the maximum value $\xi_{\max} = \eta_{\max}$ is determined by the properties of the π-particles interactions,[2] and $q_{\min}$ is determined from the conservation laws. Noting that the most important quantity in $d\sigma^c$ is $q << 1$ and setting $\varphi(q) \approx 4/3\, q^2$, we get a known result[3] for the cross section for pair formation in the Coulomb field:

$$d\sigma^c = (8e^2n^2/3\mu^2)\,\varepsilon(1-\varepsilon) \tag{10}$$

$$\times\, d\varepsilon \ln[(2\varepsilon(1-\varepsilon)\,\omega/\mu^2R]; \quad 2\mu R q_{\min} \ll 1.$$

The integral cross sections are equal to

$$\sigma^d = \frac{e^2R^2}{12}\left[\ln\frac{1+\xi^2_{\max}}{e} + \frac{1}{1+\xi^2_{\max}}\right]; \tag{11}$$

$$\sigma^c = \frac{4}{9}\frac{e^2n^2}{\mu^2}\ln\frac{2\omega}{\mu^2 R}.$$

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Translated by E. S. Troubetzkoy
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Invalidity of the Fermi-Dirac Distribution for Electrons of Semiconductor and Crystal Phosphor Impurity Centers

S. I. PEKAR
Institute of Physics, Academy of Sciences, Ukrainian SSR

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AMONG the original assumptions in introducing the Fermi-Dirac distribution we have the following: 1) The electrons must not interact with each other, in particular, the energy of a given single electronic state must not depend on the distribution of electrons in the states ; 2) subject to the well known limitations, interaction of electrons is permitted with other subsystems (for example, if the state of this subsystem follows the electronic motion adiabatically). But it is necessary that the entropy of this subsystem not depend on the electronic distribution of the state.

It is simple to demonstrate that this assumption is not usually realized for electrons of semiconductor impurity centers. For example, if the donor is an atom of a monovalent metal, then the essential interaction of the electrons (other than the valence electrons) with one another and with the valence electrons, is still not a difficulty since the state of strongly bound electrons of the ion core follows the motion of the valence electrons adiabatically (and thus the motion of the conduction electrons). Therefore the ion core can be considered as the above-mentioned subsystem and the statistical distribution can be introduced only for the valence electrons of the donor and the conduction electrons. But the essential difficulty in obtaining a Fermi distribution is the following circumstance : there exist two equilibrium states of the valence electrons corresponding to the two possible orientations of their spin; hence, if one is occupied by an electron the energy level of the second state is raised considerably and even gets into the conduction band (this is consistent with the instability of the negative ions of the alkali elements, when introduced into crystals). Hence this violates the original assumption 1).

If the donor is an atom of a divalent element, in which the valence electrons have opposite spin orientations, then the state of the atom is nondegenerate. But after a single ionization of the donor, the state of the remaining electrons shows a twofold degeneracy corresponding to the two spin orientations of a single valence electron. Thus the degeee of degeneracy of the states of the subsystem consisting of ionic core is equal to 2^{N_1}, where N_1 is the number of singly ionized donors. In this case the entropy of the subsystem depends essentially on the electron distribution, i.e., in violation of assumption 2).

In consequence of the violation of the original assumptions 1) and 2), the Fermi-Dirac distribution, generally speaking, is not applicable to the donor electrons. Instead, we are led to employ the more general Gibbs distribution for a system with a variable number of particles, and we regard the donor as a system capable of losing electrons to the surrounding medium, and absorbing electrons from the medium. The probability that a donor will contain N electrons and be found in a quantum state n, is equal to

$$w_{nN} = \exp\{(\Omega + \mu N - E_{nN})/kT\}. \tag{1}$$

Here E_{nN} is the energy of all of the electrons of the donor (the electrons may interact with each other), Ω is the thermodynamic potential of the donor electrons, determined from the normalization condition $\sum_{n,N} w_{nN} = 1$ and equal to

$$\Omega = -kT \ln \sum_{n,N} \exp \left\{ \frac{\mu N - E_{nN}}{kT} \right\}, \tag{2}$$

