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QUANTUM THEORY OF DEFECTS IN CRYSTALS

A. F. ANDREEV and I. M. LIFSHITZ

Institute of Physical Problems, U.S.S.R. Academy of Sciences

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At sufficiently low temperatures localized defects or impurities change into excitations that move practically freely through a crystal. As a result instead of the ordinary diffusion of defects, there arises a flow of a liquid consisting of "defectons" and "impuritons." It is shown that at absolute zero in crystals with a large amplitude of the zero-point oscillations (for example, in crystals of the solid helium type) zero-point defectons may exist, as a result of which the number of sites of an ideal crystal lattice may not coincide with the number of atoms. The thermodynamic and acoustic properties of crystals containing zero-point defectons are discussed. Such a crystal is neither a solid nor a liquid. Two kinds of motion are possible in it; one possesses the properties of motion in an elastic solid, the second possesses the properties of motion in a liquid. Under certain conditions the "liquid" type of crystal motion possesses the property of superfluidity. Similar effects should also be observed in quasiequilibrium states containing a given number of defectons.

A FUNDAMENTAL property of crystals is their ideal periodicity, i.e., the periodicity of the density function $\rho(\mathbf{r})$ which determines the probability of different positions of the particles in space. In general there exist two different causes which violate this periodicity. These are, in the first place, vibrations of the crystal lattice sites and, in the second place, defects (vacancies, extra atoms, dislocation loops, etc.).

In considering the vibrations it is usually assumed that at each lattice site (i.e., at a maximum of the function $\rho(\mathbf{r})$) there is always exactly one atom and these atoms undergo small vibrations. Then $3r$ (r is the number of sites in an elementary cell) vibrational branches appear. Quantum-mechanical effects require the existence of zero-point vibrations, i.e., vibrations that remain at zero temperature and therefore do not violate the periodicity of the crystal. The initial assumption about the identification of sites and atoms will here be valid only in the case when the amplitude of the zero-point vibrations turns out to be small in comparison with the lattice period, and therefore the wave functions of atoms located on neighboring sites do not overlap in practice. A numerical measure of the magnitude of the zero-point vibrations is given by the dimensionless parameter $\Lambda = h/a\sqrt{m\epsilon}$ (see [1]), where m is the mass of an atom, ϵ is the characteristic interaction energy of the atoms, and a is the interatomic distance. For example, for elements of group VIII of the periodic table, one can take as ϵ and a the parameters which determine the potential energy of the interaction of two atoms: $U(r) = 4\epsilon\{(a/r)^{12} - (a/r)^6\}$.

The parameter Λ is actually very small for the majority of crystals. However, crystals exist for which $\Lambda \gtrsim 1$. For example, $\Lambda = 0.6$ for Ne, $\Lambda = 2.7$ for He^4, and $\Lambda = 3.1$ for He^3. In addition, crystals exist in which the condition of smallness of the amplitude of the zero-point vibrations may be violated not for all but only for certain kinds of vibrations. For example, this pertains to the vibrations of hydrogen impurity atoms in lattices consisting of certain heavy metals. The appreciable magnitude of the amplitude of the zero-point vibrations is here related to the smallness of the impurity atom mass. The usual approach to an investigation of the properties of such crystals and, in particular, the vibrations is completely inapplicable (see [2–4]). We will see that even the number of normal modes may differ from $3r$.

Defects are usually regarded classically as localized objects which only occasionally move from one position to another. It is clear, however, that at sufficiently low temperatures, because of the finiteness of the parameter Λ, quantum effects must also become important for defects. And what is more, as we shall see, the existence of zero-point defects or, more accurately, "zero-point defectons" turns out to be possible; just like zero-point vibrations "zero-point defectons" exist at zero temperature and do not violate the crystal periodicity. The existence of zero-point defectons means that the number of sites in an ideal crystal lattice does not coincide with the number of atoms. This is not surprising since for finite values of Λ an atom is not localized at a definite site, and therefore the requirement that the number of sites be equal to the number of atoms is not compulsory.

In the present article the influence of quantum effects on the behavior of defects in a crystal will be considered, and it is shown that these effects lead to the existence of a number of rather unusual crystal properties.

1. DEFECTONS

Because of the quantum-tunneling effect, a defect in a crystal at zero temperature is not localized. According to quantum mechanics, in such a case the possible states are classified according to the values of the quasimomentum $\mathbf{k}$. Thus, with each type of defect there is associated a branch of excitations—the defectons. The energy of a defecton, which is a function of the quasimomentum $\epsilon(\mathbf{k})$, takes all possible values inside a certain band of width $\Delta\epsilon$ which is proportional to the probability of tunneling by the defect.

In the majority of cases the tunneling probability is relatively small; therefore one can use the tight-binding approximation in order to calculate a defecton's energy. In this connection the function $\epsilon(\mathbf{k})$ may be determined, as is well known, in explicit form for all values of $\mathbf{k}$. For example, for a simple cubic lattice we have

$$\varepsilon(\mathbf{k}) = \varepsilon_1 + \varepsilon_2(\cos \mathbf{ka}_1 + \cos \mathbf{ka}_2 + \cos \mathbf{ka}_3),$$

where ϵ_1, ϵ_2 are constants and $\mathbf{a}_1$, $\mathbf{a}_2$, $\mathbf{a}_3$ are the basis vectors of the lattice.

