Phase transition in multivalley semiconductors in a magnetic field

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The phase transition in multivalley cubic semiconductors with electron-phonon coupling via the deformation potential in a magnetic field leading to quantization of the carrier motion (variation of their energy spectrum) is considered. A nontrival distribution of the electrons over the valleys arises in the new phase as the result of a spontaneous homogeneous anisotropic deformation appearing in the crystal, which deforms the carrier energy spectrum. The phase transition region is a series of separate or overlapping regions on the "concentration-temperature" diagram, the higher regions approximately resembling the first one adjacent to the point $N = T = 0$ (N is the electron concentration and T is the temperature). In the case of a multivalley band structure of the n-Ge type, states with one, two, or three enriched valleys are possible. Each of these states is absolutely stable in a certain range of N and T values. The regions are bounded by first-order phase transition curves which contain separate second-order phase transition points.

INTRODUCTION

The deformation interaction of current carriers with the lattice can lead to a phase transition of a cubic multivalley superconductor to an anisotropic state.[1] The anisotropic phase of the semiconductor is characterized by a spontaneous homogeneous uniaxial deformation along one of the symmetric crystalline directions. The energy spectrum of the carriers is distorted here: the energy of one or several of the valleys is decreased and that of others increased. As a result, a nontrivial carrier distribution among the valleys is achieved. Generally speaking, several such states exist, to which correspond deformations along different axes of the crystal and different variations of the energy spectrum. Anisotropy of the properties of the crystal to which the carriers make a contribution (electrophysical, elastic and other characteristics of the semiconductor) should appear in the new phase properties.

The critical condition for the phase transition depends on the temperature T and the carrier concentration N, and can be represented in the form $A(N, T) \geq 1$, where the parameter $A(N, T)$ reaches a maximum as $T \to 0$; $\max A \sim b^2(\lambda d\epsilon_F/dN)^{-1}$ (b and λ are characteristic combinations of the constants of the deformation potential and the elastic modulus $\epsilon(N)$ is the Fermi energy of the carriers). If we take $b \sim E_a$ and $\lambda \sim E_a/a_0^3$,

$$\varepsilon_F \approx \frac{(3\pi^2)^{2/3}m_0}{\nu^{2/3}m^*}(Na_B^3)^{2/3}E_a$$

(here E_a is an energy of the order of atomic energies, a_0 the lattice constant, a_B the Bohr radius of the hydrogen atom, m^* the effective mass of the carriers, ν the number of valleys), then the following order of magnitude estimate is obtained for the critical concentration in the region of actual temperatures $T < \epsilon_F$:

$$N_c a_0^3 \gtrsim \frac{9\pi^4}{\nu^2}\left(\frac{m_0 a_B^2}{m^* a_0^2}\right)^3 = \xi.$$

In semiconductors in real cases, the number of carriers is much smaller than the number of atoms in the lattice ($Na_0^3 \sim 1$); therefore the effect should appear in crystals with large effective mass of the carriers.[1)] In the cases $m^* \ll m_0$, it turns out that $N_c a_0^3 \sim 1$, i.e., the critical condition has not been achieved experimentally.

A different situation obtains in the case of a strong magnetic field that leads to quantization of the motion of the carriers and which changes the dependence $\epsilon_F(N)$. Actually, when the Fermi level approaches the Landau level, the density of states in the band increases without limit and $d\epsilon_F/dN \to 0$. Then, according to the estimate given above, $A \to \infty$, i.e., the critical condition is satisfied in a number of intervals of values of N, which are determined by the equality $\epsilon_F(N) \approx \hbar\omega k$, $k = 0, 1, 2, \ldots$. For finite T, this should lead to the existence of a number of separated or overlapping regions for the thermodynamic variables N and T, in which the effect is possible. The concentration barrier which exists in the absence of a magnetic field disappears. In fact, for small N, when the ultraquantum case is achieved, we have

$$\varepsilon_F(N) \approx (Na_0^3)^2 \frac{E_a^3}{(\hbar\omega)^2}\xi < \hbar\omega,$$

so that $A \sim N^{-1}$, (ω is the cyclotron frequency). If $\hbar\omega < \xi E_a$, then an isolated interval of concentrations bordering on the value $N = 0$ must necessarily exist, and an estimate of the critical concentration gives $N_c a_0^3 \lesssim (\hbar\omega)^2/E_a^2\xi$. It is easy to determine in this case the range of temperatures for which the critical condition $T < \epsilon_F(N_c)$ is satisfied, i.e., $T_c \lesssim (\hbar\omega)^2/E_a\xi$. If $\hbar\omega > \xi E_a$, then all the regions in the NT plane overlap, and the effect is possible for any N, if $T < \hbar\omega$.

