V, when the conditions

$$\beta|\mu_i - \mu_j| \ll 1. \tag{2.8}$$

are satisfied. Here the equation of dynamic equilibrium (1.6) is easily solved and in first order in βVe we obtain the expression for the current flowing through the junction, without account of direct tunneling between the junction edges:

$$I = \frac{V}{R_{i1}+R_{i2}}P(\alpha_{ii},\varkappa,0). \tag{2.9}$$

Analaysis of (2.3) shows that if (2.7) holds then the current (2.9) is a rapidly decreasing function of the quantity κ. Over almost the entire interval $[-\frac{1}{2}, \frac{1}{2}]$ the changes of the current is exponentially small (for example, $I \sim e^{-\gamma}$ for $\kappa = 0$). The current increases sharply only near the ends of the interval ($\kappa = \pm 1/2$). For $\kappa = \pm 1/2$, the current is $I \approx V/2(R_{i1} + R_{i2})$. The width $\delta\kappa$ of the bursts near $\kappa = \pm 1/2$ is equal to

$$\delta\varkappa \sim \gamma^{-1} = (1/2\beta e^2 \alpha_{ii})^{-1}. \tag{2.10}$$

in order of magnitude.

The dependence of κ on the potential coefficients α_{ii}, α_{1i}, α_{2i} is determined by Eqs. (2.5) and (2.6), which must be considered for $V = 0$ ($\mu_i = \mu_{1,2}$). When the junction edges are made out of the same metal and one of them is grounded, the condition $V = 0$ corresponds to the absence of charge on the junction edges. Then κ is an oscillating function of only the single variable α_{ii}. If we denote by α_m the value of α_{ii} corresponding to $\kappa = \pm 1/2$, then the width of the current bursts $\delta\alpha_m$ for an α determined by Eq. (2.6), is equal to

$$\delta\alpha_m \sim \alpha_m(\beta|\bar{\mu}_1 - \dot{\mu}_{0i}|)^{-1} \sim \alpha_m/\beta\mu_1, \tag{2.11}$$

in magnitude if the chemical potential of the uncharged droplet and the junctions edge differ by several fold ($|\mu_i - \mu_{0i}| \sim \mu_1$). The interval between neighboring bursts, $\Delta\alpha_m = |\alpha_m - \alpha_{m+1}|$, is estimated from Eq. (2.6):

$$\frac{\Delta\alpha_m}{\alpha_m} \sim \frac{e^2\alpha_m}{|\mu_1 - \mu_{0i}|} \sim \frac{e^2\alpha_m}{\mu_1} \sim \frac{1}{\varepsilon}\frac{a}{r}. \tag{2.12}$$

For $a/r \sim 10^{-2}$ and $\epsilon \sim 10$, the change in α of the order of 0.1% leads to the appearance of a new current burst. Such a change in α can take place from an insignificant change in the properties of the surrounding dielectric (ϵ), and also the shape of the droplet, without any essential change in the value of $R_{i1} + R_{i2}$, which depends on the distances between the droplet and the junction edges.

The current through the junctions which contain a collection of drops that are sufficiently far removed from one another, is obtained after averaging the expression (2.9) over the parameters of the inclusions. For a rigorous calculation of the current, it is necessary to know the expression for the drop distribution function, and also the dependence of α_{ii} on the dimensions, and shape of the droplets and on their location in the dielectric layer. Only qualitative remarks on the result of such an averaging are of importance to us. The averaging can be divided into averaging over the characteristic dimensions of the droplet, its location in the oxide layer and over the changes (within prescribed limits) of the parameter ϵ and the shape of the droplet. The result of the latter averaging will be proportional to the width of the current bursts (2.11), i.e., proportional to $\beta^{-1} = kT$. Consequently, the current through the junction and the conductor will be proportional to T. Thus the system possesses a negative temperature coefficient of resistance

$$R(V=0) = (dV/dI)_{V=0} \propto T^{-1}. \tag{2.13}$$

Such a dependence has been observed experimentally by a number of authors.[2,9]

3. OSCILLATORY EFFECTS

It was noted in Sec. 2 of this paper that oscillations of the tunnel current as a function of the capacity of the

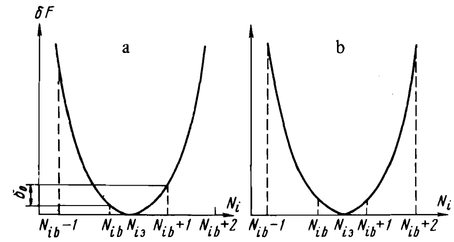

FIG. 2. Dependence of the free energy of the junction $\delta F = F - F_{min}$ on the number of particles in the droplet: a—$N_{ie} < N_{ib} + 1/2$. It is seen that the states with N_{ib} and $N_{ib} + 1$ particles on the droplet are separated by a finite energy interval δ_0; b—$N_{ie} = N_{ib} + 1/2$. In this case, the free energies of states with N_{ib} and $N_{ib} + 1/2$ particles on the droplet are equal.