At finite temperatures collisions of a defecton with other crystal excitations are possible. The increase in the number of collisions which takes place as the temperature is raised has a substantial effect on the nature of the defect motion. If the frequency of collisions is sufficiently small, then one can talk about a practically freely moving defecton which only occasionally undergoes collisions. As the collision frequency increases there appears a moment when, during the time spent by a defect on a fixed site, it is able to reach equilibrium with the lattice. Under such conditions one must talk about a localized defect which undergoes a random walk with a step equal to the lattice period a.

In the low temperature region the diffusion coefficient D for a defecton is determined by the gas-kinetic expression $D \sim vl$, where v is the velocity of the defecton, $l \sim v\tau_{\mathrm{tr}}$ is its mean free path, and τ_{tr} is the transport time that characterizes the collisions of the defecton with other excitations of the crystal. In dielectrics at temperatures much smaller than the Debye temperature Θ, collisions with long wavelength acoustic phonons play a major role; for such processes, as is well known, the collision cross section σ is proportional to the fourth power of the frequency. Therefore $\sigma \sim a^2(qa)^4$ where q is the phonon wave vector. The reciprocal of the time between collisions is given by $1/\tau \sim N_{\mathrm{ph}}c\sigma$ (where c is the speed of sound, N_{ph} is the number of phonons per unit volume). Substituting $N_{\mathrm{ph}} \sim (T/a\Theta)^3$ and $qa \sim T/\Theta$ we obtain $1/\tau \sim (c/a) \times (T/\Theta)^7 \sim (\Theta/\hbar)(T/\Theta)^7$. Since the phonon momentum is small in comparison with the defecton momentum, the transport time differs from τ by the presence of a large factor $(\Theta/T)^2$. In order of magnitude the diffusion coefficient is given by

$$D \sim \frac{\hbar v^2}{\Theta}\left(\frac{\Theta}{T}\right)^9 \sim \frac{a^2}{t}\frac{\hbar}{\Theta t}\left(\frac{\Theta}{T}\right)^9, \qquad (1)$$

where the time $t \sim a/v$ spent by a defecton on a lattice site has been introduced. On the other hand, if it is taken into consideration that $v \sim \Delta\epsilon/k \sim a\Delta\epsilon/\hbar$, then we obtain a relation between t and the width of the band: $t \sim \hbar/\Delta\epsilon$.

We note that in metals the collisions of a defecton with electrons play a fundamental role. In this connection the coefficient of diffusion for a defecton is proportional to 1/T as long as $T \gg \Delta\epsilon$.

The diffusion coefficient for a localized defect is expressed in terms of the probability w for a transition to a neighboring site by the relation $D \sim a^2 w$, which corresponds to a random walk with step a and frequency w. At not too high temperatures the probability w is determined by the above-introduced time t ($w \sim 1/t$) and does not depend on the temperature. In this connection the coefficient of diffusion also does not depend on the temperature and is equal to $D \sim a^2/t \sim a^2\Delta\epsilon/\hbar$. From the condition for matching this expression with formula (1) we obtain the temperature at which a transition occurs from freely moving defectons to localized defects: $T \sim \Theta(\Delta\epsilon/\Theta)^{1/9}$.

A further increase of the temperature leads to the result that with appreciable probability a defect is found in one of the excited states in a potential well corresponding to the position of equilibrium. In this case the probability for a transition to a neighboring site is given by

$$w = \sum_n w_n e^{-\varepsilon_n/T},$$

where w_n is the probability for a transition from the state n, ϵ_n is the energy of this state measured from the energy of the ground state (n = 0). As the temperature increases w increases from the value $w_0 \sim 1/t$, corresponding to quantum tunneling from the ground level, to the purely classical value $w \sim (\Theta/\hbar)\exp -U/T$, which is obtained at the expense of above-barrier transitions from states with $\epsilon_n > U$ (U is the height of the barrier which must be overcome in order for a transition to a neighboring site to take place).

Thus, as the temperature is lowered first the diffusion coefficient of the defects falls exponentially (classical diffusion), then a plateau appears (quantum diffusion, localized defects), and then it increases (diffusion of defectons).

In addition to the above-considered mechanism of localization of a defect, which is associated with an increase of the temperature, mechanisms due to the interaction of defects with each other or with fixed defects may play an essential role. Let $\varphi(\mathbf{r})$ be the potential energy describing the interaction of a given defect with other defects. Since φ depends on the coordinates, the energies of the states corresponding to localization on neighboring sites differ by a quantity of order $|\nabla\varphi|a$. If this quantity is larger than the width $\Delta\epsilon$, then a tunneling transition from site to site is impossible, and a defect cannot change into a defecton. Point defects interact according to a cubic law, i.e., the interaction energy of two defects separated by a distance r is given by $\varphi \sim mc^2(a/r)^3$, where m is the mass of an atom in the lattice. Differentiating and substituting $r \sim n^{-1/3}$ (n denotes the number of defects per unit volume), we find $|\nabla\varphi|a \sim mc^2(na^3)^{4/3}$. In order for this quantity to be smaller than $\Delta\epsilon$, the concentration of defects must satisfy the condition $na^3 \ll (\Delta\epsilon/mc^2)^{3/4}$.