The magnetic field not only leads to a change in the region of the phase transition, but also has a material effect on the resultant anisotropic phases. Thus, in a multivalley semiconductor with a band structure of the n-Ge type, when states with one, two or three sunken valleys are possible, the thermodynamically most favored (in the absence of a magnetic field) are the single-valley states. In a magnetic field, it turns out that there are regions of absolute stability for each of the "deformed" states. As a result, there are on the NT plane, in addition to the phase transition curves of the crystal from the initial state to the anisotropic, first-order phase-transition curves along which the different anisotropic phases coexist, and isolated points of second-order phase transitions appear, at which these curves terminate. In the two-valley situation (a two-valley semiconductor or, say, a four-valley one in which the valleys are pairwise equivalent in the aniso-

tropic phase), first or second order phase transitions can be achieved, depending on the values of N and T. Points appear on the NT plane at which the curve of second order phase transitions joins with the curve of first order phase transitions (a second order phase transition is always achieved in this situation in the absence of a magnetic field).

We shall consider below the theory of phase transitions in multivalley semiconductors in a quantizing magnetic field.

1. FUNDAMENTAL EQUATIONS

For the study of the spatially homogeneous states of a monopolar multivalley semiconductor, we write down the free energy density of the crystal in the form

$$F=\frac{1}{2}\lambda_{ijkl}u_{ij}u_{kl}+\sum_{\alpha=1}^{\nu}b_{ij}^{(\alpha)}u_{ij}n_\alpha+\sum_{\alpha=1}^{\nu}F_{\alpha e}(n_\alpha), \tag{1}$$

where λ_{ijkl}, u_{ij}, $b_{ij}^{(\alpha)}$ are the respective components of the tensors of elastic moduli, the deformation and the constants of the deformation potential; n_α and $F_{\alpha e}(n_\alpha)$ are the concentration and free energy of the carriers of valley α, ν is the number of valleys. It is convenient to express the free energy $F_{\alpha e}$ for carriers located in a quantizing magnetic field in terms of the thermodynamic potential in the variables T, V, and μ $-\Omega(T, V, \mu)$[2]:

$$F_{\alpha e}(n_\alpha)=\mu_\alpha n_\alpha+\Omega(T,\mu_\alpha)\equiv\mu_\alpha n_\alpha-g\hbar\omega_\alpha T^{3/2}\varphi_{1/2}\left(\frac{\mu_\alpha}{T}-{}^1/_2\vartheta_\alpha,\vartheta_\alpha\right). \tag{2}$$

Here $g=(1/2\pi^2)(2m^*/\hbar^2)^{3/2}$, m^* is the effective mass for the density of states, ω_α is the cyclotron frequency of the electrons of valley α, $\vartheta_\alpha=\hbar\omega_\alpha/T$; the following notation is also introduced for the Fermi integrals:

$$\varphi_s(z,\vartheta)\equiv\sum_{m=0}^{\infty}\Phi_s(z-m\vartheta),\qquad \Phi_s\equiv\int_0^\infty\frac{dx\,x^s}{(e^{x-z}+1)}. \tag{3}$$

Since the variable in $F_{\alpha e}(n_\alpha)$ is the carrier concentration n_α, we can assume $\mu_\alpha=\mu_\alpha(n_\alpha)$ in (2). The explicit form of this relation is found from the condition

$$n_\alpha={}^1/_2g\hbar\omega_\alpha T^{1/2}\varphi_{-1/2}(\mu_\alpha/T-{}^1/_2\vartheta_\alpha,\vartheta_\alpha). \tag{4}$$

Variation of the free energy (1) with respect to the variable u_{ij} gives an equation for the components of the deformation tensor:

$$\lambda_{ijkl}u_{kl}+\sum_{\alpha=1}^{\nu}b_{ij}^{(\alpha)}n_\alpha=0. \tag{5}$$

