by Nergaard[6] for the case of films thick enough to exhibit semiconducting properties.

The effect on the periodic deviations[5] from the Schottky line resulting from a deposition of SrO on molybdenum is illustrated in Fig. 1. There is a washing out of the deviations for deposits as small as 1/60 monolayer, and at approximately $\frac{1}{3}$ monolayer there are no deviations from the Schottky line greater than 1/100%. Since the surface barrier is mirror image in the λ region, as suggested above, these data would indicate that with the SrO film, electron reflections near the emitter surface cannot be associated with the simple μ coefficient[5] found for clean metals.

[6] L. S. Nergaard, RCA Rev. **18**, 464 (1952).

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Search for the Hall Effect in a Superconductor. II. Theory

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Various theoretical explanations for the absence of a Hall effect in a superconductor are considered, and none are found convincing. It is concluded that this property lies outside the existing body of theory, and the general requirements it imposes on a future theory are adduced.

I. ORIENTATION

In a previous work[1] the early inconclusive result of Kamerlingh Onnes, that the Hall coefficient of a metal vanishes when it goes into the superconducting state, was confirmed for a vanadium sample. (In fact, it was shown that the Hall coefficient was reduced to less than about 20% of its value in the normal state. It would probably be more difficult to explain its reduction to a finite smaller value than to explain its vanishing completely, so that, for the purposes of the following, we will suppose that these experiments demonstrate the disappearance of the Hall effect in the superconducting state.) It is the purpose of this note to discuss the theoretical implications, if any, of this fact.

To begin with, it is probably well to dispose of some previous arguments that have been advanced, to the effect that it is perfectly obvious that there ought to be no Hall effect in a superconductor. These arguments take several forms, and we discuss them in order.

First, it has been argued that, since a magnetic field can hardly penetrate a superconductor, and, since a magnetic field is essential to a Hall effect, such an effect is precluded. In fact, a magnetic field penetrates a superconductor to a known depth of about 10^{-5} cm, and within this penetration depth the current densities can be quite large. This property of a superconductor is fully taken into account in the earlier paper, in evaluating the magnitude of effect to be expected.

The second argument is due to Pippard[2] and is as follows: if there were a Hall effect in a superconductor it would be possible, in a static magnetic field, to impose a resistive load on the Hall voltage, and so to draw energy from the field. This would, however, cause the collapse of the magnetic field, which is in contradiction to the observed stability of the current-carrying state in a superconductor. Consequently, there must be a contact potential at the surface, which is just sufficient to cancel the Hall voltage, and to render it unobservable.

The answer to this comes in two parts. (We must grant, to begin with, that the gedanken-experiment would go as described, though it has not been tried. This is very probable.) In the first place, one must consider the magnitudes involved in this gedanken-experiment. A superconducting sphere of radius a, in an applied magnetic field H, has an energy excess over a nonsuperconducting sphere equal to $3H^2a^3/8$. The Hall voltage[1] between the pole and equator would be $9RH^2/32\pi$, where R is the Hall coefficient, and, as before, H is the applied field at infinity. If a resistive load Z is now applied, the decay time T will be given by $T=128\pi^2Za^3/27R^2H^2$. Suppose $a\approx 1$ cm, $Z\approx 1$ ohm $=10^9$ emu, $H=100$ gauss, $R=100\times 10^{-6}$ emu (tin or lead); then $T\approx 5\times 10^{14}$ sec. Thus, the field collapse of which we have spoken above would take something more than fifteen million years. The stability of the super currents can hardly be considered to be established over such periods of time. This time can, of course, be somewhat reduced by a suitable choice of different numbers from those used above, but cannot be brought down to the experimental time, which is of the order of weeks.

Thus, one is finally forced to make this argument a matter of principle, and here the question is less clear. If one accepts the idea that the field collapse will indeed occur over such a long period of time, one accepts with it the concept of a lower energy state of a supercon-

[1] H. W. Lewis, Phys. Rev. **92**, 1149 (1953).
[2] Unpublished, but quoted in D. Schoenberg, *Superconductivity* (Cambridge University Press, London, 1952), p. 49. I have had the pleasure of an interesting conversation with Professor Pippard on this question.

ductor, in which the field is no longer excluded. Thus the normal superconducting state, exhibiting the Meissner effect, must be regarded as metastable, rather than absolutely stable. This concept is distasteful to some physicists, but cannot be regarded as in any sense excluded by the information at hand. The answer to such a question must probably ultimately come from a satisfactory theory of the superconducting state.