If the written condition is fulfilled, then a defect is not localized at any specific site. However, in this connection one may find that it is localized in a certain macroscopic region. Such a situation arises in the case when the defects form a supperlattice with a macroscopically large period. For complete delocalization of a defect it is necessary that the superlattice should be unstable, which is automatically satisfied if the height of the potential barrier $\varphi \sim mc^2(a/r)^3 \sim mc^2na^3$, which a defect must overcome in order to pass from one superlattice site to another, is smaller than $\Delta\epsilon$, i.e., if the concentration na^3 is smaller than $\Delta\epsilon/mc^2$.

A question arises concerning the statistics which defectons should obey. If, for example, the question is about the defectons corresponding to vacancies, then one can easily see that their statistics coincide with the statistics of the atoms out of which the crystal is composed (it is assumed that the crystal consists of atoms of a single type). In fact, the creation operator for a vacancy, i.e., the operator which changes the ground state of the crystal into an excited state, corresponding to the presence of a single vacancy, may always be written in the form

$$\varphi^+(x) = \sum_{n=0}^{\infty} \int K_n(x, x'; x_1, \ldots, x_n; x_1', \ldots, x_n')$$

$$\times \psi(x')\psi^+(x_1)\psi(x_1') \ldots \psi^+(x_n)$$

$$\times \psi(x_n')\, d^3x'\, d^3x_1\, d^3x_1' \ldots d^3x_n\, d^3x_n',$$

where $\psi(x)$ and $\psi^+(x)$ are operators for the annihilation and creation of real atoms. Here all integrals converge for $|x - x_i| \sim |x - x_{i'}| \sim a$; terms with $n \sim 1$ are essential in the summation. The operators φ, taken at points x and x′ such that $|x - x'| \gg a$, have the same commutation relations as the operators ψ. On the other hand, since the vacancies are "good" quasiparticles (if their density is sufficiently small) they must obey either Bose or Fermi statistics. Thus, the first case is realized in a Bose crystal (for example, in solid He^4), and the second case is realized in a Fermi crystal (He^3).

Similarly one can easily convince oneself that in the general case the defecton statistics are determined by the number of atoms which must be annihilated or created in order to produce the corresponding defect. If this number is even then the defectons obey Bose statistics; if it is odd their statistics coincide with the statistics of the atoms.

Everything said at the beginning of this article also pertains to the case of quasiparticles corresponding to impurity atoms in the crystal. At sufficiently low temperatures localized impurities turn into "impuritons" which move essentially freely through the crystal. On the basis of what was said above, one can easily determine the statistics of the impuritons. Here the situation is obviously different for interstitial and substitutional impurities. Interstitial impuritons obey the statistics of the impurity atoms. Substitutional impuritons obey Bose statistics if the crystal atoms and the impurities have the same statistics, and obey Fermi statistics in the opposite case. For example, an interstitial He^4 impurity in a crystal of He^3 corresponds to a Bose impuriton, a substitutional He^4 impurity in He^3 corresponds to a Fermi impuriton, and impurities of He^3 in He^4 always correspond to Fermi impuritons.

If there are a certain number of defects of a specific type (vacancies or interstitial atoms) present in a crystal, then the number of these defects cannot change as a result of processes occurring inside the crystal. The same result is obviously valid under conditions when the defects turn into defectons. A change in the number of defectons may only take place on the surface of the crystal. The number of defectons inside the bulk changes only as a consequence of their diffusion to the surface. The corresponding relaxation time is macroscopically large. The time required to establish equilibrium for a given number of defectons is much smaller. Thus, at a sufficiently low temperature such quasi-equilibrium states exist in a crystal when the defectons constitute a strongly degenerate Fermi or Bose gas. In particular, Bose condensation of defectons occurs in the latter case.

Below we shall see that a similar situation may also be realized under complete equilibrium conditions.

2. ZERO-POINT DEFECTONS

Let us trace the change in the energy spectrum of a defecton associated with an increase of the parameter Λ, i.e., associated with an increase in the probability of quantum tunneling. In the classical limit a defect is localized and possesses a certain energy $E_0 > 0$. The presence of a small but finite tunneling probability leads to the appearance of a band of finite width where the middle of the band coincides with E_0. As the tunneling probability increases, the width of the band increases, and therefore the minimum energy ϵ_0 (the bottom of the band) is reduced. Thus, in a crystal with $\Lambda \sim 1$ a situation is possible in which the energy ϵ_0 becomes negative. This means that a reorganization of the crystal's ground state must occur. Below we shall clarify the nature of this reorganization.

In the simplest case the defecton energy $\epsilon(\mathbf{k})$ has a minimum value at $\mathbf{k} = 0$. Near this point one can expand ϵ in powers of $\mathbf{k}$:

$$\varepsilon = \varepsilon_0 + k^2/2M.$$

Here M is some effective mass which, for simplicity, we assume to be isotropic. In order of magnitude M coincides with $(\Delta\epsilon a^2/\hbar^2)^{-1}$.

