Theory of Many-Valued Equilibrium Distribution of Carriers in Many-Valley Semiconductors

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Many-valley unipolar semiconductors exhibit a homogeneous anisotropic lattice deformation which is accompanied by the formation of an energy gap between the equivalent valleys and by the redistribution of carriers between the displaced valleys. This anisotropy is the result of the electron-phonon interaction via the deformation potential and it appears when the carrier density is high. It is found that in this situation the state of a semiconductor, in which all the valleys are equally populated, is thermodynamically unstable. The stability of anisotropic states is ensured by a general lowering of the Gibbs free energy of a crystal which is associated with a reduction in the energy of carriers in some of the valleys. The many-valley energy spectrum is responsible for the many-valued nature of the equilibrium distribution of carriers, which is manifested by the existence of several stable states (corresponding to a minimum of the Gibbs free energy) in a semiconductor with an inhomogeneous distribution of carriers over the valleys. These states are characterized by different values of the strain tensor. Some of these states correspond to the same lowering of the Gibbs free energy, i.e., they are degenerate. A detailed analysis is given of an isotropic model of a semiconductor with two groups of carriers whose interaction with phonons is characterized by different deformation potentials. The results are also given for germanium and silicon, and the case of a degenerate semiconductor is considered briefly. It is shown that in many-valley semiconductors of the type represented by germanium and silicon the absolute minimum of the Gibbs free energy corresponds to degenerate states characterized by a preferential population of one of the valleys in germanium and of a pair of valleys (which can be regarded as one valley) in silicon.

THE concept of carrier groups can often be applied to semiconductors with complex energy band structures. Such groups may correspond to, for example, two or more overlapping bands, different minima in the **k** space, etc. The distribution of carriers over such groups has a strong influence on many physical properties of semiconductors. This distribution may be affected by external forces such as electric and magnetic fields, currents, or deformations.

In the present paper we shall use the deformation potential model to consider the influence of a homogeneous lattice deformation, resulting from the presence of free carriers, on the equilibrium distribution of carriers over groups. Such a deformation increases the elastic energy of the lattice and the energy of carriers in some groups but reduces it in other groups. Consequently, an equilibrium distribution of carriers over the various groups is established in such a way as to ensure a minimum of the Gibbs free energy of a crystal. We shall show that at high carrier densities such a distribution is not single-valued, i.e., that for a given value of the total carrier density there are several different equilibrium distributions and associated deformations. In this case the state with equal populations of the valleys in a semiconductor with many equivalent valleys may be thermodynamically unstable. Under these conditions the stable states are characterized by a deformed lattice, displaced energy minima, and preferential population of the lowest valleys.

We shall consider the effect just described by writing down the density of the Gibbs free energy of a homogeneous unipolar semiconductor[1] (we shall use the harmonic approximation for the elastic deformation energy and we shall assume that carriers are not degenerate):

$$F = {}^1/_2\lambda_{ijkl}u_{ij}u_{kl} - \sigma_{ij}u_{ij} + \sum_{r=1}^{\nu} b_{ij}^{(r)}u_{ij}n_r - T\sum_{r=1}^{\nu}\left(n_r - n_r\ln\frac{n_r}{n_{0r}}\right). \quad (1)$$

Here, λ_{ijkl}, u_{ij}, σ_{ij}, $b_{ij}^{(r)}$ are the tensor components of the elastic moduli, strains, stresses, and deformation potential constants, respectively; n_r is the density of carriers in the r-th group; n_{0r} is the density in the same group in the absence of deformation; ν is the number of valleys. The temperature T (expressed in energy units) is assumed to be constant and the donors are taken to be fully ionized.

The condition for an extremum of the free energy (1) with respect to the variables u_{ij} and n_r can be combined with the electrical neutrality equation

$$\sum_{r=1}^{\nu} n_r = N, \quad (2)$$

where N is the total density of carriers, to give the following system of equations:

$$\lambda_{ijkl}u_{kl} + \sum b_{ij}^{(r)}n_r = \sigma_{ij}, \quad (3)$$

$$n_r = n_{0r}\exp\{-(\Phi + b_{ij}^{(r)}u_{ij})/T\}. \quad (4)$$

The Lagrange factor Φ is found from Eq. (2).