The third argument we will discuss is given by London[3] and is substantially as follows, if we confine ourselves, for the moment, to the discussion of the forces acting on the superelectrons, and ignore the normal electrons.

Consider the Lorentz expression for the force per unit volume acting on the former

$$\mathbf{F}=\rho_s[\mathbf{E}+(1/c)\mathbf{v}_s\times\mathbf{H}], \tag{1}$$

where ρ_s is the charge density of the superelectrons, $\mathbf{v}_s$ their velocity, c the speed of light, and $\mathbf{E}$ and $\mathbf{H}$ the electric and magnetic fields. This can be transformed, by using the London equations

$$\mathrm{curl}(\Lambda\mathbf{j}_s)=\mathrm{curl}(\Lambda\rho_s\mathbf{v}_s)=-(1/c)\mathbf{H}, \tag{2}$$

$$\Lambda(\partial/\partial t)(\mathbf{j}_s)=\mathbf{E} \tag{3}$$

to eliminate the field strengths. Λ is a constant. Then (1) can be written after suitable transformation

$$\mathbf{F}=\frac{\partial}{\partial t}(\Lambda\rho_s\mathbf{j}_s)+\mathrm{div}(\Lambda\mathbf{S}), \tag{4}$$

where $\mathbf{S}$ is a tensor defined by

$$S_{\mu\nu}=j_\mu j_\nu-\tfrac{1}{2}j^2\delta_{\mu\nu}, \tag{5}$$

and which represents the kinetic stress tensor of the supercurrents. Thus (4) tells us that the momentum delivered to the supercurrents, per unit volume, and per unit time, is divided between an increase of the momentum density in the volume, and a transport of stress across the boundary of the region considered, $\Lambda S_{\mu\nu}$ representing the flow in the ν direction of the μ component of momentum density. If we were to add the stress tensor of the electromagnetic field we would find an over-all conservation law of the form

$$\partial\mathbf{P}/\partial t+\mathrm{div}(\mathbf{T})=0, \tag{6}$$

where we have derived above the expressions for the contributions of the superelectrons to $\mathbf{P}$ and $\mathbf{T}$. The contributions due to the field have the standard form.

It is now argued that, in the stationary case, the first term on the right side of (4) vanishes, as does $\mathbf{E}$, according to (3). Thus, the second term on the right side of (1), representing the magnetic force on the superelectrons, is converted completely into the kinetic stress of the supercurrents, represented by $\mathbf{S}$ in (4). We have thus an equilibrium situation, in which the magnetic forces are balanced by the inertial forces, without an electric field, hence without a Hall effect. At the surface of the material, where $\mathbf{S}$ changes discontinuously, becoming zero outside the metal, there must be surface forces which finally take up the transferred momentum, and which are responsible for the fact that even a superconducting wire can be used in an electric motor. This, then, is a coherent picture, in which the Hall effect has no place.

To study it more carefully, we must go back to the London equations (2) and (3), and to their basis. Here one can adopt one of two points of view; one can postulate the equations in the form given, or one can try to justify them, or at least make them plausible, by studying the motion of a frictionless electronic fluid in an electromagnetic field. London has done this in the book previously referred to.[3] The motion of each electron, under the force represented by (1), will be determined by

$$m(d\mathbf{v}_s/dt)=e(\mathbf{E}+(1/c)\mathbf{v}_s\times\mathbf{H}), \tag{7}$$

where m and e are the mass and charge of the electron. Further, the acceleration can be transformed into

$$\frac{d\mathbf{v}_s}{dt}=\frac{\partial\mathbf{v}_s}{\partial t}+(\mathbf{v}_s\cdot\nabla)\mathbf{v}_s=\frac{\partial\mathbf{v}_s}{\partial t}+\tfrac{1}{2}\nabla(\mathbf{v}_s^2)-\mathbf{v}_s\times\mathrm{curl}\,\mathbf{v}_s, \tag{8}$$

so that (7) can be written

$$\frac{\partial\mathbf{v}_s}{\partial t}+\tfrac{1}{2}\nabla(\mathbf{v}_s^2)-\frac{e}{m}\mathbf{E}=\mathbf{v}_s\times\left[\mathrm{curl}\,\mathbf{v}_s+\frac{e}{mc}\mathbf{H}\right]. \tag{9}$$

