Fluctuon states of electrons

M. A. Krivoglaz

Metal Physics Institute, Ukrainian Academy of Sciences, Kiev

The carrier states are considered in disordered or in not-fully-ordered nometallic systems under conditions when the internal parameters of the medium change relatively rapidly. In a definite region of temperatures and electron-medium interaction constants, there can be produced in these systems fluctuons, i.e., large-radius formations in which the electron is autolocalized near the change of the fluctuation, concentration, or internal parameter of the medium, and maintains the fluctuations stationary through its field. The characteristics of fluctuons are investigated in solutions, in para- and ferromagnetic semiconductors, in systems near the critical point in a solution, or in a gas-liquid system, and also near a first-order phase transition point. The mechanism of fluctuon mobility is discussed. A transition of electrons into fluctuonic states can have the character of a smeared first-order transition and can alter strongly different electronic properties of the system, as well as some other system properties. The possibility of spontaneous dispersion of a system with easily-alterable internal parameters is considered at a relatively high carrier density.

CONTENTS

1. INTRODUCTION, EXAMPLES OF FLUCTUONIC STATES IN VARIOUS SYSTEMS

The interaction between a conduction electron and medium is in some cases quite strong and can qualitatively alter the state of the electron. This question was examined in detail with the interaction of an electron with ion vibrations in ionic crystals as an example. This interaction leads to the formation of polarons (see, e.g. [1-3]). Depending on the ratio of the width ΔE of the conduction band to the polarization energy E_p, there appear either large-radius polarons in which the region of electron localization in the polaron potential well occupies a large number of bins (at $\Delta E \gg E_p$), or small-radius polarons where this region occupies only one bin (at $\Delta E \ll E_p$).

Special electronic states that resemble in a sense polaron-type self-localized states but differ from them significantly in some respects can be formed in disordered or incompletely ordered systems, e.g., in solutions or in systems whose internal parameters are relatively easily changed. Let, for example, a fluctuation cause a change in the concentration c or in an internal parameter η of a semiconductor. In the absence of electrons, such a fluctuation causes the thermodynamic potential (TP) of the system to grow and to become dissipated after some time. But if the changes of c and η are of suitable sign, then the fluctuation decreases the electron potential energy. If the resultant potential well is deep and wide enough, then the electron is localized in it (Fig. 1). The electron energy is reduced by the localization and under certain conditions this reduction may exceed the increase in the TP due to the fluctuation. The onset of a fluctuation near which the electron is localized is then thermodynamically favored, the change of c or η is stationary, and the fluctuation does not become dissipated. At definite values of the parameters, the radius of the electron state turns out to be large enough and the region of electron localization extends over a large number of atoms.

Such large-radius formations, in which the electron is localized near a change (fluctuation) of the concentration or an internal parameter of the medium, and in which the fluctuation is kept stationary by the electron field, have been named fluctuons [4]. They can be regarded in a certain sense as bound states of the electron and of the fluctuation (the fluctuation is unstable in the "free state"). Formations of such type were theoretically treated in [4-12].

In an external electric field, a force acts on the self-localized electron and through it on the atoms of the medium. These forces should cause translational motion of the electron together with the surrounding region in which the internal parameter is altered. Hence, if fluctuons are thermodynamically favored, they can serve as carriers.

In case of semiconducting (liquid or solid) solutions fluctuons can be formed near the region where the component whose atoms interact more strongly with the

electron has a higher concentration. The resultant cluster, made up mainly of the atoms of one component, is stable even if the direct interaction between the atoms is of no importance. The atoms in a fluctuon cluster are in fact bound by the forces of an indirect interaction due to the self-localized electron.

Fluctuon production in magnetic semiconductors may be due to the usually appreciable exchange interaction between the conduction electrons and the electrons of the unfilled shells of the magnetic atoms. This interaction leads to a large effective field with which a self-localized conduction electron acts on the magnetic atom spins and which tends to orient them parallel (or antiparallel) to the electron spin. On the other hand, the electron itself is situated in an effective field produced by the oriented spins and forming a potential well in which the electron is localized and goes over to the fluctionic state. Fluctuons in magnetic and semiconductor can therefore be due to the magnetization fluctuation and can form a ferromagnetic region in a paramagnet (see Fig. 2) or a region of enhanced magnetization in a ferromagnet.

Fluctuon production should be facilitated in systems with easily modified internal parameters, where the appearance of a fluctuation does not cause an appreciable growth of the TP. Near a first-order phase transition point, in particular, the densities of the TP of both phases are nearly equal and when the interphase surface energy is low the fluctuation-induced second-phase section causes a relatively small increase in the TP. If the electron is attracted by such a heterophase fluctuation and is localized near it, then the decrease in the electron energy can offset the aforementioned growth of the TP and stabilize the fluctuation. The resultant thermodynamically-favored state of an electron localized in the region of the second phase (which is not at equilibrium in the absence of the electron) has been named phason[4]. A phason is a particular case of a fluctuon having a fluctuating internal parameter of a special type, and is characterized by the presence of a discontinuity of this parameter. Phasons can appear also in a decaying solution if a change of concentration carries the solution beyond the decay curve.

Internal parameters are much easier to alter also in the systems that are in the critical region, e.g., in solutions near the critical point on the decay curve or near the Curie temperature of a magnet. In this region the generalized susceptibility is anomalously high and the
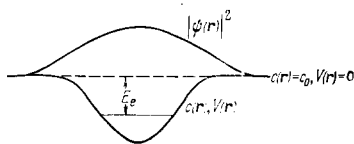

FIG. 1. Formation of localized electronic states having a wave function $\psi(r)$ and an energy E_e in a region with altered concentration $c(r)$ (or altered internal parameter) where a potential well $V(r)$ is produced.
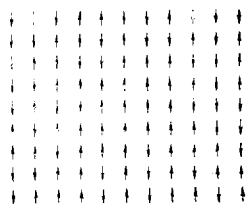

FIG. 2. Oriented-spin region near a fluctuon in a paramagnet.

internal parameter can be greatly altered by relatively weak effective fields. Fluctuon production in the critical region is therefore easier and can occur under much less stringent conditions than far from the critical point or the Curie point.

In particular, fluctuon production should be easier near the gas–liquid critical point. In this case (and in compressed gases in general) the fluctuon is the density-change region near which the electron is localized.

By way of other examples we can cite incompletely ordered molecular crystals (with orientational ordering), in which the fluctuons are due to long-range order fluctuations, substances in which the short-range order is easily altered, and so on.

The fluctuon concept is close to that of the polaron and is to some degree a generalization of the latter. However, whereas in large-radius polarons the ions experience only small harmonic displacements, in fluctuons we encounter a complete restructuring of the atomic or spin configuration, or an abrupt change of composition in some region. It is essential that, unlike polarons, the dependence of the change of the internal parameter on the effective field is highly nonlinear. It is this circumstance that ensures the macroscopic character of the fluctuon in the presence of a short-range interaction of the electron with the medium (the large radius of the polaron is connected with the long-range character of the polarization field).

The fluctuon properties are unusual also in many other respects and have no analogs with other electron formations. Thus, fluctuons are thermodynamically favored only in a limited temperature range that does not include usually low temperatures. The transition of most electrons to the fluctuonic state is possible in a narrow temperature range and is manifest in the form of a smeared phase transition in the electronic subsystem (polaron effects are most strongly manifest at low temperatures, and an increase of T leads in polarons only to a smooth decrease of the degree of electron localization). Fluctuons have a unique mobility mechanism that differs qualitatively from those of band electrons and of large- or small-radius polarons. Fluctuonic states are usually separated from band-electron states by a TP barrier, so that both fluctuons and band electrons can exist simultaneously in a system.

These features of fluctuons will be considered first by using as the simplest example ideal solutions or paramagnets, where the direct interaction between the atoms or spins is of no importance, followed by a discussion of the role of the direct interaction (Chaps. 2–4). The special case of fluctuons in the critical region is discussed in Chap. 5. The kinetic characteristics of fluctuons are described in Chap. 6.

Interactions of electrons with inhomogeneities of internal parameters can alter qualitatively the states of not only the carriers but also of the electrons localized at impurity centers. In particular, two self-consistent states (stable and metastable) having s-symmetry, viz., hydrogenlike and of the fluctuonic type, can exist in large-radius Coulomb centers. The electrons must go over from one state into another near some definite temperature. Excitons can also have self-consistent fluctuonic states of various types. These questions are briefly discussed in Chap. 7.

A number of new effects appear at appreciable car-

rier concentrations. With increasing concentration, interactions of fluctuons with one another result first in the production of fluctuon complexes containing two electrons ("bifluctuons") or several electrons. At sufficiently high concentrations above a limiting value, the electrons and impurity ions should become separated from the phase under consideration and form, e.g., intermetallic compounds. At concentrations lower than the limiting value, however, long-range Coulomb forces make it thermodynamically more expedient for the electrons to gather into large groups (e.g., about 10^2 electrons), which play the role of disperse metallic-type particles. This results in appearance of equilibrium single-phase disperse systems. Such systems are considered in Chap. 8.

Finally, Chap. 9 deals with the effect of fluctuons on various properties of semiconducting systems. It appears that transitions into fluctuonic states can alter radically all the electronic properties, e.g., the electric conductivity, the galvanomagnetic and thermoelectric effects, the light-absorption spectra and photoconductivity, magnetic properties of semiconductors with uncompensated atomic spins, as well as many atomic properties, such as phase-transition kinetics, the positions of phase-equilibrium lines, etc.

2. FUNDAMENTAL EQUATIONS

Two approaches to the investigation of electronic states in disordered or incompletely-ordered systems are possible. In the first one investigates electron motion in the random field produced by atoms that are fixed in the space (see, e.g., [13,14]). In the second (which will be used below for the investigation of the fluctuons), the case of a relatively high atom mobility is considered and it is assumed that the field sources themselves become redistributed as a result of interaction with self-localized electrons. We shall therefore consider henceforth cases when the relaxation time τ_0 of the medium in a small region of the fluctuon potential well is short compared with the electron lifetime τ' in this well:

$$\tau_0 \ll \tau'. \tag{2.1}$$

We consider first the fundamental equations that describe the fluctuon states, using as an example binary solutions A–B (solid or liquid) in which both components A and B have equal atomic volumes v. In the macroscopic approximation, the state of the solution is described by a concentration distribution $c(\mathbf{r})$ which differs significantly in the region of the fluctuon from the mean concentration $c_0 = N_A/N$ ($N = N_A + N_B$; N_A and N_B are the numbers of atoms A and B in the solution).

If an uneven distribution of the concentration $c(\mathbf{r}) - c_0$ is produced, then the TP of the solution is increased. The increase can be calculated, being the minimum work R needed to obtain this distribution (see, e.g., [15]). In case of a smooth variation of $c(\mathbf{r})$ we have

$$R = \int \left\{ \varphi [c(\mathbf{r})] - \varphi(c_0) - \frac{\partial \varphi(c_0)}{\partial c_0}(c(\mathbf{r}) - c_0) + \frac{1}{2}\beta (\nabla c)^2 \right\} d\mathbf{r}; \tag{2.2}$$

here $\varphi(c)$ is the density of TP of the solution; the next-to-last term in (2.2) results from the fact that the total number N_A of the atoms A is unaltered by the redistribution (the atoms A are transferred to the fluctuon from a remote region with concentration c_0),

and the last term takes the inhomogeneity of the concentration into account.

The disorder in the solution results in the shifting and smearing of the conduction band (see, e.g., [13,14]). However, we can conclude from the results given below that large-radius fluctuons can appear when the difference between the energies of electron interaction with atoms A and B is relatively small. In this case the smearing region is comparatively small (apart from the far tails of the state density), and it can be assumed with good approximation that the renormalized spectrum boundary coincides with the bottom of the conduction band of a perfect crystal with a medium potential energy (see p. 862). We shall reckon the electron energy from this boundary and assume for simplicity that the position of this boundary depends linearly on the concentration.

The electron potential energy in the region of the altered concentration is then

$$V(\mathbf{r}) = A [c(\mathbf{r}) - c_0]. \tag{2.3}$$

If the constant $|A|$ is large enough, $V(\mathbf{r}) < 0$, and the resultant potential well is wide enough, then the electron is localized in this potential well and its energy E_e is negative.

The change of the TP of the entire system (solution + electron) with changing concentration and upon localization of the electron in the created potential well, i.e., when the electron goes from the bottom of the conduction band to the fluctuonic state, is equal to $R + E_e$.[1] The electron energy $E_e[c(\mathbf{r})]$ at a given change $c(\mathbf{r}) - c_0$ of the concentration can be determined in the adiabatic approximation as the minimum of the functional $E_e[c(\mathbf{r}), \psi(\mathbf{r})]$ with respect to the class of normalized functions $\psi(\mathbf{r})$. This functional is the quantum-mechanical average of the energy operator. A stationary concentration distribution in the fluctuon corresponds to the minimum of the functional $R[c(\mathbf{r})] + E_e[c(\mathbf{r})]$ with respect to $c(\mathbf{r})$.

The change $\Delta\Phi$ in the TP of the system following the production of a localized fluctuon with a fixed center of gravity can be determined, together with the electron wave function $\psi(\mathbf{r})$ and the concentration change $c(\mathbf{r}) - c_0$, from the condition that the functional $I[\psi(\mathbf{r}), c(\mathbf{r})]$ be a minimum (with respect to ψ and c):

$$\Delta\Phi = \min_{\psi, c} I[\psi, c], \quad I = E_e + R = \frac{\hbar^2}{2m} \int |\nabla \psi|^2 d\mathbf{r}$$
$$+ A \int [c(\mathbf{r}) - c_0] |\psi(\mathbf{r})|^2 d\mathbf{r} + R[c(\mathbf{r})]. \tag{2.4}$$

The first two terms in I determine the average kinetic and potential energy of the electron, and m is its effective mass (we assume for simplicity a quadratic and isotropic dispersion).

The functional (2.4) can be minimized with respect to ψ and c in any order. It is obviously more convenient to find first the minimum condition with respect to $c(\mathbf{r})$ at a given $\psi(\mathbf{r})$. According to (2.4) and (2.2) this condition is

$$\frac{\partial \varphi[c(\mathbf{r})]}{\partial c(\mathbf{r})} - \frac{\partial \varphi(c_0)}{\partial c_0} - \beta \Delta c(\mathbf{r}) + A|\psi(\mathbf{r})|^2 = 0. \tag{2.5}$$

Equation (2.5) determines the distribution of the concentration $c[\psi(\mathbf{r})]$ in an effective field $A|\psi|^2$ produced by a self-localized electron. The examples given below show that Eq. (2.5) can be solved for various particular $\varphi(c)$ so that $c[\psi(\mathbf{r})]$ can be found in explicit form (since the problem is macroscopic, the term $-\beta\Delta c$ can usually be omitted).

M. A. Krivoglaz

Substituting in (2.4) the value of $c[\psi(\mathbf{r})]$ corresponding to the minimum of I with respect to c, we get a functional $I[\psi]$ that depends only on one unknown function $\psi(\mathbf{r})$:

$$I[\psi] = \min_c I[\psi, c] = \frac{\hbar^2}{2m} \int |\nabla \psi|^2 \, d\mathbf{r} \qquad (2.6)$$
$$- A \int \{c|\psi(\mathbf{r})| - c_0\} |\psi(\mathbf{r})|^2 \, d\mathbf{r} + R\{c|\psi(\mathbf{r})|\}.$$

The fluctuon ground state corresponds to a spherically symmetrical wave function. Thus $I[\psi]$ can be regarded as the functional of a function of only one variable. The minimum of such a functional can always be found in principle either numerically, by solving the corresponding (essentially nonlinear) Euler equation, or by direct variational methods. This solves the problem of finding the stationary distributions of $\psi(\mathbf{r})$ and $c(\mathbf{r})$ as well as $\Delta\Phi$.

The same method can be used to set up the basic equations describing fluctuons in magnetic semiconductors that contain atoms of transition and rare-earth elements with uncompensated spins. The formation of a region of altered magnetization near the fluctuon can be due here to exchange s-d or s-f interaction between these spins and the conduction-electron spin [16]. In the macroscopic approximation used here, the electron spin in the ground state can be assumed to be oriented parallel or antiparallel (depending on the sign of the exchange-interaction constant) to the predominant orientation of the atom spins (to the Oz axis). This is equivalent to taking only one component into account in the spinor wave function of the electron. This approximation, as well as the adiabatic approximation in which the fast electron motion in a field of fixed spins can be considered, will be corroborated later on.

When considering the electron spin direction corresponding to its lowest energy, the potential energy of the exchange interaction of the electron with the inhomogeneous change of magnetization $M_z(\mathbf{r})$ ($M_x = M_y = 0$) can be regarded as negative, characterized by an interaction constant $A > 0$, and expressed in the form

$$V(\mathbf{r}) = -A \frac{M_z(\mathbf{r}) - M_0}{M^0}. \qquad (2.7)$$

The energy is reckoned here from the bottom of the conduction band of an ideal crystal whose atoms have average magnetic moments corresponding to an equilibrium magnetization $M = M_0(T)$ ($M^0 = M_0(T=0)$).