β is the chemical potential of the electrons, which is the same for all electrons of the subsystem, which enter into the crystal. The average number of donor electrons is equal to

$$\bar{N} = \sum_{n,N} N w_{nN} \tag{3}$$
$$= \sum_{n,N} N \exp \left\{ \frac{\mu N - E_{nN}}{kT} \right\} \Big/ \sum_{n,N} \exp \left\{ \frac{\mu N - E_{nN}}{kT} \right\}.$$

This formula is the generalization of the Fermi-Dirac distribution. For not too high temperatures, we can limit our consideration to singly ionized donors only. In this case, let the number of electrons in the ion core be equal to ν, and the number of electrons in neutral donors be $\nu + 1$. Then the Fermi "occupation number" of the donor electrons in our case corresponds to the number $N' = N - \nu$, which is equal to 1, if the donor is neutral, and to 0, if the donor is singly ionized. From Eq. (3) we obtain in this case (N takes on the values ν and $\nu + 1$ only):

$$\bar{N}' = \bar{N} - \nu \tag{4}$$
$$= \left[1 + \sum_n \exp \left\{ -\frac{E_{n\nu}}{kT} \right\} \Big/ \sum_n \exp \left\{ \frac{\mu - E_{n\nu+1}}{kT} \right\} \right]^{-1}.$$

Here appear the partition functions of the ion core and the neutral donors. If we limit ourselves to the first term (low temperatures), which corressponds to the usual simplest popular variant of the theory of semiconductors, in which the interaction between the states of the ion core and the neutral donors is ignored, then we obtain from Eq. (4)

$$N' = [1 + \delta \exp \{(\varepsilon - \mu)/kT\}]^{-1}, \ \delta = f/g. \tag{5}$$

Here the zero of energy is selected, usually so that the energy of the ion core in the ground state $E_{0\nu}$ is equal to zero, the energy of the electrons at the bottom of the conduction band equals zero, the energy of the neutral donors in the ground state is $E_{0\nu+1} = \epsilon$; f is the degree of degeneracy of the ground state of the ion fragment and g is the degree of degeneracy of the ground state of the neutral donor. Equation 5 differs from the usual Fermi-Dirac distribution by the factor δ, which cannot be eliminated by means of introducing the new value of μ, because it then loses its meaning as the chemical potential and does not conform to the chemical potential of the other electronic systems which make up the crystal.

If we use Eq. (5) we derive (by the usual method) the expression for the concentration of conduction electrons in semiconductors with a single type of donor and find

$$n_e = (G\delta n_d)^{1/2} (m^* kT/2\pi\hbar^2)^{3/4} e^{-w/2kT}, \tag{6}$$
$$w = -\varepsilon > 0.$$

Here n_d is the concentration of donors, m^* is the effective mass of the conduction electrons, and G is the number of different quantum states of the conduction electrons with a given energy and quasi momentum. For example, if the conduction band is formed from atomic s-states, then $G = 2$, since there are two possible orientations of the spin of the electrons with a given energy and quasi-momentum.

Eq. (6) differs by the factor $\sqrt{\delta}$ from the analogous formula, deduced from the Fermi-Dirac statistics. Such an additional factor appears in the expression for the current in thermionic emission by semiconductors. An analogous correction appears in other equations in the theory of semiconductors, based on the statistics of electrons.

If the donor is an atom of a monovalent metal, then, as was explained above, $f = 1$, $g = 2$, $\delta = ½$. In the case when the donor is a bivalent element, then according to the above, $f = 2$, $g = 1$, $\delta = 2$. In trivalent donors the single p-electron can be in any one of the six p-states, so that after this electron leaves, the ion fragment is in the non-degenerate state. Hence $f = 1$, $g = 6$, $\delta = 1/6$. Strictly speaking, the six-fold p-levels of the donor atoms are slightly separated under the influence of the crystalline field, which does not possess spherical symmetry. This may be taken into account if we do not use Eq. (5) but the more exact, more general Eq. (4).