If we now take the curl of both sides, call the expression in the square bracket $\mathbf{\Omega}$, and use one of Maxwell's equations, it is easy to see that we have

$$\frac{\partial\mathbf{\Omega}}{\partial t}=\mathrm{curl}(\mathbf{v}_s\times\mathbf{\Omega}). \tag{10}$$

Consequently, if $\mathbf{\Omega}$ is initially zero everywhere, it will remain zero at all times. It is thus consistent to postulate, in addition to the equations of motion, the equation

$$\mathbf{\Omega}=0 \tag{11}$$

It is obvious that this is identical with London's first equation (2), if we identify Λ with $m/e\rho_s$. This is in fact the right order of magnitude for Λ, if we take for ρ_s about one electron per atom.

Thus, one is led to London's equation (2), with a meaning for the constant Λ. Now combine this with (9), to obtain

$$\partial\mathbf{v}_s/\partial t=(e/m)\mathbf{E}-\tfrac{1}{2}\nabla(\mathbf{v}_s^2), \tag{12}$$

which is, apart from the last term, identical with (3), and with the same value of Λ. London now argues that, although (12) is probably a more consistent expression

[3] F. London, *Superfluids* (John Wiley and Sons, Inc., New York, 1950), p. 70.

of the equations for a superconductor than is (3), the gradient term is always small, and (3) is simpler. We will argue that the extra term radically alters the conclusion drawn above about the absence of the Hall effect.

Indeed, if one goes through the argument contained between Eqs. (1) and (6), but using (12) instead of (3), one finds that it goes exactly as before, except that the tensor $\mathbf{S}$ is replaced by a new tensor $\mathbf{S}'$, lacking the last term in (5), and therefore given by

$$S_{\mu\nu}'=j_\mu j_\nu. \tag{13}$$

Also, it is no longer the case that $E=0$ in a stationary state, but, from (12)

$$\mathbf{E}=\frac{m}{2e}\nabla(\mathbf{v}_s^2)=\frac{e}{2m}\nabla(\Lambda^2\mathbf{j}_s^2), \tag{14}$$

since $m\mathbf{v}_s=e\Lambda\mathbf{j}_s$, with the value adopted for Λ in this picture.[4]

There are therefore two points in which the conclusions differ from those drawn by London on the basis of (2) and (3). First, the expression for the kinetic stress tensor is changed from (5) to (13), thus eliminating the Bernouilli pressure term. Thus, since the normal components of j must be zero at the surface, the discontinuity in stress across the surface no longer exists, and the same is true of the surface forces which appear in the original picture. Secondly, the electric field is no longer zero, but is given by (14), and constitutes the Hall field. The usefulness of the superconducting wire in an electric motor is still guaranteed, but the forces communicating with the surface are electric forces operating on the metallic lattice. This is the more usual situation.

To spell out this point, consider the following particularly simple stationary situation. A free plane surface of a superconducting body has a magnetic field H_0 parallel to the body just outside it, and currents j inside. Call the interior normal the z direction, the magnetic field direction y, and the current direction x, supposing them to be mutually perpendicular. Then, according to Eqs. (2) or (11), combined with Ampere's law, for the stationary case,

$$\mathrm{curl}\mathbf{H}=(4\pi/c)\mathbf{j}, \tag{15}$$

we can find that the magnetic field as well as the current decrease exponentially going into the material as

$$\begin{aligned}\mathbf{j}&=\mathbf{j}_0\exp[-z/\lambda],\\ \mathbf{H}&=\mathbf{H}_0\exp[-z/\lambda],\end{aligned} \tag{16}$$

where the penetration depth λ is given by

$$\lambda^2=\Lambda c^2/4\pi=mc^2/4\pi e\rho_s. \tag{17}$$

[4] Substantially this conclusion was reached by F. Bopp, Z. Physik **107**, 623 (1937), in a discussion of the derivation of London's equations from the acceleration theory.

