

to include β_1 and β_2 in order to prove that

$$C^+(m_s)C(m_s) + \sum_{k', m_{s'}} C^{'+}(m_{s'})C'(m_{s'}) = 1.$$

The differential cross section for elastic scattering is

$$d\sigma_{m_{s'}, m_s} = \frac{L^3 K}{ck} \sum_{k'} \frac{\partial}{\partial l} C^{'+}(m_{s'})C'(m_{s'}) = |f(m_s, m_{s'}, \theta', \varphi')|^2 d\Omega'. \quad (8)$$

If the incident Dirac particle is directed along the z axis ($\cos \theta = 1$), the scattering amplitude is given by

$$f(m_s, m_{s'}, \theta', \varphi') = \begin{cases} -\frac{1}{k} \sum_{l=0}^{\infty} \left[(l+1) \frac{c_{1l}}{1+ic_{1l}} + l \frac{c_{2l}}{1+ic_{2l}} \right] P_l(\cos \theta') & \text{when } m_{s'} = m_s, \\ -\frac{1}{k} \sum_{l=0}^{\infty} \left[\frac{c_{1l}}{1+ic_{1l}} - \frac{c_{2l}}{1+ic_{2l}} \right] 2m_{s'} e^{-2i\varphi' m_{s'}} P_l^1(\cos \theta') & \text{when } m_{s'} = -m_s. \end{cases} \quad (9)$$

The total effective elastic scattering cross section is

$$\sigma = \frac{1}{2} \sum_{m_{s'}, m_s} \oint |f(m_s, m_{s'}, \theta', \varphi')|^2 d\Omega' = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} \left[(l+1) \frac{c_{1l}^2}{1+c_{1l}^2} + l \frac{c_{2l}^2}{1+c_{2l}^2} \right] = \frac{4\pi}{k^2} \sum_{l=0}^{\infty} [(l+1) \sin^2 \eta_l^{(1)} + l \sin^2 \eta_l^{(2)}]. \quad (10)$$

¹A. A. Sokolov and B. K. Kerimov, *Nuovo cimento* **5**, 921 (1957).

Translated by E. J. Saletan

17

ON THE DESTRUCTION AND THE ONSET OF SUPERCONDUCTIVITY IN A MAGNETIC FIELD

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Transition from the superconducting state to the normal and vice versa in the presence of an external magnetic field is considered. Critical magnetic field strengths H_C , H_{C1} and H_{C2} , which correspond to equilibrium transition and to the boundaries of the supercooled and superheated regions respectively, are computed. Cases of small samples and of bulk metals are considered.

THE destruction and the onset of superconductivity in the presence of an external magnetic field proceed in entirely different ways, depending on the dimensions, shape and internal condition of the

sample (its purity, its homogeneity, etc.). In the simplest case of a bulk sample of cylindrical shape subjected to a field parallel to the axis of the cylinder, assuming that no intermediate state occurs,

the equilibrium transition from the superconducting to the normal state (and vice versa) takes place in a field given by

$$H_{cb} = \sqrt{8\pi(F_{n0} - F_{s0})},$$

Here F_{n0} and F_{s0} are the free energy densities of the normal and superconducting phases. (The change of volume associated with the transition is neglected here and throughout the paper.)

Experimentally, however, supercooling of the normal phase can occur and in fact, is often observed, so that its transition to the superconducting phase occurs in fields $H_1 < H_{cb}$. Similarly, it is also found that the superconducting phase can experience a superheating, in which case it returns to the normal phase only for $H_2 > H_{cb}$. The values of H_1 and H_2 can not be calculated. They depend on many factors and, generally speaking, differ from experiment to experiment. Nevertheless, as was shown in previous work,^{1,2} there exist certain critical fields, H_{c1} and H_{c2} , which serve as boundaries of the supercooling and superheating regions, such that $H_1 \geq H_{c1}$ and $H_2 \leq H_{c2}$ always. Thus the quantities H_{c1} and H_{c2} determine the maximum extent of the hysteresis loop, and their calculation is obviously of interest, especially since in certain cases H_{c1} has been reached experimentally.²

In small samples, i.e., when the smallest characteristic dimension of the sample, L , is commensurate with the penetration depth of a weak magnetic field into the metal (we shall denote this penetration depth by δ_0), the supercooling and superheating, generally speaking, are even more strongly pronounced than in the bulk metal. This is apparently due to the difficulty of producing sufficiently small nuclei. Indeed, in accordance with Ref. 1, the boundary between the normal and superconducting phases in bulk becomes blurred and has a width of the order of δ_0/κ . For pure superconductors, $\kappa \sim 0.1$ and, thus, it should be difficult to form nuclei in samples of dimensions on the order of $\delta_0/\kappa \sim 10\delta_0 \sim 10^{-4}$ cm.*

The circumstances noted above also hinder the formation of an intermediate state in small samples, to say nothing of the fact, that in this case, because of the increase of the surface energy density, stratification of the sample would become less advantageous even if the boundary between the

phases were sharp. Because of this, one naturally expects more pronounced hysteresis in samples of small dimensions, and in such samples the attainment of the corresponding critical values H_{c1} and H_{c2} should be relatively easy. On the other hand, for very small samples, smaller than a certain dimension, $L_c \sim \delta_0$, which depends on the shape of the sample, the transition from the superconducting state to the normal state (and vice versa) is a second order transition¹ and, consequently, superheating and supercooling are impossible (in other words, in this case $H_{c1} = H_{c2} = H_c$, where H_c is the critical field for the equilibrium transition). Hence, it is clear that supercooling and superheating are pronounced only in some "average" domain of sample sizes.

Various aspects of this problem have already been considered in the literature.¹⁻⁷ However, because of the publication of some new results⁸ of an investigation of the destruction of superconductivity in cadmium, this series of questions has again attracted attention. The corresponding results, which relate to the values of H_{c1} , H_{c2} and H_c in different cases, will be presented below.

1. Let us first write down the general thermodynamic relations for superconductors. The free energy density of a superconductor, according to Ref. 1, is given by

$$F_{sH} = F_{s0} + \frac{H^2}{8\pi} + \frac{1}{2M} \left| -i\hbar \nabla \Psi - \frac{e}{c} \mathbf{A} \Psi \right|^2, \quad (1.1)$$

$$F_{s0} = F_{n0} + \alpha |\Psi|^2 + \frac{\beta}{2} |\Psi|^4, \quad (1.2)$$

where $F_{n0}(T)$ is the free energy in the normal state in the absence of the magnetic field H ; the function Ψ plays the role of the parameter η , which enters into the theory of second-order phase transitions, and α , β , and M are certain coefficients. It is possible, in principle, to use here an expression different from Eq. (1.2) to represent $F_{s0}(|\Psi|^2)$, but for definiteness, we shall use only the expression shown above, bearing in mind certain statements made in Refs. 9 and 10.

