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NEGATIVE IONS IN SOLID HELIUM

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A self-consistent description of the structure of a negative ion in solid helium is presented. The mobility of negative ions (anions) in weak constant and variable external fields and also the first nonlinear corrections to the mobility, which appear upon increasing the intensity of the driving field, are calculated within the framework of a diffusion mechanism. The mobility of the anions is determined under conditions when the vacancies of solid helium lose their localization. The question of surface electron states on the vacuum-dielectric boundary is discussed, and also the question of the structure of these states above a helium film which has a solid dielectric as its support.

FREE electrons, introduced into solid helium, form in it, just like in liquid helium, spherical cavities which are rather large in comparison with the dimensions of interatomic distances. The self-consistent complex arising from the deformed region of helium and from the electron localized inside this region possesses many interesting properties. A description of some of these properties is given in the present article. In addition, as one of the varieties of interaction of free electrons with solids, the question of the electron surface states above a helium film, having a solid dielectric as its support, is discussed.

THE STRUCTURE OF THE NEGATIVE ION IN SOLID HELIUM

The fundamental parameters of the negative ion can be comparatively simply estimated within the framework of the model of a spherical potential well. In this model the total excess energy of the negative ion is written in the following manner:[1)]

$$W = W_e + W_p + W_{e-n} + W_\varepsilon,$$

$$W_e = \frac{\hbar^2 x^2}{2ma^2}, \quad W_p = \frac{4}{3}\pi a^3 p, \quad W_\varepsilon = -\frac{\varepsilon - 1}{2}\frac{e^2}{a}, \tag{1}$$

$$W_{e-n} = \frac{2\pi\hbar^2}{m} a_0 n f(x), \quad f(x) = \frac{\sin^2 x}{|\operatorname{ctg} x|(x - \sin x \cos x) + \sin^2 x};$$

$$\frac{\sin x}{x} = \frac{\hbar}{a\sqrt{2mU_0}} \quad U_0 = \frac{2\pi\hbar^2}{m} a_0 n. \tag{1a}$$

Here W_e denotes the kinetic energy of the electron in the ground state for a spherical well of radius a and height U_0. The value of the parameter x determines the position of the electron level in the well. A discrete level appears in the well for the first time when $x = \pi/2$. However, if the height of the barrier is very large, then $x \to \pi$. Thus, the self-consistent value of x which we are interested in is found somewhere within the limits $\pi/2 \leq x < \pi$. The relation between x and the barrier height U_0 and the ion's radius a is given by relation (1a), which is taken from [3]. As to the expression for U_0, it describes a hard-sphere type of interaction of a free electron with a medium having a particle number density equal to n (see, for example, [1]). In this definition a_0 denotes the amplitude for the scattering of an electron by an individual helium atom, m denotes the electron mass, and n denotes the number density of particles in one cubic centimeter of solid helium. W_p denotes the excess energy of the ion, resulting from its finite volume $\frac{4}{3}\pi a^3$ in the medium with an external pressure p; W_{e-n} denotes the excess energy associated with the penetration of the electron wave function into the depths of the solid helium; W_ϵ denotes the negative energy resulting from the polarization attraction of the solid helium towards the charged vacancy; ϵ is the dielectric constant of solid helium. One can use the Clausius-Mosotti formula with sufficient accuracy in order to estimate the difference $\epsilon - 1$; in units which are convenient for later use this relation is written as follows:

$$\varepsilon - 1 = 4\pi\frac{0.1245}{V_0}$$

where V_0 denotes the molar volume of solid helium at the given pressure.

Relations (1) and (1a) must be supplemented by the relation between the external pressure p and the number density n of particles of solid helium. The analytic dependence of n on p is not known. Therefore, certain numerical data, taken from experiment, will be utilized below. After this, by minimizing W with respect to a for given values of p or n, one can obtain an equation which determines the dependence of a on p or on n.

In practice it is convenient to carry out the required calculations in the following manner. From (1a) let us express the quantity a in terms of x and n:

$$a = \frac{1}{2\sqrt{a_0 n}}\frac{x}{\sin x} \tag{1b}$$

[1)] The relatively large dimensions of the negative ion in solid helium are usually associated with the smallness of the ratio $m/M \ll 1$, where m is the electron mass and M is the mass of the helium atom. Thus from [1,2] it follows that the ion's radius a is determined by the expression $a^5 \approx \hbar^2 x^2/4\pi mp$; for $p \approx 30$ atm we obtain $a \approx 10$Å; here p denotes the external pressure and x is a certain numerical parameter varying within the limits $\pi/2 \leqslant x < \pi$. However, in actual fact the problem of the calculation of the radius a contains one more small parameter, $a_0/a_1 < 1$, which influences the size of the ion (a_0 and a_1 denote the amplitudes for the scattering of an electron or a helium atom by an atom of helium; $a_0/a_1 \approx 1/5$). The self-consistent calculation of the ion's radius, carried out in this article with this additional smallness taken into account, leads to values of the radius a somewhat larger than those in [2].

and let us substitute this expression for a into W from (1). As a result the energy W turns out to depend only on x, n, V_0, and p, and moreover there is a unique relation between n, V_0, and p, so that the independent parameter is either p or n. Therefore, minimization of W with respect to x for a given value of n enables us to find the values of x corresponding to the extremum state of the ion. Specific values of x_{extr}, obtained from the equation $dW/dx|_n = 0$ by using numerical data concerning the molar volume and density of solid helium associated with certain specific pressures, are collected in the table. (The data concerning the density and molar volume is taken from [4]). Here the values of the radius a, following from Eq. (1b) for known values of n and x_{extr}, are also given (the quantity $a_0 = 6 \times 10^{-9}$ cm).