The possibility of many-valued equilibrium distributions of carriers in many-valley semiconductors has been pointed out briefly in[2]. We shall develop a detailed theory of this phenomenon in cubic crystals in the absence of external stresses ($\sigma_{ij} = 0$). In Sec. 1 we shall analyze in detail the simplest isotropic model of a semiconductor with two groups of carriers characterized by different deformation interaction constants. In Sec. 2 we shall consider the solutions of the system (3)–(4) for semiconductors whose energy structure is of the type found in n-type Ge and n-type Si and we shall also discuss the case of a degenerate semiconductor. In Sec. 3 we shall compare the values of the free energy for solutions obtained in Sec. 2.

1. UNIPOLAR SEMICONDUCTOR WITH TWO GROUPS OF CARRIERS

We shall consider a model of a semiconductor in which the two groups of carriers are electrons (or holes) characterized by an isotropic energy spectrum. We shall assume that the interaction with phonons is represented by a deformation potential which is different for each of these groups. In this case $b_{ij}^{(1)} = b_1\delta_{ij}$, $b_{ij}^{(2)} = b_2\delta_{ij}$, and Eq. (2) is of the form

$$n_1 + n_2 = n_{01} + n_{02} = N. \tag{5}$$

In the case of a cubic crystal the only components of the tensor λ_{ijkl} that do not vanish are

$$\lambda_{xxxx} \equiv \lambda_1,\ \lambda_{xxyy} \equiv \lambda_2,\ \lambda_{xyxy} \equiv \lambda_3. \tag{6}$$

It follows from Eqs. (3) and (4) that $u_{ij} = 0$ for $i \neq j$ and the diagonal components $u_{xx} = u_{yy} = u_{zz} = 2T\eta/3(b_1 - b_2)$ are defined by the equation

$$\eta / A + \beta = \mathrm{th}(\eta - \rho). \tag{7}$$

Here,

$$A = \frac{3(b_1 - b_2)^2 N}{4T(\lambda_1 + 2\lambda_2)},\quad \beta = \frac{b_1 + b_2}{b_1 - b_2},\quad \rho = \frac{1}{2}\ln\frac{n_{01}}{n_{02}}. \tag{8}$$

The ratio of the carrier densities in the two groups is

$$n_1 / n_2 = e^{2(\rho - \eta)}. \tag{9}$$

The dependences of the left-hand (L) and the right-hand (R) parts of Eq. (7) on η are plotted in Fig. 1 for different values of the parameter A (these curves are plotted for the specific case when $-\mathrm{th}\,\rho < \rho < 0$, $\rho > 0$). Depending on the values of the parameters A, β, and ρ, Eq. (7) can have between one (curves 1 and 3) and three (curves 2 and 3) real roots. An analysis of the free energy of Eq. (1) shows that a minimum of this energy F is obtained for those solutions η which satisfy

$$1 / A > \mathrm{ch}^{-2}(\eta - \rho), \tag{10}$$

i.e., in the case of thermodynamically stable states the slope of $L(\eta)$ with respect to the abscissa is greater than the slope of $R(\eta)$ (Fig. 1).

We shall now consider the dependences of the solutions of Eq. (7) and of the ratio (9) on the values of the parameters A, β, and ρ. To be specific, we shall assume that $n_{01} \geq n_{02}$, i.e., $\rho \geq 0$.[1)]

1) If $\beta \geq 1$, all finite values of A correspond to a single (stable) solution $\eta < 0$, which represents the distribution $n_1 > n_2$ (curve 1 in Fig. 2a).