From the condition that the total free energy must be a minimum, these equations result:

$$\frac{1}{2M} \left(-i\hbar \nabla - \frac{e}{c} \mathbf{A} \right)^2 \Psi + \alpha \Psi + \beta |\Psi|^2 \Psi = 0; \quad (1.3)$$

$$-\text{curl curl } \mathbf{A} = \Delta \mathbf{A} = -\frac{4\pi}{c} \mathbf{j}_s,$$

$$\mathbf{j}_s = -\frac{ie\hbar}{2M} (\Psi^* \nabla \Psi - \Psi \nabla \Psi^*) - \frac{e^2}{Mc} \mathbf{A} |\Psi|^2, \quad (1.4)$$

where it is assumed that $\text{div } \mathbf{A} = 0$.

In considering a superconductor in a uniform external field, H_0 , the role of the thermodynamic

*Here we assume (as is usually done) that far from the critical temperature, T_c , $\delta_0 \sim 10^{-5}$ cm (near T_c the values of δ_0 and of δ_0/κ are still larger). For samples with dimensions $L < \delta_0/\kappa$, the formation of a transition region between phases is still possible in principle, but involves an increase in the corresponding surface energy.

potential which has a minimum at equilibrium is not played by $\int F_{sH} dV$, but rather by another quantity, which we shall call $\Phi(T, H_0)$. This difference, which is immaterial from the standpoint of deriving Eqs. (1.3) and (1.4), is related to the existence of an "energy of interaction" between the magnetic moment of the superconductor and the external magnetic field. The expression for Φ can be obtained by means of an analogy with the theory of magnetic materials, where that part of Φ which is a function of H_0 , is determined by the expression $-\int \mathbf{M} dH_0 dV$ (here \mathbf{M} is the magnetization). If $\mathbf{M} = \text{const} \times \mathbf{H}$, then it follows that

$$\Phi_s(T, H_0) = \int \left\{ F_{s0} + \frac{\hbar^2}{2M} (\nabla \Psi)^2 \right\} dV - \frac{\beta H_0}{2}, \quad (1.5)$$

where $\mu = \int \mathbf{M} dV$ is the magnetic moment of the solid.

The derivation given above is not sufficiently rigorous, but we also arrive at Eq. (1.5) by taking it into account that during an isothermal process at equilibrium in a magnetic field, the following quantity must have a minimum:⁵

$$\Phi(T, H_0) = E - TS - \frac{1}{4\pi} \int \mathbf{B} H_0 dV + \frac{1}{8\pi} \int H_0^2 dV, \quad (1.6)$$

where E is the internal energy of the solid, S is its entropy, and the term containing H_0^2 is added for convenience. In the case of a superconductor:

$$E - TS = \int F dV = \int F_{sH} dV,$$

where F_{sH} is defined by Eq. (1.1).

In most cases the function Ψ can be considered real. Indeed, in transforming to gradients, it is necessary that

$$\Psi' = \Psi \exp \left[i \frac{e}{\hbar c} \chi(\mathbf{r}) \right], \quad \mathbf{A}' = \mathbf{A} + \nabla \chi,$$

where the only requirements on $\chi(\mathbf{r})$ are that the function Ψ' remain everywhere continuous and single valued. For a simply connected superconductor, this condition can be satisfied everywhere and at the same time one can choose χ so that the function Ψ' turns out to be real.

In this case, as is evident from Eq. (1.4), if $\Psi = \Psi^*$ (the primes on Ψ are omitted),

$$\mathbf{j}_s = - (e^2 / Mc) \Psi^2 \mathbf{A}. \quad (1.7)$$

For a bulk, multiply-connected superconductor it is possible to choose Ψ real only if the magnetic flux through any contour located in the interior of the superconductor is equal to zero. Indeed, in the interior of the superconductor the current density

is $\mathbf{j}_s = 0$, but on the other hand, under condition (1.7), the circulation of the current on such a contour is given by

$$\oint \mathbf{j}_s ds = \text{const} \cdot \oint \mathbf{A}_s ds = \text{const} \cdot \int H_{nd} \sigma,$$

i.e., it is proportional to the magnetic flux through the contour. Therefore, if this flux is different from zero, Eq. (1.7) cannot be true. The magnetic flux through a superconductor does not vanish, as is well known, only for multiply-connected samples which are transformed into the superconducting state in the presence of a magnetic field. This case will not be considered below, and Eq. (1.7) will be used when we have for the superconductor [see Eq. (1.6)]

$$\Phi_s(T, H_0) = \int \left[F_{s0} + \frac{\hbar^2}{2M} (\nabla \Psi)^2 \right] dV - \frac{1}{2c} \int \mathbf{j}_s \mathbf{A} dV + \frac{1}{8\pi} \int (\mathbf{H} - \mathbf{H}_0)^2 dV, \quad (1.8)$$

where, as before, the integration is performed over all space. (Outside the superconductor, naturally, $\Psi = 0$ and $\mathbf{j}_s = 0$; in Eq. (1.6), in addition, the substitution $\mathbf{B} = \mathbf{H}$ was made since the metal is considered to be non-magnetic.)

In the normal state, since the metal is non-magnetic,

$$\Phi_n(T, H_0) = \int F_{n0} dV. \quad (1.9)$$

Eq. (1.8) can be transformed into the form of Eq. (1.5) by using the field equations.

The function Ψ which enters into Φ_s is determined in the equilibrium or metastable state by the condition that Φ_s must have a minimum. As has been pointed out, this condition is the same as the requirement of a minimum in $\int F_{sH} dV = E - TS$, i.e., it is determined by means of Eq. (1.3). The equivalence of the expression for Φ_s and $E - TS$ in this respect is evident from Eq. (1.6), since the presence of the term

$$-\frac{H_0}{4\pi} \int \mathbf{H} dV = -\frac{H_0}{4\pi} \int \text{curl} \mathbf{A} dV$$

is immaterial when Ψ and \mathbf{A} are varied for the purpose of obtaining Eqs. (1.3) and (1.4). In this case, in the absence of a field, when one can write $\mathbf{A} = 0$ and $\nabla \Psi = 0$, we have

$$\Psi^2 = \Psi_\infty^2 = -\frac{\alpha}{\beta} = \frac{|\alpha|}{\beta}, \quad F_{s0}(\Psi_\infty^2) = F_{n0} - \frac{\alpha^2}{2\beta}. \quad (1.10)$$