As a brief comment on this table, we point out the interesting behavior of the quantity x_{extr} with increasing pressure. If one moves in pressure from the side of liquid helium, then at first x_{extr} increases monotonically, which corresponds to the unimportance of the polarization correction W_ϵ to the total energy W. However, starting with negative ion radii $\lesssim 10$ Å the situation changes. In this range of external pressures, the equilibrium state of the ion begins to be determined by competition between the contributions to the total energy W coming from W_e and W_ϵ, but not W_e and W_p, as was the case at smaller pressures. Formally this shift in the competing factors corresponds to nonmonotonicity in the behavior of x_{extr}.

MOBILITY

The question of the mobility of ions in solid helium actually arose in connection with the first successful experiments in regard to the measurement of such a mobility, which were carried out by Keshishev, Mezhov-Deglin, and Shal'nikov.[5] It should be noted that the dynamical properties of the ions in solid helium differ qualitatively from the corresponding properties of the ions in liquid helium. If one can talk about the ions in liquid helium as about quasiparticles, for which the concepts of momentum, dispersion law, and so forth are well defined, then for ions in solid helium such concepts lose their meaning over practically the entire accessible range of temperatures and pressures. Here the coordinate of the ion plays the role of the dynamical characteristic. Under such conditions the mobility of the ions must be of a diffusion, either viscous or plastic character.

One of the possible mechanisms for the mobility of negative ions in solid helium was considered by the author[6] under the assumption that the displacement of the ion with respect to the lattice of solid helium is accomplished with the aid of specific diffusion processes which arise around the negative ion due to the influence of the external electric field. The results of the calculation in [6] lead to the following expression for the mobility μ (the driving field is assumed to be constant and sufficiently small):

$$\mu = eD\frac{c_s\omega_0}{kT}\frac{\pi\hbar^2}{ma^5}\frac{\Lambda}{|\lambda_0 - \lambda_1|},$$

$$\Lambda = \frac{2\beta_1}{j_0(\pi\beta_1)j_2(\pi\beta_1)}\frac{\partial}{\partial x}j_1(\pi\beta_1 x)\Big|_{x=1}\int_0^1 j_0(\pi x)j_1(\pi\beta_1 x)x^3\,dx, \quad (2)$$

$$\beta_1 = 1.4303.$$

p, atm	V_0, cm³/mole	n, 10^{22} cm⁻³	x_{extr}	a, Å
26	20.9	1.9	2.15	12.1
30	20.6	1.94	2.17	12.0
73	18.8	3.20	2.23	10.0
142	17.0	3.65	2.13	8.5
1064	12.5	4.85	1.88	5.7

Here ω_0 and D denote the volume and diffusion coefficient of the vacancies in solid helium, c_s denotes the equilibrium concentration of vacancies on the surface of the negative ion (for the determination of c_s, see below), a denotes the radius of the ion, and the j_l are spherical Bessel functions. The constant Λ is of the order of unity, and $|\lambda_0 - \lambda_1|$ denotes the difference between the ground and the first excited electronic levels in the spherical cavity of the negative ion. In order of magnitude this difference is given by $|\lambda_0 - \lambda_1| \approx \pi^2\hbar^2/2ma^2$.

In addition to the calculations from [6] it makes sense to determine the value of the concentration of vacancies on the surface of the ion more accurately. In the indicated article the quantity c_s was assumed to be equal to the volume concentration of vacancies, c_0. In actual fact, however, the distribution of vacancies near the negative ion turns out to be nonuniform. The causes of the nonuniformity are the polarization forces, which repel the vacancies from the surface of the ion into the depths of the solid helium. As is shown in the first section of the present article, the polarization forces (or the polarization energy W_ϵ from (1)) turn out to have a pronounced effect on the structure of the ion in solid helium. These forces change the concentration of vacancies in the neighborhood of the negative ion, and therefore they must be taken into consideration in calculating the mobility of the anions. With the polarization forces taken into account, the distribution of the vacancies near a negative ion is determined from the condition that the chemical potential of the vacancies be constant:

$$\frac{\alpha e^2}{r^4}\omega_0 + kT\ln c = kT\ln c_0,$$

from which

$$c(r) = c_0\exp\left(-\frac{\omega_0}{kT}\frac{\alpha e^2}{r^4}\right). \quad (3)$$

Here α denotes the polarizability of solid helium: $\alpha = (\epsilon - 1)/8\pi$, ω_0 denotes the volume of a single vacancy, and c_0 denotes the equilibrium concentration of vacancies far away from the ion. From Eq. (3) we find that the surface concentration of vacancies is determined by the following expression:

$$c_s \equiv c(a) = c_0\exp\left(-\frac{\omega_0}{kT}\frac{\alpha e^2}{a^4}\right). \quad (3a)$$

Substituting here the values $\omega_0 \approx 10^{-22}$ to 10^{-23} cm⁻³, $\alpha \approx 3 \times 10^{-3}$ and $a \approx 10^{-7}$ cm, one can easily verify that for $T \approx 2$°K the argument δ of the exponential is of the order of $\delta \gtrsim 1$, that is, the quantity c_s is appreciably smaller than the equilibrium concentration c_0.

The value of the mobility of the anions from Eq. (2) is qualitatively in agreement with the existing experimental data.[5] However, this experimental data is still too incomplete to reach any final conclusions about the uniqueness of the description proposed in [6]. Detailed measurements of the temperature dependence of the mobility and of its dependence on the intensity of the driving field are needed. In addition, the verification of other possible consequences of the diffusion mechanism of mobility might prove to be of great assistance in regard to the final interpretation. Some of these consequences are discussed below.