If a defecton with $\mathbf{k} = 0$ appears in the crystal, then the crystal remains perfectly periodic; however, the number of crystal lattice sites becomes unequal to the number of atoms. The quantity ϵ_0 is equal to the difference between the energies of these two crystal states. Since ϵ_0 depends on the pressure, then at a certain pressure or, what is the same thing, at a certain value V_0 of the volume associated with a given total mass of the solid, ϵ_0 may tend to zero. In order to determine the properties of the crystal near this point, let us expand ϵ_0 in powers of $V_0 - V$:

$$\varepsilon(\mathbf{k}) = \lambda \frac{V_0 - V}{V_0} + \frac{k^2}{2M}. \tag{2}$$

If for definiteness we assume $\lambda > 0$, then for $V < V_0$ the number of defectons of a given type is proportional to $\exp(-\epsilon_0/T)$. The number of defectons at $T = 0$ (zero-point defectons) is equal to zero. For $V > V_0$ the situation depends on what kind of statistics the defectons obey.

First let us consider the case of Bose statistics. At $T = 0$ the defectons condense into the state with $\mathbf{k} = 0$, and the energy of the system decreases with increase of their number until the interaction is no longer effective. Since ϵ_0 is small near the point $V = V_0$, this happens at a small (in comparison with atomic) density of defectons. Therefore we may use the well-known expression for the energy of a rarefied Bose gas (see [5]). The contribution of the defectons to the total energy of the crystal is given by

$$E = \lambda \frac{V_0 - V}{V_0} N + \frac{2\pi a}{M} \frac{N^2}{V} \tag{3}$$

where N is the number of defectons, and a is the amplitude for their scattering on one another.

If $a < 0$ then a phase transition of the first kind occurs at $V = V_0$. Naturally, in the present case it is impossible to say anything definite about the properties of the resultant new phase.

However if $a > 0$ (i.e., the defectons are repulsive) then from the condition that the energy (3) be a minimum we obtain the following result for the equilibrium number of zero-point defectons:

$$\frac{N}{V} = \frac{M\lambda}{4\pi a}\frac{V - V_0}{V_0}. \tag{4}$$

Substituting (4) into (3) we obtain

$$E = -V\frac{M\lambda^2}{8\pi a}\left(\frac{V - V_0}{V_0}\right)^2, \tag{5}$$

from which it is seen that a phase transition of the second kind occurs at the point $V = V_0$. The order parameter of this transition is the square root of the number of zero-point defectons or of the difference between the number of lattice sites and the number of atoms.

At any finite temperature this transition becomes a first-order transition. Actually, for $V_0 > V$ the condensate is not present, the interaction between defectons is unimportant, and one can use the well-known formulas for the thermodynamic functions of an ideal Bose gas with chemical potential equal to zero and spectrum given by Eq. (2). The contribution of the defectons to the free energy is given by

$$F = -\frac{2}{3}V\frac{M^{3/2}}{2^{1/2}\pi^2}T^{5/2}\int_0^\infty \frac{x^{3/2}\,dx}{\exp\{x + \lambda(V_0 - V)/TV_0\} - 1}.$$

Because of the presence of V in the denominator of the integrand, the function F(V) has a singularity at the point $V = V_0$ such that for $\lambda(V_0 - V)/V_0T \ll 1$ we have

$$V\left(\frac{\partial P}{\partial V}\right)_T = -V\frac{\partial^2 F}{\partial V^2} \approx \frac{(2M)^{3/2}}{3\pi^2}T^{1/2}\lambda^2\int_0 \frac{e^{2x}x^{3/2}\,dx}{\{\exp[x + \lambda(V_0 - V)/TV_0] - 1\}^3}$$
$$\approx \frac{(2M\lambda)^{3/2}}{8\pi}T\left(\frac{V_0}{V_0 - V}\right)^{1/2}.$$

This expression is the part of the derivative $\partial P/\partial V$ which is associated with the type of defectons under consideration. However, it is such that as $V \to V_0 - 0$ the total derivative (taking the compressibility of the initial crystal into consideration) becomes positive.

For $V > V_0$ and not too high temperatures, $T \ll (N/V)^{2/3}M^{-1}$, one can use formula (5) from which it is seen that in this region the defectons introduce a small contribution to the pressure and to the derivative $\partial P/\partial V$. Therefore here this derivative is negative.

For $T \neq 0$ the pressure as a function of the volume has a minimum and a maximum near the point $V = V_0$, i.e., it has the form characteristic of a first-order phase transition.

In the case when the defectons obey Fermi statistics, at $T = 0$ the states with $k < k_0$, where $k_0 = \{2M\lambda(V - V_0)/V_0\}^{1/2}$ $(V > V_0)$, are filled and the remaining states are empty. Therefore the contribution to the energy is given by

$$E = \frac{V}{(2\pi)^3}\int_0^{k_0} 4\pi k^2\,dk\left\{-\lambda\frac{V - V_0}{V_0} + \frac{k^2}{2M}\right\}$$
$$= -\frac{V}{15\pi^2}(2M)^{3/2}\left(\lambda\frac{V - V_0}{V_0}\right)^{5/2}.$$

For the equilibrium number of zero defectons we obviously have

$$N = \frac{V}{6\pi^2}\left\{\frac{2M\lambda(V - V_0)}{V_0}\right\}^{3/2} \quad (V > V_0).$$

At the point $V = V_0$ a phase transition takes place which is completely analogous to the transitions considered previously by one of the authors[6] for electrons in a metal. At finite temperatures this transition is washed out.