From the examples considered earlier, it is clear that not only Eq. (4), but even Eq. (5) leads to results different from the results from Fermi-Dirac statistics. However the latter, in the course of many years, has been widely applied to electrons of impurity centers, beginning first in the work of Wilson[1] and Fowler[2] and ending in the latest review of Schottky.[3] One should make the appropriate corrections to the formulae of the theory of semiconductors. In Ref. 4, the correct results are derived, since we do not use the Fermi-Dirac electron statistics but use the much more general Gibbs distribution.

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Application of the Lattice Model to Semiconductors of the Lead Sulphide Type

T. K. Rebane
Leningrad State University

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THE application of the lattice model to solids was first pointed out by Coulson[1], who calculated (with the aid of this model) the band structure of the energy spectrum in metals with a cubic space lattice, and also in graphite and in boron nitride. In the present paper the lattice model is applied to semiconductors of the type PbX, where $X = $ S, Se and Te. The specified semiconductors have cubic lattices of the NaCl type. The initial electron configurations in the isolated atoms are: $\mathrm{Pb}-p^2$, $X-p^4$. For each of the paired atoms of PbX in the crystal there are six p-electrons. We may consider two lattice models of PbX crystals:

a) the three-dimensional model, analogous to the three-dimensional lattice model, proposed by Coulson for metals;

b) it is possible to describe the p-electrons in the crystal as breaking up into the groups p_x, p_y and p_z, and the electrons of each group break up into subgroups, such that all electrons of one subgroup can move in a definite plane of the tetragonal lattice, formed by the atoms of Pb and X. Each of the subgroups is similar to a system of π-electrons in conjugate organic molecules.

In the first, as well as in the second model, we set the following for the potential V along the lattice: $V = V_0$ within the Pb atoms and $V = 0$ within the X atoms (V_0 is the difference between the electronegativities of X and Pb). For conjugate organic molecules containing heterocyclic atoms, Veselov and Rekasheva[2] proposed such a form for the potential.

In order to determine the size of the atoms of Pb and X in the crystal, we start out from the value of the ionic radii of Pb^{++} and X^{--} (according to Goldshmidt). The initial values of the ionic radii r_{Pb} and r_X are changed in proportion so that in each crystal the equation $r_{\mathrm{Pb}} + r_X = a$ holds (a is the distance between the atoms Pb and X).

We have the following relation for the binding energy of the electron and its quasi-momentum **k**:

In the first model

$$f(E) = {}^1/_9\,(\cos ak_x + \cos ak_y + \cos ak_z)^2;$$

In the second model

$$f(E) = {}^1/_4\,(\cos ak_x + \cos ak_y)^2.$$

The function $f(E)$ has the following form:

$$f(E) = (\cos\omega_1 r_X \operatorname{ch}\omega_2 r_{\mathrm{Pb}} - (\omega_1/\omega_2)\sin\omega_1 r_X \operatorname{sh}\omega_2 r_{\mathrm{Pb}}) \times (\cos\omega_1 r_X \operatorname{ch}\omega_2 r_{\mathrm{Pb}} + (\omega_2/\omega_1)\sin\omega_1 r_X \operatorname{sh}\omega_2 r_{\mathrm{Pb}}),$$

if $E < V_0$ and

$$f(E) = (\cos\omega_1 r_X \cos\omega_2 r_{\mathrm{Pb}} - (\omega_1/\omega_2)\sin\omega_1 r_X \sin\omega_2 r_{\mathrm{Pb}}) \times (\cos\omega_1 r_X \cos\omega_2 r_{\mathrm{Pb}} - (\omega_2/\omega_1)\sin\omega_1 r_X \sin\omega_2 r_{\mathrm{Pb}}),$$

$$\omega_1 = \sqrt{2E};\quad \omega_2 = \sqrt{2\,|E - V|},$$

if $E > V_0$. The allowed energy values in the first and second models are determined from the equation

$$0 \leqslant f(E) \leqslant 1.$$

In this manner the three-dimensional and the plane model lead to the same band structure for the energy spectrum. At absolute zero, the first allowed band in the first as well as in the second model is completely filled with electrons, the remaining allowed zones are empty.

We calculated the width of the forbidden zone ΔE, the effective mass of the holes m_h^* and the effective mass of the electrons m_e^* (in units of the