

90 YEARS



STATES OF ELECTRONS NEAR THE PHASE TRANSITION POINT AND IN DISORDERED SYSTEMS

Translated and reprinted from Fiz. Tv. Tela **11**, No. 8 2230–2240 (1969)

M.A. KRIVOGLAZ

Institute of Metal Physics, National Academy of Sciences of the Ukrainian SSR
(Kyiv, Ukraine)

We consider a possibility of the localization of an electron near a region of the second phase which is non-equilibrium at the given temperature. We study the conditions for such stationary formations, *phasons*, that are thermodynamically favorable and take place in systems where first-order phase transitions are possible, to appear. Characteristics of macroscopic phasons in cases of the non-pyroelectric, pyroelectric, and metal second phases are determined. The possibility of the appearance of regions of the second phase with several localized electrons is considered. It is noted that the formation of phasons must lead to a sharp modification of electronic and some other parameters of the substance. The formations of a more general type, in which an electron is localized near the area with a variable internal parameter, are also considered. Such areas are unstable fluctuations if an electron is absent, but are stabilized due to the electron energy. The appearance of such stable macroscopic formations, *fluctuons*, is studied for the cases of disordered solutions and ideal paramagnetic materials with spin $S=1/2$. The existence of fluctuons (or phasons) with large radius becomes possible owing to a non-linear dependence of the thermodynamic potential on the corresponding internal parameter at reasonably large values of the ratio between the binding energy and kT . The radius of a fluctuon and its energy parameters are determined.

Under certain conditions, a conduction electron in a non-metallic substance can be localized near a small region of phase II (which is non-equilibrium at the given temperature) located within equilibrium phase I. Near the point of a first-order phase transition, the densities of the thermodynamic potential of both phases are close, so that, in the case of the relatively low interphase surface energy, a decrease of the electron energy due to its localization can compensate an increase of the volume and surface thermodynamic potentials, and the formation of a region of phase II with the electron localized near it will be thermodynamically favorable. As a result, the majority of electrons near the point of the phase transition can transfer to such self-consistent states. In some cases (at the low heat of the transition), the density differences of phases are small even at a large distance from the transition point, and stable localized electronic states can exist in a rather wide temperature range.

In an external electric field, a force inducing the translational motion of the whole formation acts on the electron localized near the region of phase II. However, the mechanism of its mobility is essentially determined by the kinetics of phase transitions. So that, depending on the specific type of a phase transition, the mobility can vary within very wide limits corresponding either to practically fixed localized formations (having only very low diffusive mobility), or to relatively fast moving quasiparticles with a significant free path length.

Such translating or slowly moving equilibrium formations, namely, electrons localized at a region of phase II and supporting the equilibrium of this region, can be naturally named as *phasons*. In some sense, they are similar to polarons [1], but differ from them in that the inertial lattice distortion in phasons is related not to harmonic displacements of ions, but to the essential reorganization of a configuration of atoms (a modification of the order) in some region of the crystal. To some extent, the phasons are similar also to electrons localized within bubbles in liquid helium [2]; however, in some ways, the former are essentially different from the latter (the role of the volume free energy, essential polarization effects in the case of pyroelectric phase II, strong temperature dependence of properties, *etc.*). The formation of phasons is related to a gain in the thermodynamic potential of the system (not just the energy, as in the case of polarons). As will be shown below, the equilibrium radius of phasons can exceed noticeably the interatomic spacing, and their qualitative consideration can invoke a macroscopic approach, with a certain error.

Phasons represent only a special case of formations of a rather general type, in which an electron is localized at some region with changed values of internal parameters, for example, at a region with disturbed order, composition, or magnetization, and the field of the electron supports the stationarity of this fluctuation of the internal parameter. It is natural to name such formations as *fluctuons*. Under certain conditions, they

can appear, in particular, in disordered non-metallic systems where second-order phase transitions occur (including those in ferromagnetics or in paramagnetic materials, where they are related to a local modification of long-range order parameters) and in disordered solutions with sufficient diffusive mobility of atoms (where they are related to a local modification of the composition). As in the case of phasons, the formation of fluctuons is due to a decrease of the thermodynamic potential of the system. It is obvious that the notions of fluctuons or phasons make sense only if their radii exceed noticeably the lattice constant. Usually, this requires the essentially non-linear dependence of a change of the free energy on a change of the corresponding internal parameter.

The phason states of electrons will be considered below in Section 1, and an example of the fluctuon states will be given in Section 2 (see also [3]). The purpose of the present work is to establish the general conditions for phasons or fluctuons to appear and to determine their basic characteristics. In this connection, the study will be carried out by using the most simplified models, and some conclusions will have character of semiquantitative estimates. We consider only the general characteristics of phasons that are not dependent on the type of a specific phase transition. Their specific properties determined by the character of a given transformation, for example, the mobility or the effective mass of phasons, need a special study in each specific case and will not be considered here.

1. State of Electrons in Systems, Where Phase Transitions are Possible

To investigate the conditions for the formation of phasons, let us first consider the case where both phases, I and II, are non-metallic and non-pyroelectric. Then we will separately consider the cases of the formation of the metallic or pyroelectric phase. Neglecting the elastic distortions (volume change at the transformation) and the anisotropy of the interphase surface energy σ , we assume the equilibrium shape of the phase-II region to be spherical.