The equations for n_α are similarly obtained from (1) with account of (3)—(5):

$$n_\alpha=\frac{1}{2}g\hbar\omega_\alpha T^{1/2}\varphi_{-1/2}\left(\frac{\varepsilon_F-b_{ij}^{(\alpha)}u_{ij}}{T}-\frac{\vartheta_\alpha}{2},\vartheta_\alpha\right) \tag{6}$$

where ϵ_F is the Fermi level in the deformed crystal, and is found from the condition of the constancy of the total concentration of the carriers:

$$\sum_{\alpha=1}^{\nu}n_\alpha=N. \tag{7}$$

Equations (5)—(7) completely describe the possible states of the crystal in a magnetic field. These states and the changes in the free energy F corresponding to them will be considered below in the example of a semiconductor with an energy band structure of the type of n-Ge. For definiteness, we renumber the valleys lying on the axes [111], [$\bar{1}$11], [$\bar{1}\bar{1}$1] and [$1\bar{1}$1] as 1, 2, 3, 4, respectively (the coordinate axes are directed along the fourfold crystallographic axes). We denote the nonzero components of the tensor λ_{ijkl} by $\lambda_{xxxx}=\lambda_1$, $\lambda_{xxyy}=\lambda_2$, $\lambda_{xyxy}=\lambda_3$. Then, with account of the symmetry properties of the tensor $b_{ij}^{(\alpha)}$, we obtain an expression from (5) for the components u_{ij}:

$$u_{xx}=u_{yy}=u_{zz}=-\frac{b_{xx}N}{\lambda_1+2\lambda_2},\qquad u_{ij}=-\frac{1}{2\lambda_3}\sum_\alpha b_{ij}^{(\alpha)}n_\alpha,\quad i\neq j. \tag{8}$$

We also assume that the magnetic field is directed along a fourfold symmetry axis, so that all the valleys remain equivalent and $\vartheta_\alpha\equiv 0$. In this case, as also for $\vartheta=0$, Eqs. (6)—(8) have solutions of the following types.

A. Two-valley solutions. These solutions possess a sixfold degeneracy and correspond to spontaneous uniaxial deformation along directions of the type [110], for example,

$$u_{xy}\lessgtr 0,\qquad u_{xz}=u_{yz}=0,\qquad n_1=n_3\gtrless n_2=n_4. \tag{9}$$

B. Single-valley and three-valley solutions. Each of these solutions has a fourfold degeneracy and corresponds to deformation along a direction of the type [111], for example,

$$u_{xy}=u_{xz}=u_{yz}\gtrless 0,\qquad n_1\lessgtr n_2=n_3=n_4. \tag{10}$$

The single-valley and three-valley states differ from one another only by the sign of the deformation and the intervalley redistribution.

2. SECOND ORDER TRANSITIONS. TWO-VALLEY STATES

We now consider the two-valley solutions. Inasmuch as it is not possible to find the explicit dependence $\mu_\alpha(n_\alpha)$ in the general case from (4), we limit ourselves at first to the case of small redistributions $((n_\alpha-n_0)/n_0=\xi_\alpha\ll 1$, $n_0=N/\nu)$, for which

$$\frac{\mu_\alpha-\mu_0}{T}\cong\frac{\zeta_\alpha\varphi}{\varphi'}\left\{1-\frac{\zeta_\alpha\varphi\varphi''}{2(\varphi')^2}+\frac{\zeta_\alpha^2\varphi^2}{2(\varphi')^4}\left(\varphi''^2-\frac{1}{3}\varphi'\varphi'''\right)+\ldots\right\}, \tag{11}$$

here and below, $\varphi=\varphi_{-1/2}(z_0)$, where $z_0=\mu_0/T$ is the reduced chemical potential for uniform filling of the valleys

$$N=\nu gT^{1/2}\hbar\omega\varphi_{-1/2}(z_0,\vartheta). \tag{12}$$

From (2) and (11), we find the variation of the free energy of the electrons from valley α upon change in their concentration:

$$\Delta F_{\alpha e}=Tn_0\left\{z_0\zeta_\alpha+\frac{\zeta_\alpha^3\varphi}{2\varphi'}-\frac{\zeta_\alpha^3\varphi^2\varphi''}{6(\varphi')^3}+\frac{\zeta_\alpha^4\varphi^3}{8(\varphi')^5}\left(\varphi''^2-\frac{1}{3}\varphi'''\varphi'\right)\right\}. \tag{13}$$

In the two-valley situation, introducing $\zeta={}^1/_2(\zeta_1-\zeta_2)$ (see (9)), we get

$$\sum_\alpha\Delta F_{\alpha e}=\frac{1}{2}TN\frac{\zeta^2\varphi}{\varphi'}\left\{1+\frac{\zeta^2\varphi^2}{4(\varphi')^4}\left(\varphi''^2-\frac{1}{3}\varphi'''\varphi'\right)\right\}. \tag{14}$$