A. The Mobility of Negative Ions in a Variable Field

We recall that in liquid helium the high-frequency mobility of the ions contains certain relaxation resonances, and the determination of the position of these resonances enables one to judge the relaxation time and the effective mass of helium ions in liquid helium. In the simplest case the existence of relaxation maxima follows from the elementary equation of motion for the helium ion

$$m^*\left(\frac{dv}{dt}+\frac{v}{\tau}\right)=eE_0e^{i\omega t},$$

where m^* is the effective mass of the ion and τ denotes the relaxation time. From here we find the following expression for the imaginary part of the mobility

$$\operatorname{Im}\mu(\omega)=\mu(0)\frac{\omega\tau}{1+(\omega\tau)^2},\tag{4}$$

that is, the imaginary part $\operatorname{Im}\mu(\omega)$ has a maximum for $\omega\tau \sim 1$. The experimental determination of such maxima in liquid helium is already a solved problem (see, for example, [7]). Similar maxima in the frequency dependence of the mobility should also be observed for the ions in solid helium. Only their specific position is, of course, determined by other physical parameters.

The problem of the frequency dependence of the mobility of negative ions in solid helium is solved with the aid of the following equations (see [6]):

$$i\omega c=D\Delta c,\qquad c|_{r=a}=\frac{c_s\omega_0}{kT}p_n,$$
$$D\nabla c|_{r=a}=v_n(\theta),\qquad \mu(\omega)=v_n/E,$$
$$p_n=\overset{\mathrm{I}}{p}_{\mathrm{el}}+\overset{\mathrm{II}}{p}_{\mathrm{el}}+p_\sigma,$$
$$\overset{\mathrm{I}}{p}_{\mathrm{el}}=\frac{\pi\hbar^2}{ma^2(2\pi a)^{1/2}}\sum_l\frac{E_{0l}}{\lambda_0-\lambda_l}\frac{\partial}{\partial r}\Big|_{r=a}j_l\left(\frac{\pi\beta_l r}{a}\right)P_l(\cos\theta)e^{i\omega t},$$
$$\overset{\mathrm{II}}{p}_{\mathrm{el}}=\overset{0}{p}_{\mathrm{el}}\sum_l 2\pi s_l\xi_lP_l(\cos\theta),\quad p_\sigma=p_\sigma^0\sum_l[l(l+1)-2]\xi_lP_l(\cos\theta),$$
$$s_l=\frac{j_l'(\pi)}{j_l(\pi)}-\frac{j_0''(\pi)}{j_0'(\pi)},\qquad a(\theta)=a\left(1+\sum_l\xi_lP_l(\cos\theta)\right),\tag{5}$$

$P_l(\cos\theta)$ are the Legendre polynomials, $c(r,\theta,t)$ is the nonequilibrium concentration of vacancies, D is their diffusion coefficient, $E_0e^{i\omega t}$ is the variable electric field, and $p_{\mathrm{el}}^{\mathrm{I}}$ denotes the electron pressure due to the perturbation of the electron wave function by the external electric field. Here the E_{0l} denote the matrix elements of the potential of the perturbing field with respect to the electron eigenfunctions of the problem, the $j_l(\pi\beta_l r/a)$ are spherical Bessel functions with the coefficients β_l chosen from the condition $j_l(\pi\beta_l)=0$, and the λ_l are the electron levels of the unperturbed problem. It is necessary to insert additional pressures $p_{\mathrm{el}}^{\mathrm{I}}$ and p_σ on the surface of the ion into the problem, because in addition to the first harmonic the pressure $p_{\mathrm{el}}^{\mathrm{I}}$ contains still higher harmonics. These higher harmonics lead to a deformation of the ion, $\xi(\theta)=[a(\theta)-a]/a$, which in turn causes the appearance of additional pressures which impede the growth of the deformation. The pressures $p_{\mathrm{el}}^0=\pi\hbar^2/4ma^5$ and $p_\sigma^0=2\sigma/a$, which appear in the definitions of $p_{\mathrm{el}}^{\mathrm{II}}$ and p_σ, correspond to the spherically symmetric values of the electron and the Laplacian pressures.

Taking the specific form of the solution of the diffusion equation

$$c(r,\theta,t)=e^{i\omega t}\sum_l c_lh_l(\gamma r)P_l(\cos\theta),$$

into consideration, where $\gamma^2=i\omega/D$ and $h_l(\gamma r)$ are the spherical Bessel functions which decay exponentially at large distances from the center of the ion (in view of the fact that their argument is imaginary), and for the sake of brevity representing $p_{\mathrm{el}}^{\mathrm{I}}$ from (5) by the summation

$$p_{\mathrm{el}}{}^{\mathrm{I}}=\sum_l q_lP_l(\cos\theta),$$

we obtain the following expression for the diffusion rate of travel $v_n(\theta)$ of the ion boundary:

$$v_n(\theta)=\sum_l v_{nl}P_l(\cos\theta),$$
$$v_{nl}=\frac{\varkappa}{h_l(\gamma a)}[q_l+\xi_lQ_l]\frac{\partial h_l(\gamma r)}{\partial r}\Big|_{r=a},\quad \varkappa=\frac{c_s\omega_0}{kT}D,$$
$$Q_l=[p_\sigma{}^0(l^2+l-2)+p_{\mathrm{el}}{}^0\cdot 2\pi s_l]\tag{6}$$

The first harmonic of the pressure $p_{\mathrm{el}}^{\mathrm{I}}$ does not cause any deformation of the ion. Therefore one immediately obtains

$$v_{n1}=q_1\frac{\varkappa}{h_1(\gamma a)}\frac{\partial}{\partial r}h_1(\gamma r)|_{r=a},$$

$$\gamma^2=\frac{i\omega}{D},\qquad h_1(z)=-\frac{z+1}{z^2}e^{iz}.\tag{6a}$$

From here one can easily find

$$\operatorname{Im}\mu_1(\omega)=\mu_1(0)\frac{\delta}{(1+\delta)^2+\delta^2},\quad \delta^2=\frac{1}{2}\frac{\omega a^2}{D}.\tag{6b}$$

This relation is completely analogous to (4) and indicates the existence of a relaxation maximum at a frequency $\omega\approx 2D/a^2$.