2) If $-\tanh\rho < \beta < 1$, we find that—beginning from $A = A_1 \geq 1$—we have not only branch 1 but also new solutions represented by curves 2 and 3 in Fig. 2a. The values of A_1 and η_1 can be found from Eq. (7) and from

$$A = \mathrm{ch}^2(\eta - \rho). \tag{11}$$

[1)]Equation (7) is symmetrical with respect to the simultaneous changes in the sign of η, β, and ρ, which correspond to a relabeling of the carrier groups. Hence, it follows that it is sufficient to consider one specific case such as $\rho \geq 0$.

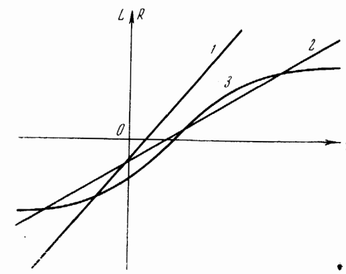

FIG. 1. Dependences of the left- and the right-hand parts of Eq. (7) on η for $-\mathrm{th}\,\rho < \beta < 0$, $\rho > 0$ and different values of A.

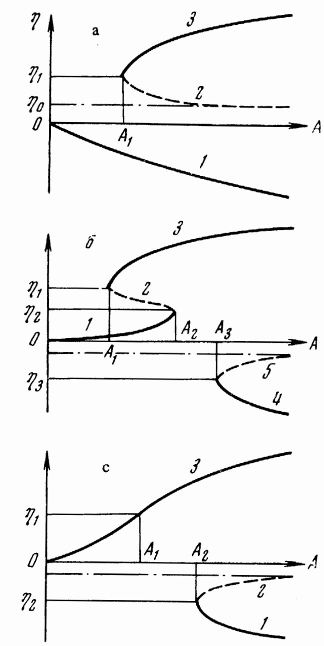

FIG. 2. Possible dependences of η on A corresponding to different values of β.

Curve 2 represents an unstable solution and curve 3 a stable solution characterized by $\eta > \rho$, i.e., by $n_1 < n_2$ [the stable solutions, in the sense of the criterion given by Eq. (10), are represented in the figures by continuous curves and the unstable solutions by dashed curves]. The unstable solution corresponding to large values of A approaches asymptotically $\eta_0 = \rho + \tanh^{-1}\beta$.

3) If $\beta < -\tanh\rho$, the dependences of the solutions on A are different for $\rho > 1$ and $\rho < 1$. In the first case, the solutions in the range $-1 < \beta < -\tanh\rho$ are given by branches 1–5 in Fig. 2b. It is evident from this figure that there are three critical values of the parameter A which are defined by Eqs. (7) and (11). Branches 1 and 4 correspond to the distribution $n_1 > n_2$, and branch 3 corresponds to $n_1 < n_2$. In the range $-\rho \leq \beta \leq -1$ the solutions are only of the type represented by curves 1–3.

4) The case when $\rho < 1$ and $-\rho < \beta < -\tanh\rho$ is of the same type as the case $\rho > 1$ and $-1 < \beta < -\tanh\rho$ (Fig. 2b). If $\rho < 1$, the possible dependences $\eta(A)$ corresponding to the range $-1 < \beta < -\rho$ are those shown in Fig. 2c. The solution represented by curve 1, which appears suddenly when $A > A_2$, as well as the solution represented by curve 3 in the range $A < A_1$, both correspond to the distribution $n_1 > n_2$ whereas curve 3 in the

range $A > A_1$ corresponds to the distribution $n_1 < n_2$. If $\beta < -\operatorname{Sup}\{\rho, 1\}$, only the solution represented by curve 1 remains valid.

Thus, when the parameter A exceeds a certain critical value, the equilibrium distribution of carriers becomes many-valued, i.e., several possible distributions of the carriers over the groups may be stable for a given total density. The free energy minima corresponding to different stable solutions are, generally speaking, different. We shall now consider the relative positions of these minima of F in the case of n-type Ge and n-type Si.

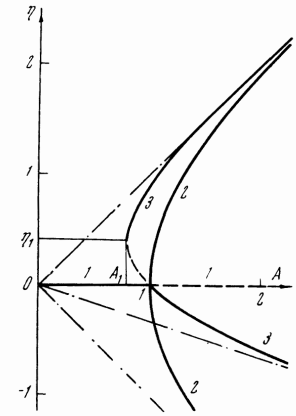

FIG. 3. Possible dependences of η on A for germainum.