metallic droplet lead to specific temperature dependence of the junction resistance. In order to understand the physical reason for these oscillations, we consider the case in which the voltage at the junction is equal to zero. We assume that the total number of electrons on both junction edge and the droplet is fixed, but an exchange mechanism of electrons is initiated between the conductors. The most probable distribution of the total number N of electrons between the conductors will be that in which the free energy of the system F is a minimum. We denote these extremal values of the numbers of particles on the junction edges and the droplet by N_{1e}, N_{2e}, N_{3e}, respectively. If the numbers of particles on the conductors differ from the extremal values by several units, then upon satisfaction of the conditions (2.1) and (2.7) the change in the free energy δF will essentially be determined by the change in the number of electrons on the droplet:

$$\delta F = F - F_{min} \approx \beta^{-1}\gamma(N_i - N_{ie})^2. \tag{3.1}$$

A plot of this function is shown in Fig. 2. It is further necessary to recognize that the number of particles on the droplet can take on only integral values. Therefore, the most probable state will be that in which the number of particles on the droplet will be the integer closest to N_{ie} (see 3.1)). However, in the case in which $N_{ie} = N_{ib} + 1/2$ (N_{ib} is an integer), there exist two values of the number of particles on the droplet, N_{ib} and $N_{ib} + 1$, with the same maximum probability. This indicates a singular degeneracy, in which the statistical weights of the states with N_{ib} and $N_{ib} + 1$ particles on the droplet are equal. On the other hand, the flow of current in the junction is connected with such processes in which the number of particles on the droplet changes by unity (we shall not consider virtual tunneling, since its probability is of second order in the transmission). In the case of degeneracy, these processes can take place for unchanged free energy of the system and, consequently, the conduction mechanism will be without a threshold. Such a situation exists also when N_{ie} differs somewhat from $N_{ib} + 1/2$, but the difference in the free energies for the numbers of particles on the drop of N_{ib} and $N_{ib} + 1$ is small in comparison with the temperature. If $N_{ie} = N_{ib} + 1/2 + \delta\kappa$, then it follows from (3.1) that the effective degeneracy takes place for $|\delta\kappa| \lesssim \gamma^{-1}$. If $|\delta\kappa| > \gamma^{-1}$, then the degeneracy disappears and the states with different numbers of electrons on the droplet are separated by an energy barrier. In this case, conduction through the junction has a threshold character.

In conclusion, we consider one more oscillation effect, which arises in a somewhat different situation. We assume that in the single droplet case considered above the distance between the droplet and one of the junction edges (i = 2) is so large that the tunnel coupling of these conductors is practically non-existence, while exchange of electrons between the droplet and the other junction edge (i = 1) is possible. If we apply a voltage to the junction, then initially a current is developed between the droplet and the nearer junction edge which ceases after the chemical potentials of these conductors become equal. Let us compute the charge on the droplet as a function of the applied voltage.

Using (2.5), we write the equilibrium condition $\mu_1 = \mu_i$ in the form

$$e^2\alpha_{ii}(N_{ie}-N_i^0) = e(V_1-V_0), \tag{3.2}$$

where

$$V_0=\mu_{01}(N_{1e})-\mu_{0i}(N_{ie}), \quad V_1=e\sum_{n=1,2}(\alpha_{1n}-\alpha_{in})(N_{ne}-N_n^0). \tag{3.3}$$

In the case in which the junction edges are made of the same metal ($\mu_{01} = \mu_{02}$) and one of them is grounded, the quantity V_1 is proportional to the voltage V on the contact:

$$V_1=\lambda V, \quad \lambda=(\alpha_{11}\alpha_{2i}-\alpha_{12}\alpha_{1i})/(\alpha_{11}\alpha_{22}-\alpha_{12}^2). \tag{3.4}$$

If we take (3.2)—(3.4) into account, we can calculate the charge Q on the droplet as a function of the voltage applied to the junction:

$$Q(V)=e\langle N_i-N_i^0\rangle=\frac{\lambda V-V_0}{\alpha_{ii}}+\frac{2\pi}{\gamma}\frac{A}{B},$$

$$A=\sum_{m=-\infty}^{+\infty} m\sin U_m e^{-\pi^2m^2/\gamma},$$

$$B=\sum_{m=-\infty}^{+\infty}\cos U_m e^{-\pi^2m^2/\gamma}, \qquad U_m=2\pi m\frac{\lambda V-V_0}{e\alpha_{ii}}. \tag{3.5}$$

It is seen from (3.5) that $Q(V)$ consists of a monotonic part and a part that oscillates with V. For $V=\lambda^{-1}V_0$, the charge on the droplet is equal to zero. For sufficiently high temperatures ($\gamma \ll 1$) the oscillating part of the charge is exponentially small. The presence in $Q(V)$ of an oscillating contribution leads to the result that the effective capacitance of the droplet $C = dQ/dV$ also contains an oscillating term. The presence of similar oscillations is the reason for the interesting effects which have been observed by Lambe and Jaklevic.[10]

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