For a bulky cylindrical superconductor in a field, parallel to the axis of the cylinder, one can assume the field to be H_0 outside the metal and by $\mathbf{H} = 0$ in the interior of the sample. Therefore

$$\mu = \frac{1}{4\pi} \int (\mathbf{H} - \mathbf{H}_0) dV = -\frac{H_0 V}{4\pi},$$

where V is the volume of the cylinder. The term with $(\nabla\Psi)^2$ in Eq. (1.5), which differs from zero only near the surface of the metal,* can be neglected in our case and, in this way, in the equilibrium state, when the external field H_0 is equal to the critical field H_{cb} for bulk metal, we have

$$H_{cb}^2/8\pi = F_{n_0} - F_{s_0} = \alpha^2/2\beta. \quad (1.11)$$

Let us introduce the notation

$$\Psi_0^2 = \frac{\Psi^2}{\Psi_\infty^2}, \quad \delta_0^2 = \frac{Mc^2}{4\pi e^2 \Psi_\infty^2} = \frac{mc^2}{4\pi e^2 \Psi_\infty^2} = \frac{2.84 \cdot 10^{11}}{\Psi_\infty^2} \text{ cm}^2,$$

$$\kappa = \frac{Mc}{e\hbar} \sqrt{\frac{\beta}{2\pi}} = \frac{V\sqrt{2}e}{\hbar c} H_{cb} \delta_0^2 = 2.17 \cdot 10^7 H_{cb} \delta_0^2. \quad (1.12)$$

Here we have taken it into account that δ_0 (the depth of penetration of a weak magnetic field into a superconductor) is the observable quantity, while the "concentration of superconducting electrons", $n_s = \Psi_\infty^2$ manifests itself through δ_0^2 . Therefore, in the expression for δ_0^2 , the coefficient M , which plays the role of an effective mass, can be set equal to the mass of the free electron m , thus uniquely relating Ψ_∞^2 with δ_0^2 . As for the charge e , it is assumed above to equal the free electron charge, an assumption having rather firm theoretical foundations.^{1,11} Making use of Eqs. (1.12) and (1.9), the potential (1.5) can be written in the form:

$$\Phi_s = \Phi_n + \frac{H_{cb}^2}{8\pi} \int [\Psi_0^4 - 2\Psi_0^2 + \frac{2\delta_0^2}{x^2} (\nabla\Psi_0)^2] dV - \frac{1}{2} \mu H_0. \quad (1.13)$$

From (1.13) it is clear that only two parameters, H_{cb} and δ_0 , enter into the theory [the parameter κ can be expressed in terms of these other two; see Eq. (1.12)], so that only the penetration depth δ_0 enters into the gradient term.

In terms of these same symbols and for a real Ψ , Eqs. (1.3) and (1.4) can be rewritten

$$\nabla^2 \Psi_0 = \frac{\kappa^2}{\delta_0^2} [\Psi_0^3 - \Psi_0 + \frac{1}{2\delta_0^2 H_{cb}^2} \Psi_0 A^2], \quad (1.14)$$

$$\text{curl curl } \mathbf{A} + \delta_0^{-2} \Psi_0^2 \mathbf{A} = 0.$$

Note, finally, that the temperature dependence of α and β , or, equivalently, of the quantities H_{cb} and δ_0 , is not fixed, and can be arbitrary within wide limits. From experimental data, it is known that quite good agreement with experiments can be usually achieved by putting

$$H_{cb} = H_{00} [1 - (T/T_c)^2], \quad \delta_0 = \delta_{00} [1 - (T/T_c)^4]^{-1/2}. \quad (1.15)$$

*It is assumed that all of the sample becomes superconducting.

2. For a number of pure metals $\kappa \ll 1$ (e.g., for aluminum at $T \rightarrow 0$, according to Ref. 9, $\kappa = 0.05$). Under such conditions, for certain problems, we can simply let $\kappa = 0$, which is the same as assuming the Ψ does not depend on the coordinates [see Eq. (1.14)]. One can proceed exactly in the same manner in analyzing the destruction of superconductivity in small samples, when

$$(\kappa L/\delta_0)^2 \ll 1, \quad (2.1)$$

where L is the characteristic dimension of the sample (the thickness of a film, the radius of a small sphere or a cylinder, etc.). Let us first dwell on this particular case.

According to Eq. (1.13) we have here

$$f = \frac{\Phi_s - \Phi_n}{(H_{cb}^2/8\pi)V} = \Psi_0^4 - 2\Psi_0^2 - \frac{4\pi}{H_{cb}^2 V} \mu H_0, \quad (2.2)$$

where V is the volume of the sample.

Since in the superconducting state, whether in equilibrium or in a metastable state, the potential Φ_s (or the potential difference f) should have a minimum, the quantities H_0 and Ψ_0 are related by the equation:

$$\partial f(H_0, \Psi_0)/\partial \Psi_0 = 0, \quad (2.3)$$

where for simplicity the value of Ψ_0 , associated with the minimum, is represented by the same symbol, Ψ_0 .

The equilibrium transition between the superconducting and normal phases occurs if

$$f(H_c, \Psi_c) = 0, \quad (2.4)$$

where H_c and Ψ_c are corresponding values of H_0 and Ψ_0 . The second equation needed to determine H_c and Ψ_c is clearly Eq. (2.3) with $H_0 = H_c$ and $\Psi_0 = \Psi_c$.

If the characteristic dimension L is less than a certain value L_c , then with increasing H_0 the function Ψ_0 decreases monotonically and $\Psi_c = 0$. In this region there occurs, as is evident, a second-order transition, when neither superheating or supercooling is possible. This is clearly seen in Fig. 1, in which we have plotted the potential difference f as a function of Ψ_0 for various values of $(H_0/H_{cb})^2$ for small spheres of radius $a = \delta_0$ [see Eqs. (2.19), (2.23) and (2.25) below].