From everything that has been said it is clear that zero-point defectons of one or the other type may exist in certain pressure intervals in a crystal that is in an equilibrium state at zero temperature and has not too small a value of the parameter Λ. In terms of its thermodynamical properties at low temperatures, such a crystal differs substantially from an ordinary crystal. In the case of Fermi defectons the heat capacity of the crystal (dielectric) must vary linearly with the temperature owing to the contribution of the defectons situated near the Fermi surface ($k = k_0$). In the boson case the excitations appearing because of the presence of the zero-point defectons have an acoustic spectrum at small energies (a Bogolyubov spectrum for small **k**) with a velocity

$$u = [\lambda(V - V_0)/MV_0]^{1/2}, \tag{6}$$

which is small in comparison with the velocity of ordinary sound in the crystal. In this case the heat capacity of the crystal is proportional to T^3; however, the coefficient of proportionality is much larger than usual.

As we already noted, in a crystal containing zero-point defectons the number of lattice sites, i.e., the number of maxima in the density function, does not coincide with the number of atoms. For this reason there are two possible types of motion in the crystal. The first of these is associated with displacement of the lattice sites and is characteristic of an elastic solid. The second is associated with mass transport by means of the motion of the zero-point defectons while the lattice sites remain essentially fixed. This kind of motion possesses the properties of motion of a liquid.[1)] Thanks to this a crystal is able to flow through a capillary in a gravitational field.

These two types of motion are related to each other by the conditions at the surface of the crystal. Namely, a single-valued relation exists (see [7]) between the stresses normal to the surface and the concentration of defects near the surface. Upon deformation of the crystal there arises therefore a self-consistent motion of the lattice sites and a flow of defectons, accompanied by a transport of mass and therefore causing quantum fluidity of the crystal.

It should, of course, be kept in mind that at finite temperatures, owing to the presence of vacancies, all crystals possess the property of fluidity. At absolute zero, however, one can discern a clear distinction between solids, liquids, and crystals containing unequal numbers of sites and atoms which occupy an intermediate position.

[1)] We note that a similar situation occurs in metals, which are crystals containing an electronic liquid. In metals, however, the situation is complicated due to the condition of electrical neutrality.

Since a nonideal Bose gas possesses the property of superfluidity, the liquid type of motion of a crystal containing Bose zero-point defectons will also possess this property (superfluid flow of the crystal through a capillary). The same also holds under well-known conditions in the case of Fermi defectons. It is of interest to note that defects of a fundamentally new type may exist in a superfluid crystal. The question concerns vortex lines, i.e., linear defects for which the phase of the condensate's wave function changes by 2π upon going around the defect.

3. MACROSCOPIC EQUATIONS OF MOTION

For finite values of Λ the usual equations of motion of a crystal, based on the identification of lattice sites and atoms, are, as mentioned above, inapplicable. But it is precisely the possibility of such an identification which enables one in the usual case to investigate the question of the nature of the crystal vibrations over the entire frequency range. In our case just as, for example, in the case of liquids, it is possible to carry out a general investigation of only the long wavelength (and low frequency) vibrations. This can be done with the aid of macroscopic equations of motion whose form is uniquely determined by the conservation laws.

Turning to a derivation of these equations, let us introduce the vector $\mathbf{u}$ that defines the displacement of the crystal lattice sites from their equilibrium positions. The derivative $\dot{\mathbf{u}}$, equal to the velocity of motion of the sites, in general does not coincide with the velocity of the crystal macroscopic motion since processes of mass transport exist for fixed sites. Moreover, in a superfluid crystal it is necessary to introduce two velocities of macroscopic motion, one of which ($\mathbf{v}_n$) determines the velocity of the "normal part," and the second ($\mathbf{v}_s$) determines the velocity of the "superfluid part." With the aid of the well-known formulas for a Galilean transformation one can express the energy E and momentum $\mathbf{j}$ per unit volume of the substance in terms of their values (ϵ and $\mathbf{p}$) in the coordinate system in which $\mathbf{v}_s = 0$:

$$E = \rho v_s^2/2 + \mathbf{p}\mathbf{v}_s + \varepsilon, \qquad \mathbf{j} = \rho\mathbf{v}_s + \mathbf{p}, \tag{7}$$

where ρ is the density of the crystal. One can regard the energy ϵ as a function of the entropy S, the density the derivatives $w_{ik} = \partial u_k/\partial x_i$ of the vector $\mathbf{u}$ with respect to the coordinates, and the momentum ρ of the relative motion of the normal and superfluid parts. We note that in our case the components of the tensor w_{ik} and the density ρ are independent variables in contrast to the usual case when the relation $\delta\rho/\rho = -w_{ll}$ holds. Let us write the differential $d\epsilon$ in the form

$$d\varepsilon = TdS + \lambda_{ik}dw_{ik} + \mu d\rho + (\mathbf{v}_n - \mathbf{v}_s)d\mathbf{p}. \tag{8}$$

Then we operate in standard fashion (see [8]), starting from the conservation laws. We seek the equations of motion in a form which will guarantee the mass and momentum conservation laws, the increase of entropy, and the potential existence of superfluid motion:

$$\dot{\rho} + \operatorname{div}\mathbf{j} = 0, \qquad \frac{\partial j_i}{\partial t} + \frac{\partial \Pi_{ik}}{\partial x_k} = 0,$$

$$\dot{\mathbf{v}}_s + \nabla\varphi = 0, \qquad S + \operatorname{div}(S\mathbf{v}_n + \mathbf{q}/T) = R/T \quad (R > 0). \tag{9}$$