In the remaining harmonics v_{nl} it is first necessary to determine the quantities ξ_l. For this purpose we write v_{nl} in the form $v_{nl}=a\dot{\xi}_l=ia\omega\xi_l$, after which from (6) we find

$$\xi_l=\frac{\varkappa q_l\ln' h_l(\gamma a)}{ia\omega-\varkappa Q_l\ln' h_l(\gamma a)};\quad \ln' h_l\equiv\frac{1}{h_l}\frac{\partial h_l}{\partial r}.\tag{7}$$

From the determination of ξ_l given by (7) it is seen that the diffusion displacements of higher order are small in comparison with ξ_1: $\xi_l/\xi_1\sim 1/l^2\ll 1$. Therefore, although the higher relaxation resonances exist in principle, their relative amplitude is small and apparently not sufficient for practical observations.

B. The Diffusion Mobility in the Presence of Strong Fields

By forgoing the assumption that the driving field is small, one can obtain one more generalization of the results of [6]. The limiting case of small fields actually corresponds to the fulfillment of the following three inequalities: 1) $V \ll D/a$ is the condition for it to be possible to describe the distribution of vacancies by the harmonic equation; 2) $eEa/W_0 \ll 1$ implies neglecting the influence of the ion's deformation on the mobility. 3) $\omega_0 p_{el}^I/kT \ll 1$ corresponds to a linear relation between the boundary values of the excess concentration of vacancies and the perturbed electron pressure p_{el}^I. In these inequalities V denotes the ion drift velocity, whose value can be estimated with the aid of (2) and the relation $V = \mu E$, E denotes the intensity of the driving field, and W_0 denotes the total self-energy of the ion; the value of the electron pressure p_{el}^I is determined in (5).

Estimates show that inequality 3) is violated first with increasing intensity of the external field.[2)] Thus, in order to describe the first effects which are nonlinear in the field, it is only necessary to define the boundary condition, relating the excess electron pressure and the concentration of vacancies on the surface of the ion, in the system of Eqs. (5) more accurately. In the general case this condition is written as follows:

$$c(r)|_{r=a} = c_s(e^{\nu} - 1), \quad \nu = \omega_0(p_{el}{}^{I} + p_{el}{}^{II} + p_{\sigma})/kT,$$

and in the range of fields $\nu \lesssim 1$ of interest to us

$$c|_{r=a} = c_s\left[\nu + \frac{\nu^2}{2} + \frac{\nu^3}{3!} + \ldots\right].$$

Now we notice that the displacement of the ion as a whole is only related to the angular harmonics of the external pressure, which are proportional to $\cos\theta$ (all the remaining harmonics deform the ion and in a constant driving field with time they are automatically cancelled by the additional pressures p_{el}^{II} and p_{σ}). Therefore, desiring to take into account the influence on the mobility in a constant field of the nonlinear terms in the expansion of c in powers of ν, it is necessary to choose in this expansion the powers of ν which contain $\cos\theta$. The first nonlinear term of such a type is $\nu^3/3!$, because $\cos^3\theta = \frac{3}{4}\cos\theta + \frac{1}{4}\cos 3\theta$. Taking account of this first nonlinear correction in the boundary condition for the excess concentration and determining the corresponding mobility, we find

$$\mu(E) = \mu(0)\left[1 + \frac{3}{4!}\left(\frac{\omega_0}{v_0}\frac{eEa}{kT}\right)^2\right],$$

where ω_0 and v_0 denote the volumes of the vacancy and of the negative ion. With regard to specific values of ω_0 and v_0, for temperatures $T \sim 1\,^{\circ}K$ the nonlinear effects should appear in fields $E \gtrsim 10^5$ V/cm.

CERTAIN QUANTUM CHARACTERISTICS OF THE MOBILITY

The determination of the mobility of ions in solid helium is of interest not only by itself. In the present case the problem excites increased interest in connection with the prospect of using charged particles to investigate different properties of lattice defects in solid helium. The rather general considerations of Andreev and I. Lifshitz[8] about the possible existence in solid helium of vacancies of quantum origin, having a nonvanishing concentration as $T \to 0$, are well known. In addition, even at rather high temperatures the helium vacancies must lose their localization, turning into "vacancy–ion" quasiparticles. All of these properties in the behavior of the vacancies have a direct relation to the mobility of the negative ions.

Upon lowering the temperature in the problem concerning the calculation of the mobility of the anions, it first becomes necessary to take account of the loss by the vacancies of their localization. According to the estimates of Pushkarov,[9] the mean free path of the vacancies becomes appreciably larger than the interatomic distances for temperatures $T < \frac{1}{8} T_D$, that is, somewhere in the region $T \lesssim 1°K$. Under such conditions the relation between the boundary values of the excess concentration of vacancies and the pressure on the surface of the ion still remains classical: $c|_{r=a} = c_s\omega_0 p_n/kT$. However, the spatial distribution of the vacancies and the corresponding vacancy–ion currents must now be determined, not with the aid of the diffusion equation but from the solution of the kinetic equation for the distribution function f of the vacancies. In the limiting case $l/a \gg 1$ (l denotes the mean free path of the vacancies and a denotes the radius of the ion) the kinetic equation for the function f can be written without the collision integral:

$$v_r\frac{\partial f}{\partial r} + \frac{v_\theta}{r}\frac{\partial f}{\partial \theta} + \left(\frac{v_\theta{}^2}{2} - \frac{1}{M}\frac{\partial U}{\partial r}\right)\frac{\partial f}{\partial v_r} - \frac{v_\theta v_r}{r}\frac{\partial f}{\partial v_\theta} = 0. \qquad (8)$$

Here v_r and v_θ are the components of the vacancy velocity in the spherical coordinate system whose origin coincides with the center of the ion, and the polar axes of the coordinate space and of the velocity space are chosen to be collinear; U(r) denotes the potential energy of the vacancies in the field of the polarization forces; M denotes the effective mass of the vacancy-ion.