By determining the energy of the electron in this field and the change of the TP when magnetization inhomogeneity is produced we obtain, just as in the derivation of formula (2.4) (i.e., using the adiabatic approximation), the functional $I[\psi(\mathbf{r}), M(\mathbf{r})]$, the minimum of which determines $\Delta\Phi$ and the stationary distribution of $M_z(\mathbf{r})$ and $\psi(\mathbf{r})$:

$$I[\psi(\mathbf{r}), M(\mathbf{r})] = \frac{\hbar^2}{2m} \int |\nabla\psi(\mathbf{r})|^2 \, d\mathbf{r} - \frac{A}{M^0} \int [M_z(\mathbf{r}) - M_0] |\psi(\mathbf{r})|^2 \, d\mathbf{r}$$
$$+ \int \left\{ \varphi[M(\mathbf{r})] - \varphi(M_0) - \frac{1}{2}\beta(\nabla M)^2 \right\} d\mathbf{r}. \qquad (2.8)$$

The last term was written out for a cubic crystal. The determination of the minimum of the functional (2.8) with respect to $M(\mathbf{r})$ for a given $\psi(\mathbf{r})$ is equivalent to the determination of the magnetization in an effective field $H_e[\psi(\mathbf{r})]$ due to the exchange interaction with the electron and equal to

$$H_{ez}[\psi(\mathbf{r})] = \frac{A}{M^0} |\psi(\mathbf{r})|^2, \quad H_{ex} = H_{ey} = 0. \qquad (2.9)$$

At a given temperature, the distribution $M(\mathbf{r})$ and the sum

$$\varphi[M(\mathbf{r})] - A|\psi|^2 \frac{M_z}{M^0} = \varphi[M(\mathbf{r})] - H_e M = \varphi_H\{H_e[\psi]\}$$

are determined uniquely by the field $H_e(\mathbf{r})$, and if the last term of (28) is neglected, then $\varphi_H\{H_e[\psi]\}$ has the meaning of the density of the TP of a magnet in a homogeneous external field H_e. Substituting this value of the magnetization in (2.8), we have a functional $I[\psi(\mathbf{r})]$ that depends only on the wave function and is analogous to the functional (2.6):

$$I[\psi(\mathbf{r})] = \frac{\hbar^2}{2m} \int |\nabla\psi|^2 \, d\mathbf{r} + \int \left\{ \varphi_H[H_e[\psi(\mathbf{r})]] \right. \qquad (2.10)$$
$$\left. - \varphi_H(0) + H_e M_0 - \frac{1}{2}\beta(\nabla M[\psi])^2 \right\} d\mathbf{r}.$$

In gases, the electron potential energy connected with the change of the density $\rho(\mathbf{r}) - \rho_0$ (ρ_0 is the gas density far from the fluctuons) can be written in the form

$$V(\mathbf{r}) = A_g \frac{\rho(\mathbf{r}) - \rho_0}{\rho_0}. \qquad (2.11)$$

which is analogous to formula (2.3) for the solution. Therefore all the results of the theory of fluctuons in solutions can be used also for gases, provided the following change is made in the formulas (and the corresponding expression for $R\{\varphi(\mathbf{r})\}$ is used)

$$\frac{c(\mathbf{r})}{c_0} \to \frac{\rho(\mathbf{r})}{\rho_0}, \quad Ac_0 \to A_g. \qquad (2.12)$$

It must be borne in mind, however, that the "local" approach used in formula (2.2) for R is valid only in sufficiently dense gases, when the atom mean free path l_a is small in comparison with the effective fluctuon radius r_0:

$$l_a \ll r_0. \qquad (2.13)$$

The expressions presented for $\Delta\Phi$ were determined for a fixed distribution of $c(\mathbf{r})$ or $M_z(\mathbf{r})$ corresponding to the minimum TP. However, $\Delta\Phi$ can have practically the same values, in an interval $\sim kT$, at different close values of the functions $c(\mathbf{r})$ or $M_z(\mathbf{r})$, corresponding to variations of the form of the fluctuon and of the distributions of the atoms (spins) inside the fluctuon. These variations should contribute to the sum of states and to the TP; these contributions can be accounted for by adding the term $-kT \ln \alpha$ to $\Delta\Phi$ (in nonmagnetic crystals, α includes also the spin factor 2).

The calculation of α is a difficult problem which has not yet been solved. On the basis of qualitative considerations we can expect α to depend little on the temperature far from the critical points, and to differ little from unity in order of magnitude. In gases, and also in the case of fluctuons of relatively weak coupling, which are produced in the critical region (see Chap. 5), α can depend strongly on the distance to the critical point and can differ from unity. In any case, $-kT \ln \alpha$ depends less on T than $\Delta\Phi$.

The foregoing calculation of the TP was carried out for an immobile fluctuon located in a definite region of space. It is necessary also to take into account the possible translational motion of the fluctuons. In the case of polarons at low temperatures this reduces to taking into account the contribution made to the sum of states by the polaron kinetic energy. Actually, however, fluctuons have no mean free path (their effective mean free path is smaller than their radius; see Chap. 6). Therefore the contribution made to the TP Φ of a system of N_f fluctuons by the translational motion is connected with the possibility of the permutations of the fluctuon

centers over the N bins. By determining the number of such permutations and taking into account the afore-mentioned contributions of the variations of the parameter $-kTN_f \ln \alpha$, we obtain

$$\Phi = N_f \Delta\Phi - N_f kT \ln \frac{e\alpha N}{N_f} . \qquad (2.14)$$

It follows from results presented later on that the fluctuonic state is usually separated by a potential barrier from the band-electron state. The system can therefore contain simultaneously both fluctuons and band electrons (some of them in a metastable state). The ratio of N_f to the number N_e of the band electrons can be obtained by taking into account formula (2.14), the expression for the TP of the band electrons

$$\Phi_e = N_e kT \ln \left[\frac{N_e}{2eNv} \left(\frac{2\pi\hbar^2}{mkT} \right)^{3/2} \right]$$

and recognizing that when the electron goes from the conduction band to the fluctuon state the summary TP at equilibrium should remain unchanged:

$$\frac{N_f}{N_e} = \frac{\alpha\zeta}{2} \exp\left(-\frac{\Delta\Phi}{kT} \right) ,$$
$$\zeta = \left(\frac{2\pi\hbar^2}{mkTv^{2/3}} \right)^{3/2} \sim \left(\frac{\Delta E}{kT} \right)^{3/2}, \quad \Delta E \sim \frac{5\hbar^2}{mv^{2/3}} . \qquad (2.15)$$

in crystals, ΔE denotes the width of the conduction band.

3. FLUCTUONS IN IDEAL SOLUTIONS AND IN IDEAL PARAMAGNETS

a) Fluctuonic states of electrons in ideal solutions. It follows from the presented general formulas that the features of the fluctuons in different systems are determined by the form of the dependence of the density of the TP on the concentration or on an internal parameter. By way of simplest examples, following [4], we consider first fluctuons in ideal systems (solutions or paramagnets), in which the direct interaction of the atoms or the spins can be neglected in the absence of the electron.

In solid solutions we have

$$\varphi (c) = \frac{kT}{v} |c \ln c - (1-c) \ln (1-c)], \quad \beta = 0. \qquad (3.1)$$

This formula is approximately valid also for liquid solutions. Substituting (3.1) in (2.5) we obtain the stationary distribution of the concentration in the field of a localized electron inside the fluctuon:

$$c (r) = c_0 \left[c_0 + (1-c_0) \exp \left(\frac{Av}{kT} |\psi|^2 \right) \right]^{-1}. \qquad (3.2)$$

The functional (2.6), the minimum of which determines the equilibrium fluctuon characteristics, is given, as follows from (2.2), (3.1), and (3.2), by

$$I [\psi] = \frac{\hbar^2}{2m} \int |\nabla\psi|^2 dr - Ac_0 \qquad (3.3)$$
$$- \frac{kT}{v} \int \ln \left[1 - c_0 + c_0 \exp \left(-\frac{Av}{kT} |\psi|^2 \right) \right] dr.$$

For the sake of argument we assume that $A > 0$ (the case $A < 0$ can be reduced to the case $A > 0$ by the substitution $c_0 \to 1-c_0$).

It is easiest to find the minimum of the functional (3.3) by a direct variational method. We use the simplest approximation for $\psi(r)$:

$$\psi (r) = \left(\frac{2\alpha}{\pi} \right)^{3/4} \exp (-\alpha r^2). \qquad (3.4)$$

This wave function is exact for the ground state of the oscillator and yields a slight overestimate of $\Delta\Phi$ for an electron in a fluctuonic potential well. Analysis

shows, however, that the approximation (3.4) usually leads to a small error (on the order of several per cent) in the calculated physical quantities. In any case, the direct variational method yields qualitatively correct results.

After substituting (3.4) in (3.3), the functional $I[\psi]$ reduces to a function of one variable a, inversely proportional to the effective volume of the fluctuon:

$$I [\psi] = I (a) = -Ac_0 + \frac{4}{3 \sqrt{\pi}} A \left[B \left(\frac{kT}{1} \right)^{2/3} a^{2/3} + b \frac{1}{a} f (a) \right], \qquad (3.5)$$

$$a = \frac{Av}{kT} \left(\frac{2\alpha}{\pi} \right)^{3/2}, \quad b = \frac{c_0}{1-c_0}, \quad B = \frac{9\pi^{3/2}}{16} \frac{\hbar^2}{mv^{2/3}A} \sim \frac{\Delta E}{2A} ,$$

$$f (a) = \int_0^a \frac{e^{-x}}{1+be^{-x}} \left(\ln \frac{a}{x} \right)^{3/2} dx. \qquad (3.6)$$

We have

$$f (a) \approx \frac{3 \sqrt{\pi}}{4} \frac{a}{1+b} \left[1 - \frac{a}{4 \sqrt{2}(1+b)} \right]$$

at $a \ll 1 + b$, $f(a) \sim 1$ at $a \sim 1$ and $b \sim 1$, and $f(a) \approx b^{-1} \ln(1 +b)(\ln a)^{3/2}$ at $a \gg \ln(1+b)$. Tables of this function at $b = 1$ and $b \ll 1$ are given in [4].

The electron energy can be written in this case in accord with (2.4) and (3.2), in the form

$$E_e = E_p (a) = -Ac_0 + \frac{4}{3 \sqrt{\pi}} A \left[B \left(\frac{kT}{A} \right)^{2/3} a^{2/3} + bf' (a) \right]. \qquad (3.7)$$

Obviously, there can be talk of fluctuonic states only if $E_e < 0$. Moreover, in order for the contribution of the stationary change of the concentration (3.2) to exceed the contribution of the fluctuation changes, and in order for the role of the latter to reduce only to the appearance of the quantity $\alpha \sim 1$ in (2.14), as well as to be able to neglect the contribution of the excited states of the electron in the fluctuon well, it is necessary to satisfy the condition

$$-E_e \gg kT. \qquad (3.8)$$

The stationary state of the electron is determined by the minimum of the function $I(a)$. The behavior of this function is different at different temperatures (Fig. 3). In the region of small a the term $\sim a^{2/3}$ in (3.5) predominates, and when a increases $I(a)$ always increases from the value $I(0) = 0$. At sufficiently high temperatures, this monotonic growth of $I(a)$ continues for all a (curve 1 of Fig. 3; the dashed curve in this figure indicates those sections of the curves which have no physical meaning, where $E_e(a) > 0$ or where the condition (3.8) is not satisfied). In this temperature region there are no fluctuonic states, even metastable ones, and the electrons are in band states.

At lower temperatures, a maximum and minimum appear on the $I(a)$ curve; the minimum first lies far above the abscissa axis (curve 2 on Fig. 3). In addition to the band electrons corresponding to the point $a = 0$ (infinitely large radius of wave function) there appear now also fluctuons that are, however, in a metastable state that is thermodynamically less advantageous.
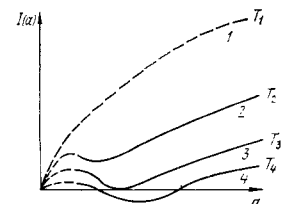
FIG. 3. Approximate plots of $I(a)$ in ideal solutions or paramagnets at different temperatures $T_1 > T_2 > T_3 = T^* > T_4$.

M. A. Krivoglaz

With decreasing temperature, the minimum of I(a) drops lower, becoming tangent to the abscissa axis at a certain temperature T* (curve 3 in Fig. 3). In this case $\Delta\Phi = 0$ and, in accordance with (2.15) ($\zeta \ll 1$), almost all the electrons are in fluctuonic states. With further lowering of the temperature, in an ideal solution, $\Delta\Phi$ continues to decrease (curve 4 of Fig. 3).

From the condition $I'(a) = 0$ (at $I''(a) > 0$) we can find the value $a = a_0$ corresponding to the minimum of the function I(a) at given values of B and kT/A, and then the change $\Delta\Phi = I(a_0)$ of the TP following the formation of the fluctuon, the electron energy $E_e = E_e(a_0)$, and also the effective number n of atoms inside the fluctuon and its effective radius r_0, which can be naturally determined from the relations

$$\frac{4\pi}{3} r_0^3 |\psi(0)|^2 = 1, \quad n = \frac{4\pi}{3} \frac{r_0^3}{r} \cdot \frac{1}{|\psi(0)|^2 r} . \tag{3.9}$$

These quantities can be expressed in the form

$$a_0 = \gamma_1(a_0) \left(\frac{b}{B}\right)^{3/5} \left(\frac{A}{kT}\right)^{2/5}, \quad n = \frac{1}{\gamma_1(a_0)} \left(\frac{B}{b}\frac{A}{kT}\right)^{3/5},$$

$$\Delta\Phi = -Ac_0 + \gamma_2(a_0) B^{3/5} b^{2/5} \left(\frac{kT}{A}\right)^{2/5} A, \tag{3.10}$$

$$E_e = -Ac_0 + \gamma_3(a_0) B^{3/5} b^{2/5} \left(\frac{kT}{A}\right)^{2/5} A,$$

where

$$\gamma_1 = \left[\frac{3}{2}(f - a_0 f')\right]^{3/5}, \quad \gamma_2 = \frac{4}{3\sqrt{\pi}}\left(\gamma_1^{2/3} + \frac{f}{\gamma_1}\right),$$

$$\gamma_3 = \frac{4}{3\sqrt{\pi}}\left(\gamma_1^{2/3} + \frac{a_0 f'}{\gamma_1}\right) \tag{3.11}$$

the quantities $\gamma_i = \gamma_i(a_0)$ are tabulated in [4].

From formula (3.10) and the tables γ_i we can obtain the temperature T* at which $\Delta\Phi$ vanishes, and the effective number n of the atoms in the fluctuon:

$$kT^* = 0{,}0040 \left(A \frac{mv^{2/3}}{\hbar^2}\right)^{3/2} A \sim \frac{1}{20}\left(\frac{A}{\Delta E}\right)^{3/2} A \quad (b = 1), \tag{3.12}$$

$$kT^* \sim \frac{1}{30\ln(1+b)}\left(\frac{A}{\Delta E}\right)^{3/2} A \ (b \gg 1), \quad kT^* \sim \frac{1}{10} b^{3/2}\left(\frac{A}{\Delta E}\right)^{3/2} A \quad (b \ll 1),$$

$$\left. \begin{array}{l} n \approx 50\left(\frac{\hbar^2}{mv^{2/3}A}\right)^{3/2} \sim 3\left(\frac{\Delta E}{A}\right)^{3/2} \quad (b = 1, \ T = T^*), \\[2mm] n(T^*) \sim 3\left(\frac{\Delta E}{A}\right)^{3/2} (b \gg 1), \quad n(T^*) \sim 3b^{-3/2}\left(\frac{\Delta E}{A}\right)^{3/2} \quad (b \ll 1), \\[2mm] n(T) \sim \frac{1}{3}\left(\frac{\Delta E}{kT}\right)^{3/5} \quad (T \ll T^*, \ b \sim 1). \end{array} \right\} \tag{3.13}$$

At a given temperature $T < T^*(c_0 = 1/2)$, the quantity $\Delta\Phi$ vanishes at certain concentrations $c_1^* < 1/2$ and $c_2^* > 1/2$.

b) Singularities of fluctuonic states in ideal systems. It is seen from the estimate (3.13) that large-radius fluctuons with $n \gg 1$ should be produced at $T \sim T^*$ in solutions for which the condition

$$\Delta E \gg A \tag{3.14}$$

is satisfied. In these systems, at temperatures $T < T^*$, the condition

$$A \gg 20\, kT \tag{3.15}$$

is also satisfied automatically and the criterion (3.8) holds true ($E_e = -0.12A$ at $T = T^*$ and $b-1$). Naturally, in this case the temperatures in questions should lie much higher than the solution decay or ordering curve, so as to be able to neglect the direct interaction of the atoms (see Chap. 4).

The foregoing estimates of T* and n (without the numerical factors) can be easily obtained also from elementary qualitative considerations. To this end it is necessary to take account of the fact that when condition (3.14) is satisfied the potential wells of the individual atoms of the solution are not deep enough for

localized states of the electron to be formed. Such states can arise only near groups consisting of a sufficiently large number n of atoms, when the kinetic energy $\sim \hbar^2/mr_0^2 \sim \Delta E n^{-2/3}$ becomes smaller than the potential energy $\sim A$ taken with a negative sign. This formation is thermodynamically favored if the increase $\sim nkT$ of the TP following the joining of n atoms of an ideal solution (with $c_0 \sim 1/2$) into a group is smaller than the lowering of the energy $\sim A$ upon localization of the electron. It is this which yields the estimates of T* and n(T*).

A distinguishing feature of fluctuons in ideal solutions is the abrupt change of the concentration in the region of electron localization. As follows from (3.2), (3.12), and (3.13) we have at $A > 0$ in the center of the fluctuon

$$c(0) \ll c_0 \tag{3.16}$$

($c(0)$ is close to unity at $a < 0$ and $1 - c(0) \ll 1 - c_0$). The potential energy at the center of the fluctuon then takes on the minimum value $-Ac_0$. With decreasing temperature, the region of this low potential energy broadens, as seen from (3.2). Consequently the volume nv of the fluctuon increases like $T^{-3/5}$, and the electron energy $\Delta\Phi$ decrease, tending to limiting values $-Ac_0$, from which they differ by terms proportional to $T^{2/5}$ (neglecting the weak dependence of the logarithmic factors on T).

The fact that the concentration change $c - c_0$ depends nonlinearly on the effective field $A|\psi|^2$ and that it is bounded by the limiting value $-c_0$ is (as well as the relatively small depth of the potential well) indeed the reason (when the condition (3.14) is applied) for the macroscopic character of the fluctuon, wherein the localized electronic state can arise only via broadening but not deepening of the potential well. In this respect this problem differs greatly from that of electron-phonon interaction, where the potential well can become infinitely deep in the armonic approximation, and only small-radius autolocalized states can be formed in the case of short-range forces (in homopolar crystals)[17]. Large-radius polarons, on the other hand, can be produced only in ionic crystals as a result of long-range forces.

Inasmuch as $\zeta \gg 1$ in (2.15) when the condition (3.14) is satisfied, the temperature of the transition to the fluctuonic states, at which $N_f = N_e$ is somewhat higher than T* at $\Delta\Phi > 0$. Since, however

$$\frac{\partial\Delta\Phi}{\partial T} \approx \frac{2}{5T^*}(\Delta\Phi + Ac_0) \approx nk,$$

at $T \approx T^*$ and $c_0 = 1/2$, the temperature shift $(1/n)T^* \ln(\alpha\zeta/2) \sim (5T^*/2n)\ln n$ is small in comparison with T*.