Expressing u_{ij} in terms of ζ with the aid of (8), and denoting

$$\eta=2bu_{xy}/T=-\zeta A\varphi/\varphi',\qquad b\equiv b_{xy}^{(1)},$$

we get for the change in the total thermodynamic potential (1) and small solutions η:

$$\Delta\mathcal{F}\equiv\frac{2b^2}{\lambda_3T^2}\Delta F=(1-A)\eta^2+C(N,T)\eta^4+\ldots, \tag{15}$$

$$\eta=\pm[(A-1)/2C]^{1/2},\qquad A>1,\qquad (A-1)\ll 1. \tag{16}$$

Here the parameters A and C are defined by the expressions

$$A\equiv\frac{b^2N}{\lambda_3T}\frac{\varphi'(z_0,\vartheta)}{\varphi(z_0,\vartheta)}, \tag{17}$$

$$C \equiv {}^1/_4(\varphi')^{-2}(\varphi''^2 - {}^1/_3\varphi'\varphi'''). \qquad (18)$$

The expression (15) has the form of the characteristic Landau[2] expansion of the thermodynamic potential near a second order phase transition point. As an expansion parameter, we use the quantity η, which determines the degree of deviation from the state with uniform filling of the valleys. The transition takes place under constant external stresses, the thermodynamic variables are the carrier concentration, the temperature and the magnetic field; for example, the curve A(N, T) = 1 on the NT plane is the continuous line of points of the phase transition. The results (15)–(16) are valid for C > 0. At the points C = 0, joining of the curves of the first and second order transitions takes place. The total change in the free energy for the phase transition is found from (15), (16):

$$\Delta\mathcal{F} = -(A-1)^2(\varphi')^2 / [(\varphi'')^2 - {}^1/_3\varphi'\varphi'''] \qquad (15')$$

and allows us to calculate the entropy change ($\Delta S \sim (A-1)$) and the jump in the specific heat in the usual way.

We analyze (in the variables N and T) the region of existence of the two-valley anisotropic states, whose boundary, in accord with (12) and (17), is determined by the conditions

$$\sqrt{t} \leqslant \varphi_{-1/2}'(z_0, \vartheta), \quad \varkappa = \sqrt{t}\,\varphi_{-1/2}(z_0, \vartheta), \qquad (19)$$

where the dimensionless concentration and temperature have been introduced:

$$\varkappa \equiv N\lambda_3 / (2g\hbar\omega b)^2, \quad t \equiv T\lambda_3^2 / (2b^2 g\hbar\omega)^2. \qquad (20)$$

Equations (19) become simplified for $\hbar\omega > T$. As $T \to 0$, when the Fermi level satisfies the conditions $r - 1 < \bar{z} < r$, $\bar{z} \equiv z_0/\vartheta$, i.e., when it is populated by r Landau levels (r = 1, 2, ...) and the electrons on the levels are strongly degenerate, while the contribution of the highest levels is insignificant, Eqs. (19) take the form

$$1 \leqslant A(\Theta) \equiv \sqrt{\Theta}\sum_{m=0}^{r-1}\frac{1}{\sqrt{\bar{z}-m}},$$
$$\varkappa = \frac{2}{\sqrt{\Theta}}\sum_{m=0}^{r-1}\sqrt{\bar{z}-m}, \qquad \Theta \equiv \hbar\omega\left(\frac{2gb^2}{\lambda_3}\right)^2. \qquad (21)$$

It is seen that in this case the dependence of A on z takes on the same character as the dependence of the density of states on the energy in a magnetic field, i.e., A becomes infinite for the values $\bar{z} = 0, 1, 2, \ldots$. This leads to the result that (21) is satisfied in a number of intervals of values of the concentration κ. Each of these intervals begins at

$$\varkappa_{ir} = \frac{2}{\sqrt{\Theta}}\sum_{m=0}^{r-1} m^{1/2}.$$

Depending on the values of the magnetic field Θ, we can have either separated intervals or overlapping ones. For $\Theta \geq 1$, the separated intervals are absent, and the effect takes place for any value of the concentration. For $\sqrt{2}/(1+\sqrt{2}) < \sqrt{\Theta} < 1$, a single interval exists, which is separated and adjoins $\kappa = 0$. It terminates at $\kappa = 2$. In the general case, for

$$\sum_{m=1}^{r+1} m^{-1/2} > \Theta^{-1/2} > \sum_{m=1}^{r} m^{-1/2}$$

the first r intervals will be separated and all the subsequent ones overlap, forming a continuous interval of values of κ in which (21) is satisfied.