Equation (8) is solved with the aid of the method of characteristics and in the general case the solution can be written in the form of an arbitrary function of the total energy, the angular momentum of the vacancy-ion, and some angle θ:

$$f = f\left[\frac{M}{2}(v_r{}^2 + v_\theta{}^2) + U(r); Mv_\theta r; \theta - rv_\theta\int_a^r \frac{dr}{r^2 v_r}\right]. \qquad (9)$$

In the absence of a perturbing electric field the distribution of the vacancies around the ion is spherically symmetric and must go over into a Maxwellian distribution at large distances from the ion. These requirements uniquely determine the specific form of the arbi-

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[2)] Let us compare, for example, the left-hand sides of inequalities 2) and 3). Taking the estimate for $p_{el}^I \sim eEa/v_0$ into account, where v_0 denotes the volume of the negative ion, and also the numerical values $\omega_0 \approx 10^{-22}$ to 10^{-23} cm^3, $v_0 \approx 10^{-20}$ cm^3, we find that for $T \approx 1°K$ and $W_0 \sim 10^3$ to 10^4 °K

$$\frac{eEa}{W_0}\frac{kT}{\omega_0 p_{el}{}^{I}} = \frac{kT}{W_0}\frac{v_0}{\omega_0} \ll 1,$$

that is, the left-hand side of inequality 3) is larger than the left-hand side of inequality 2).

trary function from (9) for the stationary distribution $f_0(r, v_r, v_\theta)$:

$$f_0 = c_0 \left(\frac{M}{2\pi kT}\right)^{3/2} \exp\left[-\frac{M(v_r^2+v_\theta^2)/2+U(r)}{kT}\right] \qquad (9a)$$

where c_0 denotes the equilibrium concentration of vacancies far away from the ion. Now calculating the local density of the vacancies by the usual method

$$c(r) = 2\pi \int f_0(r, v_r, v_\theta)\, dv_r v_\theta\, dv_\theta,$$

with the aid of Eq. (9a) we obtain

$$c(r) = c_0 e^{-U(r)/kT}.$$

This distribution turns out to be in perfect agreement with the distribution (3), (3a) obtained above, that is, the surface concentration of vacancies, c_s, which enters into the determination of the anion's mobility, is not sensitive to the nature of the motion of the vacancies in solid helium.

Before going on to the case involving an external field, it is still necessary to discuss the question of the behavior of vacancies whose trajectories either begin or end on the surface of an ion. The basic property of the ion's surface, which is essential for the entire problem about diffusion mobility, is its ability to absorb and emit vacancies. Therefore, in solving the kinetic equation it is natural to assume that all of the vacancies, falling onto the ion's surface from the volume of the crystal, are absorbed by this surface. In the equilibrium case the flux of particles, impinging on a given element of the ion's surface, is given by

$$j_n = \int_0^\infty v_z dv_z \int_{-\infty}^{+\infty} dv_x \int_{-\infty}^{+\infty} dv_y f_0(a, \mathbf{v}) = \frac{c_s v_T}{2\sqrt{\pi}}, \quad v_T = \sqrt{\frac{2kT}{M}}. \qquad (10)$$

The z axis in the cited integral is chosen in the direction of the inward normal to a given point on the surface of the sphere, $f_0(a, \mathbf{v})$ is taken from Eq. (9a), and v_T denotes the thermal velocity of the vacancy-ions.

Assuming the possibility of absorbing the currents (10) on the surface of the ion, it is necessary to postulate that in the equilibrium situation there simultaneously occurs an emission of vacancies by the ion surface in the volume of the crystal with an output which is equal to the value of the current from expression (10). It is natural to assume the velocity distribution of these vacancies to be Maxwellian, with a characteristic temperature equal to the temperature of the crystal. This assumption is quite reasonable, since a source of vacancies on the surface of an ion has a fluctuating thermal origin and may impart only thermal velocities to the vacancies which are leaving the surface.

The considerations discussed here enable us to describe relatively simply the situation when an external electric field is switched on. In this connection the distribution of the vacancies incident on the ion and also the corresponding currents remain the same as before, given by expressions (9a) and (10). As to the distribution function of the vacancies which are leaving the ion surface, it acquires a small correction, having a Maxwellian shape in velocity space (here considerations about the nature of the emission of vacancies by the ion surface are utilized; a weak external electric field $eEa/kT \ll 1$ should not influence the emission mechanism, operating under equilibrium conditions) and depending on the angular variables in coordinate space. The angular dependence of the correction is selected to be such that, on the one hand, it would allow the general solution (9) and, on the other hand, it would permit one to satisfy the boundary condition

$$\delta c = \frac{c_s \omega_0}{kT} p_{\text{el}}^{\text{I}}; \qquad (10')$$

δc denotes the nonequilibrium concentration of vacancies on the surface of the ion, and p_{el}^{I} denotes the perturbing electron pressure. For simplicity the pressure p_{el}^{I} contains only one angular harmonic $\propto \cos\theta$. Consequently the total distribution function has the following form:

$$f(r, \theta, \mathbf{v}) = \begin{cases} f_0(r, \mathbf{v}), & v_r < 0, \\ f_0(r, \mathbf{v}) \left[1 + \text{const}\cdot\cos\left(\theta - r v_\theta \int_a \frac{dr}{r^2 v_r}\right)\right], & v_r > 0 \end{cases} \qquad (11)$$

$f_0(\mathbf{r}, \mathbf{v})$ is obtained from expression (9a).