It is important that the transition of most electrons to fluctuonic states takes place in a narrow temperature region. Indeed, as follows from (2.15) and from the presented estimate of $\partial\Delta\Phi/\partial T$, the temperature difference δT at which N_f/N_e changes from a value 1/3 to 3 is equal to

$$\delta T \approx \frac{2.2}{n} T^* \ll T^*. \tag{3.17}$$

This means that the transition into the fluctuonic states should be interpreted as a smeared first-order phase transition. In such a transition, various properties of the semiconductor should change strongly (see Chap. 9).

M. A. Krivoglaz

In particular, the electronic specific heat should have a peak with a height $\sim N_f(\partial\Delta\Phi/\partial T)T^*/\delta T \sim N_f m^2 k$. No such abrupt transitions to self-localized states take place in either polarons or other formations of the polaron type.

Since the fluctuonic states are separated by a TP barrier from the band states (see Fig. 3), fluctuon formation can take place quite slowly. From this point of view, the fluctuons are easier to form in liquid solutions, where the atom mobility is larger. As follows from (3.5), the height of the barrier I_{max} at $c_0 \sim 1/2$ is of the order of

$$\frac{I_{max}}{kT} \sim 5\left(\frac{\Delta E}{A}\right)^3 \frac{kT}{A}, \qquad (3.18)$$

i.e., $I_{max}/kT \sim (1/4)(\Delta E/A)^{3/2} \sim (1/10)n$ at $T = T^*$ and decreases in proportion to T with decreasing temperature.

Although there is no direct interaction between atoms in ideal solutions, a localized electron can lead to a considerable indirect interaction between them. This interaction appears in the microscopic description of the change of the concentration. The distribution of the atoms over the lattice sites is characterized then by the quantities $c_s - \bar{c}_s$ ($c_s = 1$ or 0 if the atom A or B is located respectively on the site s; $\bar{c}_s$ is the mean value of c_s in the field $A|\psi|^2$). In second-order perturbation theory, the energy of the localized electron turns out to depend on the occupation of pairs of various sites s and s' by the atoms A or B. In the adiabatic approximation, it corresponds to indirect interaction between the atoms. An interaction of this type, as can be readily shown, has a large radius $\sim r_0$ and an order of magnitude

$$-\left\{\frac{A^2}{\Delta E}v|\psi(0)|^2 \frac{v^{1/3}}{|r_s - r_{s'}|}\exp\left[-\alpha_1\left(\frac{A}{\Delta E}\right)^{1/2}\frac{|r_s - r_{s'}|}{v^{1/3}}\right]\right.$$
$$\left. + \alpha_2 A v^2|\psi(0)|^4\right\}(c_s - \bar{c}_s)(c_{s'} - \bar{c}_{s'}) \quad (|r_s - r_{s'}| < r_0, \; \alpha_i \sim 1). \qquad (3.19)$$

The interaction (3.19) introduces in $\Delta\Phi$ a contribution that vanishes in first-order approximation of the thermodynamic perturbation theory, and whose order of magnitude in second-order perturbation theory is smaller than $A/n(T^*) \ll A$. For a large-radius fluctuon, this leads to small corrections to the computed quantities.

Satisfaction of the condition (3.14) is necessary also in order that the linear approximation (2.3) of the electron potential energy be applicable. This approximation is obtained in natural fashion in a perturbation-theoretical calculation of the end point of the energy band in regions with concentrations $c(r)$ and c_0 in first-order approximation relative to the small difference between the interaction energies of the electrons and atoms A and B. In second-order perturbation theory, the shift of the end point and the corresponding correction to $V(r)$ depend in nonlinear manner on $c(r)$, but this correction is of the order of $A^2/\Delta E \ll A$ and is small when the condition (3.14) is satisfied. It is possible here to neglect also the contribution of the smearing of the edge of the band to the free energy of the band electrons. The violations of the linear dependence (2.3) may also be due to many-particle effects of the influence of the type of the neighboring atoms on the interaction energy of the given atom with the electron, with the dependence of the atomic volume on the composition of the solution, etc. However, the nonlinear terms in (2.3) should not influence the presented qualitative results and lead apparently to small quantitative corrections, especially in

systems where the position of the edge of the conduction band depends almost linearly on the composition.

Another physical situation arises if the condition (3.14) is not satisfied. It is seen from (3.13) that at $|A| \sim \Delta E$ we have $n \sim 1$ in the region $T \sim T^*$, i.e., no macroscopic fluctuons are produced. This is directly connected with the fact that at $|A|$ larger than a certain limiting value $\sim \Delta E$ localized electronic states are produced already near single impurity atoms A in the crystal B (or of B in the crystal A). At a noticeable concentration c_0 (or $1 - c_0$) and at $\Delta E \gg kT$, only a small fraction of the thermally excited electrons is in "band" states, and the temperature T^* is meaningless.

At sufficient atom mobility, however, the condition (2.1) is satisfied and in this case it should be borne in mind that the energy of the electron decreases if the electron is close to a complex of several atoms. Therefore, at not too high temperatures, when the conditions

$$|A| > \Delta E \gg 20kT \quad \text{at} \quad c_0 \sim 1/2$$

or

$$A > \Delta E \gg 30kT \,|\ln(1 - c_0)| \quad \text{at} \quad 1 - c_0 \ll 1, \; A > 0 \qquad (3.20)$$

are satisfied, it is thermodynamically more profitable for the electron to form a complex containing a large number n of atoms. Just as in the case when the condition (3.14) is satisfied, the value of n is determined by formulas (3.10) or (3.13) (at $T \ll T^*$). The temperature dependences of $\Delta\Phi$ and E_e at $|A| > \Delta E$ can also be determined from formula (3.10). These quantities are now determined, however, only accurate to a constant, since the position of the end point of the band spectrum cannot be determined with any degree of rigor. The change of the concentration in accordance with (3.16) is also large. We note that although the effective-mass method cannot be used at $|A| \sim \Delta E$ and $n \sim 1$, at small values of T and at $n \gg 1$ the electron kinetic energy is $\Delta E \cdot n^{-2/3} \ll \Delta E$ and the condition for the applicability of this method is again satisfied in the case of a broad forbidden band $E_0 \gg |A|$.

Thus, although at $|A| \sim \Delta E$ (or $|A| \gg \Delta E$) there is no abrupt transition of the electrons into the fluctuonic states, and only a gradual decrease of the sizes of the complexes near which the electrons are localized[21] takes place at $T < T^* \sim \Delta E/20k$ ($c_0 \sim 1/2$), fluctuonic states of the same type as when conditions (3.14) are satisfied are produced in the temperature interval (3.20) nonetheless.

The foregoing results of fluctuon theory were obtained under the assumption that the local connection (2.3) exists between the changes of the concentration and of the potential energy of the electron. They are valid for systems in which the radius r^0 of the difference $w(r)$, between the interaction energies of the electron with the atoms of the solution is small in comparison with the fluctuon radius $r_0 \sim (nv)^{1/3}$. If $r^0 \gtrsim (nv)^{1/3} \sim v^{1/3}(\Delta E/A)^{1/2}$ (at $T \sim T^*$), then the connection between $V(r)$ and $c(r) - c_0$ becomes nonlocal and the results should change. This case was considered in [18] (in a somewhat simplified manner) and later in [12].

In the case of large r^0, the radius of the fluctuons that are produced at the transition temperature T^* is also of order r^0, and the concentration change $|c(0) - c_0|$ is relatively small (and is not ~ 1 as in the local theory):

$$kT^* \sim \frac{1}{10}c_0(1 - c_0)\frac{A}{\Delta E}\frac{v^{1/3}}{r^0}\mathscr{A}, \quad r_0 \sim r^0, \; |c(0) - c_0| \sim \frac{\Delta E}{A}\frac{v^{2/3}}{(r^0)^2} \ll 1 \left(r^0 \gg v^{1/3}\left(\frac{\Delta F}{A}\right)^{1/2}\right),$$
$$\qquad (3.21)$$

where $\mathscr{A} = \int w(\mathbf{r})\,d\mathbf{r}$. When the temperature is lowered, the concentration change $|c(0) - c_0|$ first decreases, the potential well becomes deeper, and r_0 decreases (like $T^{1/4}$). However, at a certain temperature $kT \sim c_0(1-c_0)\,Av/(r^0)^3$ the concentration at the center of the fluctuon reaches a maximum possible value $|c(0)-c_0| \sim 1$, after which the lowering of the temperature increases r_0 in proportion to $T^{-1/4}$. Finally, at $kT \sim (1/10)\Delta E[v^{5/3}(r^0)^5] \times [\ln(Av/kT(r^0)^3)]^{3/2}$ the fluctuon radius is again proportional to r^0, and at lower temperatures we have $r_0 \gg r^0$ and the results of the local theory become applicable (see [12] for details).

Another approach to the problem of the interaction of an electron with fluctuation inhomogeneities in an ideal disordered system was used in [6]. It was taken into account that fluctuation energy levels are formed below the renormalized smeared boundary of the band spectrum. When conditions (3.14) are satisfied, such levels correspond to fluctuations in relatively large volumes and, in the macroscopic approximation, each electron energy E_e corresponds to a definite probability $p_0(E_0)$ of formation of such a fluctuation[19-21]. The distribution of the electrons over the fluctuonic levels is determined by the product $p(E_e) = p_0(E_e)\exp(-E_e/kT)$. For each temperature we can find an energy $E_e = E_e(T)$ at which the quantity

$$\Delta F(E_e) = -kT \ln p(E_e) = E_e - kT \ln p_0(E_e) \qquad (3.22)$$

is minimal, and also the corresponding change of the concentration and the electron wave function. These states are the most probable at the considered temperature.

This formulation of the problem corresponds more readily to the case when the electron is in a field of fixed atoms, and does not manage to cause a self-consistent redistribution of the atoms during its lifetime in the potential well, as was assumed in the case considered above, when the condition (2.1) was satisfied. Accordingly, the function $\Delta F(E_0)$ does not coincide, generally speaking, with the function $\Delta\Phi(E_0)$ that can be obtained from the formulas given above. It can be shown, however, that at the energy E_{em} determined from the condition $\partial\Delta F(E_e)/\partial E_e = 0$, the values of $\Delta F(E_{em})$ and $\Delta\Phi$ coincide, and the equations for $\psi(\mathbf{r})$ and $c(\mathbf{r})$ turn out to be the same as in the previously considered formulation of the problem. Both approaches to the equilibrium states of fluctuons therefore lead to the same results.

The case of low concentration $1 - c_0 \ll 1$, when the fluctuonic potential wells are almost rectangular (the latter is seen from (3.2)), was investigated in this manner in detail in [6]. Not only the three-dimensional problem, but the one-dimensional and two-dimensional ones were also considered. A feature of the latter cases is the absence of a TP barrier to fluctuon formation.

Since the results of the calculation of $\Delta\Phi$ in systems with high and low atom mobility are the same, formula (2.15), which determines the fraction of the electrons in the fluctuonic states, is valid at low carrier density not only when condition (2.1) is satisfied but also for an arbitrary ratio of τ_0 and τ'. However, if $\tau_0 \gg \tau'$ and the composition fluctuations are quenched, then states of the fluctuonic type are possible only near fluctuations that have been formed. Therefore Eq. (2.15) holds only if N_f/N is small compared with the concentration of necessary fluctua-

tions $p_0 \sim \exp(-\Delta\Phi_p/kT)$ ($\Delta\Phi_p$ is the change of the TP when fluctuations are produced in the absence of an electron). But if the number of electrons exceeds the number of places with ready-made fluctuations then Eq. (2.15) does not hold at $\tau_0 \gg \tau'$. On the other hand, when τ_0 are small enough the electron can produce during its lifetime the stationary fluctuation needed for the appearance of fluctuonic states. The aforementioned results are then valid at significant carrier densities. We note that the kinetics of electron transition into fluctuonic states was not investigated in detail. It can only be assumed that the barrier that determines the temperature dependence of this kinetic has a height on the order of I_{max}

c) Fluctuons in ideal paramagnets. We consider now fluctuons in ideal paramagnets[4,5]. These fluctuons result from exchange interaction between a conduction electron and magnetic atoms. The state of the fluctuon is determined in this case by the condition that the functional (2.10) be a minimum. In ideal paramagnets there is no direct interaction between the magnetic-atom spins, $\beta = 0$, and the TP density $\varphi_H(H_e)$ in the effective field H_e (2.9) is determined in the case of pure spin paramagnetism from

$$\varphi_H = -\frac{kT}{v}\ln\sum_{m=-S}^{S}\exp\left(-\frac{\mu H_e}{kTS}m\right) \qquad (3.23)$$
$$= -A|\psi|^2 - \frac{kT}{v}\ln\left\{1 - \exp\left[-\frac{Av}{SkT}|\psi|^2(2S+1)\right]\right\}$$
$$+ \frac{kT}{v}\ln\left[1 - \exp\left(-\frac{Av}{SkT}|\psi|^2\right)\right],$$

where S is the spin of the atom and $\mu = vM^0$ is its magnetic moment. We consider crystals with one magnetic atom per cell.

Substituting (3.23) in (2.10) and using the trial function (3.4) we reduce the minimization of the functional $I[\psi]$ to the task of finding the minimum of the function $I(a)$, which can be determined from (3.5) and (3.6) by making these substitutions

$$c_0 \to S, \quad b \to 1, \quad A \to \frac{A}{S}, \quad f(a) \to f_p(a) \qquad (3.24)$$
$$= \int_0^a dx\left(\ln\frac{a}{x}\right)^{3/2}\left[\frac{1}{e^x-1} - \frac{2S+1}{e^{(2S+1)x}-1}\right].$$

We have $f_p(a) \approx (3\sqrt{\pi}/4)\,aS[1 - (1/12\sqrt{2})a(S+1)]$ at $a(S+1) \ll 1$, $f_p(a) \sim 1$ at $a(S+1) \sim 1$ and $f_p(a) \approx (\ln a)^{3/2} \times \ln(2S+1)$ at $a \gg 1$. Tables of $f_p(a)$ and $f_p'(a)$ at different S are given in [5].

The stationary values of $\Delta\Phi$, E_e, and n for fluctuons in ideal paramagnets are determined accordingly from (3.10) and (3.11), in which the substitution (3.24) should also be made.

In case of a spin $S = 1/2$, as can be seen from (3.24), if A is replaced by $2A$ the problem of a fluctuon in an ideal paramagnet coincides exactly with that of a fluctuon in an ideal solution of concentration $c_0 = 1/2$, so that the foregoing analysis holds also for paramagnets. The obtained estimates can be used also as order-of-magnitude estimates for paramagnets with $S \sim 1$. If, for example, $S = 1/2$, $\Delta E = 5$ eV, and $A = 0.5$ eV, then (3.12) and (3.13) yield $T^* \sim 50°K$, $n(T^*) \sim 30$, and $n(T = 5°K) \sim 100$. Since the spin-relaxation time is small, fluctuons can be easily produced in magnets even at the presence of the TP barrier. It is essential that the change of magnetization at the fluctuon center in paramagnets is close to saturation magnetization at $T = 0$

$$M_z(0) \approx M^0, \qquad (3.25)$$

i.e., the fluctuon produces a ferromagnetic region of sorts in a paramagnetic crystal (see Fig. 2).

The distribution of the magnetization $M_z(\mathbf{r})$ produces a magnetic moment M_f parallel to the electron spin, where M_f can be regarded as the renormalized electron moment which turns out to be much higher in the case of fluctuon formation than the true magnetic moment. In an ideal paramagnet we have

$$M_f = \int M_z(\mathbf{r})\, d\mathbf{r} = \frac{2\mu}{\sqrt{\pi}\, S^2}\, \frac{f_{1p}(a_0)}{a_0}\, \frac{A}{kT},$$

$$f_{1p}(x) = \int_0^a \frac{dx}{x} \left(\ln \frac{a}{x}\right)^{1/2} \left[S - \frac{1}{e^x - 1} + \frac{2S+1}{e^{(2S+1)x} - 1} \right]. \quad (3.26)$$

At $S \sim 1$ and $T \sim T^*$ we have in order of magnitude $M_f \sim n\mu$. The orientation of M_f is determined by the magnetic-anisotropy field.

4. THE ROLE OF DIRECT INTERACTION. FLUCTUONS IN FERROMAGNETS

a) Influence of direct interaction between spins on fluctuon production in magnetic semiconductors. In real systems there is always a definite direct interaction between the atoms or spins. This interaction can be approximately neglected at temperatures that are high compared with the ordering or decay temperature of the solution or compared with the Curie (Neel) temperature T_C of the magnet. The foregoing results for fluctuons in an ideal system are therefore valid only if $T^* \gg T_C$, i.e., if (at $S \sim 1$)

$$\varkappa = \frac{1}{7} \frac{A}{\Delta E} \left(\frac{A}{kT_c}\right)^{2/3} \gg 1. \quad (4.1)$$

According to (3.14), $A \gg 20kT_C$.

However, even in this case the direct interaction manifests itself at temperatures $T \sim T_C \ll T^*$. With decreasing temperature it leads to the appearance of short-range and subsequently long-range order in the system (or to decay of the solution). The character of the long-range order and of the direct interaction itself influence appreciably the dependence of the intrinsic parameter on the effective field produced by the electron, and thus affect the conditions of fluctuon production and the features of the fluctuons.

We consider these effects using first as an example fluctuons in magnets with positive direct exchange, assuming the s-d or s-f exchange interaction to be large so that condition (4.1) is satisfied, but at the same time the conduction band is broad enough to satisfy also the condition (3.14) [5,10]. At $T < T_C$ such magnets become ferromagnetic state and acquire a spontaneous magnetization $M_0(T)$ along a certain axis Oz.