2. MANY-VALLEY SEMICONDUCTORS OF THE n-TYPE Ge OR n-TYPE Si KIND

We shall consider the distribution of electrons over the valleys in semiconductors with energy structures of the kind encountered in n-type Ge or n-type Si.

1. n-Type Germanium

This semiconductor has four equivalent valleys oriented along the threshold axes. In a coordinate system whose axes xyz coincide with the fourfold crystallographic axes, the tensor $b_{ij}^{(r)}$ is of the form[3]

$$b_{ij}^{(r)} = b_1\delta_{ij} + b_2 e_i^{(r)} e_j^{(r)}, \tag{12}$$

where $\mathbf{e}^{(r)}$ is a unit vector directed along a threefold axis into the r-th valley. The valleys oriented along the [111], [$\bar{1}11$], [$\bar{1}\bar{1}1$], [$1\bar{1}1$] axes will be denoted by the subscripts 1, 2, 3, and 4, respectively. In the absence of deformation and also under hydrostatic compression or expansion all the valleys have the same populations: $n_{0r} = N/4$.

In the case we are considering we can separate the equations for the diagonal components of the strain tensor from the system (3)—(4): these components are independent of the distribution of electrons over the valleys are given by

$$u_{xx} = u_{yy} = u_{zz} = -(b_1 + {}^1\!/_3 b_2)N/(\lambda_1 + 2\lambda_2). \tag{13}$$

The nondiagonal components are defined by the equations

$$2\lambda_3 u_{ij} = -N\Sigma_{ij}^{(s)}/\Sigma^{(s)}, \quad i \neq j, \tag{14}$$

where

$$\Sigma_{ij}^{(s)} = \sum_{r=1}^{4} b_{ij}^{(r)} \exp\left(-\frac{b_{mn}^{(r)} u_{mn}}{T}\right), \quad \Sigma^{(s)} = \sum_{r=1}^{4} \exp\left(-\frac{b_{mn}^{(r)} u_{mn}}{T}\right). \tag{14$'$}$$

The system of transcendental equations (14) has—apart from the trivial solution $u_{ij} = 0$, which corresponds to the state with the same population in all valleys—solutions of the following three types.

a) Two-valley solutions. In the sixfold-degenerate solutions of this type the only nonvanishing nondiagonal component of the strain tensor is

$$\begin{aligned} &u_{xy} \lessgtr 0, \ n_1 = n_3 \gtrless n_2 = n_4; \\ &u_{xz} \lessgtr 0, \ n_1 = n_4 \gtrless n_2 = n_3; \\ &u_{yz} \lessgtr 0, \ n_1 = n_2 \gtrless n_3 = n_4. \end{aligned} \tag{15}$$

These solutions correspond to the anisotropic state of a semiconductor in which any one pair of valleys can be enriched with electrons at the expense of depletion of the other valleys and the valley populations are the same in each pair. The equations which determine the deformation and the corresponding intervalley redistribution are identical in all three cases. We shall consider the specific case when $u_{xy} \neq 0$, $u_{xz} = u_{yz} = 0$. If we introduce the notation

$$u_{xy} = 3T\eta/2b_2, \quad A = b_2^2 N/9\lambda_3 T, \tag{16}$$

we find that Eq. (14) yields an equation for η which is identical with Eq. (7) if we substitute $\beta = \rho = 0$ into the latter equation. The dependences of the solutions on the parameter A are plotted for this case in Fig. 3 (curves 1 and 2). If $A < 1$, the only stable solution is the trivial case when $\eta = 0$, $n_1 = n_2 = n_3 = n_4$. If $A > 1$, there are three solutions: the trivial solution, which is now unstable, and two nontrivial stable solutions (curve 2). The stable solution characterized by $\eta > 0$ corresponds to the carrier distribution $n_1 = n_3 < n_2 = n_4$, whereas the solution characterized by $\eta < 0$ corresponds to the distribution $n_1 = n_3 > n_2 = n_4$. A simple analytic dependence $\eta = \eta(A)$ can be obtained in the following two limiting cases:

$$\eta \approx \pm\sqrt{3(A-1)}, \quad |\eta| \ll 1; \tag{17}$$

$$\eta \approx \pm A, \quad |\eta| \gg 1. \tag{18}$$

b) One-valley and three-valley solutions. In the solutions of this type, which correspond to the identical population of any three valleys as a result of enrichment (one valley case) or depletion (three-valley case) of the fourth valley, none of the nondiagonal components of the strain tensor is equal to zero and these components differ only in sign:

$$\begin{aligned} -u_{xy} = -u_{yz} = u_{xz} \gtrless 0, &\quad n_4 \lessgtr n_1 = n_2 = n_3; \\ u_{xy} = u_{yz} = u_{xz} \gtrless 0, &\quad n_1 \lessgtr n_2 = n_3 = n_4; \\ u_{xy} = -u_{yz} = -u_{xz} \gtrless 0, &\quad n_3 \lessgtr n_1 = n_2 = n_4; \\ -u_{xy} = u_{yz} = -u_{xz} \gtrless 0, &\quad n_2 \lessgtr n_1 = n_3 = n_4. \end{aligned} \tag{19}$$

Equations for solutions of this type are identical in all cases. We shall consider the first of them. We shall introduce the notation

$$u_{xy} = 3T\eta/4b_2, \quad A = 4b_2^2 N/27\lambda_3 T; \tag{20}$$

then, the equation for η is of the Eq. (7) type in which $\beta = -\tanh\rho = -1/2$. The roots of this equation are represented by curves 1 and 3 in Fig. 3 (the axes represent $\eta/2$ and $3A/4$ for convenience of comparison with the case a solutions). The critical point (η_1, A_1), like the point (0, 1), is determined from Eqs. (7) and (11). Only the trivial solution exists for values of A up to A_1.

A stable one-valley solution appears suddenly at $A = A_1 < 1$: this solution corresponds to the range $\eta > \eta_1$ in curve 3 and to the distribution $n_4 > n_1 = n_2 = n_3$. If $A > 1$, the trivial solution is always unstable and that part of curve 3 which corresponds to the three-valley solution of the $\eta > 0$, $n_4 < n_1 = n_2 = n_3$ type becomes stable. In the limiting cases the analytic dependences of these solutions are of the form

$$\eta = 1 - A, \quad |\eta| \ll 1; \tag{21}$$

and

$$\eta = \begin{cases} A, & \eta > 0 \\ -{}^1/_3 A, & \eta < 0; \quad |\eta| \gg 1. \end{cases} \tag{22}$$

The asymptotes corresponding to the limiting case represented by Eqs. (18) and (22) are plotted as chain lines in Fig. 3. In view of the exponential dependence of the carrier density n_r on the deformation, the asymptotic forms of the solutions are close to the true solutions at values of the parameter A which exceed only slightly the critical value. At these values of A the solutions correspond to an anisotropic state of a crystal with the number of valleys governed by the nature of the solutions.

2. n-Type Silicon

This semiconductor has three pairs of equivalent valleys (each of these pairs can be regarded as one valley), which are oriented along directions coinciding with the fourfold crystallographic axes. If the coordinate system is selected as in the case of n-type germanium, it is found that the tensor $b_{ij}^{(r)}$ is of the form given by Eq. (12), where $e^{(r)}$ is a unit vector directed along a fourfold axis into the r-th valley. The tensor $b_{ij}^{(r)}$ expressed in terms of these axes is diagonal. We shall now relabel the valleys elongated along the x, y, and z axes as valleys 1, 2, and 3 and we shall denote the electron densities in these valleys by $2n_1$, $2n_2$, and $2n_3$, respectively; here, $n_{0r} = N/6$.