The value of the constant in this distribution is found with the aid of the indicated boundary condition, that is, from the equation

$$2\pi \int [f(a, \theta, \mathbf{v}) - f_0(a, \mathbf{v})] v_\theta dv_\theta dv_r = \frac{c_s \omega_0}{kT} p_{\text{el}}^0 \frac{eEa}{W_0} \cos\theta.$$

Here the perturbing electron pressure is represented by the estimated expression

$$p_{\text{el}}^{\text{I}} \approx p_{\text{el}}^0 \frac{eEa}{W_0} \cos\theta,$$

where p_{el}^0 denotes the spherically symmetric electron pressure: $p_{\text{el}}^0 \approx W_0/v_0$, W_0 is the self-energy of the anion, and v_0 is the volume of the ion. Now using the distribution function from (11) to calculate the radial nonequilibrium current on the surface of the ion and relating the value of this current with the velocity of motion of a given element of the ion's surface, we obtain the following expression for the velocity of motion of the ion as a whole:

$$\delta j_n |_{r=a} = V \cos\theta,$$

$$V = c_s \frac{eEa}{kT} \frac{\omega_0}{v_0} \sqrt{\frac{kT}{2\pi M}}, \quad \mu = \frac{V}{E}. \qquad (12)$$

This result for the velocity V differs qualitatively from the diffusion expression (2) and has a simple physical meaning. Under conditions when the vacancy-ions are free, that is, they arrive at and leave the ion surface without collisions, the velocity of displacement of the ion as a whole is limited by only two factors: the concentration of nonequilibrium vacancies on the surface of the ion, which is estimated to be

$$\delta c \approx c_s \frac{eEa}{kT} \frac{\omega_0}{v_0},$$

and the velocity of escape (or arrival) of the vacancies from the surface, that is, the thermal velocity of the vacancies $v_T = \sqrt{2kT/M}$. Therefore $V \approx v_T \delta c$, which is also obtained in (12).

Upon a further reduction of the temperature, the classical boundary condition (10′) loses meaning. However, the specific range of temperatures, where degeneracy of the vacancy-ion gas begins, is still unclear.

Therefore, a discussion of the question of the modification of this boundary condition is not given in the present article.

THE INTERACTION OF ELECTRONS WITH THE FREE SURFACE OF A SOLID DIELECTRIC. SURFACE ELECTRONS ABOVE A HELIUM FILM

Surface electron states exist on the free boundary of a solid dielectric, just like on a liquid-vapor boundary; the concept of these states is introduced independently in articles [10, 11]. The difference between the cases of solid and liquid boundaries consists only in the numerical difference of the discontinuities of the dielectric constant, as a consequence of which the localization of the electrons above a solid dielectric turns out to be much stronger than above a liquid. The presence of surface states above liquid helium was recently confirmed by the experiments of Williams, Crandall, and Willis.[12] Therefore, there is no doubt at all about the existence of such states above a solid surface. However, by themselves the surface states above a solid dielectric are apparently of little interest. It is much more attractive to utilize the strong interaction between the electron and a solid dielectric in order to increase the effectiveness of the interaction between the electron and a liquid dielectric. The reasons for the appearance of such a problem require explanations.

The surface electrons above a liquid boundary can be utilized in order to investigate the spectrum of thermal surface excitations in liquid helium, where there is practically no information about this spectrum in the region of large values of the wavenumbers of the thermal excitations. However, as is shown in [13], the natural surface electrons interact weakly with the surface vibrations of liquid helium, and therefore are not very suitable for the indicated purpose. The situation is improved considerably if an external field is enlisted in forming the electron-phonon interaction. The simplest possibility of this type is the inclusion of an additional electric field $E_\perp$, pressing the free electron from the side of the gaseous phase toward the liquid-vapor surface. This possibility is investigated by the author in [13]. But the field $E_\perp$ cannot be very large, since with increasing $E_\perp$ the probability of breakdown phenomena in the gaseous phase rapidly increases. Therefore, from the point of view of strengthening the electron-phonon interaction for surface electrons one can advance much further by studying the surface electrons above a helium film (in connection with this, also see [14]). Here the additional image force, acting on the charge from the side of the dielectric backing, plays the role of an external field.

Let us consider a helium film of thickness d, situated on a planar dielectric backing having a typical value of the dielectric constant $\epsilon \approx 2$ to 5. Let a free electron be located above this film; thanks to the attractive image forces acting on it, and thanks to the repulsive potential that prevents the electron from penetrating into the liquid film, the electron is localized above the surface of the film. The wave equation describing the state of the electron in such a situation, taking account of the existing small deviations of the shape of the free surface of the film from its equilibrium planar shape, appears in the following form (the z axis is directed along the normal to the interface, and the gaseous phase corresponds to the region $z - d \geq 0$; for simplicity the perturbation $\delta(x)$ of the shape of the surface is assumed to be one-dimensional):

$$\Delta\psi + \frac{2m}{\hbar^2}[\lambda - W(z,\delta)]\psi = 0,$$
$$\psi|_{z=d-\delta(x)} = 0, \quad \psi|_{z\to+\infty} \to 0, \tag{13}$$