Let us determine the energy of the system in the adiabatic approximation, considering the energy $E(R)$ of an electron localized near a spherical particle of the second phase with radius R as a term in the potential energy of the system. If the widths of the conduction bands in both phases are large enough (in comparison with $E(R)$), the energy of the electron can be determined by using the effective mass method. To

avoid complications due to boundary conditions for the wave function at the interface, we restrict ourselves to the case where differences of the effective masses of the electron in both phases from the free electron mass m , as well as differences of the smoothed wave functions from the detailed ones, can be neglected. For simplicity, let us suppose that the inertial polarizabilities of both phases are small, and their inertialess polarizabilities are identical. Then we can neglect the energy of the electrostatic interaction of the electron with the interface (an estimate of the contribution of this energy will be given below) and assume that the interaction of the electron with a particle of phase II is only due to the fact that the bottom of the conduction band of phase II lies below the bottom of the conduction band of phase I by V .

Let the energy of the electron and the thermodynamic potential be reckoned, respectively, from the bottom of the conduction band of phase I and from the value corresponding to the first phase containing no electrons. Then, by determining the energy of the ground state of an electron in a spherical potential well, $E(R)$, in a usual way, we can write the thermodynamic potential $\Delta\Phi$ of phase I containing a fixed region of phase II, at which one electron is localized (without regard for the possibility of a displacement of this formation), as

$$\Delta\Phi(R) = \frac{4\pi}{3} R^3 \varphi + 4\pi R^2 \sigma + E(R);$$

$$E(R) = -V + \frac{\hbar^2 k^2}{2m}. \quad (1)$$

Here, φ is the difference of the densities of the thermodynamic potentials of both phases (if the elastic energy is taken into account, the corresponding term should be added to φ), and k is determined by the equation

$$k \operatorname{ctg} kR = -\sqrt{\frac{2mV}{\hbar^2} - k^2}. \quad (2)$$

If the possibility of a displacement of phasons is taken into account, the expressions for the thermodynamic potential will vary depending on whether they are quasiparticles moving rectilinearly with effective mass M or localized formations displacing due to a mechanism of the diffusion type. In the first case, with regard for the contribution due to a translation motion in the nondegenerate gas, it is easy to obtain an expression for

the thermodynamic potential of N_{ph} phasons,

$$\Phi = N_{\text{ph}}\Delta\Phi(R) - N_{\text{ph}}kT \ln \left[e \frac{N}{N_{\text{ph}}} v \left(\frac{MkT}{2\pi\hbar^2} \right)^{3/2} \right], \quad (3)$$

where v is the volume of a lattice cell of the first phase, and N is the number of cells. In the second case, considering the configuration contribution to Φ due to a permutation of N_{ph} phasons over N cells, we obtain

$$\Phi = N_{\text{ph}}\Delta\Phi(R) - N_{\text{ph}}kT \ln \left(e \frac{N}{N_{\text{ph}}} \right). \quad (4)$$

Taking into consideration that, for a system of N_e electrons in the conduction band of phase I in the absence of degeneration,

$$\Phi = -N_e kT \ln \left[e \frac{N}{N_e} v \left(\frac{mkT}{2\pi\hbar^2} \right)^{3/2} \right]$$

and that, in the equilibrium, the total thermodynamic potential should remain constant at the transition of one electron from the conduction band to a localized state, we can find the ratio of the equilibrium concentrations of phasons and electrons

$$\frac{N_{\text{ph}}}{N_e} = \zeta \exp \left(-\frac{\Delta\Phi}{kT} \right). \quad (5)$$

Here, $\zeta = (M/m)^{3/2}$ if the appearing formations are quasiparticles and $\zeta = \left(\frac{2\pi\hbar^2}{v^{2/3}mkT} \right)^{3/2}$ if they are localized.

If we neglect the dependence of ζ on R , the most probable radius $R = R_0$ is determined from the requirement that $\Delta\Phi$ take the minimal value. We should also take into account that $E(R)$ should be negative for the phason state to appear, i.e., as seen from (1), the radius R should exceed $R_{\text{min}} = \left(\frac{\pi^2\hbar^2}{8mV} \right)^{1/2}$ [$kR = \pi/2$ at $E(R) = 0$]. If the condition

$$\frac{\partial\Delta\Phi}{\partial R} = 4\pi R^2\varphi + 8\pi R\sigma - \frac{\hbar^2}{mR^3} \frac{(kR)^3}{kR - \text{tg } kR} = 0 \quad (6)$$

is not satisfied for any values of $R > R_{\text{min}}$ [here, the derivative $\partial(kR)/\partial R$ is determined by Eq. (2)], then $\Delta\Phi$ takes the minimal value

$$\Delta\Phi_{\text{min}} = \frac{4\pi}{3} R_{\text{min}}^3 \varphi + 4\pi R_{\text{min}}^2 \sigma = \frac{\pi^3 \hbar^2}{2mV} \left(\sigma + \frac{\pi \hbar \varphi}{6\sqrt{2mV}} \right) \quad (7)$$

at $R = R_{\text{min}}$. If condition (6) is satisfied at some $R = R_0 > R_{\text{min}}$, this value of R_0 will determine the equilibrium radius of a phason, and the minimal value of $\Delta\Phi$ will be equal to $\Delta\Phi(R_0)$. For specified values of σ , φ , and V , it is easy to find R_0 (and $\Delta\Phi(R_0)$) by solving Eqs. (6) and (2) simultaneously.