With this distribution of field and current we note that $(\mathbf{v}_s\cdot\nabla)\mathbf{v}_s=0$, so that there are no so-called "inertial forces." This is true in both representations of the London equations. Indeed, the "inertial forces" in the version given by Eqs. (2) through (5) can be regarded as arising in breaking up this relation into

$$(\mathbf{v}_s\cdot\nabla)\mathbf{v}_s=\tfrac{1}{2}\nabla(\mathbf{v}_s^2)-\mathbf{v}_s\times\mathrm{curl}\mathbf{v}_s, \tag{18}$$

and then ignoring the first term on the right-hand side, as negligible. In fact, in the case here presented, it is equal and opposite to the last term, which is usually kept, and the electric field given by (14) is easily seen to be equal to the usual Hall field. Since the net force on the electrons is now zero, it is clear that the magnetic force has been turned into electric forces that act on the metallic lattice.

In conclusion, then, we may say that there are available two forms of London's equations, (2) and (3), and (11) and (12), respectively. We may denote them by I and II. They differ by terms which are usually negligible, but which are of utmost interest here. I is the set originally proposed by London, and leads to the prediction that the Hall effect is absent. II is the set that appears naturally from a study of the dynamics of a frictionless electronic fluid, and leads to a normal Hall effect. II is probably, according to London, a somewhat more consistent expression of the electrodynamics of a superconductor, if we believe that frictionless motion of electrons is in any way involved. It is probably also worth noting that the equations II constitute, to second order, a relativistically covariant set, whereas the equations I do not. At the very least, it appears that from this type of argument one cannot predict whether or not a superconductor ought to exhibit a Hall effect.

Note added in proof.—Professor Bardeen has kindly called to my attention an article by J. Lindhard [Phil. Mag. **44**, 916 (1953)] in which it is argued that the London equations do not represent a limiting case of a frictionless electronic fluid. This argument depends upon the zero-point velocity of the electrons in a metal, and must be regarded as rendering still more mysterious the origin of the London equations.

In all the above we have ignored the role of the "normal" electrons in the superconductor. The next sections will be devoted to a study of their influence.

II. THE TWO-FLUID MODEL

We want here to set out briefly those characteristics of the "two-fluid" model[5] which will be essential to the subsequent discussion. The model has been developed in much greater specificity than we need for our purposes. Indeed, for these off-equilibrium situations the specific forms of the model that are currently in vogue cannot be considered well established.

[5] Gorterand Casimir, Physik. Z. **35**, 963 (1934); Z. tech. Phys. **15**, 539 (1934); see also reference 2, pp. 194 ff.

We consider the electrons to divide themselves into two groups, with the relative populations of these groups determined by a parameter f that can vary between zero and unity, and which we call the "fraction of normal electrons." These two groups are supposed to coexist in the same volume, and to be in thermal, but not mechanical interaction. Thus they have, in local equilibrium, the same temperature T and Gibbs free energy density μ (per unit mass) but not necessarily the same pressures.[6,7] It follows that in transport equilibrium we have

$$\begin{aligned} \nabla p_n &= \rho_n \nabla \mu + \sigma_n \nabla T, \\ \nabla p_s &= \rho_s \nabla \mu + \sigma_s \nabla T, \end{aligned} \tag{19}$$

where p, ρ, and σ are the pressure, density, and transport entropy per unit volume, and the subscripts refer to normal and superconducting components. These equations determine the thermomechanical forces on the two groups of electrons in terms of the gradients of the macroscopic thermodynamic quantities. We will suppose that the transport entropy of the superconducting electrons is zero, i.e., $\sigma_s = 0$.

If Eqs. (19) were coupled with suppositions about the kinetics of entropy transport in the electron fluid, we would have a complete scheme for treating the dynamical properties of the two fluid model. In the case of liquid helium II, where analogous considerations apply, they lead to the phenomena of second sound, fountain effect, anomalous heat conductivity, etc. All these are associated with relative motions of the two components, which bring the thermomechanical forces into play.