We investigate first fluctuons in ferromagnets at relatively low temperatures, when the spin-wave approximation holds. In this case the TP density $\varphi_H(H_e)$ and the magnetization $M_z(H_e)$ can be written as

$$\varphi_H = E_0 - M^0 H_{ez} + \frac{kT}{8\pi^3} \int \ln\left[1 - \exp\left(-\frac{\varepsilon_k}{kT}\right)\right] d\mathbf{k},$$

$$M^0 - M_z = \frac{g\mu_B}{8\pi^3} \int n_\mathbf{k}\, d\mathbf{k}. \quad (4.2)$$

Here E_0 is the ferromagnet ground-state energy when there is no field, $M^0 = M_0(0) = \mu/v$, g is the spectroscopic splitting factor (g = 2 for pure spin magnetism), and μ_B is the Bohr magneton. Taking only the principal (exchange) interaction into account, the spin-wave energy ε_k in a cubic ferromagnet is

$$\varepsilon_k = \hbar\omega_0 + \frac{\hbar^2 k^2}{2M_s}, \quad \hbar\omega_0 = g\mu_B |\mathbf{H}_e| = g\frac{\mu_B v}{\mu} A |\psi(\mathbf{r})|^2. \quad (4.3)$$

If the fluctuon is considered in the macroscopic approximation, we can substitute in (2.10) the expression for φ_H with the coordinate-dependent local field $H_e[\psi(\mathbf{r})]$ (and with the local spin-wave spectrum) and neglect the last term of (2.10). The error in this approximation will be discussed below. Using the approximation (3.4) for $\psi(\mathbf{r})$ and taking (4.2) and (4.3) into account, we reduce the functional (2.10) to the function

$$I(a) = -\zeta\left(\frac{3}{2}\right) A' \left(\frac{T}{\theta}\right)^{3/2} + \frac{4}{3\sqrt{\pi}} A' \left(\frac{T}{\theta}\right)^{3/2} \times \left[B\left(\frac{kT}{A'}\right)^{2/3} \left(\frac{\theta}{T}\right)^{3/2} a^{2/3} + \frac{1}{a} f_F(a)\right] \quad \left(T \ll \frac{T_c}{S}\right), \quad (4.4)$$

where

$$A' = g\frac{\mu_B}{\mu} A, \quad \theta = \frac{2\pi\hbar^2}{kM_s v^{2/3}} \sim \frac{2nT_c}{S+1},$$

$$f_F(a) = \sum_{n=1}^{\infty} \frac{1}{n^{5/2}} \int_0^{an} \left(\ln \frac{an}{x}\right)^{3/2} e^{-x}\, dx, \quad (4.5)$$

while B and a are defined in (3.6), where A should be replaced by A'.

The functions $f_F(a)$ and $f_F'(a)$ are tabulated in [5]. At large and small a, the function $f_F(a)$ tends to the limits

$$f_F(a) \approx \frac{3\sqrt{\pi}}{4} \zeta\left(\frac{3}{2}\right) a - \pi \left(\frac{2}{3} a\right)^{3/2} \quad (a \ll 1),$$

$$f_F(a) \approx \zeta\left(\frac{5}{2}\right) (\ln a)^{3/2} \left(1 + \frac{1.30}{\ln a}\right) \quad (a \gg 1). \quad (4.6)$$

Unlike in ideal paramagnets, in ferromagnets the function I(a) has no maximum in the harmonic approximation for spin waves, and can be seen from (4.4) and (4.6) to decrease as a increases from the point $a = 0$ ($I(a) = 0$) and to go through a minimum at some value $a = a_0$ (see Fig. 4). The values of a_0, $\Delta\Phi$, and the effective number n of atoms in the fluctuon (see (3.9)), corresponding to the minimum of I(a), i.e., to the fluctuon stationary state, can be expressed in the form

$$\Delta\Phi = -\zeta\left(\frac{3}{2}\right) A' \left(\frac{T}{\theta}\right)^{3/2} + \gamma_2(a_0) B^{3/5} A' \left(\frac{T}{\theta}\right)^{3/5} \left(\frac{kT}{A'}\right)^{2/5} \quad (4.7)$$

$$n = \frac{1}{a_0} \frac{A'}{kT} = \frac{1}{\gamma_1} \left(\frac{A'}{kT} B\right)^{3/5} \left(\frac{\theta}{T}\right)^{9/10}.$$

In the analogous equation for E_e we replace $\gamma_2(a_0)$ by $\gamma_3(a_0)$. The quantities γ_1, γ_2, and γ_3 are expressed in terms of $f_F(a_0)$ in accordance with (3.11). At not too low temperatures, so long as $a_0 \gg 1$, γ_i depends little on T. In order of magnitude we have then

$$n \sim \frac{1}{3} \left(\frac{\Delta E}{kT}\right)^{3/5} \left(\frac{\theta}{T}\right)^{9/10}, \quad \Delta\Phi + \zeta\left(\frac{3}{2}\right) A' \left(\frac{T}{\theta}\right)^{3/2} \sim 2 \left(\frac{T}{\theta}\right)^{3/5} \left(\frac{kT}{\Delta E}\right)^{2/5} \Delta E,$$

$$M^0 - M_z(0) \ll M^0 - M_0 \quad \left(\frac{T_c}{S} \gg T \gg \left(\frac{\Delta E}{A'}\right)^{6/5} \left(\frac{k\theta}{A'}\right)^{4/5} \theta\right). \quad (4.8)$$

In this temperature interval, just as in ideal paramagnets, the effective field changes the magnetization near the fluctuon center to almost the maximum value M^0. Now, however, the fluctuon radius decreases (like $T^{-1/2}$) with rising rather than decreasing temperature.

At lower temperatures the equation $I'(a) = 0$ has a solution at $a_0 \ll 1$ and we can use the expansion (4.6) for $f_F(a)$. Then the formulas for I(a), $\Delta\Phi$, E_e, and n simplify to

$$\Delta\Phi = \frac{1}{3} E_e = -\frac{\pi^3 \sqrt{\pi}}{81} \frac{1}{B^3} \left(\frac{A'}{kT}\right)^2 \left(\frac{T}{\theta}\right)^6 A',$$

$$n = \frac{1}{a_0} \frac{A'}{kT} = \left(\frac{6}{\pi^2}\right)^3 B^6 \frac{(k\theta)^9}{A'^3 (kT)^6} \quad \left(T \ll \frac{1}{2} \left(\frac{\Delta E}{A'}\right)^{6/5} \left(\frac{k\theta}{A'}\right)^{4/5} \theta\right). \quad (4.9)$$
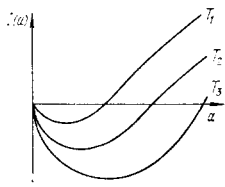
The magnetization change in the fluctuon region is then

FIG. 4. Typical plots of I(a) in ferromagnets at various temperatures $T_1 < T_2 < T_3$.

of order $M_Z(0) - M_0 \sim (M^0 - M_0)\sqrt{a_0} \ll M^0 - M_0$ and is comparatively small.

It is seen from (4.9) that $|\Delta\Phi|$ and the electron energy $|E_e|$ decrease rapidly with decreasing temperature. At a certain temperature, $|E_e|$ becomes of the order of kT. Near a temperature T_1^* on the order of

$$T_1^* \sim 20 \frac{\Delta E k T_c}{A^2} \left(\frac{S}{S+1}\right)^2 T_c, \qquad (4.10)$$

the condition (3.8), which permits the employed fluctuon description, in particular the adiabatic approximation, no longer holds. (At $|E_e| > kT$ the criterion for the applicability of this approximation is satisfied for the spin waves excited at the given temperature.) At lower temperatures one cannot speak of fluctuonic states of electrons. The electrons are then in band-type states with renormalized energy and magnetic moment (owing to interaction with the spin waves), and the calculations should be made in some variant of perturbation theory by taking the smallness of the magnon density into account. Such a calculation using an improved perturbation theory (for the case $A \gg kT_c$, $T \ll T_1^*$) has yielded an upper bound for the temperature interval of the band states.[22] It turned out to equal the lower bound (4.10) of the interval of fluctuonic states.

The behavior of the electron transition from the fluctuonic into the band states near the lower bound T_1^* turned out to be quite different from that near the upper bound T^*. Whereas near T^* the derivative is $|\partial\Delta\Phi/\partial T| \sim kn \gg k$ and the transition in the narrow temperature interval (3.17) takes the form of a smeared first-order phase transition, it can be seen from (4.9) and (4.10) that near T_1^* we have $|\partial\Delta\Phi/\partial T| \sim |E_e|/T \sim k$. Therefore the transition of the electrons into fluctuonic states is accompanied by a gradual decrease of the energy in a relatively wide temperature interval $\delta T_1 \sim T_1^*/3$ (δT_1 is not very large numerically because of the very strong temperature dependence of $\Delta\Phi$ and $E_e \sim T^6$). This transition recalls the smooth transition of electrons from polaron to band states in ionic crystals [23], but whereas the autolocalization of polarons takes place at decreasing temperature, in the case of fluctuons in ferromagnets it takes place when the temperature rises. The absence of a TP barrier for fluctuons in ferromagnets and the aforementioned character of the transition at T_1^* are actually due to the specific relation $M_0(T, H) - M_0(T, 0) \sim \sqrt{H}$ (at small H) in the ferromagnetic region.

Thus, when account is taken of the direct ferromagnetic interaction, fluctuon formation turns out to be possible in the limited temperature interval

$$T_1^* < T < T^*, \quad 0 < T_1^* < T_c, \; T^* > T_c, \qquad (4.11)$$

that includes the Curie temperature but does not extend to absolute zero (see Fig. 5). Physically this is connected with the fact that at $T = 0$ the atomic spins are already parallel (or antiparallel) to the electron spin and any kind of spin flip only increases the energy of an electron situated in a lower spin subband (the electrons

FIG. 5. Temperature range in which fluctuons exist in ferromagnetic semiconductors.
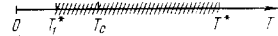
in an upper subband can go into fluctuonic states even as $T \to 0$, but their equilibrium fraction is exponentially small). At $T \sim T_1^*$, when there is already a marked spin disorder, the formation of a region of almost-parallel spins can lead to the onset of fluctuonic states with sufficiently low energy. A further rise in temperature increase in the ferromagnetic region, by increasing the spin disorder, contributes to further decrease of the electron potential energy and, in accord with (4.8) and (4.9), makes fluctuonic states thermodynamically more favored. To the contrary the main effect when the temperature is increased in the paramagnetic region is an increase of the spin part of $\Delta\Phi$, which makes the fluctuonic states less and less favored, until all the electrons go over into band states at $T \approx T^*$.

To make the employed macroscopic description of the fluctuon valid, most spin waves excited at a given temperature should have wavelengths smaller than the fluctuon dimension, i.e., the condition

$$(M_s kT)^{1/2} (nv)^{1/3} \hbar^{-1} \gg 1, \quad \text{or} \quad n^{1/3} (T/\theta)^{1/2} \gg 1.$$

should be satisfied. Taking expressions (4.8) and (4.9) for n into account, we find that this condition holds. From the estimates (4.8)–(4.10) it follows also that the last term discarded from (2.10)

$$\frac{1}{2} \int \beta\,(\nabla M)^2\,d\mathbf{r} \sim \beta\,(M_z(0) - M_0)^2\,(nv)^{1/3} \quad (\beta \sim k\theta\,(4\pi\,(M^0)^2 v^{1/3})^{-1})$$

is really small relative to the other terms of $\Delta\Phi$, e.g., relative to the average electron potential energy $\sim A(M_Z(0) - M_0)/M^0$.

Just as in ideal systems, a localized electron leads to indirect interaction of the type (3.19) between the spins (this interaction was considered in [24]) for large radius electronic states, which changes the spin excitation spectrum. It can be shown by using the results of [24] that this interaction contributes to $\hbar\omega_0$ the spin wave energy much less. At low temperatures, in the region where Eqs. (4.9) hold we have $\hbar\omega_0 \sim a_0 kT \ll kT \sim \epsilon_k$ and the indirect interaction leads to corrections of the higher order of smallness to both the spin-wave energy (compared with the contribution of the direct interaction) and to the fluctuon characteristics. At higher temperatures, when $a_0 \gtrsim 1$, this indirect interaction can make no less a contribution to the spin wave-energy than the direct one (but much less than $\hbar\omega_0$). However, this fact affects only the terms in φ_H and $I[\psi]$, which are in any case exponentially small (owing to the large gap $\hbar\omega_0$ in the spectrum), and hence leads to only small corrections to $\Delta\Phi$.

Obviously, the assumption made above that the electron spin is strictly parallel to the magnetization in the crystal (see p. 859), which leads in the zeroth approximation to the spin-wave spectrum (3), is only approximated if spin disorder obtains in the region of the fluctuon. This assumption does lead, however, to a small error, if the characteristic dimension of the spin homogeneity, i.e., the wavelength of the spin waves excited at the temperature in question, is small enough (then the growth of the kinetic energy of the electron leads to a suppression of this component if a second electron-spinor component that varies rapidly in space appears). The indicated assumption and the results

M. A. Krivoglaz

given above for fluctuons in ferromagnets turn out to be justified at $T > \tilde{T} \sim T_C A/\Delta E$ (for $S \sim 1$). If $T_1^* < \tilde{T}$, then the character of the transition to fluctuonic states and the singularities of the fluctuons at $T < \tilde{T}$ can differ greatly from those described above. Violation of the rule (4.3) at large ψ-function radii can lead also to a suppression of the small maxima on the curves of Fig. 4 at small a.

Fluctuon formation in a ferromagnet, as in a paramagnet, causes an anomalously large electron-induced change in the magnetization

$$M_f \sim \int [M_z(\mathbf{r}) - M_0]\, d\mathbf{r} = \frac{4}{3\sqrt{\pi}}\, g\mu_B \frac{1}{a}\, f_{1F}(a)\, \frac{A'}{kT}\left(\frac{T}{\theta}\right)^{3/2} \gg \mu, \ (4.12)$$

where

$$f_{1F}(a) = \sum_{n=1}^{\infty} \frac{1}{n^{3/2}} \int_0^{an}\left(\ln\frac{an}{x}\right)^{3/2} e^{-x}\, dx,$$

$$f_{1F} \approx \zeta\left(\frac{3}{2}\right)(\ln a)^{3/2}\left(1 + \frac{2,82}{\ln a}\right) \quad (a \gg 1). \tag{4.13}$$

The foregoing results for fluctuons in ferromagnets are valid only in the spin-wave region. To consider ferromagnets at higher temperatures, and also nonideal paramagnets in the case $\kappa \gg 1$, the molecular-field approximation can be used. For a pure spin magnetism at $S = 1/2$ ($g = 2$, $\mu = \mu_B$) we have in this approximation

$$\varphi_H = \frac{kT}{2v}[(1 + \eta)\ln(1 + \eta) + (1 - \eta)\ln(1 - \eta)] - \frac{kT_c}{2v}\eta^2 - \frac{\mu H_e}{v}\eta. \ (4.14)$$

The relative magnetization $\eta = \eta(\mu H_e/kT) = M_0/M^0$ is determined here by the equation

$$\eta(x) = \operatorname{th}\left[\frac{T_c}{T}\eta(x) + x\right], \quad x = \frac{\mu H_e}{kT}. \tag{4.15}$$

Substituting (4.14) and (3.4) in (2.10), it is easy to verify that the function I(a) and the quantities $\Delta\Phi$, E_e, and n are likewise determined in this case by (3.5), (3.6), (3.10), and (3.11), as in ideal solutions, provided we make the substitutions

$$2c_0 \to 1 - \eta(0), \quad b \to 1, \quad A \to A' = 2A,$$

$$f(a) \to f_M(a) = \frac{1}{2}\int_0^a\left(\ln\frac{a}{x}\right)^{3/2}\left[1 - \eta\left(\frac{x}{2}\right)\right] dx. \tag{4.16}$$

Tables of the function $f_M(a)$ for some values of T/T_c are given in [5].

Analysis of these results shows that in a ferromagnet the conditions for fluctuon production are easier and that $\Delta\Phi$ and E_e decrease as the Curie temperature is approached. In paramagnets, the direct interaction between the spins facilitates fluctuon production and raises T^*, and when the temperature is lowered and approaches T_C the quantities $\Delta\Phi$ and E_e also decrease. For example, at $S = 1/2$, $B = 3$, $A'/kT_C = 10^3$, and $T = 1.5T_C$ we have in an ideal paramagnet $\Delta\Phi = -0.25A$, and allowance for the interaction yields $\Delta\Phi = -0.40A$.

The Curie point itself is not singled out in this approximation when the condition (4.1) is satisfied. The reason is that at $\kappa \gg 1$ the strong effective field in the fluctuon region brings the magnet out of the critical region and changes $M_z(0)$ almost to the value of M^0. The fluctuon-existence region extends in this case over a wide temperature range around T_C, since

$$T^* \sim \varkappa^{3/2}T_c \gg T_c, \quad T_1^* \sim 3\left(\frac{S}{S+1}\right)^2\left(\frac{kT_c}{A}\right)^{1/3}\frac{1}{\varkappa}T_c \ll T_c \quad (\varkappa \gg 1). \tag{4.16'}$$

On the other hand when $\kappa < 1$ the effective field H_e is insufficient to bring the system out of the critical region, the molecular-field approximation does not hold,

and the fluctuons must be investigated by some other method (see Chap. 5).

The foregoing results were obtained in [5]. Similar calculations in the molecular-field approximation were performed in [9], where it was also concluded that there exist autolocalized electronic states (called there paramagnetic polarons)[3]. We note that a qualitative assumption of the possible existence of autolocalized states in paramagnets was advanced in [25].

An important role can be played in ionic magnetic crystals also by interaction between electrons and polarized oscillations. Simultaneous allowance for exchange and polarization interactions shows that the polarization interaction stabilizes the fluctuons and facilitates their production [26].

The described theory of fluctuons in magnetic semiconductors was developed in a macroscopic approximation. It is valid so long as $n \gg 1$. Autolocalized electronic states in paramagnets were investigated recently also by using a microscopic theory within the framework of the molecular-field approximation[27a] and by the Green's-function method [27b]. The results agreed there agree with those of the macroscopic theory.

It appears that the condition $A \gg kT_C$, kT is satisfied in almost all real magnetic semiconductors. In compounds of rare-earth elements and in some transition-metal compounds the conduction band is broad enough, the condition (3.14) is satisfied, and the large-radius fluctuons considered above appear. Many transition-metal compounds, however, have narrow conduction bands and the inverse condition $A \gg \Delta E \gg kT_C$ is satisfied instead of (3.14).