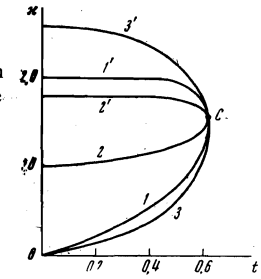

FIG. 1. Dependence of the concentration on the temperature. The first region of phase change $\kappa = \kappa_1(t)$—curves 1 and 1'. Curves 2 and 2' bound the region of absolute stability of states of the two-valley type, and curves 2, 3 and 2', 3' pertain to one- and three-valley states, respectively.

At a finite temperature, these intervals indicate the presence of a series of regions, part of which is separated on the NT plane under consideration. The boundaries of these regions depend in general on Θ. For the first isolated region ($\bar{z} < 1$), it is necessary to take into account only the first component in $\varphi_{-1/2}$. In this case, the explicit dependence on the magnetic field drops out, and in place of (19) we find

$$t^{1/2} \leqslant \Phi_{-1/2}'(z_0), \quad \varkappa = t^{1/2}\Phi_{-1/2}(z_0). \qquad (19')$$

The $\kappa_1(t)$ dependence that follows from (19') is shown in Fig. 1 by the lines 1 and 1'. For small κ, the boundary of the region coincides with the straight line x = t, i.e., it is determined by the expression for the parameter A, which is characterized for the case of nondegenerate carriers. In the region of maximal temperatures, for which the effect still exists, the curve $\kappa_1(t)$ takes the form

$$\varkappa - \varkappa_c = \pm\delta(t_c - t)^{1/2}, \quad \delta^2 \equiv (\varphi'^3/|\varphi'''|)_{z=z_c}, \qquad (22)$$

where $\kappa_C = {}^1/_2(\varphi^2)_{z_C}'$, $t_C = (\varphi)_{z_C}^2$ and z_C is found from the condition

$$(d^2\varphi_{-1/2}/dz^2)_{z_c} = 0. \qquad (23)$$

The upper boundary of the region is determined as $t \to 0$ by the line $\kappa = 2$. Here, according to (18), the coefficient C(N, T) in the expansion (15) vanishes at some point N_λ, T_λ (actually, $C \approx -\pi^2/48z_0^4 < 0$ as $t \to 0$, κ_λ and $t < t_\lambda$, as $t \to 0$, the solution can be obtained by using the general formulas (2)–(4) without assuming smallness of ζ_α. We then get for the free energy of the electrons

$$\sum_\alpha F_{\alpha e} = \frac{\hbar\omega}{2}N + \frac{N^3}{3v^2(g\hbar\omega)^2}\sum_\alpha(1+\zeta_\alpha)^3. \qquad (24)$$

Using (1) and (24), we can find that a nontrivial solution appears only jumpwise, so that all the carriers turn out to be in a single valley and correspondingly $\zeta_\alpha = 1$. The decrease in the thermodynamic potential and the limiting expression for the parameter A have the following forms in this case:

$$\Delta F = -\frac{N^3(A-1)}{(4g\hbar\omega)^2}, \quad A = b^2(4g\hbar\omega)^2/2\lambda_3 N. \qquad (25)$$

The approximate course of the curves $\kappa_r(t)$, (r > 1)—the boundaries of the succeeding regions—can be obtained for $\Theta \ll 1$, when there are several isolated regions. For

$$t < t^* = \frac{\pi}{q^2(r)}\exp\left\{\frac{2q(r)}{q(r)-1}\right\}, \qquad q(r) \equiv 1 - \sqrt{\Theta}\sum_{m=1}^{r-1} m^{-1/2},$$

close to κ_{ir} we find

$$\varkappa - \varkappa_{ir} = t\ln\left(\sqrt{\frac{t}{\pi}}q(r)\right)(1-q(r)). \qquad (26)$$

Outside this exponentially small region, for $t > t^*$, the $\kappa_r(t)$ dependence differs from the $\kappa_1(t)$ dependence

considered above only by a change in scale, i.e., the following similarity holds approximately:

$$\varkappa_r(t)=\varkappa_{ir}+\frac{1}{q(r)}\varkappa_1[tq^2(r)],\qquad r=1,2,\ldots \tag{27}$$