In the case of superconductors, however, the friction involved in the mass motion of the normal electrons serves to destroy some of these effects. For example, one might expect, in a superconductor, an anomalous heat conductivity produced by the counterflow of the two components, as in helium. However,[6] the resistance to the motion of the normal electrons reduces this to an unobservable fraction of the normal heat conductivity, and it has never been observed. Similarly for the "second sound" phenomenon in a superconductor. Here the resistance can be expected to attenuate the wave in much less than one wavelength, and it too has never been observed. The same argument applies to the absence of thermoeffects in a superconductor. Clearly, if one is to observe the effects of (19) in a superconductor, one must do so without moving the normal electrons.

The Hall effect situation is one in which currents are carried by the superelectrons alone, so that only they experience the magnetic forces. A complete discussion of the behavior of the electrons in the skin must therefore take into account the details of the two-fluid model. This is the subject of the next section.

III. THE HALL EFFECT IN THE TWO-FLUID MODEL

In the presence of electric and magnetic fields the forces on both the normal and superconducting electrons are given by combining (19) with the Lorentz force. If we suppose that only the superelectrons are moving (with a mean velocity v_s), we have, for the forces on the electrons (per unit volume)

$$\begin{aligned} \mathbf{F}_n &= \rho_n \nabla \mu_e + \sigma_n \nabla T, \\ \mathbf{F}_s &= \rho_s \nabla \mu_e + (e/mc)\rho_s [\mathbf{v}_s \times \mathbf{H}], \end{aligned} \tag{20}$$

where we have introduced the electrochemical potential μ_e to include the electric forces. Equilibrium is determined by the absence of a net force on the superelectrons, so that

$$\nabla \mu_e + (e/mc)[\mathbf{v}_s \times \mathbf{H}] = 0. \tag{21}$$

We have now to consider the normal electrons. If there is a net force on them, it will result in an internal circulation of current, and therefore a dissipative effect.[8] Within this framework, the only way this can be avoided is for the thermoelectric force, represented by the term in the gradient of the temperature in (20) to cancel the electrochemical force—so that we would have a thermal gradient in the presence of a magnetic field. This would amount to substituting an Ettingshausen effect for the Hall effect, and is doubtless what would happen if the metal were a thermal insulator. It is not hard to see, however, that the actual thermal gradient will be severely reduced by heat transport in the metal, and, in fact, by a factor of approximately $(kT/E_F)^2$ which is of order 10^{-8}. This can be estimated by writing down the entropy flow balance in the steady-state condition. Thus, the metal can be considered to be isothermal, and a net force equal to $\rho_n \nabla \mu_e$ must be supposed to act on the normal electrons. Thus we have both a dissipative normal current, and a Hall effect.

Deferring for a moment discussion of the fact that the two-fluid model fails to account for the absence of the Hall effect, let us consider first the magnitude of the resistive dissipation predicted above. We can express it in terms of the time constant for the decay of the diamagnetic state of the superconductor, which we have already calculated in Sec. I. We have only to use for

[6] Considerations of this sort have been discussed by V. L. Ginzburg in his book *Superconductivity* (in Russian), Moscow (1946), and in Uspekhi Fiz. Nauk 42, 169 (1950), and by P. M. Marcus at the Schenectady Cryogenics Conference, October, 1952 (unpublished). Particularly the latter anticipates the argument to be presented here.

[7] Dr. Herring has kindly pointed out to me that the formal expression of the assumption of thermal but not mechanical equilibrium is not immediately obvious in the presence of a magnetic field. The form that we have chosen is consistent with a treatment of the problem by the methods of irreversible thermodynamics, and is, in fact, just analogous to the corresponding treatments of the liquid helium problem.

[8] This is not at all unfamiliar. In an ordinary metal that has overlapping bands, so that there are two distinct groups of electrons, there is an internal circulation when a current flows in the presence of a magnetic field. The same applies to the holes and electrons in a semiconductor.

the impedance Z which loads the Hall voltage, some estimate of the resistance of the skin layer to the flow of normal currents. For an area of about 1 cm^2, a penetration defth of about 10^{-5} cm, and a resistivity of about $10^{-6}\Omega$ cm, the impedance may be estimated to be of the order of 10^{-11} ohm. This is more likely high than low for a typical sample. Thus the decay time, which was 5×10^{14} sec with a loading of one ohm, is reduced to a few hours at most. This is much too short, so that we can be sure that loading of the Hall voltage by the normal electrons does not occur on anything like the scale suggested by the two fluid model.