Thus, as V increases at given σ and φ , the radius R_0 and $\Delta\Phi(R_0)$ decrease. First, they coincide with R_{min} and $\Delta\Phi(R_{\text{min}})$, respectively, and then they are determined by formulae (6), (2), and (1). At some value $V = V^0$, $\Delta\Phi(R_0)$ vanishes, so it becomes negative at larger V . By determining V^0 and the corresponding radius of a phason $R_0 = R^0$ from the conditions $\Delta\Phi(R_0) = 0$ and $\partial\Delta\Phi/\partial R = 0$ (with regard for Eq. (2)), it is easy to find that, near the transition point (as $\varphi \rightarrow 0$) and at large distances from this point (at small σ), these quantities are determined by the formulae

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

$$V^0 = 5.81 \left(\frac{\hbar^2}{m\varphi} \right)^{3/5}; \quad R^0 = 0.73 \left(\frac{\hbar^2}{m\varphi} \right)^{1/5}$$

$$(\text{at } \varphi R^0 \gg \sigma). \quad (8)$$

With a further increase of V , R_0 continues to decrease, and $|\Delta\Phi(R_0)|$ continues to increase, by tending to their limiting values R_∞ and $\Delta\Phi_\infty$ as $V \rightarrow \infty$:

$$R_\infty = \left(\frac{\pi\hbar^2}{8m\sigma} \right)^{1/4}; \quad \Delta\Phi_\infty = -V + (2\pi)^{3/2} \hbar \sqrt{\frac{\sigma}{m}}$$

$$(\text{at } \varphi R_\infty \ll \sigma);$$

$$R_\infty = \left(\frac{\pi\hbar^2}{4m\varphi} \right)^{1/5}; \quad \Delta\Phi_\infty = -V + \frac{10\pi}{3} \left(\frac{\pi\hbar^2\varphi^{2/3}}{4m} \right)^{3/5}$$

$$(\text{at } \varphi R_\infty \gg \sigma). \quad (9)$$

For example, if $\sigma = 20$ erg/cm² and $\varphi = 0$, then $V^0 \approx 1$ eV, $2R^0 \approx 10$ Å. The quantities V^0 and $2R^0$ are of the same order if $\varphi \sim 10^9$ erg/cm³ (for example, if the molar heat of the transition $\sim R$, and the system is removed from the transition point by ~ 300 K) and $\sigma \ll 10^2$ erg/cm². As $\zeta \gg 1$ (for localized phasons, $\zeta \sim 10^3$) at $V > V^0$ when $\Delta\Phi(R_0) < 0$, relation (5) implies that the majority of electrons is in the phason state. Even at smaller V (but $V > 0$) when $\Delta\Phi(R_0) > 0$,

if the value of (7) does not exceed $10kT$, the considerable part of electrons will transfer into phason states, being localized on the Frenkel heterophase fluctuations [4] and making them more stable.

In the above consideration, in order to determine the equilibrium radius R_0 , we considered the dependence $\Delta\Phi$ on R only, neglecting the dependence $\zeta(R)$ (i.e. $M(R)$ for the case of non-localized phasons). In addition, we supposed that all the regions of the second phase are of the same spherical shape and the same radius R_0 , i.e. the contribution of fluctuations of the size and the shape of these regions to $\Delta\Phi$ was not considered. For these approximations to be valid, the derivative $\partial^2\Delta\Phi/\partial R^2$ (at $R = R_0$) should be large enough. It is easy to see that the corresponding criterion can be written in the form

$$-E(R_0) \gg kT. \quad (10)$$

Even if this requirement is fulfilled, $\Delta\Phi$ is determined with the error of several kT and, as a result, the preexponential factor in (5) is determined only by the order of magnitude. Let us note that if requirement (10) is fulfilled, the validity criterion for the adiabatic approximation used above is also fulfilled, and, in addition, a contribution of the excited electron states in the potential well to $\Delta\Phi$ can be neglected.

As follows from the estimates presented above, at small values of σ and φ , a phason can be indeed considered within the macroscopic approach with certain accuracy. As σ and φ increase, this approach becomes less accurate, and the considered region should be described as a region with disturbed short-range order rather than as a region of formed phase II. Even for small σ and φ , a more strict consideration should take the dependence of these quantities on the radius R , as well as their variation under the action of the electric field of the electron, into account. Changes in the long-range and short-range orders and the density in each of the phases should also be taken into account, as they can be rather substantial, especially if the first-order phase transition is close to the second-order one.

In addition, in the case of the different dielectric constants ε_1 and ε_2 of the phases, one should consider a change in the electron potential caused by the image forces. In the absence of the inertial polarizability of both phases, for the electron located at the center of a spherical region of the second phase, the corresponding contribution to the potential energy is equal to $V'(0) = \frac{e^2(\varepsilon_2 - \varepsilon_1)}{2R\varepsilon_1\varepsilon_2}$. If, for example, $\varepsilon_2 - \varepsilon_1 = \frac{1}{10}\varepsilon_1\varepsilon_2$, $2R = 10 \text{ \AA}$, then $V'(0) < 0.1 \text{ eV}$ (the average value of V' is

less than $V'(0)$), i.e. V' is usually noticeably less than the indicated values of V^0 , at which a macroscopic phason is formed. Though the approximations mentioned above can influence the value of $\Delta\Phi$, they do not change, obviously, the order of magnitude of the estimates.