The boundaries of the considered regions $\kappa_r(t)$ are curves of second order phase transitions only for $C(N, T) > 0$. In the general case, C vanishes at finite t for the isolated regions; as $\kappa \to \kappa_{in}$, $t \to 0$, the coefficient $C(N, T) \to 1/6$ and at the ends of the curves, when $\kappa \to \kappa_{fr}$, $t \to 0$, $r > 1$,

$$C(N,T)=\frac{(\Theta t)^2\left(\sum_0^{r-1}(\bar z-m)^{-1/2}\right)^{-2}}{16}\left\{\left(\sum_0^{r-1}(\bar z-m)^{-5/2}\right)^2-\left(\sum_0^{r-1}(\bar z-m)^{-1/2}\right)\left(\sum_0^{r-1}(\bar z-m)^{-5/2}\right)\right\}<0. \tag{28}$$

(The latter follows directly from the well-known Cauchy-Bunyakovskiĭ inequality.) Thus the points

$$A(N_\lambda,T_\lambda)=1,\qquad C(N_\lambda,T_\lambda)=0, \tag{29}$$

exist on the curves $\kappa_r(t)$ at which the first two terms of the expansion (15) vanish. In the vicinity of these points, one must keep the term in (15) with η^6 $-(1/3)D\eta^6$. We then get as a solution, in place of (16),

$$\eta^2=D^{-1}(-C\pm\sqrt{C^2+(A-1)D}), \tag{30}$$

$$D(N_\lambda,T_\lambda)=D(z_\lambda)=\frac{\varphi''\varphi^{(IV)}}{8(\varphi')^2}-\left(\frac{\varphi''}{\varphi'}\right)-\frac{\varphi^{(V)}}{120\varphi'}; \tag{31}$$

here the value of the argument of D corresponds to the points (29).

If $C > 0$, then the solution with the plus sign in front of the radical of (30), for $C^2 \gg |D(A-1)|$ goes over into (16). If $C < 0$ and $D > 0$, then the solution with the plus sign (in the vicinity of the points (N_λ, T_λ), this solution still appears small) shows up as a jump at $C^2 = (1-A)/D$ and corresponds to the minimum of ΔF. The second solution of (30) corresponds to the maximum of ΔF and determines the height of the barrier which separates the trivial state from the "deformed" state. Thus, for $C < 0$, the phase transition turns out to be a transition of first order, i.e., the points N_λ, T_λ are points of joining of the first and second order phase-transition curves (λ points). The first order transition curve is found from the condition $\Delta F(\eta) = 0$, where η is taken from (30) and is determined by the condition

$$C^2=4/3(1-A)D. \tag{32}$$

It is easy to show that all the phase transition curves do not undergo a discontinuity at the λ points. In the vicinity of these points, we have in place of (15′)

$$\Delta\mathcal{F}=-2/3[(A-1)^3/D]^{1/2}, \tag{33}$$

whence it follows that the entropy change for a phase transition of the system $\Delta S \sim (A-1)^{1/2}$ and the unbounded increase in the specific heat is $\Delta c_0 \sim (A-1)^{-1/2}$.

In the case $D < 0$, both types of solutions of Eq. (30) for η^2 near N_λ, T_λ have a meaning for $C > 0$. The solution which transforms into (16) corresponds to a relative minimum in ΔF, while the second, larger solution is a maximum. Consequently, there should exist one more type of minimum of ΔF with, generally speaking, large deformations and repopulations ($\eta \sim 1$) for which (15) and (30) are unsuitable. The point N_λ, T_λ itself is unstable in this case "accumulation" takes place for it (without an activation barrier) in the state with $\eta \sim 1$. Thus, the case $D < 0$ indicates the existence of a region of values of N and T at which two stable states exist, one of which corresponds to a relative minimum in ΔF and is metastable. Close to the point (29), states with small repopulation are metastable. We note that the presence of two stable states should lead to hysteresis effects in the spontaneous deformation and intervalley redistributions for a change in N and T.

3. FIRST ORDER TRANSITIONS. STATES OF THREE AND SINGLE-VALLEY TYPES

Results similar to those given above can be obtained also for single-valley (three-valley) states (see (10)): for them there is also a number of separated (or overlapping) existence regions on the N, T plane, always bounded, in contrast with (9), by curves of first order phase transitions. One can show that in each of these separated regions, a region is preserved which corresponds to two-valley solutions, so that the states of type (10) are realized over a broad range of values of N and T.