It is to be emphasized that this conclusion is independent of the possible existence of a contact potential that may cancel the Hall voltage at the surface of the specimen, and is a direct consequence of the systematic application of the two-fluid model to the problem. We can therefore only conclude that, if cancellation of the magnetic forces on the superelectrons takes place in the interior of the sample, then the forces responsible for this cancellation (the Hall forces) cannot act also on the normal electrons. This is a new feature of a superconductor, and is not contained in the existing phenomenological theories.

It is not hard to see that the new phenomenological theories[9] do not improve the situation, at least in their present form. What they provide for is a reluctance (because of the uncertainty principle) of the electrons to change their wave functions over distances shorter than $\sim10^{-4}$ cm, and this is not required by our considerations.

[9] Ginzburg and Landau, J. Exptl. Theoret. Phys. (U.S.S.R.) **20**, No. 12 (1950). J. Bardeen, Phys. Rev. **94**, 554 (1954).

IV. CONCLUSIONS

We have considered all possible explanations of the absence of a Hall effect in a superconductor, which both lie in the framework of existing theory, and are known to the author. All have been found wanting. The simple assumption of a contact potential that just cancels the Hall voltage has been found to beg the question, since we are still in trouble in the interior of the sample, as discussed in Sec. III.

We therefore conclude that an explanation of the absence of a Hall effect in a superconductor will require an extension of present theory in a direction not easily foreseen. It will require a long-range cooperative interaction among the electrons, that is not contained in the present phenomenological theories, and which will serve to transfer the magnetic forces on the superconducting electrons directly to the metallic lattice in such a way that the noncurrent carrying electrons are not affected. Whether the present beginnings of a molecular theory of superconductivity contain the seeds of such an interaction, we do not know.

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Theory of the Magnetic Susceptibility of Graphite*

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The theory of the magnetic susceptibility of graphite is presented in terms of a three-dimensional Wallace electron energy band structure. The experimentally observed variation with temperature is explained in a satisfactory manner, provided the interplane resonance integral occurring in the band approximation is given a value of about 0.5 ev. This is about five times larger than the previously used estimate and implies that a two-dimensional band approximation may be invalid in many cases. The inplane resonance integral is obtained by fitting the variation, with electron concentration, of the electrical resistivity of a graphite-bisulphate residue compound. In this way a value of 1.63 ev for this integral is obtained. It might be noted that these values enabled a better fit of the resistivity over the entire range of bisulphatization than could be obtained by a two-dimensional theory. On the other hand, the value thus obtained for the actual magnitude of the susceptibility is lower than that observed by a factor of about 40. The (room temperature) variation of the susceptibility of bromine graphite is then analyzed on the basis of the above theory, using the indicated values of the constants. In this way, a value is obtained for the percentage of the bromine which is ionized. This is found to be weakly dependent on the amount of bromine, varying between 18% at 0.3 atomic percent bromine to 13% at 0.8 atomic percent bromine. The experimental value has been found to vary slightly around 18%. This agreement is very good and indicates that the theory is valid in explaining relative variations of the susceptibility, even though there is difficulty in predicting the absolute magnitude. The latter is the only serious discrepancy found in the present work and has not yet been explained.

I. INTRODUCTION

GRAPHITE shows a very high diamagnetic susceptibility which is, in addition, extremely anisotropic.[1] These properties have been explained by Eatherly[2] and Smoluchowski[3] as due to the highly anisotropic Brillouin zone structure of the conduction band.[4] It was originally shown by Peierls,[5] and later

* This paper is based on studies conducted for the U. S. Atomic Energy Commission.

[1] N. Ganguli and K. S. Krishman, Proc. Roy. Soc. (London) **177**, 168 (1940).

[2] W. P. Eatherly, see comments in discussion following reference 3.

[3] R. Smoluchowski, Revs. Modern Phys. **25**, 178 (1953).

[4] P. R. Wallace, Phys. Rev. **71**, 622 (1947).

[5] R. Peierls, Z. Physik **80**, 763 (1933).