The estimates presented above are applicable also in the case where phase II has metallic conduction (and phase I is non-metallic). In this case, V should be considered as the distance from the bottom of the conduction band of phase I to the Fermi level of phase II, and the contribution of the Coulomb energy $\frac{e^2}{2R\varepsilon_1}$ to $\Delta\Phi(R)$ should be taken into account. However, as noted above, the consideration of this energy does not change the order of magnitude of the estimates made in case of the applicability of the macroscopic approach.

In the case where phase II is pyroelectric one and has spontaneous polarizability P , we will carry out only a qualitative investigation. A special feature of this case is the appearance of both the additional potential energy $V_P(\mathbf{r})$ of an electron in the field created by the spontaneous polarization and the electrostatic energy U_P related to this polarization. The equilibrium shape of a phase-II region is now not spherical, and its sizes R_{\parallel} and R_{\perp} in the directions parallel and perpendicular to P (along the z - or x - and y -axes) will be different. For estimations, this shape will be considered as ellipsoidal.

For simplicity, let us neglect the inertial polarization created by the electron (the polaron effect) and assume that $\varepsilon_2 \sim \varepsilon_1 = \varepsilon$. Then V_P takes the minimal value $V_{\min} \sim -2E_P R_{\parallel} n_z$ (where $E_P = 2\pi eP$, and n_z is the depolarization coefficient) at the point $z = -R_{\parallel}$, $x = y = 0$ corresponding to the edge of the region of phase II (the origin of coordinates is chosen at the region center). Near this point within the region, $V_P - V_{\min} \sim E_P n_z |R_{\parallel} + z|$. At large distances from the region, V_P decreases as the dipole potential. The energy U_P is of the order of $\alpha_1 \varepsilon E_P^2 e^{-2} n_z^2 R_{\perp}^2 R_{\parallel}$ (α_i are positive quantities of the order of unity).

Let us restrict ourselves to the case where the polarization effects are most pronounced, and E_P is so large that the conditions $E_P R \gg \hbar^2 (R^2 m)^{-1}$, $|V_{\min}| \gg V$ are satisfied for the considered values of R . Then the distribution of the electron density (with widths r_{\parallel} and r_{\perp} along the z - and x -axes) has a maximum near the minimum of V_P and lies, as follows from the results presented below, mainly in the area where the specified approximation for V_P is applicable. Using the given expressions for U_P and V_P and estimating the average kinetic and potential energies of the electron,

we get the formula

$$\Delta\Phi = \alpha_1 \varepsilon \frac{E_P^2}{e^2} n_z^2 R_\perp^2 R_\parallel + \frac{4\pi}{3} \alpha_2 R_\parallel R_\perp^2 \varphi + S(R_\parallel, R_\perp) \sigma + \frac{\hbar^2}{m} \left(\frac{\alpha_3}{r_\perp^2} + \frac{\alpha_4}{r_\parallel^2} \right) - 2\alpha_5 E_P n_z R_\parallel + 2\alpha_6 E_P n_z r_\parallel, \quad (11)$$

where $S(R_\parallel, R_\perp)$ is the surface area, and $r_\perp \sim \left(\frac{r_\parallel R_\perp^2}{R_\parallel} \right)^{1/2}$ is determined by the order of magnitude as a coordinate $\sqrt{x^2 + y^2}$ of the ellipsoid at $R_\parallel + z \sim r_\parallel$.

To determine stationary sizes of a phason and the corresponding value of $\Delta\Phi$, one should find the minimum of expression (11) with respect to the variables r_\parallel , R_\parallel , and R_\perp . With regard for the known expressions for n_z , it is easy to verify that, although the values of R_\parallel and R_\perp corresponding to the minimum of $\Delta\Phi$ are different, they are of the same order of magnitude ($R_\perp \sim R_\parallel \sim R_0$) at $\varepsilon P^2 R_0 \lesssim \sigma$ or $\varepsilon P^2 \lesssim \varphi$. Moreover, the condition $r_\parallel, r_\perp \lesssim R_0$ is satisfied at $E_P R_0^3 m \gg \hbar^2$. The estimates for R_0 and $\Delta\Phi(R_0)$ follow from expression (11):

$$R_0 \sim \frac{eP}{\sigma}; \quad \Delta\Phi(R_0) \sim -\frac{10(eP)^2}{\sigma}$$

(at $3\sigma \gg (\varphi + \alpha'_2 \varepsilon P^2) R_0$);

$$R_0 \sim \left(\frac{eP}{\varphi + \alpha'_2 \varepsilon P^2} \right)^{1/2}; \quad \Delta\Phi(R_0) \sim -\frac{10(eP)^{3/2}}{(\varphi + \alpha'_2 \varepsilon P^2)^{1/2}}$$

(at $3\sigma \ll (\varphi + \alpha'_2 \varepsilon P^2) R_0$; $\varepsilon P^2 \lesssim \varphi$). (12)

For example, for $P \sim 10^4$ electromagnetic units and $\sigma \sim 30$ erg/cm² $\sim \frac{1}{3}(\varphi + \alpha'_2 \varepsilon P^2) R_0$, $R_0 \sim 10$ Å according (12), and a change of $\Delta\Phi \sim -5$ eV is rather large.