In this case it follows from Eqs. (3)—(4) that all the strain tensor components vanish ($u_{ij} = 0$) if $i \neq j$. The diagonal components are given by the equations

$$\lambda_{ijkk} u_{kk} = -N\Sigma_{ij}^{(6)}/\Sigma^{(6)}, \quad i = j, \tag{23}$$

where the quantities $\Sigma_{ij}^{(6)}$ and $\Sigma^{(6)}$ are defined in Eq. (14′). The system of transcendental equations (23) has a trivial solution as well as triply degenerate solutions corresponding to identical populations in any two pairs of valleys as a result of depletion (two-valley case) or enrichment (one-valley case) of the third pair:

$$\begin{aligned} &u_{xx} = u_{zz}, \quad u_{xx} - u_{yy} \gtrless 0, \quad n_2 \gtrless n_1 = n_3; \\ &u_{yy} = u_{zz}, \quad u_{zz} - u_{xx} \gtrless 0, \quad n_1 \gtrless n_2 = n_3; \\ &u_{yy} = u_{xx}, \quad u_{yy} - u_{zz} \gtrless 0, \quad n_3 \gtrless n_2 = n_1. \end{aligned} \tag{24}$$

In all these cases Eq. (23) reduces to the same form. We shall consider briefly the first case. If we use the notation

$$u_{xx} - u_{yy} = 2T / b_2, \quad A = 3Nb_2^2 / 8T(\lambda_1 - \lambda_2), \tag{25}$$

we find that η is given by Eq. (7) in which $\beta = -\text{th}\,\rho = -1/3$. It follows from Eq. (23) that

$$u_{xx} = u_{zz} = \frac{2T}{3b_2}\eta - \frac{(b_1 + {}^1/_3 b_2)}{\lambda_1 + 2\lambda_2} N. \tag{26}$$

The qualitative nature of the dependence of β on A is of the same kind as in Fig. 3 (curves 1 and 3). In this case that part of curve 3 for which $\eta > \eta_1$ corresponds to the distribution $n_2 > n_1 = n_3$ and the stable part of curve 3 for which $\eta < 0$ corresponds to $n_2 < n_1 = n_3$. A uniaxial shear strain corresponds to the stable nonequilibrium distributions of electrons over the valleys.

3. Numerical Estimates and Degenerate Case

In numerical estimates of the critical value of the carrier density in n-type Ge we may assume that $b_2 = 20$ eV and $\lambda_3 = 0.5 \times 10^{12}$ dyn/cm². Then, at T = 100°K the value $A = A_1$ is reached at $N = 4.8 \times 10^{19}$ cm⁻³.

The electron gas may become degenerate at high carrier densities and low temperatures. We shall now consider how the basic equations are modified in the case of strong degeneracy. The contribution of the electron component to the Gibbs free energy, which is the last term in Eq. (11), can be represented in the form

$$\frac{3}{5}\varepsilon_F\left(\frac{\nu}{N}\right)^{2/3}\sum_{r=1}^{\nu} n_r^{5/3}, \tag{27}$$

where ϵ_F is the Fermi energy of the electron gas whose density is N in the case of uniform population of the valleys. For the sake of simplicity we shall consider a two-valley solution for n-type Ge ($n_1 = n_3$, $n_2 = n_4$; $u_{xy} \lessgtr 0$, $u_{xz} = u_{yz} = 0$). If we introduce the notation

$$\eta = \frac{6\lambda_3}{b_2 N} u_{xy}, \quad A = \frac{b_2^2 N}{6\lambda_3 \varepsilon_F}, \tag{28}$$

we find that Eq. (7) is replaced by

$$ {}^4/_3 A\eta = (1 + \eta)^{2/3} - (1 - \eta)^{2/3}. \tag{29}$$

The parameter A differs from its nondegenerate value given by Eq. (16) in that T is replaced by $2\epsilon_F/3$. If $A < 1$, we obtain a solution with a uniform population of the valleys: $\eta = 0$. In the $1 < A < 3/2^{4/3}$ range we have, in addition to the unstable trivial solution $\eta = 0$, two symmetrical stable solutions whose absolute values increase with A from $\eta = 0$ to $|\eta| = 1$. If $A \geq 3/2^{4/3}$, one of the valley pairs becomes completely empty and $|\eta| = 1$.