The unknown quantities π_{ik}, φ, $\mathbf{q}$, and R must be determined from the requirement that the law of energy conservation,

$$\dot{E} + \operatorname{div}\mathbf{Q} = 0. \tag{10}$$

should follow from Eqs. (9). Differentiating the first of the equations (7) with respect to time and using Eqs. (8), (7), and (9), we obtain

$$\begin{aligned}\dot{E} = {} & T\dot{S} + \lambda_{ik}\frac{\partial \dot{u}_k}{\partial x_i} - \mu\operatorname{div}\mathbf{j} - \operatorname{div}\left(\frac{v_s^2}{2}\mathbf{j}\right) + \mathbf{j}\nabla\frac{v_s^2}{2} \\ & - (\mathbf{j} - \rho\mathbf{v}_n)\nabla\varphi - v_{ni}\frac{\partial \Pi_{ik}}{\partial x_k} + \mathbf{v}_n\mathbf{v}_s\operatorname{div}\mathbf{j} \\ = {} & -\operatorname{div}\left\{\mathbf{j}\frac{v_s^2}{2} + ST\mathbf{v}_n + \mathbf{v}_n(\mathbf{v}_n\mathbf{p})\right\} + T(\dot{S} + \operatorname{div}S\mathbf{v}_n) \\ & + \lambda_{ik}\frac{\partial \dot{u}_k}{\partial x_i} + (\mathbf{j} - \rho\mathbf{v}_n)\nabla\left(\varphi - \frac{v_s^2}{2}\right) - \rho\mathbf{v}_n\nabla\mu \\ & - v_{ni}\frac{\partial}{\partial x_k}\{\Pi_{ik} - \rho v_{si}v_{sk} + v_{si}p_k + v_{nk}p_i \\ & + [-\varepsilon + TS + (\mathbf{v}_n - \mathbf{v}_s)\mathbf{p} + \mu\rho]\delta_{ik}\} - \mu\operatorname{div}\mathbf{j},\end{aligned}$$

where we have neglected the term $v_{ni}\lambda_{kl}\partial w_{kl}/\partial x_i$, which is cubic in the "normal" motion of the crystal, and which corresponds to a linear theory with respect to the "rigid" type of crystal motion.

With the aid of simple transformations one can rewrite the last formula in the form

$$\begin{aligned}\dot{E} + \operatorname{div}\Big\{\Big(\frac{v_s^2}{2} + \mu\Big)\mathbf{j} + ST\mathbf{v}_n + \mathbf{v}_n(\mathbf{v}_n\mathbf{p}) + \mathbf{q} + \psi(\mathbf{j} - \rho\mathbf{v}_n) \\ + v_{nk}\pi_{ki} - \lambda_{ik}\dot{u}_k\Big\} = R + \pi_{ik}\frac{\partial v_{ni}}{\partial x_k} + \psi\operatorname{div}(\mathbf{j} - \rho\mathbf{v}_n) \\ + \frac{\mathbf{q}\nabla T}{T} + (v_{nk} - \dot{u}_k)\frac{\partial \lambda_{ik}}{\partial x_i},\end{aligned} \tag{11}$$

where the following notation has been introduced:

$$\begin{aligned}\Pi_{ik} = \rho v_{si}v_{sk} + v_{si}p_k + v_{nk}p_i + [-\varepsilon + TS \\ + (\mathbf{v}_n - \mathbf{v}_s)\mathbf{p} + \mu\rho]\delta_{ik} - \lambda_{ki} + \pi_{ik},\end{aligned}$$

$$\varphi = v_s^2/2 + \mu + \psi. \tag{12}$$

Comparing (11) with (10) we obtain an expression for the energy current

$$\mathbf{Q} = \left(\frac{v_s^2}{2} + \mu\right)\mathbf{j} + ST\mathbf{v}_n + \mathbf{v}_n(\mathbf{v}_n\mathbf{p}) + \mathbf{q} + \psi(\mathbf{j} - \rho\mathbf{v}_n) + v_{nk}\pi_{ki} - \lambda_{ik}\dot{u}_k \tag{13}$$

and for the dissipation function of the crystal

$$R = -\pi_{ik}\frac{\partial v_{ni}}{\partial x_k} - \psi\operatorname{div}(\mathbf{j} - \rho\mathbf{v}_n) - \frac{\mathbf{q}\nabla T}{T} - (v_{nk} - \dot{u}_k)\frac{\partial \lambda_{ik}}{\partial x_i}. \tag{14}$$

From the condition of positiveness of the dissipation function, with the Onsager symmetry principle taken into account, we obtain the following relations:

$$\begin{aligned}q_i &= -\varkappa_{ik}\frac{\partial T}{\partial x_k} - \alpha_{ik}\frac{\partial \lambda_{kl}}{\partial x_l}, \\ v_{ni} - \dot{u}_i &= -\alpha_{ik}\frac{\partial T}{\partial x_k} - \beta_{ik}\frac{\partial \lambda_{kl}}{\partial x_l}; \\ \pi_{ik} &= -\eta_{iklm}\frac{\partial v_{nl}}{\partial x_m} - \zeta_{ik}\operatorname{div}(\mathbf{j} - \rho\mathbf{v}_n), \\ \psi &= -\zeta_{ik}\frac{\partial v_{ni}}{\partial x_k} - \chi\operatorname{div}(\mathbf{j} - \rho\mathbf{v}_n),\end{aligned} \tag{15}$$

where κ, α, β, η, ξ, and χ are certain kinetic coefficients. The quantities κ have the meaning of the thermal conductivity tensor; η, ξ, and χ are the coefficients of viscosity; β and α are stipulated by the processes of diffusion and thermodiffusion of defects. We note that the obtained equations are also applicable to nonsuperfluid crystals in which the density of the superfluid component vanishes.