The formation of phasons can be considerably facilitated if several, n , electrons, rather than a single one, are localized at the region of phase II. In the determination of $\Delta\Phi_n$ for non-pyroelectric phase II, we should take into consideration that, according to Pauli's exclusion principle, the electronic energy of n electrons in a potential well of radius R is equal to

$$E_n(R) = -\alpha'_3 nV + \alpha'_4 \frac{\hbar^2 n^{2/3}}{mR^2} + \alpha'_5 \frac{e^2}{\varepsilon_\infty R} \frac{n(n-1)}{2}, \quad (13)$$

where ε_∞ is the high-frequency dielectric constant. Let us consider the case where $\Delta\Phi_n = 0$ on the formation of a phason with n electrons. According to (1) and (13), the relevant values of $V_n^{(0)}$ and the limiting values of $R_{n\infty}$

and $\Delta\Phi_{n\infty}$ (as $V \rightarrow \infty$) in the case where $V \gg \frac{e^2 n}{\varepsilon_\infty R_{n\infty}}$, $\frac{\pi^2 \hbar^2}{mR_{n\infty}^2} \gg \frac{n^{4/3} e^2}{\varepsilon_\infty R_{n\infty}}$, and $2\sigma \gg \varphi R_{n\infty}$ are related to the corresponding values $V_1^0 \equiv V^0$, $R_{1\infty} \equiv R_\infty$ and $\Delta\Phi_{1\infty} \equiv \Delta\Phi_\infty$ given by Eqs. (8) and (9) as follows:

$$V_n^0 \sim V^0 n^{-2/3}, \quad R_{n\infty} \sim R_\infty n^{1/6}, \quad \Delta\Phi_{n\infty} \sim n \Delta\Phi_\infty. \quad (14)$$

With the further growth of n at $\frac{\pi^2 \hbar^2}{mR_{n\infty}^2} \ll \frac{n^{4/3} e^2}{\varepsilon_\infty R_{n\infty}}$ and $2\sigma \gg \varphi R_{n\infty}$, the quantities $R_{n\infty}$ and $\Delta\Phi_{n\infty}$ are determined by the formulae

$$R_{n\infty} \sim \left(\frac{n^2 e^2}{16\pi\sigma\varepsilon_\infty} \right)^{1/3};$$

$$\Delta\Phi_{n\infty} = -Vn + \alpha'_6 \left(\frac{e^4 \sigma}{\varepsilon_\infty^2} \right)^{1/3} n^{4/3} \quad (n \gg 1). \quad (15)$$

The quantity $\Delta\Phi_{n\infty}$ reaches its minimum value $\approx -\frac{1}{4} V n^0 \sim \frac{1}{10} \frac{V^4 \varepsilon_\infty^2}{e^4 \sigma}$ at $n^0 \sim \frac{1}{10} \frac{V^3 \varepsilon_\infty^2}{e^4 \sigma}$ (this estimate was obtained for $n^0 \gg 1$). Obviously, if the total concentration of electrons is very small, the concentration of such complicated complexes (which is determined, for example, by the law of mass action) is rather small.

Obviously, the formation of phasons should lead to a change of all the electronic properties of the substance (in particular, to the formation of a new light absorption band due to transitions of electrons in the phason potential well), which would be especially pronounced in the region of a phase transition. In addition, some of its atomic properties can change as well. So, by causing the formation of stable regions of phase II even in the equilibrium range of phase I, the electrons can essentially accelerate the rate of the phase transition I \rightarrow II under the transition of the system to the equilibrium range of phase II. This effect should be manifested especially sharply if R_0 exceeds the critical radius of nuclei of phase II.

Note that phasons are, to some extent, similar to formations of phase II nearby impurity ions (see, for example, [5]). But, in the case of phasons, the above-described quantum effects related to the small mass of an electron and its high kinetic energy are of importance.

2. State of Electrons in Disordered Systems

To illustrate the possibility of the formation of fluctuons with relatively large radii, we consider an electron in a disordered solid solution containing one atom per a cell. In fact, these results are also applicable to an electron in the ideal paramagnetic material and (qualitatively) to an electron in the liquid non-polar solution. Unlike the usual statement of the problem (see, for example, [6]), we consider a region with relatively high mobility of atoms and assume that the redistribution of atoms in a small region of the fluctuon potential well has time to happen for the lifetime of an electron in this well.

In the case of an inhomogeneous distribution of the concentration $c(\mathbf{r})$ of atoms A in solution $A - B$, the electron potential energy can be written in the macroscopic approach as

$$V(\mathbf{r}) = A[c(\mathbf{r}) - c_0]. \quad (16)$$

Here, c_0 is the average concentration, the energy is reckoned from the bottom of the conduction band of the perfect crystal corresponding to the average potential energy in the solution with concentration c_0 , and the parameter A is small in comparison with the conduction band width ΔE but is large in comparison with the other characteristic energy of the problem, kT .