If $A \gg \Delta E$, strong interaction produces bound states of a conduction electron situated on some atom with the spin of this atom (with a total spin $S \pm 1/2$) [28]. Such spin-electron complexes move in the crystal as single quasiparticles with a somewhat modified effective mass ($<2m$). At low temperatures, these quasiparticles are in band-type states. But if the ratio $\Delta E/kT_C$ is large enough, then at higher temperatures the interaction between the quasiparticles and the spin deviations can greatly modify the carrier states and make autolocalized states of the fluctuonic type thermodynamically favored [29]. At large $\Delta E/kT_C$ the temperature interval in which fluctuons exist can extend much above the Curie point in the paramagnetic region but somewhat below T_C in the ferromagnetic region (usually not below $(1/2)T_C$). If $A \gg \Delta E$ it is not the electrons themselves that are autolocalized, but the spin-electron complexes, and their interactions with the spin deviations are determined by ΔE and not by A. Therefore the characteristics of the produced fluctuons and the character of transition into fluctuonic states differ appreciably from the fluctuon characteristics at $A \ll E$ (see [29] for details).

We note that the foregoing results refute the conclusion that an analog of a small-radius polaron with a diffusion mobility mechanism is produced in ferromagnetic semiconductors [30], which is sometimes used to interpret the experimental data (see [5,31] for details).

Direct antiferromagnetic interaction between spins in the paramagnetic region hinders fluctuon production, as is easily seen from an analysis of the results of the molecular-field approximation. Electron autolocalized states in the antiferromagnetic region were studied in a number of investigations starting with the pioneer work

of De Gennes [32]. In this region the fluctuons become more stable with decreasing temperature [9]. As $T \to 0$ they go over continuously into the states considered previously in [33] and called these "magnetic polarons."

b) <u>Phasons.</u> The direct interaction determines also the properties of the fluctuons that are produced near a first-order phase transition in single-component systems. If the electron is attracted to the region of the second phase, which is unstable at the given temperature, and is localized near this region, then the lowering of the electron energy can cancel out both the difference of the volume TP and the surface energy of the interphase boundary, which can be regarded as sharp enough in the macroscopic approximation. The resultant stable formation—phason—is a particular case of a fluctuon in which the electron is localized at the heterophase fluctuation [34] and a sufficiently abrupt change of the internal parameter takes place. In a certain sense, phasons are similar to electrons localized in bubbles inside liquid helium [35], but in many respects they differ significantly from them (in the role of the exchange TP, in the strong temperature dependence of the properties, and in the character of the mobility mechanism). They are also analogous to a certain degree to the formation of a second phase near impurity ions (see, e.g., [36]), but in the case of phasons the decisive role is played by quantum effects connected with the small electron mass.

In the case of nonpyroelectric phases, in the absence of elastic stresses, and in the case of anisotropy of the surface energy, the phason can be regarded as a spherical particle (radius R) of a second phase, in which the bottom of the potential well is lowered by a certain constant value $V > 0$. Calculating the electron energy E_e in the effective-mass approximation (for $V \ll \Delta E$), we can find the change $\Delta\Phi$ of the TP following formation of a phason, by determining the minimum of the function $\Delta\Phi(R)$, where

$$\Delta\Phi(R) = \frac{4\pi}{3} R^3 \varphi' + 4\pi R^2 \sigma + E_e(R), \quad E_e(R) = -V + \frac{\hbar^2 k_e^2}{2m}. \quad (4.17)$$

Here φ' is the difference of the phase TP densities, σ is the interphase surface energy, and k_e is determined from the equation

$$k_e \operatorname{ctg} k_e R = -\sqrt{\frac{2mV}{\hbar^2} - k_e^2}.$$

By determining the smallest value $\Delta\Phi = \Delta\Phi(R_0)$ under the condition $E_e(R_0) < 0$ (for details see [4]) we can verify that $\Delta\Phi$ becomes negative (and the phasons are stable) at V larger than a certain value V^0. Near the phase transition itself ($\varphi' \to 0$) and at noticeable distances from this point (at small σ), the values of V^0 and of the corresponding phason radius $R_0 = R^0$ are given by

$$V^0 = 11.5\hbar\sqrt{\frac{\sigma}{m}}, \quad R^0 = 0.60 \left(\frac{\hbar^2}{m\sigma}\right)^{1/4} \quad (\text{if } \varphi' R^0 \ll \sigma), \quad (4.18)$$

$$V^0 = 5.81 \left(\frac{\hbar^2}{m\varphi'}\right)^{3/5} \varphi', \quad R^0 = 0.73 \left(\frac{\hbar^2}{m\varphi'}\right)^{1/5} \quad (\text{if } \varphi' R^0 \gg \sigma). \quad (4.19)$$

At large $V \gg V^0$ the values of $\Delta\Phi$ and E_e tend to the limiting value $-V$, while R_0 tends to a value R_∞, where

$$R_\infty = \left(\frac{\pi}{8} \frac{\hbar^2}{m\sigma}\right)^{1/4} \quad (\text{if } \varphi' R_\infty \ll \sigma),$$
$$R_\infty = \left(\frac{\pi}{4} \frac{\hbar^2}{m\varphi'}\right)^{1/5} \quad (\text{if } \varphi' R_\infty \gg \sigma). \quad (4.20)$$

If, e.g., $\sigma = 20$ erg/cm² and $\varphi' = 0$, then $V^0 \sim 1$ eV and $2R^0 \sim 10$ Å. The quantities V^0 and $2R^0$ are of the same order at $\varphi' \sim 10^9$ erg/cm³ and $\sigma \ll 10^2$ erg/cm².

The equilibrium concentration of the phasons is determined by the general formula (2.15). Most electrons go over into the phason states in the vicinity of the transition temperature T_0 in systems with small σ, if V exceeds (or, taking $\zeta \gg 1$ into account, is somewhat smaller than) the value V^0 (4.18). With increasing distance from the transition point, when $\varphi' = q|T - T_0|v^{-1}$ increases (q is the heat of transformation per atom), $\Delta\Phi$ increases and vanishes at a certain temperature T^*. According to (4.19) we have

$$|T^* - T_0| \sim \frac{1}{7} \left[\frac{V^5}{(\Delta E)^3 (qT_0)^2}\right]^{1/2} T_0 \quad \left(\text{if } 0.1 \frac{V^2}{\Delta E} \gg \sigma v^{2/3}\right). \quad (4.21)$$

Since $|\partial\Delta\Phi/\partial T| \sim (4\pi/3)(R^3/v)q \gg k$ (at not too small $q \sim k$), the electrons should go over into band states at a somewhat larger distance from the point T_0, and this transition should have, just as in the case of fluctuons in ideal systems, the character of a smeared (in the interval $\delta T \sim (3v/4\pi R^3)(k/q)T_0$) first-order phase transition.

Allowance for the polarization effects connected with the difference between the dielectric constants of the phases in homopolar mediums, introduces small corrections into these estimates. The polarization effects play a more important role if the second phase is pyroelectric (e.g., in ferroelectric phase transitions). Then the phase-transition region has not a spherical but an ellipsoidal form and the conditions for the production of phasons are altered [4].

If the specific volumes of the phases differ appreciably, the production of phasons in crystals is hindered by the elastic energy. In this case the phasons (or the fluctuons in the analogous situations) can become predominantly localized at the crystal surface or near dislocations (especially if the electrons are attracted to the surface.

c) <u>Role of direct interaction in solutions.</u> To investigate the influence of the direct interatomic interaction on the production of fluctuons in solutions when condition (4.1) is satisfied [12] we can use the simplest nearest-neighbor model, in which correlation is disregarded. In this model we have

$$\varphi(c) = \frac{kT}{v} [c \ln c + (1-c) \ln (1-c)] + \frac{zw}{2v} c^2,$$
$$\beta \sim 4kT_0 v^{-1/3}, \quad z|w| = 4kT_c, \quad (4.22)$$

where w is the ordering energy, z is the coordination number, and T_c is the maximum decay or ordering temperature.

In the macroscopic approximation (at $n \gg 1$) it is possible to neglect the term with $\beta(\nabla c)^2$ in (2.2), and then (2.5), with (4.22) taken into account, takes the form

$$\ln \frac{c}{1-c} + \frac{zw}{kT} c = \ln \frac{c_0}{1-c_0} + \frac{zw}{kT} c_0 - x, \quad x = \frac{Av}{kT} |\psi|^2. \quad (4.23)$$

From (2.6), (2.2), (3.4) and (4.22) it follows that in nonideal solutions with temperatures higher than T_c the values of $I(a)$, $\Delta\Phi$, E_e, and n are determined formally by the same expressions (3.5), (3.6), (3.10), and (3.11) as in ideal solutions. It is only necessary to define the function $f(a)$ as

$$f(a) = \int_0^a dx \left(\ln \frac{a}{x}\right)^{3/2} c(x), \quad (4.24)$$

where $c = c(x)$ is a solution of Eq. (4.23). For $c_0 = 1/2$, the formulas turn out to be the same as in nonideal paramagnets with spin $S = 1/2$.

An analysis of these results shows that direct interaction shifts the transition temperature by an amount

$$\delta T^* \sim -T_c \frac{w}{|w|} \sim -T^* \varkappa^{-3/2} \frac{w}{|w|}. \quad (4.25)$$

In decaying solutions we have $w < 0$, i.e., direct interaction raises the temperature T^* and leads at a given T to a decrease of n and to stabilization of the fluctuons. In solutions that become ordered we have $w > 0$ and T^* decreases. In the considered case of large κ, the change δT^* is small. The changes of $\Delta\Phi$ and n at temperatures close to T_C are much larger (by several times).

Below the temperature T_C in decaying solutions, the effective field of the electron can bring the concentration to the decay curve, and then a second phase is produced in the center of the fluctuon, and an interphase boundary appears, on which the concentration changes jumpwise. In this case the fluctuon is a phason, but one in which the concentration in each of the phases is not constant but changes somewhat. If the solution is near the decay curve, then the formation of the second phase changes the TP of the system little, and at the same time leads immediately to the formation of a deep potential well for the electron. Under these conditions the production of fluctuons is therefore greatly facilitated even at low concentrations c_0, and their characteristics differ from the characteristics of fluctuons in ideal solutions (see [12] for details).

An appreciable influence can be exerted on fluctuon production also by long-range order in both single-component ordered systems of the molecular type [7] and in solid solutions [12].

5. FLUCTUONS NEAR CRITICAL POINTS AND SECOND-ORDER PHASE TRANSITION POINTS

As already noted above, at sufficiently large A, when the criterion (4.1) is satisfied, the temperatures T^* and T_1^* of the electron transition into fluctuonic states lie far enough away from the Curie point or from the critical temperature, and the strong effective field of the electron in the vicinity of the critical point takes the medium immediately out of the critical region, so that the vicinity of T_C is not singled out from the point of view of the singularities of the fluctuon properties.

A special case arises, however, if the condition (4.1) no longer holds. At $\kappa \lesssim 1$, as seen from (4.16) the boundaries of the interval T^* and T_1^* approach T_C. At sufficiently small A, when $\kappa \ll 1$, the effective fields are relatively weak and the system, even if perturbed by the electron field, remains in the critical region. In this region, as is well known, weak fields can produce appreciable changes of the internal parameter, so that the conditions for fluctuon production are greatly facilitated. It turns out as a result that in the critical region fluctuations can be produced even if the criterion inverse at (4.1) is satisfied (but, as before, $A \gg 10kT_e$). Only the temperature interval in which fluctuons exist will be much narrower, and the fluctuon characteristics are changed.

The molecular-field method does not hold generally speaking in the critical region, so that the case of small κ calls for a special analysis [7]. We carry out this analysis using as an example solutions that are near the critical point on the deacy curve. The results, however, hold also for paramagnets near the Curie temperature and for systems near the gas–liquid critical point.

The problem of determining the fluctuon state in a solution reduces to a determination of the minimum of

the functional (2.4). After minimization with respect to $c(\mathbf{r})$, the sum of the integrands of the second and third terms in (2.4) can be regarded as a change $\delta\varphi$ in the TP density following a change of the chemical potentials of the solution atoms by an amount $\delta\mu' = Av|\psi(\mathbf{r})|^2$ ($\delta\mu'$ is proportional to the effective field).

The form of the functional $J[\psi]$ is determined therefore by the dependence of $\delta\varphi$ on $\delta\mu'$. In the case of short-range interatomic forces, in a uniform effective field, this dependence can be specified with the aid of the scaling hypothesis (see, e.g., [37]):

$$\delta\varphi = -\frac{kT_c}{v}\,\tau^\rho g\left[\left(\frac{\delta\mu'}{kT_c}\right)^{(\delta+1)/\delta}\tau^{-\rho}\right],$$
$$\rho = \gamma\frac{\delta+1}{\delta-1},\quad \delta\mu' = Av|\psi(\mathbf{r})|^2; \tag{5.1}$$

here $\tau = (T - T_C)/T_C > 0$, while γ and δ are the known critical exponents for the dependence of the susceptibility on τ and of the effective field on the magnetization; we have $g(t) \sim t$ as $t \to \infty$ and $g(t) \to \mathrm{const} \sim 1$ as $t \to 0$. In particular, at the critical point itself we have

$$\delta\varphi = A(c-c_0)|\psi|^2 + \varphi(c) - \varphi(c_0) - \frac{\partial\varphi(c_0)}{\partial c_0}(c-c_0)$$
$$= -P\frac{kT_c}{v}\left(\frac{Av|\psi(\mathbf{r})|^2}{kT_c}\right)^{(\delta+1)/\delta},\quad P \sim 1. \tag{5.2}$$

The effective field in the fluctuon is in fact not uniform. The corresponding effects, however, can frequently be neglected (see the estimates given below). We put therefore $\beta = 0$ in (2.2) and (2.5).

We consider first the critical point itself. To determine the minimum of the functional $I[\psi]$, obtained after substituting (5.2) in (2.4), it is convenient to introduce in lieu of $\mathbf{r}$ and $\psi(\mathbf{r})$ the dimensionless quantities $\mathbf{r}'$ and $\psi'(\mathbf{r}')$:

$$\mathbf{r} = p\mathbf{r}',\quad \psi(\mathbf{r}) = p^{-3/2}\psi'(\mathbf{r}'),$$
$$p^2 = P^{-\lambda\delta}A^{-\lambda(1+\delta)}\left(\frac{kT_c}{v}\right)^\lambda\left(\frac{\hbar^2}{2m}\right)^{\delta\lambda},\quad \lambda = \frac{2}{2\delta-3}. \tag{5.3}$$

The calculation of $\Delta\Phi$ reduces then to a determination of the minimum $-I'$ of a functional containing no parameters whatever

$$-I' = \min_{\psi'}\left[\int|\nabla'\psi'|^2\,d\mathbf{r}' - \int|\psi'|^{2+(2/\delta)}\,d\mathbf{r}'\right]$$
$$= -(2\delta-3)(2\delta)^{-\lambda\delta}\left(\frac{2}{\pi}\right)^{3\lambda/2}\left(\frac{\delta}{1+\delta}\right)^{3\lambda\delta/2} \tag{5.4}$$

(I' was calculated approximately with an accuracy $\sim 1\%$).

We then obtain for $\Delta\Phi$, E_e, n, and the maximum change $|c(0) - c_0|$ of the concentration in the fluctuon the expressions

$$\Delta\Phi = \frac{2\delta-3}{2\delta-1}E_e = -I'\frac{\hbar^2}{2mp^2} \sim -x^{3\lambda/2}A,\quad x = \frac{1}{7}\frac{A}{\Delta E}\left(\frac{A}{kT_c}\right)^{2/3},$$
$$n = \left(\frac{\pi}{2}\frac{2\delta-3}{I'}\right)^{3/2}\frac{p^3}{v} \sim x^{-9\lambda/4}\left(\frac{\Delta E}{A}\right)^{3/2},\quad |c(0)-c_0| \sim x^{3\lambda/2}. \tag{5.5}$$

The exponents in these formulas can be estimated by recognizing that in the Ising model we have $\gamma = 5/4$, $\delta \approx 5$, and $3\lambda/2 \approx 0.43$. In order for the system to remain in the critical region, $|c(0) - c_0|$ should be small compared with unity. By stipulating also that E_e exceed kT_c, we obtain the conditions

$$x^{3\lambda/2} \ll 1,\quad A x^{3\lambda/2} \gg kT_c, \tag{5.6}$$

which can be compatible if ΔE is large enough. From a comparison of (5.5) and (3.13) it follows that fluctuons with small κ have in the critical region much larger dimensions than under ideal conditions.

It is seen from (5.4) that the positive term in the expression for $I[\psi]$ depends on the effective radius $\tilde{r}$ of the wave function like $\tilde{r}^{-2}$, while the negative term

depends like $\tilde{r}^{-3/\delta}$. Therefore when $\tilde{r}$ changes from ∞ to the equilibrium value r_0, the value of $I[\psi]$ decreases monotonically ($\delta > 3/2$), i.e., fluctuons at a critical point, unlike fluctuons in ideal systems, are produced without overcoming the TP barrier (see Fig. 6, curve $\tau_1 = 0$).

We consider now a temperature different from critical (assuming as before that c_0 is equal to the critical concentration c_C). To investigate this case we recognize that at large radii $\tilde{r}$, when $A|\psi|^2$ is small enough $((\delta\mu'/kT_C)^{\delta+1} \ll \tau^{-\rho\delta})$, we have $\delta\varphi - \delta\varphi_0 \sim (kT_C/v)\tau^\gamma(c-c_0)^2$. According to (2.5) we then have in the fluctuon $|c - c_0| \sim (A|\psi|^2v/kT_C)\tau^{-\gamma}$ and the negative term in the expression for $I[\psi]$ is proportional to $\tilde{r}^{-3}$ (the positive term is $\sim \tilde{r}^{-2}$), i.e., $I[\psi] = I(\tilde{r}^{-1})$ increases when $\tilde{r}^{-1}$ increases from zero. On the other hand if $A|\psi|^2$ is large enough $((\delta\mu'/kT_C)^{\delta+1} \gg \tau^{-\rho\delta})$, then $\delta\varphi$ is approximately determined by the same formula (5.2) as at $\tau = 0$.

At sufficiently small τ the function $I(\tilde{r}^{-1})$ should therefore first have, with increasing $\tilde{r}^{-1}$, a positive maximum

$$I_{max} \sim \varkappa^{-3}A\tau^{2\gamma}, \tag{5.7}$$

which determines the order of magnitude the height of the thermodynamic barrier for fluctuon production, followed by a minimum whose depth is close to expression (5.5) for $\Delta\Phi$ (see Fig. 6, curve τ_2).