The value $L = L_c$ corresponds to the critical Curie point, when the specific-heat discontinuity is infinite at the transition. For $L > L_c$, a first-order transition takes place. Plots of $f(\Psi_0)$ for this case are presented in Fig. 2 for small spheres with $a/\delta_0 = 8$. It is already evident from this fig-

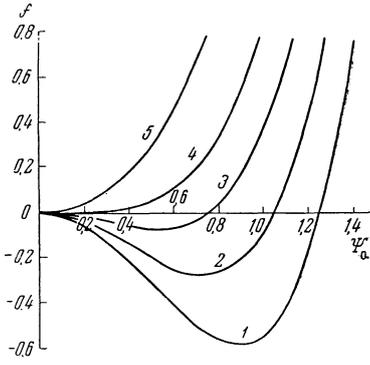


FIG. 1. Curves 1 through 5 correspond to values of $(H_0/H_{cb})^2$ equal to 5, 10, 15, 20, and 30, respectively.

ure, that the metastable (supercooled) normal phase, which accounts for the relative minimum in f at $\Psi_0 = 0$, can exist only in fields $H_0 > H_{c1}$. The value of H_{c1} is obtained from the condition

$$\partial^2 f(H_{c1}, 0) / \partial \Psi_0^2 \equiv (\partial^2 f / \partial \Psi_0^2)_{H_0=H_{c1}, \Psi_0=0} = 0. \quad (2.5)$$

As for the metastable (superheated) superconducting phase, it can exist only for fields $H_0 < H_{c2}$, where for $\Psi_{c2} \neq 0$:

$$\partial^2 f(H_{c2}, \Psi_{c2}) / \partial \Psi_0^2 = 0, \quad \partial f(H_{c2}, \Psi_{c2}) / \partial \Psi_0 = 0. \quad (2.6)$$

In this case, when $\Psi_0 = \text{const.}$, the magnetic moment of the sample is calculated in the same way as in the Londons' theory [see the second of Eqs. (1.14)]. The solutions of the corresponding problems are presented in detail in Ref. 12. For a field parallel to a thin film of thickness $2d$

$$\frac{\mu}{V} = \frac{\mu}{2dS} = - \left(1 - \frac{\tanh(\Psi_0 d / \delta_0)}{\Psi_0 d / \delta_0} \right) \frac{H_0}{4\pi}. \quad (2.7)$$

For a sphere of radius a :

$$\frac{\mu}{V} = \frac{\mu}{4\pi a^3/3} = -3 \left\{ 1 - \frac{3\delta_0}{\Psi_0 a} \coth \frac{\Psi_0 a}{\delta_0} + \frac{3\delta_0^2}{(\Psi_0 a)^2} \frac{H_0}{8\pi} \right\}. \quad (2.8)$$

For a circular cylinder with radius r in a field parallel to its axis,

$$\begin{aligned} \frac{\mu}{V} &= \frac{\mu}{\pi r^2 l} = - \left[1 - \frac{2\delta_0}{\Psi_0 r} \frac{I_1(\Psi_0 r / \delta_0)}{I_0(\Psi_0 r / \delta_0)} \right] \frac{H_0}{4\pi} \\ &= - \frac{I_2(\Psi_0 r / \delta_0)}{I_0(\Psi_0 r / \delta_0)} \frac{H_0}{4\pi}, \end{aligned} \quad (2.9)$$

where $I_n(x) = i^{-n} J_n(ix)$ and J_n is the Bessel function. For the case of a circular cylinder perpendicular to the field, the value of μ/V is twice as large as that given in Eq. (2.9).

For a film, the quantity f assumes a form that is clear from Eqs. (2.2) and (2.7), and Eqs. (2.3) and (2.4) yield*

*The case of a thin film was previously considered in Ref. 3, where, however, the expression for the field H_{c2} was not included.

$$\left(\frac{H_0}{H_{cb}} \right)^2 = \frac{4\Psi_0^2 (\Psi_0^2 - 1) \cosh^2(\Psi_0 d / \delta_0)}{1 - \sinh(2\Psi_0 d / \delta_0) / (2\Psi_0 d / \delta_0)}; \quad (2.10)$$

$$\left(\frac{H_c}{H_{cb}} \right)^2 = \frac{\Psi_c^2 (2 - \Psi_c^2)}{1 - \tanh(\Psi_c d / \delta_0) / (\Psi_c d / \delta_0)}. \quad (2.11)$$

Using the first relation in (2.6) we find:

$$\left(\frac{H_{c2}}{H_{cb}} \right)^2 = \frac{2\Psi_{c2}^2 (1 - 3\Psi_{c2}^2) \cosh^3(\Psi_{c2} d / \delta_0)}{\cosh\left(\frac{\Psi_{c2} d}{\delta_0}\right) \left[1 - \frac{\sinh(2\Psi_{c2} d / \delta_0)}{2\Psi_{c2} d / \delta_0} \right] + \frac{\Psi_{c2} d}{\delta_0} \sinh\left(\frac{\Psi_{c2} d}{\delta_0}\right)}. \quad (2.12)$$

The second equation for H_c and Ψ_c or H_{c2} and Ψ_{c2} is obtained, as has already been remarked, from Eq. (2.10) by replacing H_0 and Ψ_0 with H_c and Ψ_c or with H_{c2} and Ψ_{c2} . The value of the field H_{c1} determined from Eq. (2.5) is equivalent to Eq. (2.12) with $\Psi_{c2} \rightarrow 0$. This same result is obtained directly from Eqs. (2.10) and (2.11) also for $\Psi_0 \rightarrow 0$, i.e., by expanding into a series in terms of $\Psi_0 d / \delta_0$. The result is:

$$H_{c1} / H_{cb} = \sqrt{6} \delta_0 / d. \quad (2.13)$$

For $d < d_c$, where d_c is the half thickness associated with the Curie point (in this case $L_c = 2d_c$), we have $H_{c1} = H$ i.e., Eq. (2.13) also determines the critical field in the region of a second-order transition.

From Eq. (2.10), for small Ψ_0 , as a result of expanding the hyperbolic functions into a series and retaining terms of the order of $(\Psi_0 d / \delta_0)^*$, we obtain

$$\begin{aligned} \Psi_0^2 &\simeq \frac{1 - 1/6 (H_0/H_{cb})^2 (d/\delta_0)^2}{1 - (d/\delta_0)^2 + 1/30 (H_0/H_{cb})^2 (d/\delta_0)^4} \\ &\simeq \frac{1 - 1/6 (H_0/H_{cb})^2 (d/\delta_0)^2}{1 - 4/5 (d/\delta_0)^2}. \end{aligned} \quad (2.14)$$

Hence for $\Psi_0 \rightarrow 0$, one necessarily obtains Eq. (2.13), but, in addition to this, it is clear that the form of the solution is changed for different values of d/δ_0 . Thus, if $d/\delta_0 < \sqrt{5}/2$ then for $H_0 > H_{c1}$ no real solution for Ψ_0 exists in general. On the other hand, when $d/\delta_0 > \sqrt{5}/2$, such a solution does exist. This denotes the presence of a first-order transition. Thus, for a film

$$d_c / \delta_0 = \sqrt{5}/2 = 1.12. \quad (2.15)$$

The character of the $\Psi_0(H_0)$ curves is shown in Fig. 3, as a function of different sample dimensions, for the case of small spheres (see below). For