For simplicity, let us consider the ideal solution, by neglecting the difference between the interaction energies of atoms of different types. Then the minimum work necessary to create the concentration distribution $c(\mathbf{r})$ is written in the macroscopic approach as

$$R = \frac{kT}{v} \int \left[\varphi \{c(\mathbf{r})\} - \varphi(c_0) - \frac{\partial \varphi(c_0)}{\partial c_0} (c(\mathbf{r}) - c_0) \right] d\mathbf{r};$$

$$\varphi(c) = c \ln c + (1 - c) \ln(1 - c), \quad (17)$$

where v is the atomic volume. If the electron is localized in a potential well created by the concentration distribution $c(\mathbf{r})$, and a fluctuon is formed, then the wave function of the electron and a change of the thermodynamic potential for the fixed location of the fluctuon can be determined from the requirement of minimum of the functional $J[\psi(\mathbf{r}), c(\mathbf{r})]$ with respect to ψ and c :

$$\Delta \Phi = \min J[\psi, c];$$

$$J = \frac{\hbar^2}{2m} \int |\nabla \psi|^2 d\mathbf{r} + \int V(\mathbf{r}) |\psi(\mathbf{r})|^2 d\mathbf{r} + R. \quad (18)$$

The first two terms in J determine the average kinetic and potential energies of the electron K and \bar{V} (m is the effective electron mass).

By minimizing functional (18) with respect to $c(\mathbf{r})$ at specified ψ , we obtain the corresponding distribution $c(\mathbf{r})$ and the functional $J[\psi]$ depending only on $\psi(\mathbf{r})$,

$$c(\mathbf{r}) = \frac{b \exp\left(-\frac{Av}{kT} |\psi|^2\right)}{1 + b \exp\left(-\frac{Av}{kT} |\psi|^2\right)}; \quad b = \frac{c_0}{1 - c_0};$$

$$J[\psi] = \frac{\hbar^2}{2m} \int |\psi|^2 d\mathbf{r} - Ac_0 - \frac{kT}{v} \int \ln \left[1 - c_0 + c_0 \exp\left(-\frac{Av}{kT} |\psi|^2\right) \right] d\mathbf{r}. \quad (19)$$

The minimum of the functional $J[\psi]$ can be found by means of the direct variational method. Let us use the simplest approximation for $\psi(\mathbf{r})$,

$$\psi(\mathbf{r}) = \left(\frac{2\alpha}{\pi}\right)^{3/4} \exp(-\alpha r^2); \quad (20)$$

then the problem is reduced to the determination of a minimum of the function of the variable α ,

$$J[\psi] = J(a) = -Ac_0 + \frac{4A}{3\sqrt{\pi}} \left[Ba^{2/3} + b \frac{1}{a} f(a) \right];$$

$$a = \frac{Av}{kT} \left(\frac{2\alpha}{\pi}\right)^{3/2}; \quad B = B' \left(\frac{kT}{A}\right)^{2/3};$$

$$B' = \frac{9\pi^{3/2}}{16} \frac{\hbar^2}{mv^{2/3}A}; \quad f(a) = \int_0^a \frac{e^{-x}}{1 + be^{-x}} \left(\ln \frac{a}{x}\right)^{3/2} dx. \quad (21)$$

In the case of large a , the function $f(a) \approx (\ln a)^{3/2} [1 + 0.86(\ln a)^{-1}]$ (at $b \ll 1$) or $f(a) \approx \ln 2 (\ln a)^{3/2} + 0.54(\ln a)^{1/2}$ (at $b = 1$) depends slightly on a . For the sake of definiteness, let us assume that $A > 0$.

The condition $\partial J / \partial a = 0$ yields the values $a = a_0$ (at small B , the equation $\partial J / \partial a = 0$ has two roots, the smaller of which $a_0 \ll 1$ corresponds to the maximum of J , and the larger one corresponds to its minimum) and the average integral width $r_0 = (3Av)^{1/3} (4\pi kTa)^{-1/3}$ of the electron density distribution $\left(\frac{4\pi}{3} r_0^3 |\psi(0)|^2 = 1\right)$ which correspond to the minimum of $\Delta \Phi$ and the equilibrium state of a fluctuon at the given B . Then

we can find $\Delta\Phi = J(a_0)$ and the average energy of the electron

$$E = K + \bar{V} = -Ac_0 + \frac{4A}{3\sqrt{\pi}} [Ba_0^{2/3} + bf'(a_0)].$$

These quantities can be written in the form

$$\begin{aligned} a &= \gamma_1 \left(\frac{b}{B}\right)^{3/5} = \gamma_1 \left(\frac{b}{B'}\right)^{3/5} \left(\frac{A}{kT}\right)^{2/5}; \\ \frac{4\pi r_0^3}{3v} &= \frac{1}{\gamma_1} \left(\frac{B'}{b} \frac{A}{kT}\right)^{3/5}; \\ \Delta\Phi &= -Ac_0 + \gamma_2 B'^{3/5} b^{2/5} \left(\frac{kT}{A}\right)^{2/5} A; \\ E &= -Ac_0 + \gamma_3 B'^{3/5} b^{2/5} \left(\frac{kT}{A}\right)^{2/5} A; \\ \gamma_1 &= \left(\frac{3}{2}\right)^{3/5} (f - af')^{3/5}; \quad \gamma_2 = \frac{4}{3\sqrt{\pi}} \left(\gamma_1^{2/3} + \frac{f}{\gamma_1}\right); \\ \gamma_3 &= \frac{4}{3\sqrt{\pi}} \left(\gamma_1^{2/3} + \frac{af'}{\gamma_1}\right). \end{aligned} \quad (22)$$

Here, the coefficients γ_i are functions of a and b . Their values for different a (i.e. for different B/b) are presented in Table 1 together with the values of the functions f and af' for the cases $b \rightarrow 0$ ($b \approx c_0$ for weak solutions) and $b = 1$ ($c_0 = 1/2$).