Let us consider in more detail the first region of existence of solutions of type (10). At $T = 0$, when the electron part of the free energy is given by the expression (24), it is easy to find that one-valley solutions exist in the range $0 \le \kappa \le 2$, while for $0 \le \kappa \le 1$, this solution corresponds to complete redistribution of the carriers in one valley ($\zeta_1 = 3$) and for $1 \le \kappa \le 2$, for the partial one: $\zeta_1 = 3(2-\kappa)/\kappa$. For $2 \le \kappa \le 3$, this latter goes over into a solution of the three-valley type. Another solution of this type with destruction of one of the valleys ($\zeta_1 = -1$, $\zeta_2 = \zeta_3 = \zeta_4 = 1/3$) is realized in the interval $0 \le \kappa \le 3$. For $T \ne 0$, we can find the change in the thermodynamic potential in the following form by using the formulas (11)—(13):

$$1/3\Delta\mathcal{F}=(1-A)\eta^2+2/3B\eta^3+1/2C'\eta^4+\ldots,\qquad |\eta|\ll 1. \tag{34}$$

Here $C' = 14C$, A and C are determined by formulas (17) and (18), and $B = \varphi''/\varphi$; according to (23), it changes sign at $z = z_c$, which on the (κ, t) plane corresponds to the parabola $\kappa = \sqrt{t}\Phi_{-1/2}(z_c)$. In the region $\kappa < \sqrt{t}\Phi_{-1/2}(z_c)$, it turns out that $B > 0$. The extremum of the expression (34) is achieved at

$$\eta=\frac{1}{2C'}(-B\pm\sqrt{B^2-4(1-A)C'}). \tag{35}$$

Both these values are suitable only near the point $B = 0$, $A = 1$. The absolute minimum of ΔF corresponds, in the region $B > 0$, to the solution with a minus sign ($\eta < 0$, the one-valley solution), and in the region $B < 0$ to the one with a plus sign ($\eta > 0$, the three-valley solution). These solutions appear jumpwise (for $B \ne 0$) and for them $\Delta F \sim (A-1)$, $\Delta S = \text{const}$ (first-order transition). The transition curve can be found from the condition $\Delta F(\eta) = 0$, near κ_c and t_c it has the form $\kappa - \kappa_c = \pm\delta_1\sqrt{t_c - t}$, where $\delta_1^2 = (21/13)\delta^2$ (compare with (22)). The point $B = 0$, $A = 1$, according to[3], is a separated point of a second order phase transition ($\eta \sim \pm\sqrt{t_c - t}$ for $\kappa = \kappa_c$). Far away from this point, the solution and the curve of first order phase transitions can only be obtained numerically by using Eqs. (5) and (6), with (10) taken into account.

Other solutions of (35) appear for $A \ge 1$, varying smoothly from zero, are small and are suitable near

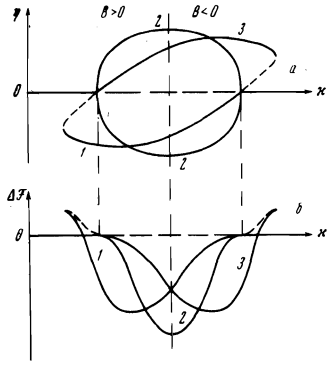

FIG. 2. Qualitative dependences of η and $\Delta\mathcal{F}$ on κ for fixed t. The broken lines correspond to stable states, the dashed lines to unstable. The path of $\eta(\kappa)$ and $\Delta\mathcal{F}(\kappa)$ for states of the two-valley type are indicated by the curves 2, while curves 1 and 3 give the corresponding curves for one- ($\eta < 0$) and three-valley ($\eta > 0$) states, respectively.

the whole curve A (κ, t) = 1. For B $\neq$ 0, we obtain η = (A − 1)/B, i.e., this solution corresponds to the three-valley state in the region B > 0 and to the one-valley one at B < 0. The expression (34) takes the form $\Delta F = -3(A-1)^3/B^2$ near A = 1, B = 0. In the vicinity of (κ_c, t_c), the explicit curve $\eta(\kappa, t)$ can be obtained:

$$\eta = \frac{3}{7(\varphi')^2}\left(\varkappa - \varkappa_c \pm \sqrt{\frac{7\delta^2}{3}(t_c - t) - \frac{4}{3}(\varkappa - \varkappa_c)^2}\right). \qquad (36)$$

This character of the $\eta(\kappa, t)$ dependence is preserved qualitatively over the entire region of existence of the solutions and is illustrated in Fig. 2a. In this drawing the stable states (corresponding to minimum F) are shown as solid lines, while the dashed lines indicate unstable states.