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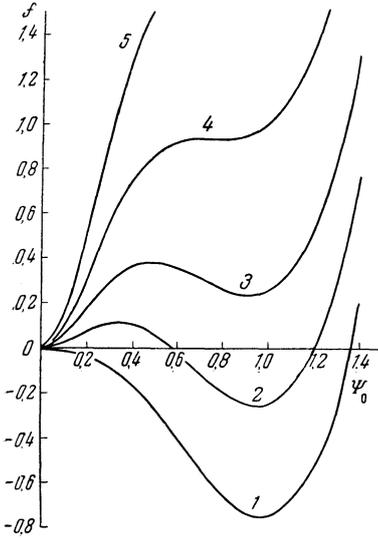


FIG. 2. Curves 1 through 5 correspond to values of $(H_0/H_{cb})^2$ equal to 0.25, 0.75, 1.25, 2.00, and 3.00, respectively.

sufficiently thick films, when

$$d/\delta_0 \gg 1 \quad (2.16)$$

and Ψ_0 is of the order of unity, Eqs. (2.11) and (2.12) are greatly simplified. They assume the form

$$\frac{H_c}{H_{cb}} = 1 + \frac{\delta_0}{2d}, \quad \Psi_c = 1 - \frac{\delta_0}{8d}; \quad (2.17)$$

$$\frac{H_{c2}}{H_{cb}} = \frac{2\sqrt{2}}{5} \left(\frac{27}{5}\right)^{1/4} \sqrt{\frac{d}{\delta_0}} = 0.86 \sqrt{\frac{d}{\delta_0}}; \quad (2.18)$$

$$\Psi_{c2} = \sqrt{\frac{3}{5}} = 0.772.$$

Eq. (2.13) for H_{c1}/H_{cb} remains valid also when condition (2.16) is satisfied.

For small spheres we have ($x_1 = \Psi_1 a/\delta_0$):

$$f = \Psi_0^2 (\Psi_0^2 - 2) + \frac{3}{2} \left(\frac{H_0}{H_{cb}}\right)^2 \left[1 - \frac{3 \coth x_0}{x_0} + \frac{3}{x_c^2}\right]; \quad (2.19)$$

$$\left(\frac{H_0}{H_{cb}}\right)^2 = \frac{8}{9} \Psi_0^2 (1 - \Psi_0^2) \sinh^2 x_0 \left[1 + \frac{\sinh 2x_0}{2x_0} - \frac{2 \sinh^2 x_0}{x_0^2}\right]^{-1}; \quad (2.20)$$

$$\left(\frac{H_c}{H_{cb}}\right)^2 = \frac{2}{3} \Psi_c^2 (2 - \Psi_c^2) \left[1 - \frac{3 \coth x_c}{x_c} + \frac{3}{x_c^2}\right]^{-1}; \quad (2.21)$$

$$\left(\frac{H_{c2}}{H_{cb}}\right)^2 = \frac{4(1 - 3\Psi_{c2}^2) \Psi_{c2}^2 \sinh^2 x_{c2}}{9[3 \sinh^2 x_{c2} - x_{c2}^3 \coth x_{c2} - x_{c2}^2 - 1/2 x_{c2} \sinh 2x_{c2}]}; \quad (2.22)$$

$$H_{c1}/H_{cb} = 2\sqrt{5} \delta_0/a. \quad (2.23)$$

For small Ψ_0 , it follows from Eq. (2.21) that

$$\Psi_0^2 \approx \frac{1 - 1/20 (H_0/H_{cb})^2 (a/\delta_0)^2}{1 - 4/21 (a/\delta_0)^2}, \quad (2.24)$$

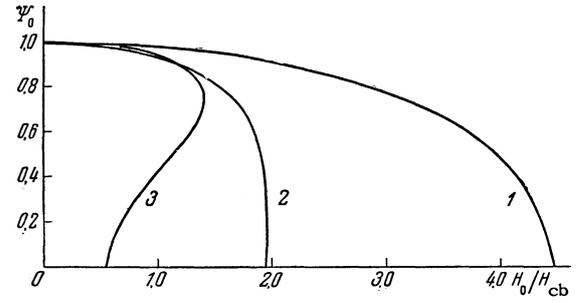


FIG. 3. Curve 1 - $a/\delta_0 = 1.00$; 2 - $a/\delta_0 = 2.29$; 3 - $a/\delta_0 = 8.00$.

whence we obtain Eq. (2.23), as well as the critical value of the radius, a_c , associated with the onset of first-order transitions (for $a > a_K$):

$$a_c/\delta_0 = \sqrt{21}/2 = 2.29. \quad (2.25)$$

For

$$a/\delta_0 \gg 1 \quad (2.26)$$

we obtain

$$H_c/H_{cb} = \sqrt{2/3} (1 + 3\delta_0/2a), \quad \Psi_c = 1 - 3\delta_0/8a; \quad (2.27)$$

$$H_{c2}/H_{cb} = 4/5 \cdot 15^{-1/4} \sqrt{a/\delta_0} = 0.407 \sqrt{a/\delta_0}, \quad \Psi_{c2} = \sqrt{3/5}. \quad (2.28)$$

The values of H_{c1}/H_{cb} , H_c/H_{cb} and H_{c2}/H_{cb} , obtained from Eqs. (2.20) through (2.23), are shown in Fig. 4. In exactly the same way as was done for

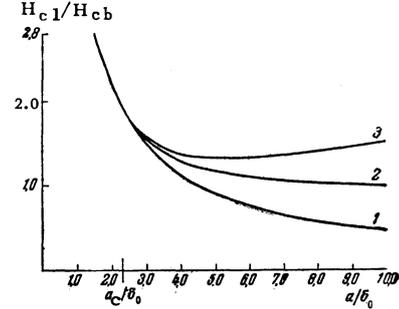


FIG. 4. Curve 1 - H_{c1}/H_{cb} ; 2 - H_c/H_{cb} ; 3 - H_{c2}/H_{cb} .

the film and the small sphere, it is possible to determine the fields H_{c1} , H_c and H_{c2} for a cylinder by using Eqs. (2.2) through (2.9). It is especially easy to show by expanding the function I_n in Eq. (2.9) in a series, that for a cylinder, in a parallel field

$$H_{c1}/H_{cb} = 4\delta_0/r, \quad r_c/\delta_0 = \sqrt{3}, \quad (2.29)$$

and for a cylinder, with a perpendicular field

$$H_{c1}/H_{cb} = \sqrt{8} \delta_0/r, \quad r_c/\delta_0 = \sqrt{3}. \quad (2.30)$$

Equations (2.20), (2.23), (2.25), (2.29) and (2.30)

were previously obtained by Silin,⁵ but in a somewhat more cumbersome way [this was because he did not make use of the general expression Eq. (1.13)]. The case of small spheres was also investigated in Ref. 4, but with the use of a different, more complicated, and at the same time, apparently less justifiable functional relation between F_{S0} and Ψ^2 . The results obtained, concerning the dependence of H_{C1} , H_C and H_{C2} on the dimensions of the samples at least in their qualitative relations, are confirmed by experiments (see Refs. 13 through 16, 4, and 10).