With increasing τ, the height of the barrier increases and the entire $I(\tilde{r}^{-1})$ curve rises. At a certain $\tau = \tau^*$, when I_{max} is of the order of expression (5.5) for $-\Delta\Phi$ (or when the argument of the function g in (5.1) is ~ 1), the minimum of this curve turns out to be on the abscissa axis, i.e., $\Delta\Phi = 0$. Somewhat above this value,

$$\tau^* \sim \varkappa^{\rho_1} \ll 1, \quad \rho_1 = \frac{3(\delta-1)}{\gamma(2\delta-3)}, \tag{5.8}$$

the fluctuons go over into band states. It is easy to find in similar fashion that the concentration interval in which the fluctuons exist is bounded by the limits

$$|c^* - c_0|^* \sim \varkappa^{\rho_2}, \quad \rho_2 = \frac{3}{2\delta-3}. \tag{5.9}$$

Thus, the interval of fluctuon existence is small near the critical point and depends strongly on the coupling constant A. The interval $\delta\tau$ in which most electrons go over into fluctuonic states can in this case be even smaller if the second condition of (5.6) is satisfied:

$$\delta\tau \sim \frac{kT_C}{A}\varkappa^{-\frac{3}{2}\lambda}\tau^* \ll \tau^*, \tag{5.10}$$

i.e., a smeared first-order phase transition takes place in this case.

It should be borne in mind that the results for the fluctuons in the critical region, as well as far from it, were obtained assuming the linear approximation (2.3) for the electron potential energy, and neglecting the shift δE of the renormalized edge of the band electron. In the critical region, δE can be much larger than the value of $A^2/\Delta E$ shown in p. 862. It does, however, remain much smaller than A. At sufficiently large A, when the condition (4.1) is satisfied, the quantity $-E_e$

is of the order of A at $T \sim T_C$, i.e., the electron level in the fluctuon lies lower than the renormalized edge of the band also at $T \approx T_C$, corresponding to the region of the fluctuation tail of the state density. The fluctuons produced at $T \approx T^* \gg T_C$ therefore remain stable also in the critical region, in spite of the aforementioned increase of the shift of the edge of the band. Inasmuch as in the fluctuon region the effective field suppresses the critical fluctuations, this effect leads only to small corrections to the fluctuon characteristics.

In the case of small A, when the condition (5.6) is satisfied, rough estimates show that $\delta E \ll |E_e|$ and the energy renormalization of the band electron is immaterial if (neglecting numerical coefficients) $(A/kT_C)^\lambda \gg (\Delta E/A)^{\rho_3}$, where $\rho_3 = [3/(2\delta-3)] - [(1-\eta_0)/(3+\eta_0)]$, and η_0 is the critical exponent for the correlation function at the critical point ($\sim r^{-(1+\eta_0)}$). In the case of short range forces at $\delta \approx 5$ and $\eta_0 \approx 0.03$ we have $\rho_3 \approx 0.1$, and this condition is usually satisfied. Even if the opposite condition is satisfied, it must be borne in mind that the difference of the energy renormalizations of the band and self-localized electrons can be small. The question of the required corrections to $\Delta\Phi$ and E_e (and also the question of the value of the coefficient ζ in (2.15) in the critical region) calls for further investigation.

Although the results presented in this chapter were formulated for solutions, they apply equally well, in accordance with the statements made in Chap. 2, to single-component systems near the gas-liquid critical point. It is necessary only to make the substitution (2.12) in all the formulas. Thus, by replacing c with M/M^0 and c_0 with M_0/M^0 we can easily see that these results are applicable also to paramagnets near the Curie temperature, at $T > T_C$.

At $T < T_C$ in the ferromagnetic region, the fluctuons can have near the Curie point certain singularities connected with the long-wave spin-wave modes, and a resultant dependence in the form $M_0(T, H) - M_0(t, 0) \sim \sqrt{H}$ at small values of H.[38] An analysis carried out for the case of a large radius of the exchange interaction between the atoms [10] has shown that at very small τ, just as at the Curie point itself, the function $I(a)$ has only one minimum. At somewhat larger τ there appear two minima, i.e., a thermodynamic barrier to fluctuon production appears. At a certain value of the relative temperature $\tau_1^* \sim \tau^*$ of the same order as in paramagnets (at $\varkappa \ll 1$), the fluctuons are no longer thermodynamically favored and go over into band states. Unlike the smooth transition in the spin-wave region, in the critical region there is produced in this case a smeared first-order phase transition. It was impossible to carry out a similar analysis for the case of short-range exchange forces, and it is unclear whether the transition from the fluctuonic to the band states in a ferromagnet is a smeared phase transition or whether it proceeds smoothly. However, even in the latter case the transition interval $\delta\tau_1^*$ is several times smaller than τ_1^*, and since τ_1^* is also small, the order of magnitude of the temperature interval $\delta T_1 = \delta\tau_1 T_C \sim (1/3)\tau_1^* T_C \ll T_C$ should be quite small.

It was assumed above that the connection between the effective field and the change of the concentration is local, and no account was taken of effects due to the inhomogeneity of the field. An analysis shows that in the case of short-range interatomic forces these effects practically do not influence the distribution of the concentration or of the internal parameter in the region of the fluctuon center. In the case when the interaction

FIG. 6. Typical plots of I vs a (or $\tilde{r}^{-3}$) in solutions or in paramagnets in the critical region at different relative temperatures $\tau_1 = 0 < \tau_2 < \tau_3 = \tau^*$.

M. A. Krivoglaz

radius r' is large and $r'^3/v \gg A/kT_C$, these effects, according to [7], alter significantly the singularities of the fluctuons (if $r' \gg v^{1/3}$ but $r'^3/v < A/20kT_C$, the results presented above are valid, and the critical exponents $\gamma = 1$ and $\delta = 3$ correspond approximately to the self-consistent-field approximation).

It must be borne in mind that even in the case of short-range forces far from the fluctuon center, at $r > (vn)^{1/3}$, the nonlocality near T_C becomes appreciable and leads to a relatively slowly decreasing (in proportion to $r^{-1} \exp(-\sqrt{(\partial^2\varphi/\partial c^2)/\beta}\,r)$ change of $c - c_0$. The most important role is played by these effects when it comes to determining the magnetic moment of a fluctuon in a magnet. They come into play, however, only in a relatively narrow temperature interval, when $\tau^{3\delta} \ll (n^{2\delta-3}\kappa^3)\rho_1$. Outside this interval, the problem can be regarded as local. We then have in a paramagnet

$$M_f \sim \mu \left(\frac{\Delta E}{A}\right)^{3/2} x^{-3\lambda/4}. \qquad (5.11)$$

6. KINETIC CHARACTERISTICS OF FLUCTUONS

a) Fluctuon mobility. Large-radius fluctuons at not too high temperatures, just like band electrons, have an appreciable mean free path l and move in straight lines over sections of length $\sim l$, being scattered from time to time by vibrations or defects. In the case of fluctuons, on the other hand, the effective free path is smaller than their radius, i.e., the fluctuons do not have the usual mobility mechanism. At the same time, the hopping conductivity is likewise inoperative in this case, just as for small-radius polarons.

The fluctuon motion is actually connected with a specific mobility mechanism wherein diffusion of the atoms or spins sets in, or else viscous flow in the medium, and the localized electron executes a motion that is coordinated with that of the surrounding region in which the internal parameter is altered. The fluctuon mobility can therefore not be calculated by the usual method of solving the kinetic equation, and another "hydrodynamic" approach must be used, in which the energy dissipated in the medium during the translational motion of the fluctuon is calculated [8].

To illustrate this approach, we consider a fluctuon in an ideal solution moving with a translational velocity V. The moving concentration distribution $c(\mathbf{r} - \mathbf{V}t)$ is connected with the diffusion fluxes in the medium, and its form differs somewhat from the distribution $c^0(\mathbf{r})$ for an immobile fluctuon. The form of this distribution can be determined by recognizing that in the coordinate system that moves together with the fluctuon this distribution is stationary and satisfies the equation

$$\mathbf{V}'\nabla c\,(\mathbf{r}) = -\,v\,\mathrm{div}\,\mathbf{I}_1, \quad c\,(r = \infty) = c_0; \qquad (6.1)$$

here $\mathbf{V}'$ is the velocity of the medium in the moving coordinate system and $\mathbf{I}_1$ is the diffusion flux of the atoms A.

In the general case $\mathbf{V}'$ depends on $\mathbf{r}$. However, if we confine ourselves to liquid solutions, in which the density and viscosity depend little on the composition, or to interstitial solid solutions, then we can neglect the viscous fluxes in the medium. Then $\mathbf{V}' = -\mathbf{V} = \mathrm{const}$, and the diffusion flux is proportional to the gradient of the difference between the chemical potentials μ' of the atoms A and B: $\mathbf{I}_1 = -L\nabla\mu'$. Neglecting for simplicity the dependence of the kinetic coefficient L on the con-

centration c and on the electron density $|\psi|^2$, we can express it in terms of the coefficient D of mutual diffusion far from the fluctuon: $L = (D/vkT)c_0(1-c_0)$. Then (6.1) takes the form

$$\mathbf{V}\nabla c^0\,(\mathbf{r}) = -\frac{D}{kT}\,c_0\,(1-c_0)\,\Delta\mu'. \qquad (6.2)$$

This equation has been linearized with respect to V (with $c(r)$ replaced by $c^0(r)$).

The diffusion processes that accompany the fluctuon motion are irreversible and lead to energy dissipation. Using the known formula for the thermodynamics of irreversible processes [39], we can determine the energy transferred per unit time from the moving fluctuon to the medium:

$$Q = -\int \mathbf{I}_1\nabla\mu'\,d\mathbf{r} = \int L\,|\nabla\mu'|^2\,d\mathbf{r} = \frac{Dc_0\,(1-c_0)}{vkT}\int|\nabla\mu'|^2\,d\mathbf{r}. \qquad (6.3)$$

According to (6.2) and (6.3), Q is proportional to V^2. In order for the fluctuon to move with constant velocity, it should acquire an energy Q from the external electric field E. Writing down Q in the form $Q = eEV = eV^2/u$ ($V = uE$), we can express the fluctuon mobility u in term of Q: $u = eV^2/Q$. By determining the integral in (6.3) with the aid of (6.2) and formulas (3.2) and (3.4) for $c^0(\mathbf{r})$, we obtain a formula for u:

$$u = \frac{1}{f_2\,(a)}\frac{eD}{kTn} \sim \frac{eD}{kTn}, \qquad (6.4)$$

where

$$f_2\,(a) = \frac{2}{3\sqrt{\pi}}\,c_0\,(1-c_0)\int_0^a \frac{dx}{x}\left(\ln\frac{a}{x}\right)^{1/2}\left(\frac{1-e^{-x}}{1-c_0+c_0e^{-x}}\right)^2. \qquad (6.5)$$

The ion mobility in electrolytes is of the order of eD/kT. As seen from (6.4), the fluctuon mobility is smaller by a factor $\sim n$ and is usually very small. For example, at $c_0 \sim 1/2$, $T \sim 300°K$, $n \sim 10^3$, and $D \sim 10^{-4}$ cm^2/sec we have $u \sim 10^{-3}$ cgs esu. Such low mobility are connected in natural fashion with the diffusion mechanism of fluctuon motion. The temperature dependence of u is determined mainly by the factor D, i.e., the mobility increases exponentially with increasing temperature.

Fluctuon motion in paramagnets is connected with spin-diffusion processes. To estimate the mobility in this case we can also use formula (6.4), taking D to mean the spin-diffusion coefficient D_S. It must be borne in mind, however, that if condition (4.1) is satisfied (when $T^* \gg T_C$) the electron-induced indirect interaction between the spins is much larger than the direct interaction, and it is indeed the indirect interaction that determines D_S. Taking this circumstance into account, we obtain the following estimate for u in paramagnets[8]:

$$u \sim \frac{eA'v^{2/3}}{\hbar kTn^{11/6}\,(T)} \sim \frac{ev^{2/3}}{\hbar\,[n\,(T^*)]^{5/6}}\left(\frac{T}{T^*}\right)^{1/10} \quad (T_c \ll T \ll T^*). \qquad (6.6)$$

The mobility (6.6) is, naturally, much larger than in solution. For example, $u \sim 1$ cgs esu at $v \sim 10^{-23}$ cm^3 and $n \sim 10^3$. It is important that u depends little on the temperature (by far not exponentially as in the case of small-radius polarons).

It must be borne in mind that formulas (6.4) and (6.6) were obtained in the approximation linear in E. Even at not too large V, the distortion of the form of the internal-parameter distribution and the change of the effective value of n lead us to expect a noticeable dependence of u on E.

We note that fluctuon mobility in paramagnets was considered also in [40]. However, the use of a different description of the spin-relaxation processes, where, in particular, no account was taken of the appreciable role of the indirect interaction, has led to somewhat different results. In [8] the author determined also the mobility of the phasons. For example, for phasons in a liquid it was determined by the Stokes formula and $u \sim e/6\pi\eta R \sim eD/kTn^{1/3}$, where η is the viscosity.

Fluctuon mobility in a liquid (or gas) is of the same order if the viscosity or density in the fluctuon region is strongly altered. We note that the fluctuon mobility should have characteristic singularities in the critical region. In particular, it should decrease abruptly when the fluctuon radius becomes smaller than the correlation radius of the critical fluctuations.

Formulas (6.4) and (6.6) determine the drift mobility of the fluctuons. If, however, we neglect the "Brownian trembling" in the fluctuon motion and assume that the charge moves uniformly with constant velocity V, then the drift mobility coincides with the Hall mobility (this is easiest to verify by changing over to a moving coordinate system in which the magnetic field vanishes and the electric field changes by an amount $(1/c)\mathbf{V} \times \mathbf{H}$), i.e., these formulas can be used also to determine the Hall mobility. The Hall constant R_H is accordingly expressed in terms of the volume concentration of the fluctuons n_f with the aid of the simple formula

$$R_H = \frac{1}{ecn_f}. \qquad (6.7)$$

Allowance for the fact that the fluctuon executes also random Brownian motion can lead to the appearance of a numerical coefficient ~ 1 in formula (6.7).

b) Fluctuon effective mass. Inasmuch as the fluctuons have no mean free path, their effective mass should drop out of the kinetic characteristics in constant external fields. When fluctuons move in rapidly-alternating fields, however, the inertial force, determined by the effective mass M, can turn out to be comparable with the dissipative force.

To determine M, we take account of the fact that the change of the TP upon production of a moving fluctuon, $\Delta\Phi(V) = \Delta\Phi(0) + (1/2)MV^2$, is a certain function of the velocity, quadratic at small values of V. In the case of solutions, $\Delta\Phi(V)$ is determined by a general formula like (2.4), as in the case of an immobile fluctuon. It is more convenient, however, to minimize it first with respect to ψ:

$$\Delta\Phi(V) = \min_{\psi,c} I[\psi, c] = \min_c I[c], \quad I[c] = E_e[c(r)] + R[c(r)]. \qquad (6.8)$$

After determining $\Delta\Phi(V)$ at small V from (6.8), we can obtain M. Just as in the case of strong-coupling polarons[1,41,42], the effective mass is much larger than the free-electron mass and is determined by the dynamics of the change of the internal parameter, which determines in this case (via formula (6.2)) the dependence of the form of the function c(r) on V.

In the case of ideal solutions at $c_0 \sim 1/2$, calculation leads to the following estimate of M [8]:

$$M \sim \frac{v^{2/3}kT}{D^2} n^{5/3} \qquad (6.9)$$

(M depends exponentially on T), and for ideal paramagnets we have

$$M \sim \frac{\hbar^2}{v^{2/3}kT^*} n^{4/3} \quad (T \sim T^*) \qquad (6.10)$$

and depends little on the temperature. For example, at $v \sim 10^{-23}$ cm^3 and $T^* \sim 300°$K we have according to (6.10) $M \sim 10^{-25}n^{4/3}$ gram, i.e., $M \gg m$ and is numerically comparable with the atom mass.

For phasons in a liquid, M can be determined from the known hydrodynamic formula for the effective mass of a sphere of radius R moving in a liquid, viz., $M = (4\pi/3)R^3(\rho_0 + (1/2)\rho)$ (ρ and ρ_0 are the densities of the first and second phases).

In the equation of motion of the fluctuons in rapidly-alternating fields, $M\dot{\mathbf{V}} + eu^{-1}\mathbf{V} = e\mathbf{E}$, the first term determines the inertial force and the second the friction force connected with the considered dissipation processes. Obviously, the inertial force becomes comparable with the friction force at frequencies

$$\omega \sim \frac{e}{Mu}, \qquad (6.11)$$

i.e., at $\omega \sim D(vn)^{-2/3}$ in solutions and $\omega \sim (kT/\hbar)n^{-1/2}$ (at $T \sim T^*$) in paramagnets. These frequencies are quite high ($\omega \sim 10^9$ sec^{-1} at $D \sim 10^{-4}$ cm^2/sec, $v \sim 10^{-23}$, and $n \sim 10^3$).

7. FLUCTUONIC STATES OF ELECTRONIC IMPURITY CENTERS AND EXCITONS

The interaction between electrons and inhomogeneities of an internal parameter or of the concentration can greatly influence not only the state of the carriers, but also the state of localized impurity-center electrons. In particular, they can go over into fluctuonic-type states in certain cases[26,43]. To investigate these effects, a calculation was performed of a model of large-radius impurity centers (analogous to some degree with the F-center model in ionic crystals [1]). The Coulomb potential energy of a defect with charge Ze

$$V_c = -\frac{Ze^2}{\epsilon r} \qquad (7.1)$$

(ϵ is the dielectric constant) was added to the potential energy (2.3) or (2.7) connected with the change of the internal parameter.

In the adiabatic approximation, the problem reduces to minimization of a functional $I[\psi]$ of the type (2.6), (2.10), to which a term $\int V_c |\psi|^2 d\mathbf{r}$ is added, or to minimization of functions I(a) of the type (3.5) and (4.4), to which a corresponding term $\sim -(Ze^2/\epsilon)(kT/Av)^{1/3}a^{1/3}$ is added ($a \sim \tilde{r}^{-3}$, where $\tilde{r}$ is the radius of the wave function). Analysis shows that the behavior of the function I(a) depends strongly on the ratio of the interaction constant to the characteristic Coulomb energy $E_c = mZ^2e^4/2\epsilon^2\hbar^2$.