The existence of several types of states in a single region of the variables (κ, t) requires the determination of the thermodynamic suitability of these states. This can be accomplished in the two limiting cases. As T → 0, we obtain the following change in the thermodynamic potential for one-, two-, and three-valley states, respectively:

$$\Delta F_{\mathrm{I}} = -F_0\varkappa^2(6-5\varkappa), \quad 0 \leqslant \varkappa \leqslant 1,$$
$$\Delta F_{\mathrm{II}} = -F_0\varkappa^2(2-\varkappa), \quad 0 \leqslant \varkappa \leqslant 2,$$
$$\Delta F_{\mathrm{III}} = -F_0\frac{\varkappa^2}{27}(18-\varkappa), \quad 0 \leqslant \varkappa \leqslant 3,$$
$$\Delta F_{\mathrm{I-III}} = -F_0(2-\varkappa)^3, \quad 1 \leqslant \varkappa \leqslant 3,$$
$$F_0 \equiv \left(\frac{\hbar\omega\Theta}{2b}\right)^2\lambda_3. \qquad (37)$$

The first three states correspond to an intervalley redistribution with a complete destruction of the valleys in the corresponding states, the fourth is the partial repopulation in the single valley ($1 \leq \kappa \leq 2$) and three-valley ($2 \leq \kappa \leq 3$) states (the latter do not generally correspond to minimum in F). From (37) we obtain the result that, in the range of values κ[0, 1], an absolute minimum F is achieved for single-valley states, in the range [1, $^9/_5$] for two valley, and in the range [$^9/_5$, $^{18}/_7$] for three-valley (for $^{18}/_7 \leq \kappa \leq 3$, the three-valley solution is metastable). For T $\neq$ 0, one can equate the different phases near the point (κ_c, t_c). From (15), (16) and (34)–(36) we find the equilibrium curve of two-valley states with states of the type (10). This curve touches the line A(N, T) = 1 at the point (κ_c, t_c) and has the form: $\kappa = \kappa_c = \pm\delta_2(t_c - t)^{1/2}$, where $\delta_2 < \delta$ (compare with (22)); in the continuation into the low temperature region, its branches should terminate at the points (1, 0) and ($^9/_5$, 0). It is easy to show that, on the line of coexistence of one- and three-valley states: $\kappa - \kappa_c = (t - t_c)\varphi/2\varphi')_{z=z_c}$. Similarly, with the help of (15), (16) and (34), (35), we can investigate the dependence of $\Delta T(\kappa, t)$ in the vicinity of B = 0, A = 1, which is represented in Fig. 2b. Such a character for the behavior of ΔT is maintained qualitatively through the entire range of values of κ.

CONCLUSION

On the basis of the results given above, we can draw the following picture of phase changes in multivalley semiconductors. In a quantizing magnetic field, a series of regions of phase transitions appears on the concentration-temperature plane, which, for high concentrations, overlap with one another. The number of overlapping regions increases with increase in the magnetic field, and for $\hbar\omega > (\lambda_3/2gb^2)^2$ all the regions overlap. The higher separated regions are approximately similar to the first, which is shown in Fig. 1. The effect on them of a magnetic field, in accord with (20) and (27), reduces to a change in scale (following a change in the value of the magnetic field). The first region is bounded by the curves of the first order phase transitions 3 and 3′. Single-valley states appear upon passage through the first of these, and three-valley states upon passage through the second. One-, two- and three-valley states exist in the overlapping regions, bounded by the curves 3, 1′; 1, 1′ and 3′, 1, respectively. However, the regions of their absolute stability are different and are located between the curves 3, 2; 2, 2′; 2′, 3′ (compare with Fig. 2b). Curves 2 and 2′ are coexistence lines of these phases, i.e., curves of first-order phase transitions between states of types (9) and (10). One- and three-valley states can exist only as metastable states. The regions of metastability of one-, two- and three-valley states are bounded by the lines 2, 1′; 1, 2 and 1′, 2′; 1, 2′. The one- and three-valley metastable states terminate on curves of their absolute instability (1′ and 1), on which the minimum F for them disappears and accumulation of the system should take place in the corresponding stable state (see also Fig. 2). In each of the separated regions, there is an isolated second order phase transition point (the point C in Fig. 1). At this point, contact takes place between the lines of the first and second order phase transitions, and all four states become identical. We note that in the regions which lie between the curves 1, 3 and 1′, 3′, the initial isotropic state of the crystal is stable, but appears to be metastable.

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[1)] At the present time, a number of multivalley crystals with a large density of states is known, for example, the n-type $SrTiO_3$ and $KaTaO_3$, the p-type SnTe and GeTe, and so forth.

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