3. CONCLUSIONS

We have considered the influence of a homogeneous anisotropic deformation resulting from the presence of free carriers on the distribution of these carriers over the valleys in a many-valley semiconductor. We have found that when the total carrier density is higher than the critical value—determined by the deformation potential constants, the elastic moduli, and the temperature—the state of a semiconductor with a uniform population of the valleys is thermodynamically unstable in the absence of shear strain. The stable states correspond to a nonzero shear strain, an energy gap between the equivalent valleys, and a redistribution of carriers over the displaced valleys. These states correspond to a minimum of the Gibbs free energy F. The unstable states are characterized by the absence of an extremum of F [F has a maximum in terms of the strain tensor components subject to the conditions (2) and (4)]. There are several stable states which correspond to different values of the strain tensor components and this is responsible for the many-valued nature of the equili-

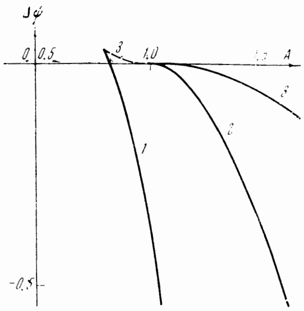

FIG. 4. Change in the Gibbs free energy plotted as a function of A for germanium. The value $\Delta\psi = 0$ corresponds to the state with the same population of all the valleys.

brium distribution of carriers between the valleys.[2)] Some of these states correspond to the same lowering of the free energy of a crystal, i.e., they are equivalent or degenerate. The multiplicity of degeneracy is determined by the number of valleys and their relative positions in the **k** space.

In the case of n-type Ge we can have a total of 14 states with nonuniform distributions of carriers over the valleys:

1) sixfold-degenerate states of the two-valley type (any two valleys are preferentially populated);

2) fourfold-degenerate states of the one-valley type (one valley is preferentially populated);

3) fourfold-degenerate states of the three-valley type (three valleys are preferentially populated).

Similarly, n-type Si has triply degenerate states of the one- and two-valley types.

The different inequivalent states correspond, generally speaking, to different reductions in the free energy. In the case of n-type Ge and two-valley states the change (relative to the trivial state) in the free energy ΔF is of the form

$$\Delta F \equiv 2\lambda_3 (3T/2b_2)^2 \Delta\psi, \qquad \Delta\psi = \eta^2 - 2A \ln \operatorname{ch} \eta, \tag{30}$$

[2)]The possibility of a many-valued distribution of carriers between valleys in a different situation (a strong "heating" electric field) has been pointed out in[4].

where η and A are given by Eq. (16) and represent the solution of Eq. (7) (curve 2 in Fig. 3). The dependence of $\Delta\psi$ on A is represented by curve 2 in Fig. 4. The corresponding change in the free energy for the one- and three-valley solutions is given by the expression

$$\Delta\psi = \frac{3}{4}\eta^2 - \frac{3}{2} A \ln\left(\frac{e^{-3\eta/2} + 3e^{\eta/2}}{4}\right), \tag{31}$$

where η and A are defined by Eq. (20) (curve 3 in Fig. 3). The dependences $\Delta\psi$ on A for the one- and the three-valley solutions are represented by curves 1 and 3 in Fig. 4, respectively. It follows from this figure that, at a fixed value of the parameter A (fixed value of the carrier density), the absolute minimum of the Gibbs free energy corresponds to the one-valley states. A similar situation occurs also in n-type Si because the absolute minimum again corresponds to the one-valley solutions.

The presence of degenerate states may give rise to splitting of a semiconductor into domains each of which corresponds to one of the spatially homogeneous equivalent solutions. We note also that a spatially homogeneous state may be unstable with respect to space-charge fluctuations even in the case of a one-valley semiconductor (see[5]). These points deserve separate discussion.

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