3. If one makes use of the equations obtained in Sec. 2, one can conclude, that as L/δ_0 increases, the field H_{C1} approaches zero, and the field H_{C2} approaches infinity [see Eqs. (2.13) and (2.18) or (2.23) and (2.28)]. In actuality, however, all these expressions are strictly applicable only subject to condition (2.1), which does not permit consideration of sufficiently thick samples. By taking into account the parameter κ , the values of the fields H_{C1} , H_C and H_{C2} are changed, and, for example, for thin films, one obtains⁷ to terms in κ^2

$$\left(\frac{H_{C1}}{H_{Cb}}\right)^2 = 6 \left(\frac{\delta_0}{d}\right)^2 \left[1 + \frac{8}{105} \left(\frac{\kappa d}{\delta_0}\right)^2\right]. \quad (3.1)$$

Hence, it follows that Eq. (2.13) can be used in practice, as long as $\kappa d/\delta_0 \lesssim 1$ or, if $\kappa \sim 0.1$, as long as $d/\delta_0 \lesssim 10$. Since $\delta_0 \gtrsim 5 \times 10^{-6}$ cm, this means that the thickness of the film $2d$ can reach 10^{-4} cm or even somewhat more (except near T_C , where δ_0 increases.)

A general investigation of the critical field values in the region $\kappa L/\delta_0 \sim 1$ is rather complicated, and we shall therefore dwell only on the second limiting case, when

$$\kappa L/\delta_0 \gg 1. \quad (3.2)$$

Since the width of the transition region between the superconducting and normal phases at equilibrium (i.e., for $H = H_{Cb}$) is of the order of δ_0/κ (see Ref. 1.), condition (3.2) has an obvious physical meaning. Samples whose smallest dimensions L satisfy the inequality (3.2) will behave like bulk samples. For such samples, the boundary of the region of supercooling of the normal phase is determined from the condition of stability of this phase with respect to a transition into the superconducting state.^{1,2} Thus

$$H_{C1}/H_{Cb} = \sqrt{2} \kappa. \quad (3.3)$$

In external fields such that $H_0 < H_{C1}$ the normal phase is unstable and cannot exist.

By comparing (3.3) with (2.13), (2.23), (2.29), and (2.30), which are valid in the second limiting

case (2.1), the following becomes clear. As L increases, H_{C1} first decreases as $H_{C1}/H_{Cb} = \text{const.} \times \delta_0/L$, but afterwards, when $\kappa L/\delta_0 \gg 1$, this decrease slows down and for the field H_{C1} , probably approaches monotonically the constant limit (3.3).

As regards the equilibrium critical field H_C , it approaches H_{Cb} for cylindrical samples with axes parallel to the field, when condition (3.2) applies. For a slab of thickness $2d \gg \delta_0/\kappa$ we have^{1,3}

$$H_C/H_{Cb} = 1 + (\delta_0/2d) (1 + \kappa/8\sqrt{2}). \quad (3.4)$$

The limit of the superheated region of the superconducting phase, i.e., the field H_{C2} , increases in certain ranges of values of L according to the law $H_{C2}/H_{Cb} = \text{const.} \sqrt{L/\delta_0}$ [see Eqs. (2.18) and (2.28)]. For $\kappa L/\delta_0 \sim 1$, this increase slows down and when condition (3.2) applies, the field H_{C2} , most probably, approaches smoothly a certain constant limit, which is a function of κ .

We now proceed to calculate H_{C2} for the bulk metal, considering for this purpose the superconducting half-space, on whose boundary (at $z = 0$) the external magnetic field, parallel to this boundary, is equal to H_0 . The problem is one dimensional and Eqs. (1.14) become

$$d^2\Psi_0/d\xi^2 = \kappa^2 [-(1 - a^2)\Psi_0 + \Psi_0^3], \quad (3.5)$$

$$d^2a/d\xi^2 = \Psi_0^2 a, \quad (3.6)$$

where

$$\xi = z/\delta_0, \quad a = A/\sqrt{2} H_{Cb} \delta_0,$$

$$h = da/d\xi = H/\sqrt{2} H_{Cb}. \quad (3.7)$$

Equations (3.5) and (3.6) must be solved subject to the boundary conditions¹

$$\begin{aligned} \xi = \infty: & \Psi_0^2 = 1, \quad d\Psi_0/d\xi = 0, \quad h = 0, \quad a = 0, \\ \xi = 0: & h = (da/d\xi)_0 = h_0, \quad d\Psi_0/d\xi = 0, \end{aligned} \quad (3.8)$$

where $h_0 = H_0/\sqrt{2} H_{Cb}$ is the field on the boundary in the new units, and the value $\xi = \infty$ corresponds to a layer of superconductor.

From Eqs. (3.5), (3.6), and (3.8), it follows that

$$(da/d\xi)^2 \equiv h^2 = 1/2 - \frac{1}{\kappa^2} \left(\frac{d\Psi_0}{d\xi}\right)^2 - (1 - a^2) \Psi_0^2 + \Psi_0^4/2. \quad (3.9)$$

Making use of the integral of Eq. (3.9), and denoting $d\Psi_0/d\xi$ by y , we can write Eqs. (3.5) and (3.6) as

$$\begin{aligned} d\Psi_0/da &= y [1/2 - (y/\kappa)^2 - (1 - a^2) \Psi_0^2 + \Psi_0^4/2]^{-1/2}, \\ dy/da &= \kappa^2 [-(1 - a^2) \Psi_0 + \Psi_0^3] [1/2 - (y/\kappa)^2 - (1 - a^2) \Psi_0^2 \\ &\quad + \Psi_0^4/2]^{-1/2}. \end{aligned} \quad (3.10)$$

The problem consists of finding an integration curve, which satisfies (3.10), goes out from the singular point $y = 0$, $a = 0$, $\Psi_0 = 1$, and intersects the plane $y = 0$ (in a coordinate system with variables y , a and Ψ_0) at the point a_0 and $\Psi_0(0)$, so that in accordance with (3.9)

$$h_0^2 = 1/2 - (1 - a_0^2)\Psi_0^2(0) + \Psi_0^4(0)/2. \quad (3.11)$$

For a given applied field, h_0 , Eq. (3.11) determines a certain curve in the plane $y = 0$. Near the singular point one can write $\Psi = 1 + \varphi$, where $|\varphi| \ll 1$, and, thus, the equation can be made linear. Consequently, near the singular point,

$$\begin{aligned} \Psi_0 &= 1 + x^2 a^2 / (2 - x^2) + C(-a)^{\sqrt{2}x}, \\ y &= -x^2 a^2 / (2 - x^2) - \sqrt{2} x C(-a)^{\sqrt{2}x}, \end{aligned} \quad (3.12)$$

where C is an integration constant.