If we neglect the dissipative terms, then from Eq. (12) we obtain the following expression for the momentum current:

$$\Pi_{ik} = \rho v_{si} v_{sk} + v_{si} p_k + v_{nk} p_i + [-\varepsilon + TS + (\mathbf{v}_n - \mathbf{v}_s)\mathbf{p} + \mu\rho]\delta_{ik} - \lambda_{ki}.$$

The tensor π_{ik} is always symmetric, a result that follows from the law of conservation of angular momentum. Therefore, in general the quantities λ_{ik} are not symmetric; their antisymmetric part is given by

$$\lambda_{ik} - \lambda_{ki} = (v_{ni} - v_{si}) p_k - (v_{nk} - v_{sk}) p_i.$$

For not too large values of the velocities one can expand the momentum $\mathbf{p}$ in powers of $\mathbf{v}_n - \mathbf{v}_s$ and limit our attention to the linear terms:

$$p_i = \rho_{ik}^{(n)} (v_{nk} - v_{sk}).$$

Here the tensor $\rho_{ik}^{(n)}$ plays the role of the density of the normal component. It is symmetric since the quantities $[\rho_{ik}^{(n)}]^{-1}$ are equal to the second derivatives of the energy ϵ with respect to the components of the relative momentum $\mathbf{p}$. One can write the total momentum per unit volume in the form of the sum of the momenta associated with the normal and superfluid motions:

$$j_i = \rho_{ik}^{(s)} v_{sk} + \rho_{ik}^{(n)} v_{nk},$$

where $\rho_{ik}^{(S)} = \rho - \rho_{ik}^{(n)}$ is the density of the superfluid part.

With the aid of the derived equations let us consider the problem of the spectrum of the long wavelength crystal vibrations at zero temperature. Linearizing Eqs. (9) and neglecting the dissipative terms, we obtain the following system of equations:

$$\dot{\mathbf{v}}_s + \nabla\mu = 0, \quad \dot{\rho} + \operatorname{div}(\rho_{ik}^{(s)} v_{sk} + \rho_{ik}^{(n)} \dot{u}_k) = 0,$$
$$\partial j_i / \partial t = \partial\sigma_{ik} / \partial x_k, \tag{16}$$

where $\sigma_{ik} = \lambda_{ik} - [-\epsilon + \mu\rho]\delta_{ik}$. Assuming that all quantities depend on the coordinates and time by means of the factor $\exp(i\mathbf{k}\cdot\mathbf{r} - i\omega t)$, and eliminating $\mathbf{v}_s$ with the aid of the first of Eqs. (16), we find

$$\omega^2\rho' + i\omega^2 \rho_{ik}^{(n)} k_i u_k = \rho_{ik}^{(s)} k_i k_k \mu',$$
$$i\omega^2 \rho_{ik}^{(n)} u_k - \rho_{ik}^{(s)} k_k \mu' = \sigma_{ik} k_k, \tag{17}$$

where the primes denote the deviations of the quantities from their equilibrium values. It is convenient to carry out further calculations in terms of the variables μ and $u_{ik} = \frac{1}{2}(\partial u_i/\partial x_k + \partial u_k/\partial x_i)$ (in the linear approximation the energy depends on only the symmetric part of the quantities w_{ik}). From the relations between the differentials

$$d\sigma_{ik} = d\lambda_{ik} - \delta_{ik}\rho\, d\mu$$

in the linear approximation we obtain

$$\sigma_{ik} = \frac{\partial\lambda_{ik}}{\partial u_{lm}} u_{lm} + \frac{\partial\lambda_{ik}}{\partial\mu}\mu' - \delta_{ik}\rho\mu' = \frac{\partial\lambda_{ik}}{\partial u_{lm}} u_{lm} - \left(\frac{\partial\rho}{\partial u_{ik}} + \rho\delta_{ik}\right)\mu', \tag{18}$$

where the thermodynamical identity $d(\epsilon - \mu\rho) = \lambda_{ik} du_{ik} - \rho d\mu$ has been used. After substituting (18) into (17) we have

$$\rho\omega^2 u_i - \frac{\partial\lambda_{ik}}{\partial u_{lm}} k_l k_k u_m = i\rho_{ik} k_k \mu' - i\rho_{ik}^{(s)} (k_k\mu' + i\omega^2 u_k),$$
$$\omega^2 \frac{\partial\rho}{\partial\mu}\mu' = \rho_{ik}^{(s)} k_i (k_k\mu' + i\omega^2 u_k) - i\omega^2 \rho_{ik} k_i u_k, \tag{19}$$

where $\rho_{ik} = \partial\rho/\partial u_{ik} + \rho\delta_{ik}$.