Δ is the two-dimensional Laplacian operator, m is the mass of a free electron, λ is the eigenvalue of the equation, and $W(z, \delta)$ is the potential energy of the electron in the field of the image forces associated with the presence of a deformation of the free surface of the helium film. In the case when no such deformation is present, one can determine the value of the potential $W_0(z)$ for an electron, located in the gaseous phase above two planar boundaries dividing the media with dielectric constants ϵ_1 (for the gaseous phase), ϵ_2 (for the liquid phase), and ϵ_3 (for the backing), by using the method of successive images:

$$W_0(z) = \frac{\alpha_0}{z-d} + \frac{\alpha_1}{z} + \alpha_1 \sum_{n=1} \frac{q^n}{z+nd},$$
$$\alpha_0 = \frac{e^2}{2\varepsilon_1}\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+\varepsilon_2} < 0, \quad q = \frac{\varepsilon_2-\varepsilon_1}{\varepsilon_2+\varepsilon_3}\frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3} < 0,$$
$$\alpha_1 = \frac{e^2}{2\varepsilon_1}\left(\frac{2\varepsilon_1}{\varepsilon_1+\varepsilon_2}\right)^2 \frac{\varepsilon_2-\varepsilon_3}{\varepsilon_2+\varepsilon_3} < 0, \varepsilon_1 < \varepsilon_2 < \varepsilon_3, \tag{14}$$

where e is the charge of a free electron and d is the thickness of the helium film. One can approximately obtain from (14) the expression for the potential $W(z, \delta)$ above the perturbed surface of the film, by having replaced the thickness d in W_0 by its variable value $d - \delta(x)$. Such an approximation is applicable for $W(z, \delta)$ if the average distance from the electron to the liquid-vapor surface is smaller than the characteristic scales of variation of δ along x.

Let us make the following change of variables in (13): $\xi = z + \delta$, $x = x$, which enables us to get rid of the perturbation δ in the boundary conditions:

$$\frac{\partial^2\psi}{\partial\xi^2} + \frac{\partial^2\psi}{\partial x^2} + \frac{2m}{\hbar^2}\left[\lambda - \frac{\alpha_0}{\xi-d} - \frac{\alpha_1}{\xi-\delta} - \alpha_1\sum_{n=1}^{\infty}\frac{q^n}{\xi-\delta+n(d-\delta)}\right]\psi$$
$$= (\delta')^2\frac{\partial^2\psi}{\partial\xi^2} - 2\delta'\frac{\partial^2\psi}{\partial x\partial\xi} + \delta''\frac{\partial\psi}{\partial\xi},$$
$$\psi|_{\xi=d} = 0, \quad \psi|_{\xi\to+\infty} \to 0, \quad \delta' \equiv d\delta/dx. \tag{15}$$

From the derived equation it is clear that in the absence of the backing, that is, for $\alpha_1 = 0$, there is no perturbation, which is linear in δ, present in the problem. In fact, formally the right-hand side of Eq. (15), where the perturbing terms which are not related to the backing are collected, has linear-in-δ terms which are proportional to δ' and δ''. However, one can show that in the linear approximation of perturbation theory, these terms do not operate.[3] However, if $\alpha_1 \neq 0$ then a term

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[3] The solution of the unperturbed equation (15) has the form $\psi = f_n(\xi)\, e^{ikx}$, where $f_n(\xi)$ satisfies the boundary conditions $f_n(d) = f_n(\infty) = 0$. In the process of interaction with thermal vibrations of the surface, the quantum number n of the electron's wave function is fixed and equal to its minimum value n = 1, and the interaction only changes the value of the electron's wave vector k along the surface. Noticing this, let us calcu-

which is linear in δ appears as a perturbation, and the major portion of this term has the form

$$W_d \approx \frac{\alpha_1}{\xi^2}\delta \approx \frac{\alpha_1}{(d+\gamma^{-1})^2}\delta.$$

Here γ^{-1} denotes the average distance from the electron to the free surface of the film; for $d \gg \gamma^{-1}$ the quantity γ is of the order of magnitude cited in [11], $\gamma_\infty^{-1} \approx 5 \times 10^{-7}$ cm. Comparing the value of W_d with the linear perturbation $W_{E_\perp}$, which arises in the problem in the presence of the external pressing field $E_\perp$ ($W_{E_\perp} = eE_\perp\delta$[13]), one can conclude that for $d \approx 10^{-5}$ cm the effect of the backing is equivalent to a field $E_\perp \approx 300$ V/cm. With a reduction of the film thickness to a value $d \approx 10^{-6}$ cm, this effect of the backing on the interaction of the electrons with the surface waves is increased again by an order of magnitude.

Now let us go on to a more detailed investigation of Eq. (15).

A. The degree of localization. It has not been possible to solve the unperturbed wave equation (15) exactly. Therefore, in order to determine the degree of localization of the electron above the helium film it is necessary to use a variational approach. Assuming that the wave function of the electron's ground state has the form

$$f_1(\xi) = 2\gamma^{3/2}(\xi - d)e^{-\gamma(\xi-d)}, \quad \int_d^\infty f_1^2(\xi)\,d\xi = 1, \tag{16}$$

we find the minimum of the integral

$$J(\gamma) = \int_d^\infty \left[(\nabla f)^2 + \frac{2m}{\hbar^2} W_0(\xi) f^2(\xi) \right] d\xi.$$

Here $W_0(\xi)$ is the total potential energy of the electron near the film. As a result we have

$$J(\gamma) = \gamma^2 + \frac{2m}{\hbar^2}\gamma \left\{ -|\alpha_0| - 4|\alpha_1|\gamma^2 d^2 \left[\frac{1}{4\gamma^2 d^2} - \frac{1}{2\gamma d} - e^{2\gamma d}\mathrm{Ei}(-2\gamma d) \right] \right\},$$

where $|\alpha_0|$ and $|\alpha_1|$ are given in (14), and $\mathrm{Ei}(-\xi)$ is the exponential integral function. Minimizing $J(\gamma)$ with respect to γ in the case $\gamma d > 1$ of practical interest, we obtain the following equation for the determination of γ:

$$\gamma = \frac{m}{\hbar^2}\left(|\alpha_0| + \frac{3|\alpha_1|}{\gamma^2 d^2} \right). \tag{17}$$