The behavior of the integral curves at sufficiently large values of $|a|$ is determined from Eq. (3.10) and, generally speaking, can be calculated quantitatively only by numerical methods. In the case of small κ , it turns out that it is more effective to get a direct solution of Eqs. (3.5) and (3.6), using, for large values of ξ , a solution equivalent to (3.12), obtained by the method of successive approximations.¹ As a result of such calculations, one can establish that the sought solution exists only so long as the field h_0 is less than a certain field $h_{C2} = H_{C2} / \sqrt{2} H_{Cb}$, which plays the role of the boundary for superheating of the superconducting phase. Incidentally, the very fact that the field H_{C2} exists can be ascertained, naturally, even without numerical calculations. Thus, in the limiting case of very large κ , $H_{C2} = H_{Cb}$. In fact, as $\kappa \rightarrow \infty$, we have from Eqs. (3.5) and (3.6)

$$\begin{aligned} \Psi_0^2 &= 1 - a^2, \quad a = \sqrt{2} / \cosh(\xi + C), \\ h &= da/d\xi = \sqrt{2} \sinh(\xi + C) / \cosh^2(\xi + C), \\ H/H_{Cb} &= \sqrt{2} h = 2 \sinh(\xi + C) / \cosh^2(\xi + C), \end{aligned} \quad (3.13)$$

where C is an integration constant, and we have taken into account the boundary condition $a(\xi = \infty) = 0$. From the requirement, that $H = H_0$ when $\xi = 0$ (i.e., $z = 0$), the following condition is obtained:

$$\cosh^2 C = 2(H_{Cb}/H_0)^2 \pm 2\sqrt{(H_{Cb}/H_0)^4 - (H_{Cb}/H_0)^2}.$$

Hence the possible existence of a solution only when $H_0 \leq H_{Cb}$ is evident, since otherwise $\cosh^2 C$ becomes complex. Thus, when $\kappa \rightarrow \infty$, $H_{C2} = H_{Cb}$. For $\kappa = 0$, on the other hand, the field $H_{C2} = \infty$, since the solution $\Psi_0 = 1$ exists in any field. For $\kappa \ll 1$, by using the method of successive approximations,¹ one can show, that on the boundary $z = 0$

the function $\Psi_0(0)$ is equal to

$$\Psi_0(0) = 1 - x h_0^2 / 2 \sqrt{2} - 9(x h_0^2)^2 / 16 - \dots \quad (3.14)$$

Hence, it is evident, that the expansion variable is the quantity κh_0^2 , and Eq. (3.14) is valid so long as $1 - \Psi_0(0) \ll 1$. For this last reason, the absence of a maximum in the curve of Eq. (3.14) at $\Psi_0(0, h)$, corresponding to the field h_{C2} , means that the value $\Psi_0(0, h_{C2}) \equiv \Psi_{C2}$ is substantially different from unity.

On the other hand, for $\Psi_0(0) \rightarrow 0$, as can be seen from Eq. (3.9), $h_0 \rightarrow 1/\sqrt{2}$ and, thus, the curve of $\Psi_0(0, h_0)$ must have a maximum. From Eq. (3.14), and from an analysis of Eqs. (3.5) and (3.6) with the introduction of the variables $\xi = \sqrt{\kappa} \xi$, $\chi = \Psi/\sqrt{\kappa}$ and $b = \sqrt{\kappa} a$, it can be inferred that, for $\sqrt{\kappa} \ll 1$ and $h_{C2} = \text{const}/\sqrt{\kappa}$, i.e.,

$$H_{C2}/H_{Cb} = \sqrt{2} h_{C2} = 0.89/\sqrt{\kappa}, \quad (3.15)$$

where the constant was obtained by numerical integration of the equations, with $\kappa = 0.02$, for $H_{C2}/H_{Cb} = 6.28$ and $\Psi_{C2} = 0.73$.

By way of example, $\Psi_0(0, h_0)$ has been plotted for $\kappa = 0.165$ in Fig. 5. The values of H_{C2}/H_{Cb} ,

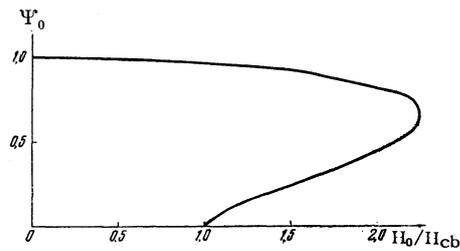


FIG. 5

obtained by means of numerical calculation, are shown in Fig. 6. We also tabulate the values of H_{C2}/H_{Cb} and Ψ_{C2} for some values of κ , as follows.

κ	0.10	0.165	0.4	0.5	0.6	0.7	0.8
H_{C2}/H_{Cb}	2.87	2.25	1.64	1.52	1.45	1.39	1.34
Ψ_{C2}	0.72	0.67	0.65	0.63	0.62	0.615	0.61

Experimentally it is difficult to observe superheating of the superconducting phase in bulk samples, but for samples of "average" dimensions (see the introduction) one can expect a different situation. Therefore, in particular, the thought arises that Hein and Steele observed not the equilibrium value of H_C for small superconducting cadmium spheres, but rather some value H_2 lying in the interval $H_C < H_2 < H_{C2}$. Indeed, by considering the transition to be an equilibrium one, in the value obtained in Ref. 8, $\delta_{00} = 8.8 \times 10^{-4}$ cm, was two orders of magnitude larger than the quantity δ_{00} in Sn, Al, and other superconductors. Hence, as $T \rightarrow 0$, if $H_{Cb} = 27.6$, we obtain $\kappa_0 = 2.16 \times$

$10^7 H_{Cb} \delta_{00}^2 \approx 460$, which seem unlikely ($\kappa_0 = 0.17$ for Sn and $\kappa_0 = 0.05$ for Al). Recent measurements by Chaikin* on Cd confirm directly the incorrectness of the conclusion drawn by Hein and Steele, since Chaikin's data lead to $\delta_{00} = (10.2 \text{ to } 11.5) \times 10^{-6}$ and $\kappa_0 = 0.07$. In this connection it seems natural to assume that superheating was observed in Ref. 8, especially since only the destruction of superconductivity in a given field with increasing temperature was investigated. Even for the smallest spheres, like those investigated in Ref. 8, the condition $\kappa_0 a / \delta_{00} \gg 1$ is satisfied. Making use, therefore, of Eq. (3.15) or of the data presented in Fig. 6, we obtain† $H_{C2} / H_{Cb} \approx 2.3$ at $T = 0$ whereas experimentally $H_2 / H_{Cb} \approx 2$. How-