For the fluctuon states to appear, the energy E should be negative¹. This implies that the parameter B' should be not very large, and the ratio kT/A should be small enough. In addition, as seen from (21) and (22), $E > 0$ both at very small b (when $b \approx c_0$) and at $c_0 \approx 1$ ($b \gg 1$), when (if $A > 0$) $f(a) \approx 3\sqrt{\pi}a/4$.

If, for example, $b = 1$ and $A = 100kT$, then, as follows from (22) and from Table 1, $4\pi r_0^3/3v = 9$, $\Delta\Phi = -0.10A$, $E = -0.21A$ for $B' = 1$ (both E and $\Delta\Phi$ are negative), and $4\pi r_0^3/3v = 32$, $\Delta\Phi = 0.03A$, $E = -0.07A$ at $B' = 2$ ($\Delta\Phi > 0$, but $E < 0$). With further increase of B' , for example, at $B' = 2.5$, $E > 0$, and a fluctuon is not formed. At high values of A/kT , the conditions for the formation of a fluctuon become more favorable. For example, at $b = 1$, $B' = 3$, $A = 1000kT$, $4\pi r_0^3/3v = 57$, $\Delta\Phi = -0.17A$, and $E = -0.26A$.

It is significant that, at given values of B' , the formation of fluctuons becomes possible ($E < 0$) only at

Table 1. Values of the coefficients γ_i

a	$b = 1$						$b \rightarrow 1$					
	$\frac{B}{b} \times 10^2$	$f(a)$	$af'(a)$	γ_1	γ_2	γ_3	$\frac{B}{b} \times 10^2$	$f(a)$	$af'(a)$	γ_1	γ_2	γ_3
1	8.61	0.607	0.550	0.230	2.27	2.08	19.3	1.132	1.003	0.373	2.67	2.41
2	9.51	1.106	0.904	0.487	2.17	1.86	21.2	1.973	1.525	0.788	2.53	2.1
3	9.36	1.518	1.129	0.724	2.18	1.78	19.3	2.63	1.832	1.117	2.58	2.04
4	8.75	1.864	1.276	0.927	2.23	1.75	17.0	3.18	2.03	1.383	2.66	2.04
5	8.01	2.16	1.38	1.099	2.28	1.75	15.0	3.63	2.17	1.601	2.74	2.05
6	7.28	2.42	1.458	1.246	2.33	1.75	13.3	4.03	2.28	1.785	2.81	2.07
7	6.62	2.65	1.519	1.373	2.38	1.76	11.8	4.38	2.36	1.943	2.87	2.09
8	6.03	2.86	1.570	1.484	2.43	1.77	10.6	4.70	2.43	2.08	2.92	2.11
9	5.52	3.05	1.613	1.582	2.47	1.79	9.57	4.98	2.49	2.20	2.97	2.13
10	5.07	3.22	1.650	1.670	2.51	1.80	8.71	5.24	2.55	2.31	3.02	2.14
11	4.67	3.38	1.683	1.751	2.54	1.82	7.97	5.48	2.59	2.41	3.06	2.16
12	4.33	3.53	1.713	1.824	2.58	1.83	7.33	5.71	2.63	2.50	3.10	2.18
13	4.03	3.67	1.739	1.892	2.61	1.84	6.78	5.92	2.67	2.59	3.14	2.19
14	3.76	3.80	1.763	1.955	2.64	1.85	6.30	6.12	2.70	2.67	3.17	2.21
15	3.52	3.92	1.785	2.01	2.67	1.87	5.87	6.31	2.74	2.74	3.21	2.22
16	3.29	4.03	1.804	2.06	2.69	1.88	5.46	6.46	2.76	2.79	3.23	2.24
17	3.09	4.14	1.823	2.11	2.71	1.89	5.12	6.62	2.79	2.86	3.26	2.25
18	2.92	4.24	1.84	2.16	2.74	1.90	4.81	6.78	2.81	2.92	3.28	2.26
19	2.76	4.35	1.857	2.20	2.76	1.91	4.54	6.93	2.84	2.97	3.31	2.27
20	2.62	4.44	1.872	2.25	2.78	1.92	4.29	7.08	2.86	3.02	3.33	2.28
21	2.48	4.53	1.887	2.29	2.80	1.93	4.07	7.21	2.88	3.07	3.36	2.29
22	2.36	4.62	1.901	2.33	2.82	1.94	3.86	7.35	2.90	3.12	3.38	2.31
23	2.25	4.71	1.912	2.36	2.83	1.94	3.68	7.47	2.92	3.17	3.40	2.32
24	2.15	4.79	1.927	2.40	2.85	1.95	3.50	7.60	2.94	3.21	3.42	2.33

¹More exactly, the energy E must apparently lie below the renormalized edge of the conduction band, and the requirement $-E > A^2 \frac{c(1-c)}{\pi} \frac{mv^{2/3}}{\hbar^2}$ or $-E > \frac{c(1-c)A}{B'}$ should be fulfilled. However, in the macroscopic approximation, B' is assumed to be large, and this condition can be considered as fulfilled. For the applicability of the effective mass method, the conduction band width should exceed A . Otherwise ($A > \Delta E$), the above consideration is not applicable, and only a fluctuon with small radius can appear.

temperatures less than some characteristic temperature T^* . In a small temperature interval $\delta T \ll T^*$ close to T^* , the majority of electrons passes into the fluctuon states, and a dramatic change of all the electronic properties should take place.