For sufficiently large values of the film thickness d, the approximate solution (17) can be written as follows:

$$\gamma \approx \gamma_\infty(1 + \Delta), \quad \gamma_\infty = m\hbar^{-2}|\alpha_0|,$$
$$\Delta = 3\frac{m}{\hbar^2}\frac{|\alpha_1|}{\gamma_\infty{}^3 d^2} < 1. \tag{17a}$$

Here γ_∞ denotes the value of γ corresponding to $d \to \infty$. The value of γ_∞, obtained by the variational method, coincides with the exact value of γ_∞ from [11]. The determination of γ from (17a) is valid as long as $\Delta < 1$. For the specific values of the dielectric constants $\epsilon_1 \approx 1$, $\epsilon_2 \approx 1.06$, and $\epsilon_3 \approx 2$ to 4, one can use formula (17a) in the range of thicknesses $d \gtrsim 5 \times 10^{-6}$ cm without violating the condition $\Delta < 1$.

B. Mobility. The scheme of calculation of the mobility of electrons above a helium film is completely analogous to the scheme used in [13]. Only the specific form of the interaction of the electron with the surface phonons

$$W_{E_\perp} = eE_\perp\delta \to W_d = \alpha_1\delta / \xi^2$$

and the dispersion law of the surface waves are changed; the dispersion law now has the form

$$\omega^2 = (\sigma/\rho)q^3 \,\mathrm{th}\, qd, \tag{18}$$

where ρ is the density of liquid helium, σ is the coefficient of surface tension on the liquid-vapor boundary, and q is the wave vector of the phonon.

The corresponding mobility of the surface electrons, calculated under the assumption $2\bar{k}d > 1$, where $\bar{k}$ is the thermal value of the wave number of the electrons, is written down as follows:

$$\mu = \frac{4e\hbar\sigma d^4}{\alpha_1^2 m}\left(1 + \frac{3}{16}\frac{\hbar}{d}\sqrt{\frac{\pi}{2k_B T m}} \right). \tag{19}$$

Here k_B is the Boltzmann constant. Formula (19) is accurate as long as the second term inside the circular brackets is smaller than unity. At temperatures $T \approx 1$°K this condition is satisfied for thicknesses $d \gtrsim 5 \times 10^{-6}$ cm. Assuming $\sigma = 0.36$ erg/cm^2, $T \approx 1$°K, $d \approx 10^{-5}$ to 5×10^{-6} cm, and taking into account that $\alpha_1 \approx \frac{1}{3}e^2$ for the values of the dielectric constants indicated above, we obtain the following estimate for the mobility in CGS units: $\mu \sim 10^6$ to 10^8.

CONCLUSION

Now let us summarize the results. The results discussed above show that the model of a negative ion in the form of an empty bubble of quasi-macroscopic dimensions together with the assumption about the diffusion character of the anion's mobility permits us to give definite answers to practically all of the questions which arise in connection with the experimental investigation of the properties of negative ions. In this connection the parameters of the problem (the ion's radius a, the diffusion coefficient D of the vacancies, and the equilibrium concentration c_0 of vacancies) can be determined by several independent methods, which supplement and check each other. Thus, a numerical relation between a, D, and c_0 can be obtained from data about the mobility of anions in a weak constant field. The measurement of the characteristic frequency of the first relaxation resonance gives one more relation between a and D. Finally, optical absorption or elastic resonances give direct information about the radius a of the ion. Incidentally, experimental confirmation of the correctness of the characteristic dimensions of the anion's radius, $a \approx 10^{-7}$ cm, is apparently unnecessary, since this quantity is determined rather accurately the-

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late the value of the matrix element of the transition between electron states with different values of k for the perturbations indicated in the main text. For example,

$$\int e^{i(k-k_1)x}\delta''(x)\,dx \int_d^\infty f_1(\xi)\frac{df_1}{d\xi}\,d\xi = \frac{1}{2}[f_1^2(\infty) - f_1^2(d)] \int e^{i(k-k_1)x}\delta''\,dx.$$

By virtue of the boundary conditions for $f_1(\xi)$, the square bracket vanishes, and with it this entire matrix element. A similar situation also occurs for the perturbation involving δ'.

oretically and, most importantly, this quantity depends weakly on the external parameters of the problem (pressure, temperature).

The situation is somewhat more complicated with regard to the interpretation of the experimental data concerning the mobility of positive ions. With definiteness one can only state that the displacement of positive ions, corresponding to charged particles with a mass of the order of helium atoms and therefore interacting with the lattice primarily in a polarization way, is not at all related to the presence of vacancies in the helium lattice. In fact, estimates of the degree of inhomogeneity of the distribution of vacancies around a charged particle, carried out for a negative ion (formula (3)), are also quite suitable for positive ions with the only difference being that now we will be interested in the concentration of vacancies, not at distances of 10^{-7} cm as was true in the case of anions, but at distances of the order of interatomic distances. Substituting the value $a \approx 3 \times 10^{-8}$ cm into the relation (3a), one can easily verify that the probability for the approach of a vacancy to within an interatomic distance of a positively charged particle is insignificantly small. Therefore, in contrast to the anions, the mobility of the cations does not have any clear connection with the imperfection of the helium lattice. Possible mechanisms for the mobility of the cations will be discussed in detail in a separate article.

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