The system of equations (19) determines four eigenfrequencies $\omega(\mathbf{k})$ for each value of the wave vector $\mathbf{k}$. The physical meaning of the corresponding eigenvibrations is especially simple in the case of a slightly anomalous crystal, i.e., when the quantities $\rho_{ik}^{(S)}$ and ρ_{ik} are small in comparison with the total density of the crystal (in an ordinary crystal $\partial\rho/\partial u_{ik} = -\rho\delta_{ik}$

If we neglect the right-hand part in the first of Eqs. (19), then we obtain an equation for the acoustic vibrations of a crystal with moduli of elasticity $\partial\lambda_{ik}/\partial u_{lm}$. Let $\omega_0(\mathbf{k})$ and $u_i^{(0)}$ be the frequency and unit polarization vector of one of these vibrations. Taking the discarded terms into account by using perturbation theory, we find the frequency with the linear terms in the small $\rho_{ik}^{(S)}$ and ρ_{ik} taken into account:

$$\omega(\mathbf{k}) = \omega_0(\mathbf{k}) + \frac{\omega_0(\mathbf{k})}{2\rho} u_i^{(0)} \rho_{ik}^{(s)} u_k^{(0)}. \tag{20}$$

The fourth solution of the system (19) corresponds, as we shall see, to a frequency $\omega \propto \rho^{(S)}$ which is low in comparison with ω_0. In this case one can consider $u_i = 0$. The second of Eqs. (19) then gives

$$\omega^2 = (\partial^2\varepsilon/\partial\rho^2)_{u_{ik}} \rho_{ik}^{(s)} k_i k_k, \tag{21}$$

where it has been taken into consideration that $\partial\mu/\partial\rho = (\partial^2\epsilon/\partial\rho^2)u_{ik}$.

Solutions with the dispersion law (21) represent oscillations of the crystal density with fixed lattice sites ($u_i = 0$). One can also show that these correspond to oscillations of the density of defectons. For this reason the velocity of the oscillations, calculated with the aid of formula (21), must coincide for the model considered in Sec. 2 with expression (6) for the velocity of the one-particle excitations.

We further note that in a crystal (which is not superfluid) containing Fermi zero-point defectons along with ordinary acoustic vibrations, vibrations of the zero sound type can exist which (for a small number of defectons) are also accompanied by oscillations of the crystal density for fixed lattice sites.

For simplicity we assumed everywhere above complete equilibrium between the crystal and the zero-point defectons. However, everything that was said also pertains to the quasiequilibrium states containing a given number of defectons which were mentioned at the end of Sec. 1. In addition, similar effects should be observed in solid solutions if they can exist at zero temperature. For example, it is quite possible that, just as in the case of liquids, a nonstratifying weak solid solution of He^3 in He^4 may exist at zero temperature. The He^3 atoms in such a solution would behave like a degenerate Fermi gas of impuritons.

Finally let us consider the question of to what extent, on the basis of existing experimental data, can one regard solid helium as a crystal containing zero-point defectons There are indications (for example, [9]) from the discrepancy between the density of helium measured by ordinary methods (measurements of the number of atoms) and with the aid of x-rays (measurements of the number of lattice sites). A linear term was observed in the heat capacity of He^3,[10] which could be explained as the defecton contribution (however, a similar result was also obtained in He^4, for which there is no reason provided a sufficiently large number of He^3 impurities were not present). On the other hand, there are significant discrepancies between the measured coefficient of the T^3 term in the heat capacity and the values calculated with the aid of the velocities of sound.[11] However, all of this data is not sufficiently reliable so it is impossible to say anything definite in answer to the posed question.[2)]

[2)] A. I. Shal'nikov has informed us of experiments involving the measurement of the velocity of motion of a small steel sphere in solid He^4 due to the influence of an external force. Investigation of the temperature dependence of the velocity of motion would enable one to obtain important information about the nature of the motion of defects and, in particular, would enable one to answer the question about the existence of zero-point defectons. Recently an upper limit on the velocity, $v < 10^{-6}$ cm/sec, was obtained for a sphere of radius 0.8 mm at a temperature $T \geqslant 0.5$ °K and pressure of 64 atm under the influence of a force of 50 mg.

[1] J. de Boer, Physica **14**, 139 (1948).

[2] F. W. de Wette and B. R. A. Nijboer, Phys. Lett. **18**, 19 (1965).

[3] L. H. Nosanow, Phys. Rev. **146**, 120 (1966).

[4] F. W. de Wette, L. H. Nosanow, and N. R. Werthamer, Phys. Rev. **162**, 824 (1967).

[5] L. D. Landau and E. M. Lifshitz, Statisticheskaya fizika (Statistical Physics), Nauka, M. 1964, Sec. 78 (English Transl. of an earlier edition, Addison-Wesley, 1958).

[6] I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **38**, 1569 (1960) [Sov. Phys.-JETP **11**, 1130 (1960)].

[7] I. M. Lifshitz, Zh. Eksp. Teor. Fiz. **44**, 1349 (1963) [Sov. Phys.-JETP **17**, 909 (1963)].

[8] I. M. Khalatnikov, Vvedenie v teoriyu sverkhtekuchesti (An Introduction to the Theory of Superfluidity), Nauka, M. 1965 (English Transl., Benjamin, 1965).

[9] R. L. Mills and A. F. Schuch, Phys. Rev. Lett. **6**, 263 (1961).

[10] E. C. Heltemes and C. A. Swenson, Phys. Rev. **128**, 1512 (1962).

[11] L. P. Lipschultz, Thesis, Cornell University (1966).

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