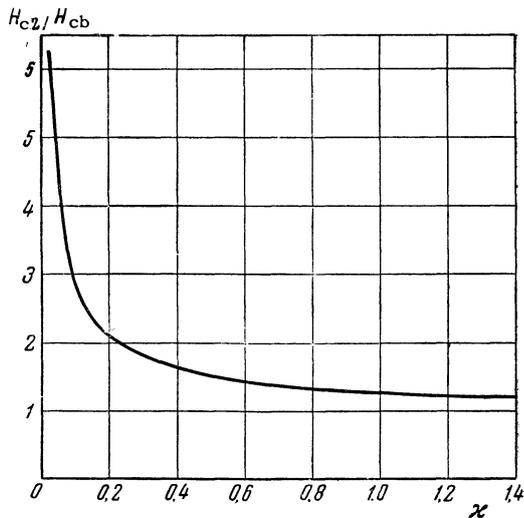


FIG. 6

ever, in Ref. 8, the field H_2 / H_{Cb} increased with increasing temperature by nearly a factor of four, whereas

$$\kappa(T) = \kappa_0 [1 + (T/T_c)^2]^{-1}, \quad (3.16)$$

i.e., the field H_{C2} / H_{Cb} increases only by approximately a factor of 1.4. On the other hand, for temperatures attained near T_c , the parameter $\kappa a / \delta_0$ equals approximately 3 or 4, i.e., it is not large enough to make use of the values H_{C2} obtained for the superconducting half-space.

Thus, the assumption of superheating still cannot be considered as contradicting the theory. In view of all this, further investigation of the problem of the boundary regions of superheating and

*The work was reported at the Fourth All-Union Conference on Low-Temperature Physics (July, 1957).

†Since the field on the surface of the sphere reaches $\frac{3}{2}$ of its value at infinity, the quantity H_{C2} for the sphere is taken to be smaller by a factor of $\frac{2}{3}$ than was calculated above for a superconductor with a plane interface.

supercooling, in particular in samples of "average" dimensions, is of interest.

Note added in proof (December 19, 1957).

In November, 1957, we received in Moscow the manuscript of the detailed work of Bardeen, Cooper, and Schrieffer (henceforth BCS) in which a microscopic theory of superconductivity is formulated. It is shown that the London equation, generally speaking, does not hold even in a weak field, and the current is connected with the field in an integral way, as was already proposed by Pippard earlier. However, in the vicinity of T_c , subject to the condition $\xi_0 / \delta_0(T) \lesssim 1$, the London equation, is still good to within an accuracy of not less than 10 or 15%, which is about the accuracy claimed by the BCS theory in its simplest version. The parameter is $\xi_0 = 0.18 \hbar v_0 / k T_c$, where v_0 is the velocity at the Fermi surface. For tin, $\xi_0 = 2.5 \times 10^{-5}$ cm, and the London equation can be used in a region of about 0.1 to 0.15° near T_c (this conclusion pertains directly only to bulk metals, but probably has a more general significance).

In the paper above, we have leaned on the work of Ref. 1 which transforms to the London theory in weak fields $H \ll H_c$. In view of what has been said, that work, and the results obtained on the basis thereof, can be quantitatively true only near T_c , as was assumed in Ref. 1, albeit for different reasons. In the general case, as one may believe and as is indicated at the end of the BCS article, the theory of Ref. 1 and its general conclusions probably retain a certain significance, but on the whole this question remains open.

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18

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MOTION OF IONS IN A MIXTURE OF ISOTOPES

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Expressions are derived for the drift velocity of ions of isotopes in a mixture of isotopes. The principal interaction between the ions and atoms is assumed to be pure charge exchange.

IN connection with the problem of the distribution of isotopes in a direct current discharge, the question of the mobility of an ion of an isotope in an isotopic mixture becomes of interest. In view of the possibility of charge exchange between an ion of one isotope and an atom of another isotope, Blank's rule for the mobility of ions in a mixture is not applicable in the given case.

Let there be a mixture of two isotopes with concentrations of neutral atoms N_1 and N_2 . We shall denote the Maxwellian velocity distributions of the atoms by $n_1(\mathbf{v})$ and $n_2(\mathbf{v})$. Let the concentration of ions be N_1^+ and N_2^+ and their velocity distribution functions be $f_1(\mathbf{v})$ and $f_2(\mathbf{v})$. As is usual in problems on mobility, we shall disregard the effect of the ions on the velocity distribution function of the atoms and the interaction of the ions among themselves. The chief process of interaction between the ions and atoms is, in the given case, the exchange of charge without an exchange of momentum (pure charge exchange model), for which the charge-exchange cross section $q(u)$ can be considered the same in all four processes A^+A , A^+B , B^+B and B^+A . In the presence of a constant homogeneous electric field E , directed along the z axis, the velocity distribution function for the ions is found from a system of two kinetic

equations, the first of which has the form

$$\begin{aligned} \frac{eE}{M_1} N_1^+ \frac{\partial f_1}{\partial v_z} = & N_1 N_1^+ \int u q(u) [n_1(v) f_1(v') - f_1(v) n_1(v')] dv' \\ & + N_1 N_2^+ \int u q(u) n_1(v) f_2(v') dv' \\ & - N_1^+ N_2 \int u q(u) f_1(v) n_2(v') dv', \end{aligned} \quad (1)$$

where M_1 is the mass of an atom of the first isotope and $u = |\mathbf{v} - \mathbf{v}'|$. The second and third terms on the right describe the appearance of A ions as a result of impacts of the type B^+A and their disappearance upon impacts of the type A^+B . The second kinetic equation is obtained from Eq. (1) by an interchange of indices.

Let us solve the system of kinetic equations in the limiting cases of weak and strong fields. For small fields, when the energy acquired by an ion over a mean free path is much less than the thermal energy, we apply the method of Langevin, who assumes the velocity distribution of the ions to be Maxwellian with a small superimposed drift in the direction of the field:

$$\begin{aligned} f_1(\mathbf{v}) = & A_1 \exp \left\{ -\frac{M_1}{2kT} [v_x^2 + v_y^2 + (v_z - v_1)^2] \right\} \\ \approx & n_1(v) + \frac{M_1}{kT} v_1 v_z n_1(v). \end{aligned} \quad (2)$$