Knowing a value of $\Delta\Phi$, one can determine the thermodynamic potential N_{fl} of fluctuons using Eq. (3) or (4) (for their rectilinear or diffusion motion, respectively). Obviously, the more strict determination of $\Delta\Phi$ should include a contribution from the excited states corresponding to fluctuations of $c(\mathbf{r})$ near the potential well. The present approach is valid only when the condition of type (10),

$$-E \gg kT, \quad (23)$$

is satisfied.

In this situation, we may neglect the dependence of the effective mass M on α on the minimization of Φ with respect to α . However, in this case, $\Delta\Phi$ is also determined with the accuracy of $\sim kT$, and the preexponential factor in the expression for the fluctuon concentration is determined to within a factor of $\sim 1 - 10$.

For fluctuons to be considered as stationary formations, it is necessary that the relaxation time $\sim r_0^2/D$ of the concentration be small in comparison with the lifetime of an electron in the fluctuon potential well. This requirement can be approximately written as $|E| > Q$, where Q is the activation energy for diffusion. It seems likely that this requirement is not often fulfilled in solid solutions, but, at higher A , it is fulfilled in liquid solutions.

The conditions for the formation of fluctuons are apparently fulfilled much easier not in solutions but in paramagnetic materials where a fluctuon is an electron localized near a local change of the magnetization. Here, the spin relaxation occurs quickly enough, the adiabaticity requirement is satisfied if condition (23) is satisfied, and the ratio A/kT is high enough at low temperatures, which is favorable for the formation of a fluctuon. If the spin-spin interaction can be neglected, then the calculation in the case where $S = 1/2$ is reduced to the determination of a minimum of the functional $J[\psi]$ defined by Eq. (19), where $c_0 = 1/2$ ($b = 1$), and $A/2$ has sense of the exchange interaction energy of the conduction electron with a magnetic atom. Therefore, all the results obtained in this section are also applicable to the ideal paramagnetic materials with $S = 1/2$. The case of large spins will be considered separately [3].

It is obvious that the results presented above are applicable not only to electrons or holes, but also to

Frenkel excitons or to Mott excitons, for which the Bohr radius is small in comparison with the radius of a phason or a fluctuon to be formed. These results can also be generalized to the case of phasons or fluctuons localized near impurity centers.

In conclusion, I would like to express my gratitude to S.I. Pekar for his interest in this study and the discussion of results and to G.I. Gudzenko for numerical calculations.

1. S.I. Pekar, *Investigations on Electronic Theory of Crystals* (GITTL, Moscow, 1951) (in Russian).
2. R. Ferrel, Phys. Rev. **108**, 167 (1957); C.G. Kuper, Phys. Rev. **122**, 1007 (1961); J. Jortner, N.R. Kestner, S.A. Rice, and M.H. Cohen, J. Chem. Phys. **43**, 2614 (1965); E.P. Gross and H. Tung-Li, Phys. Rev. **170**, 190 (1968); G. Baym, R.G. Rarrera, and C.J. Petnik, Phys. Rev. Lett. **22**, 20 (1969).
3. M.A. Krivoglaz and A.A. Trushchenko, Fiz. Tv. Tela **11**, 3119 (1969).
4. Ya.I. Frenkel, *Kinetic Theory of Liquids* (Izd. AN SSSR, Moscow, 1945) (in Russian).
5. K.R. Atkins, Phys. Rev. **116**, 1339 (1959).
6. I.M. Lifshitz, Usp. Fiz. Nauk **83**, 617 (1964).

Received April 12, 1969

**KRIVOGLAZ MIKHAIL ALEKSANDROVICH
(18.05.1929–30.06.1988)**

Mikhail Aleksandrovich Krivoglaz is a prominent scientist in the area of solid state physics, Corresponding member of AS of UkrSSR, laureate of State's prizes of UkrSSR in science and technique. From 1951 to 1988, he had worked in G. V. Kurdyumov Institute for Metal Physics, NAS of the Ukraine. M.A. Krivoglaz made a fundamental contribution to the development of the theory of non-ideal crystals and laid the foundation of a number of trends in this field. In the theory of light absorption spectra by the impurity centers, he predicted (together with S.I. Pekar) the existence of narrow phononless lines in the electron-vibration spectra before the discovery of the Mössbauer effect. Together with A.A. Smirnov, he essentially developed the theory of properties of ordered alloys [M.A. Krivoglaz, A.A. Smirnov, *Theory of Order-Disorder in Alloys* (Elsevier, N.-Y., 1965)]. He is one of the founders of the theory of the scattering of X-rays and neutrons in non-ideal crystals, in which he developed the method of fluctuation waves, proposed a new systematics of impurities in crystals, and predicted some important effects (M.A. Krivoglaz, *X-Ray and Neutron Diffraction in Non-Ideal Crystals* (Springer, Berlin, 1996); M.A. Krivoglaz, *Diffuse Scattering of X-Rays and Neutrons by Fluctuations*, ibid., 1996). In the theory of electron states in crystals, he developed a theory of fluctuons – autolocalized electron states of a new type that can appear in the systems with easily changing parameters (see the article in the present issue). The full bibliography of the works by M.A. Krivoglaz is presented in the book: M.A. Krivoglaz, *Life and Scientific Activity. Reminiscences. Selected Works* (Publ. House "Akademperiodyka", Kyiv, 2004) (in Russian).