If the Coulomb interaction prevails in the impurity centers and $E_c \gg A$ ($A > 10kT$, $10kT_c$), then the function I(a) has only one minimum corresponding to a hydrogenlike state. The interaction with an internal parameter leads to a change of this parameter near the center and to a temperature dependence of the electron energy and of other characteristics of the center. At appreciable values of A (at the limit of satisfaction of the criterion) these effects can be appreciable (see [26] for details). A similar picture with a single electronic state of 1s type is obtained also in the model of small-radius impurity centers, in which the electron is localized only near the atoms of the first coordination sphere [44,45].

If, however, the Coulomb energy is not very high and, e.g., in ideal solutions or paramagnets, the condition

$$E_c \ll A, \tag{7.2}$$

is satisfied, then the function I(a) can have two minima (separated by a maximum), corresponding to states of the 1s type (this is possible because the wave equation of the self-consistent problem is essentially nonlinear). The first of them is located at small $a \ll 1$ and corresponds to hydrogenlike states of large radius, slightly distorted by an internal-parameter change that is weak in this region. The second minimum, corresponding to $a \gtrsim 1$, does not appear at very high temperatures, but appears only starting with a certain temperature and then decreases with decreasing T. This minimum corresponds to states with much smaller radius, formed in the fluctuon potential well, which is produced by the strong change of the internal parameter and which is only slightly distorted by the Coulomb potential.

At a certain temperature T'^*, the depths of the minima become equal, and states of fluctuonic type become thermodynamically favored at $T < T'^*$, while the hydrogenlike state, separated by a potential barrier, can exist only as a metastable excited self-consistent state of the 1s type (at $T > T'^*$ it is the fluctuonic states that are metastable). The electrons in impurity states of the fluctuonic type can be regarded as localized fluctuons. Unlike the case of free fluctuons, the electrons do not become free when the localized fluctuons are destroyed, but remain localized at the Coulomb centers and go over into hydrogenlike states of much larger radius.

The Coulomb energy is much larger in small-radius states. Therefore the Coulomb interaction stabilizes the fluctuonic states, raising the temperature T'^* (in comparison with T^*) by an amount

$$\delta T^* \sim T^* \left(\frac{E_c}{A} \right)^{1/2}. \tag{7.3}$$

It must be borne in mind, however, that the free carriers, owing to the factor $\zeta \gg 1$ in (2.15), go over into fluctuonic states somewhat above T^*, so that at very small E_c and δT^* the transition in impurity centers can be somewhat lower than for free carriers. Just as in the case of free fluctuons, the transition occurs in a narrow temperature interval (3.17) as a smeared out phase transition. It should be accompanied by a strong change in the wave-function radius, the electron energy, the optical spectrum, the ionization probability, and other characteristics of the centers. The considered transition takes place only at small Z/ϵ, and there is no transition starting with a certain value E_c, while the properties of the centers should vary smoothly with temperature.

In ferromagnets, the function I(a) has in the spin-wave region only one minimum, and a smooth transition from the hydrogenlike to the fluctuonic state takes place with increasing temperature at small E_c. Numerically, however, the interval T'_1 in which this transition takes place may not be very broad, just as in the case of the fluctuons. This interval is particularly small if the transition temperature T'^*_1 falls in the critical region where $\delta T'_1 \sim (1/3)\tau'^*_1 T_c \ll T_c$ (inasmuch as $\tau'^*_1 \ll 1$).

At the Curie point or at the critical point itself, I(a) has also one minimum. If, however, E_c and κ are small enough, so that

$$\varkappa \ll 1, \quad E_c \ll A\varkappa^{\rho_2}, \quad \rho_2 = \frac{3}{2\delta - 3}, \tag{7.4}$$

then the electrons should go over in the critical region from fluctuonic to hydrogenlike states at certain values of $|\tau'^*|$ of the same order as τ^* (5.8).[46]

Fluctuonic states can be possessed also by excitons. In the case of Frenkel excitons or Mott excitons and a strong Coulomb interaction between the electron and hole, the exciton can be regarded as a single quasiparticle moving in the field of an altered internal parameter, and all the results presented above for fluctuonic states of electrons can be literally applied also to excitons (with suitable modification of the values of m, A, and ΔE).

On the other hand, in the case of a relatively weak Coulomb interaction between the electron and the hole, fluctuonic states of another type are produced in a Mott exciton[47]. If the effective masses of the electron and hole as well as the constants of their interaction with the internal parameter do not differ greatly, then the two particles move in the fluctuonic state in an almost uncorrelated manner in a common potential well, and there exists one temperature for the transition to this state. But if the particle masses (or the coupling constants) differ significantly, then, as the temperature is lowered (in an ideal solution or in a paramagnet), only one particle (say a hole) first goes over into the fluctuonic state at $T \approx T^*_h$, while the other remains in the hydrogenlike state. Only at lower temperatures, $T \approx T^*_e$, does the second particle go over into the fluctuonic state (of much larger radius than for the first).

8. SPONTANEOUS DISPERSION IN SYSTEMS WITH INTERNAL PARAMETERS

Localization of several electrons near one fluctuonic potential well is energywise favored, and appreciable attraction forces act between the fluctuons. Therefore the conditions for the formation of complexes containing two (bifluctuons) or several electrons may be less stringent than for the formation of isolated fluctuons [4,48]. However, the concentration c_n of complexes with n electrons is proportional to $(c_e)^n$, and at low carrier densities c_e they are in the state of isolated fluctuons or band electrons. On the other hand, when c_e increases the fraction of complexes with several electrons increases continuously.

With further increase of the concentration c of the ionized donor impurities and of the carriers, the system should break up into two phases. The reason is that, e.g., in a solution A–B, the electrons capable of producing fluctuons interact much more strongly with atoms of one type (A) than with atoms of another (B). Therefore, starting with a definite carrier density c_e, it is thermodynamically more profitable to separate from the solution a compound consisting of ions C, electrons, and atoms A (with a small admixture of atoms B). A similar decay should take place also in systems in which phasons are produced.

However, if certain conditions are satisfied at somewhat lower concentrations $c_e < \tilde{c}_e$, before a decay into two phases can occur, formation is possible of a unique equilibrium structure consisting of regions with modified composition (or internal parameter, say magnetization) and with high electron concentration [49]. The ap-

pearance of such metallic-type particles is due to long-range Coulomb forces.

The indicated disperse structure can appear if the transition of the donor ion C into the region of the modified internal parameter is energywise unprofitable (or much less profitable than the electron transition). Then, in the absence of Coulomb interaction and at a certain concentration $c_e' < \tilde{c}_e$, conditions would be thermodynamically more favored for a system decay in which the electrons would go over into the region where the concentration or an internal parameter is altered, forming a new phase, and the ion would remain in the matrix. However, the tremendous Coulomb-repulsion forces make this process impossible for a massive second phase, so that the electrons and ions can be dissolved only in pairs. On the other hand, if the sizes of the produced regions in which the parameter is modified, and consequently also the numbers of the electrons contained in them, are small, then the Coulomb energy is also small, and the "dissolution" of the electrons alone can become thermodynamically favored. The ions, on the other hand, remain in the semiconductor and form a Debye atmosphere that screens the electron charge. In a certain concentration region $c_e > \tilde{c}_e'$ the resultant disperse single-phase system can be thermodynamically more favored than either a mixture of two massive phases produced upon decay of the solution, or the usual atomic solution of the ions C and fluctuons or electrons in the system (localized large electron groups can be thermodynamically favored even if the fluctuonic states of the individual electrons are not stable). The equilibrium characteristics of the produced particles depend on the ratio of the electron-dissolution energy V, the Coulomb energy, the surface energy, and difference of the TP densities φ' in the particle and in the medium.

To investigate qualitatively the characteristics of a disperse system, let us consider the case of spherical regions with altered internal parameter, of radius R and with sharp boundary, in which the ions C are not dissolved in practice, while the electron energy $-V$ is constant. The change of the TP of the system following the formation of N^0 such regions, containing n electrons each, can be expressed in the form

$$N^0 \Delta \Phi_{n_e} = N^0 \left[-\alpha_1 n_e V + \alpha_2 \frac{\hbar^2 n_e^{5/3}}{m R^2} + \alpha_3 \frac{e^2}{\epsilon R} n_e (n_e - 1) + 4\pi\sigma R^2 + \frac{4\pi}{3} \varphi' R^3 \right]. \quad (8.1)$$

Here $\alpha_i \sim 1$, the second term determines the electron kinetic energy (with allowance for the Pauli principle), and the third term determines the Coulomb energy. Considering, for simplicity, the case when all the donor centers are ionized and the total number of electrons in the system is fixed, we can determine the equilibrium values of n and R from the condition that (8.1) be a minimum and the additional condition $N^0 n = \text{const}$. As a result, for example at small φ' and $n \gg 1$, we obtain the estimate

$$n_e \sim 10 \frac{\hbar^2}{m} \left(\frac{\epsilon}{e^2} \right)^{4/3} \sigma^{1/3}, \quad R \sim 3 \left(\frac{\hbar^2}{m} \right)^{2/3} \left(\frac{\epsilon}{e^2} \right)^{5/9} \frac{1}{\sigma^{1/9}}$$

$$\left(V > 5\alpha_4 \left(\frac{\hbar^2}{m} \right)^{1/3} \left(\frac{e^2 \sigma^2}{\epsilon} \right)^{2/9}, \quad \varphi'^{9/10} \left(\frac{\hbar^2}{m} \right)^{3/5} \left(\frac{\epsilon}{e^2} \right)^{1/2} \ll \sigma \right). \quad (8.2)$$

When the characteristics of a disperse system are calculated in detail, one can use the Thomas-Fermi approximation for an electron gas in the particles and the equation of the Debye screening theory to describe the distribution of the ions around the particles. This makes it possible to obtain the distribution of the potential at the particles and the change that occurs in the

TP when the particles are produced. The condition that the TP of the entire system be a minimum makes it possible to determine the equilibrium dimensions of the particle and their form, and to investigate the conditions under which disperse systems are stable against a transition to a homogeneous state or against a decay with separation of a massive phase.

An analysis of this type [49] shows that the transition from the homogeneous state to the disperse states is a first-order phase transition that is somewhat smeared out because of the finite particle dimensions. Systems favoring production of a stable disperse state have small φ' and σ ($\sigma \lesssim 30$ erg/cm^2) and large ϵ. The produced particles can have dimensions on the order of 10–100 Å (larger, the smaller m and the larger ϵ). It is important here that, depending on the values of the parameters, the particles can be either spherical or platelet-like. In some cases the particles can correspond not to a uniformly distributed degenerate electron gas, but to an aggregate of somewhat distorted fluctuonic (or polaronic) potential wells in which collectivized electrons are present to one degree or another.

These heterogeneous states can arise, for example, in semiconductor solutions, in magnets, in a system near a phase-transition point, or in a gas in which a certain fraction of the atoms is ionized.

It is obvious that such a disperse system containing particles of metallic type can have a number of distinctive properties. For example, at high particle concentration, when the particles are contiguous (or almost contiguous), the system can have metallic-type conductivity and interesting superconducting properties.

In metal-ammonia solutions are concentrations 0.1–0.3 molar per cent of metal, it is indicated by a number of experimental data that clusters are produced, containing $\sim 10^2$ polarons [50]. It is possible that these are examples of the considered dispersed particles.

In some experimental situations, total equilibrium is not reached and therefore the particle charge is fixed and does not agree with the equilibrium value as in the presented approach. This case was considered in [51]. "Metallic" drops can be produced also in single-component strongly-doped semiconductors as a result of fluctuations of ionized impurities [52]. Unlike the considered systems with internal parameters, in this case the drops likewise constitute nonequilibrium formations.

9. INFLUENCE OF FLUCTUONS ON THE PROPERTIES OF SEMICONDUCTORS

a) Equilibrium fluctuon concentration, electric conductivity, and thermoelectric power. The equilibrium fluctuon concentration in an impurity semiconductor can be determined from the condition of equilibrium of a system of N_f fluctuons (with TP (2.14)), a system of N_e band electrons, and a system of N' electrons distributed over N_i impurity centers. An elementary calculation [11] shows that in a compensated semiconductor ($N_i \gg N' + N_f + N_e$) we have

$$\frac{N_f}{N} = \frac{\alpha}{\alpha'} \frac{N'}{N_i} \exp\left(\frac{\Delta\Phi' - \Delta\Phi}{kT} \right) \quad (9.1)$$

and in a fully non-compensated semiconductor ($N_i = N' + N_f + N_e$) at $N_f \gg N_e$ we have

$$\frac{N_f}{N} = \frac{\alpha}{\alpha'} \frac{N'}{N} \exp\left(\frac{\Delta\Phi' - \Delta\Phi}{2kT} \right); \quad (9.2)$$

here $\Delta\Phi - kT \ln \alpha'$ is the change of the TP when the band electrons go from the bottom of the band to a localized impurity-center state (α', as in (2.14), takes into account the fluctuation effects).

Formulas (9.1) and (9.2) are analogous to the usual formulas for the carrier density in the semiconductor. Now, however, the quantity $\Delta\Phi' - \Delta\Phi$ depends strongly on the temperature. Therefore the fluctuon concentration, generally speaking, has a non-exponential dependence on $1/T$ (especially near the temperatures T^* and T_c). In principle, even an anomalous growth of N_f with decreasing temperature is possible. Since the fluctuons and band electrons exist simultaneously, the electric conductivity ρ^{-1} of the semiconductors of the type considered is a sum of the electronic and fluctuonic electric conductivities

$$\rho^{-1} = \rho_e^{-1} + \rho_f^{-1} = e n_e u_e + e n_f u_f; \qquad (9.3)$$

here n_e and n_f are the volume concentrations of the band electrons and the fluctuons, while u_e and u_f are their mobilities ($e > 0$). From the results of Chap. 6 it follows that $u_f \equiv u \ll u_e$.

Self-localized states of the fluctuonic type were recently discussed also for the case of electrons in high-density gases [64]. The transition to these states at a definite temperature or density is quite abrupt (see Chap. 3) and lowers the carrier mobility by several orders of magnitude. This has made it possible to explain the experimentally observed [65] sharp decrease of the electron mobility in He and H_2 gases when the densities are increased above certain characteristic values.

In compensated semiconductors, as follows from (9.1) and (3.15), the formation of fluctuons at $T < T^*$ does not influence the concentration of the band electrons, which is determined by the same factor $\exp(\Delta\Phi'/kT)$ as above T^*. In this case the onset of fluctuons does not change the temperature dependence of ρ (so long as $\rho_f^{-1} \ll \rho_e^{-1}$) nor does it increase ρ^{-1}. On the other hand, according to (9.2) and (2.15), in the case of uncompensated (or intrinsic) semiconductors, an extra factor $\exp(\Delta\Phi/2kT) < 1$ appears in the formulas for $n_e \sim N_e$ when fluctuons are produced, and this factor decreases ρ_e^{-1} if $T < T^*$. Therefore if the increase of the number of carriers following fluctuon formation does not compensate for the decrease of their mobility (in comparison with the electrons), fluctuon production is accompanied in this case by a lowering of the conductivity.

Fluctuonic effects should also influence strongly the hopping conductivity in the impurity band. The change of an internal parameter in the region of impurity-electron localization, as demonstrated with magnetic semiconductors as an example [44], leads to an increase of the potential barrier to the electron hopping between neighboring centers, and to a temperature dependence of the height of the barrier. If a transition to fluctuonic states of the type considered in Chap. 7 is possible in impurity centers, then the strong contraction of the electron wave function and the appreciable lowering of the electron energy should lead to an abrupt decrease of the hopping probability and to an increase of the corresponding activation energy. As a result, as noted in [11,43], the impurity conductivity (which has a metallic character at $T < T_1'^*$ and $T > T'^*$ if the activation energy is low) may turn out to be completely suppressed. This can lead in experiment to a strong decrease (by several orders of magnitude) of the conductivity in the tempera-

ture interval $\delta T'$ when the temperature is increased above $T_1'^*$.[4] Such an effect is sometimes observed in experiment, but so long as there are no detailed data on the character of the states of the impurity electrons in particular semiconductors it is difficult to say whether this effect is due to a transition, of the type considered in [44], to a fluctuonic state, with a temperature-dependent activation energy, or to other causes. In the region of the Curie point, the section near the center, in which the magnetization is altered, becomes broader at a given wave function. This can lead to a lowering of the potential barrier and to the inverse effect—an increase of the impurity conductivity [57].

As shown with fluctuons in paramagnets as an example, the formation of fluctuons should greatly alter the absolute thermoelectric power Q of the semiconductors. If the fluctuons are the only carriers, then we can obtain for Q the expression

$$Q = -\left[(\Delta\Phi - \xi_e)\frac{1}{T} - \frac{\partial\Delta\Phi}{\partial T}\right]\frac{1}{e}, \qquad (9.4)$$

where ξ_e is the chemical potential of the electrons. The contribution of the spin entropy $-\partial\Delta\Phi/\partial T$ ($\sim nk$ at $T \sim T^*$) to Q is large and depends strongly on the temperature.

b) Effect of fluctuons on phase transitions. Fluctuons and phasons, forming a region of modified composition or order, can be regarded in a certain sense as nuclei of a second phase. Therefore if the electrons are in a fluctuonic state, they should have a very strong effect on the kinetics of a first-order phase transition. The increase of the transition rate should be particularly large if the fluctuon dimension exceeds the dimensions of the critical nuclei.

At noticeable fluctuon concentrations $c_f = N_f/N$ the fluctuons can lead also to an appreciable shift of the phase-equilibrium curves. For example, in the case of decaying solutions far from the critical point, the shift of the decay temperature T_p and the change of the concentration δc_p of the atoms A in the precipitating phase are estimated at [11]

$$\delta T_p \sim T_p n |c_f' - c_f''|, \qquad |\delta c_p| \sim n |c_f' - c_f''|, \qquad (9.5)$$

where c_f' and c_f'' are the fluctuon concentrations in the first and second phase ($c_f' \gg c_f''$ or $c_f' \ll c_f''$, depending on the sign of A). The macroscopic character of the fluctuon (the large n) leads to an appreciable shift of the lines on the phase diagram. At $T_p \sim T^*$, smeared-out kinks should be observed on these lines. An estimate similar to (9.5) holds also for the shift of a first-order transition curve in single-component systems when phasons are produced.

Fluctuons can affect strongly the phase equilibrium curves in the critical region. This question, however, is not clear enough and will not be discussed here (the results obtained in [11], which pertain to the critical region and to the vicinity of the Curie point of a ferromagnet, are plainly preliminary and doubtful in a number of respects).

Fluctuonic effects can play a definite role when it comes to explaining the properties of metals near the gas—liquid critical point. When the density is varied it is possible to have in this case a transition from the metallic into a nonmetallic state [58-60]. It was suggested that electrons in the plasma region are in states of the

fluctuonic type [18]. We note that near the critical point itself these states should be described by the formulas of Chap. 5 (if $\kappa < 1$). If, indeed, the principal role is played here in the conductivity by the fluctuons, then this explains the decrease of the conductivity with increasing T in the critical region, which was observed in [59] (the move away from the critical point increases $\Delta\Phi$ and decreases the fluctuon concentration). We note also that in this region, at definite densities and concentrations of the carriers, the formation of "metallic drops" of the type considered in Chap. 8, which strongly affect the conductivity of the system, becomes possible. Naturally, other factors influencing the behavior of these systems are also possible, in particular the Mott transition[14,61], the lowering of the ionization energy as a result of electron interaction with neutral atoms[62], etc.

c) Effect of fluctuons on the magnetic properties of semiconductors. The anomalously large magnetic moment M_f of the fluctuon should lead to a strong change $\delta\chi$ of the magnetic susceptibility of paramagnets and of the paramagnetic Curie point when fluctuons are introduced into a crystal. At $\kappa \gg 1$ we have, according to (3.26),

$$\delta\chi = \frac{n_f M_f^2}{3kT} \sim \frac{\mu^2}{vkT}\, c_f n^2 \sim \chi c_f n^2, \qquad (9.6)$$

i.e., $\delta\chi$ is larger by $\sim n^2$ times then when ordinary atomic impurities are added. The susceptibility $\delta\chi$ in relatively weak fields should depend strongly on the external field H when $M_f H \sim kT$, and also when H is comparable with the magnetic-anisotropy field (which orients the fluctuons). In the latter case, a strong angular dependence of $\delta\chi$ may be observed.

At $\kappa \ll 1$ and at a certain distance from the Curie point we obtain, taking (5.11) into account,

$$\delta\chi \sim \frac{\mu^2}{vkT}\left(\frac{\Delta E}{A}\right)^3 x^{-3\lambda/2} c_f. \qquad (9.7)$$

Near the Curie point itself, when the nonlocality is significant, relation (9.7) becomes invalid. In the ferromagnetic region, the magnetic moments of the fluctuons are oriented mainly parallel to the magnetization M_0 and can lead to a noticeable increase of M_0 and to a certain change of the temperature dependence of the magnetization. At low temperatures we have

$$\delta M_0 \sim c_f n(M^0 - M_0). \qquad (9.8)$$

The band electrons also produce a certain average effective field $c_e' A/\mu\,(c_e' = N_e/N)$ that changes the magnetization by an amount $\delta M_0' \sim \chi c_e' A/\mu$. If the transition into the fluctuonic states in the ferromagnet occurs in a narrow temperature interval, then at $T \approx T_1^*$ one should expect a relatively abrupt change of the magnetization by an amount $\delta M_0 - \delta M_0'$.

We note that effects of the same type, particularly near the Curie point, may be produced by large-radius impurity electronic states.

d) Interaction of fluctuons with electromagnetic radiation. In a fluctuonic potential well there can exist not only the ground (1s) state, but also excited states, e.g., 2p. Infrared light can produce phototransitions between these states, leading to the appearance of new bands in the absorption spectrum. The most intense band corresponds to the transition 1s–2p. Its maximum occurs at a frequency $\hbar\omega_{1\to2} \sim (0.1-0.3)A$. Since a definite state of the fluctuon corresponds to different distributions of the atoms or spins, this band should be broad. Estimating the width $\delta_{1\to2}$ by means of the formulas obtained

for large-radius impurity centers [24] we find that in ideal paramagnets (with $S \sim 1$) or solutions we have

$$\delta_{1\to2} \sim \frac{1}{\sqrt{n}}\,\omega_{1\to2} \quad \text{at} \quad T \sim T^*. \qquad (9.9)$$

A broad band, due to the transition of an electron to the conduction band, should also appear in the spectrum. If the time of the hopping of the electron from the band state to the fluctuonic state is long enough, then such a transition leads to a sharp increase of the photoconductivity.

Inasmuch as the fluctuons form a region of modified composition or of modified order, with a relatively large radius, they should lead to a noticeable small-angle scattering of light, x-rays, or neutrons in the vicinities of the reciprocal-lattice points [63]. For example, in the case of magnetic scattering of neutrons by fluctuons in magnets, a region of increased intensity, with dimension $\sim (nv)^{-1/3}$, is produced near each reciprocal-lattice point. At small angles, the angular width of such a region, for scattering of x-rays of neutrons in solutions, is of the order of $\lambda(nv)^{-1/3}$. In these regions (and at arbitrary angles in the case of light scattering), the scattering cross section is proportional to $c_f n^2$, and if $c_f \sim 10^{-4}$ and $n \sim 10^2-10^3$ it can greatly exceed the background scattering in the absence of fluctuons.

Fluctuons should cause, analogously, intense scattering of long-wave phonons and of spin waves, and can therefore greatly influence the background thermal conductivity and the ferromagnetic-resonance line width.

---

[1] This expression for the change of the TP is valid in the adiabatic approximation if the electron-induced change of the interatomic interaction in the solution can be neglected. It will be shown below (see p. 862) that this is justified in a certain approximation.

[2] At sufficiently small $c_0 \approx b \ll 1$ and at $A \sim \Delta E$, as seen from (3.13) and (3.17), we have $n(T^*) \sim 3b^{-3/2} \gg 1$ and $\delta T \sim b^{3/2} T^* \ll T^*$, i.e., the transition to the fluctuonic states is abrupt. These estimates remain in force also when $A \gg \Delta E$.

[3] Taking into account the described significant differences between the characteristics of polarons in ideal ionic crystals and of electronic auto-localized states in partially-ordered systems (where the usual electric polarization, strictly speaking, may not exist at all), it seems more expedient to use for the latter states the special name "fluctuons."

[4] Arguments concerning the suppression of impurity conductivity when electrons of shallow impurity centers go over into states of the fluctuonic type were advanced also in [53], where the experimentally observed [54] increase of the conductivity (by more than 13 orders of magnitude) in EuO with excess Eu somewhat below the Curie point was explained from this point of view.

In [55] they considered strongly doped ferromagnetic semiconductors under conditions when the principal role is played by collective effects with a carrier density close to the limiting concentration at which a Mott type metal-dielectric transition takes place. The interaction of the electrons with the magnetization at increased temperature favors the production of an inhomogeneous electron distribution and causes a Mott transition at a definite temperature. The case when an essential role is played by collective effects was discussed also in [56] (with the aid of the linear theory).

We note that the abrupt change of conductivity, observed in [11,43,53] in a transition of impurity electrons into fluctuonic states, is not necessarily connected with a Mott transition. It can take place, in particular, in compensated semiconductors, where there is no Mott transition. In fully uncompensated semiconductors the transition of the impurity electrons into fluctuonic states may be accompanied by a Mott transition. If, however, as is frequently the case, the Fermi energy of the electrons in the impurity band and the Coulomb energy of the electrons of shallow impurity centers E_C are small in comparison with A, then the collective effects can be neglected and one can consider the problem

with one electron in an impurity center. The Mott transition is then a secondary effect due to the fact that the radius of the impurity electron on going to the fluctuonic state decreases abruptly and becomes smaller than the screening radius (i.e., the well known Mott criterion is satisfied for the dielectric phase).

[1] S. I. Pekar, Zh. Eksp. Teor. Fiz. 16, 341 (1946); Issledovaniya po elektronnoi teorii kristallov (Studies in the Electronic Theory of Crystals), Gostekhizdat, 1951.

[2] Polarons and Excitons, Ed. C. G. Kuper and G. D. Whitefield, Oliver & Boyd, 1963; J. Appl. Sol. State Phys. 21, 193 (1968).

[3] I. B. Austin and N. F. Mott, Adv. Phys. 18, 41 (1969); M. I. Klinger, Rept. Progr. Phys. 31 (pt. 1), 225 (1968).

[4] M. A. Krivoglaz, Fiz. Tverd. Tela 11, 2230 (1969) [Sov. Phys.-Solid State 11, 1802 (1970)].

[5] M. A. Krivoglaz and A. Trushchenko, ibid. 11, 3119 (1969) [11, 2531 (1970)].

[6] I. M. Lifshitz and S. A. Gredeskul, Zh. Eksp. Teor. Fiz. 57, 2209 (1969) [Sov. Phys.-JETP 30, 1197(1970)].

[7] A. M. Dykhne and M. A. Krivoglaz, Fiz. Tverd. Tela 12, 1705 (1970) [Sov. Phys.-Solid State 12, 1349 (1970)].

[8] M. A. Krivoglaz, ibid. 12, 3496 (1970) [12, 2840 (1970)].

[9] T. Kasuya, A. Yanase, and T. Takeda, Solid State Comm. 8, 1543 (1970).

[10] M. A. Krivoglaz, Fiz. Tverd. Tela 15, 1141 (1973) [Sov. Phys.-Solid State 15, 773 (1973)].

[11] M. A. Krivoglaz, ibid. 14, 2092 (1972) [14, 1801 (1973)].

[12] M. A. Krivoglaz and V. S. Lechtsier, Ukr. Fiz. Zh. 18, 463 (1973).

[13] I. M. Lifshitz, Usp. Fiz. Nauk 83, 617 (1964) [Sov. Phys.-Usp. 7, 549 (1965)].

[14] N. F. Mott, Adv. Phys. 16, 39 (1967).

[15] L. D. Landau and E. M. Lifshitz, Statisticheskaya Fizika (Statistical Physics), Nauka, 1964 [Pergamon, 1971].

[16] S. V. Vonsovskiy, Zh. Eksp. Teor. Fiz. 16, 981 (1946); Magnetizm (Magnetism) Nauka, 1971; S. V. Vonsovskii and E. A. Turov, Zh. Eksp. Teor. Fiz. 24, 419 (1953).

[17] M. F. Deĭgen and S. I. Pekar, Zh. Eksp. Teor. Fiz. 21, 803 (1951); Y. Toyozawa, Progr. Theor. Phys. 26, 29 (1961).

[18] A. G. Khrapak and I. T. Yakubov, Zh. Eksp. Teor. Fiz. 59, 945 (1970) [Sov. Phys.-JETP 32, 514 (1971)].

[19] I. M. Lifshitz, ibid. 53, 743 (1967) [26, 462 (1968)].

[20] B. I. Halperin and M. Lax, Phys. Rev. 148, 722 (1966).

[21] J. Zittartz and J. S. Langer, Phys. Rev. 148, 741 (1966).

[22] I. Ya. Korenblit and Yu. P. Lazarenko, Fiz. Tverd. Tela 12, 2624 (1970) [Sov. Phys.-Solid State 12, 2110 (1971)].

[23] M. A. Krivoglaz and S. I. Pekar, Izv. Akad. Nauk SSSR, Ser. Fiz. 21, 16 (1957).

[24] M. A. Krivoglaz and G. F. Levenson, Fiz. Tverd. Tela 12, 362 (1970) [Sov. Phys.-Solid State 12, 293 (1970)].

[25] S. von Molnar and S. Methfessel, J. Appl. Phys. 38, 959 (1967).

[26] M. A. Krivoglaz and A. A. Trushchenko, Ukr. Fiz. Zh. 15, 1940 (1970).

[27] a) A. Yanase, Int. J. Magn. 2, 99 (1972); b) J. Kübler, Zs. Phys. 250, 324 (1972).

[28] É. L. Nagaev, Zh. Eksp. Teor. Fiz. 56, 1013 (1969) [Sov. Phys.-JETP 29, 545 (1969)]; Yu. A. Izyumov and M. V. Medvedev, ibid. 59, 553 (1970) [32, 302 (1970)]; S. Klama and M. I. Klinger, Acta Phys. Polon. A40, 619 (1971).

[29] M. A. Krivoglaz, ZhETF Pis. Red. 17, 262 (1967) [JETP Lett. 17, 188 (1967)]; Fiz. Tverd. Tela 15, 1765 (1973) [Sov. Phys.-Solid State 15, 1180 (1973)].

[30] T. Wolfram and J. Callaway, Phys. Rev. 127, 1605 (1962).

[31] M. A. Krivoglaz, Usp. Fiz. Nauk 106, 360 (1972).

[32] P. G. DeGennes, Phys. Rev. 118, 141 (1960).

[33] E. L. Nagaev, ZhETF Pis. Red. 6, 484 (1967) [JETP Lett. 6, 18 (1967)]; Zh. Eksp. Teor. Fiz. 54, 228 (1968) [Sov. Phys.-JETP 27, 122 (1968)].

[34] J. I. Frenkel, Kinetic Theory of Liquids, Dover, 1954.

[35] R. A. Ferell, Phys. Rev. 108, 167 (1957); C. G. Kuper, ibid. 122, 1007 (1961); J. Jortner et al., J. Chem. Phys. 43, 2614 (1965); E. P. Gross and H. Tung-Li, Phys. Rev. 170, 190 (1968); G. Baym et al., Phys. Rev. Lett. 22, 20 (1969).

[36] K. R. Atkins, Phys. Rev. 116, 1339 (1959).

[37] L. P. Kadanoff et al., Rev. Modern Phys. 39, 395 (1967); V. L. Pokrovskiĭ, Usp. Fiz. Nauk 94, 127 (1968) [Sov. Phys.-Usp. 11, 66 (1968)].

[38] V. G. Vaks, A. I. Larkin, and S. A. Pikin, Zh. Eksp. Teor. Fiz. 51, 361 (1966) [Sov. Phys.-JETP 24, 240 (1967)].

[39] L. D. Landau and E. M. Lifshitz, Mekhanika sploshnykh sred, Gostekhizdat, 1953 [Fluid Mechanics, Addison-Wesley, 1959].

[40] T. Kasuya, A. Yanase, and T. Takeda, Solid State Comm. 8, 1551 (1970).

[41] L. D. Landau and S. I. Pekar, Zh. Eksp. Teor. Fiz. 18, 419 (1948).

[42] N. N. Bogolyubov, Ukr. Matem. Zhurn. 2, 3 (1950); R. P. Feynman, Phys. Rev. 97, 660 (1955).

[43] T. Kasuya, Proc. 10th Internat. Conf. on the Physics of Semiconductors, Cambridge, Mass., 1970, p. 243.

[44] A. Yanase and T. Kasuya, J. Phys. Soc. Japan 25, 1025 (1968); Rev. Modern Phys. 40, 684 (1968).

[45] É. L. Nagaev, Fiz. Tverd. Tela 11, 3438 (1969) [Solid State Phys. 11, 2886 (1970)].

[46] M. A. Krivoglaz and A. A. Trushchenko, Ukr. Fiz. Zh. 15, 1956 (1970).

[47] M. A. Krivoglaz and A. A. Trushchenko, ibid. 16, 833 (1971).

[48] A. A. Trushchenko, ibid. 17, 2016 (1972).

[49] M. A. Krivoglaz, Zh. Eksp. Teor. Fiz. 63, 670 (1972) [Sov. Phys.-JETP 36, 354 (1973)].

[50] M. H. Cohen and J. C. Thompson, Adv. Phys. 17, 857 (1968).

[51] Ya. E. Geguzin, Yu. S. Kagonovskiĭ, V. V. Kalinin, and V. V. Slezov, Fiz. Tverd. Tela 12, 1953 (1970) [Sov. Phys.-Solid State 12, 1553 (1971)].

[52] B. I. Shklovskiĭ and A. L. Éfros, Zh. Eksp. Teor. Fiz. 61, 816 (1971) [Sov. Phys.-JETP 34, 435 (1972)].

[53] J. B. Torrance et al., Phys. Rev. Lett. 29, 1168 (1972).

[54] M. R. Oliver, J. A. Kafalas, J. O. Dimmock, T. B. Reed, ibid. 24, 1064 (1970); S. von Molnar, IBM J. Res. Develop. 14, 269 (1970); G. Petrich et al., Phys. Rev. Lett. 26, 855 (1971); T. Penney et al., Phys. Rev. B5, 3669 (1972).

[55] E. L. Nagaev, A. P. Grigin, Phys. Lett. A38, 469 (1972).

[56] P. Leroux-Hugon, Phys. Rev. Lett. 29, 939 (1972).

[57] A. Yanase, Solid State Comm. 9, 2111 (1971).

[58] I. K. Kikoin et al., Zh. Eksp. Teor. Fiz. 49, 129 (1965) [sic!]

[59] F. Hensel and E. U. Franck, Rev. Modern Phys. 40, 697 (1968).

[60] V. A. Alekseev et al., Usp. Fiz. Nauk 106, 393 (1972) [Sov. Phys.-Usp. 15, 139 (1972)].

[61] N. F. Mott, Proc. Phys. Soc. A62, 416 (1949); Phil. Mod. 6, 287 (1961).

[62]V. A. Alekseev and A. A. Vedenov, Usp. Fiz. Nauk **102**, 665 (1970) [Sov. Phys.-Usp. **13**, 830 (1971)].

[63]M. A. Krivoglaz, Ukr. Fiz. Zh. **17**, 1390 (1972).

[64]T. P. Eggarter, M. H. Cohen, Phys. Rev. Lett. **25**, 807 (1970); T. P. Eggarter, Phys. Rev. A5, 2496 (1972); L. S. Kukushkin and V. B. Shikin, Zh. Eksp. Teor. Fiz. **63**, 1830 (1972) [Sov. Phys.-JETP **36**, 969 (1973)];

J. P. Hernandes, Phys. Rev. A7, 1755 (1973).

[65]J. L. Levine, T. S. Sanders, ibid. **A154**, 138 (1967); H. R. Harrison, B. E. Springett, Phys. Lett. **35**, 73 (1971); Chem. Phys. Lett. **10**, 418 (1971).

Translated by J. G. Adashko