

directly, and determination of density at extremely high pressure these constants are important.

Lazarus<sup>11</sup> studied the variation of the moduli of several cubic crystals under hydrostatic pressures up to 1000 bars. Hearmon<sup>13</sup> has used his data to compute three relations between the third-order constants of the cubic crystals. The methods of measurement under anisotropic stress described here in addition to measurements under hydrostatic stress would in principle make possible the evaluation of all the third-order constants of cubic crystals of both classes.

Several authors<sup>4,9,14</sup> have considered the effect of stress upon elastic wave velocities. Brillouin<sup>4</sup> in the first approximation concluded that pressure decreased

<sup>13</sup> R. F. S. Hearmon, *Acta. Cryst.* 6, 331 (1953).

<sup>14</sup> F. Birch, *J. Appl. Phys.* 9, 279 (1938).

the velocity of both dilational and rotational waves. This was obtained by neglecting the third-order terms in the energy. When these terms are included, however, [Eqs. 76, 77 of reference 4] results agreeing exactly with the first two equations of set (12) of the present paper are obtained. It is necessary in Brillouin's equation to set the initial pressure equal to zero since our equations are referred to zero strain as the initial state.

As was forecast by Brillouin,<sup>5</sup> the third-order constants appear to be in general negative and an order of magnitude larger than the second-order constants  $\lambda$  and  $\mu$ . Our present data are not conclusive on this point, but reference to Eq. (12) shows that this is true for any material if the elastic velocities increase with applied hydrostatic pressure. This is the case for every material that has been studied except glasses.

## Search for the Hall Effect in a Superconductor. I. Experiment

H. W. LEWIS

*Bell Telephone Laboratories, Murray Hill, New Jersey*

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A search has been made for a Hall effect in superconducting vanadium, using a new method that avoids some of the difficulties previously encountered. The result is negative, with an upper limit of  $150 \times 10^{-6}$  emu, which can be compared with the value of  $800 \times 10^{-6}$  emu for normal vanadium. The theoretical implications will be discussed in a separate paper.

### I. INTRODUCTION

SINCE the early work of Kamerlingh Onnes and Hof,<sup>1</sup> it has been generally supposed that there is no Hall effect in a superconductor. Kamerlingh Onnes and Hof searched for the effect in tin and lead samples, and showed that, within the sensitivity of their method, the Hall voltage disappeared when the magnetic field was below the critical field for the sample. Since, however, they were working as pioneers in the study of superconductivity, they were unaware of some of the properties of the superconducting state that we now understand, in particular, the existence of the intermediate state. We wish to point out that their samples were almost certainly in the intermediate state, and that this alone would probably have been sufficient to lead to their negative result. Consequently, the experimental question must still be considered open, and, in view of the significance attached to the Hall coefficient in the study of any phenomenon of electrical conduction,<sup>2</sup> it has seemed

<sup>1</sup> H. Kamerlingh Onnes and K. Hof, *Leiden Comm. No. 142b* (1914); see comments by D. Schoenberg, *Superconductivity* (Cambridge University Press, London, 1952).

<sup>2</sup> In the cases in which current carriers of only one sign are involved, it is well known that the Hall coefficient measures (inversely) the number of current carriers per unit volume. This is, from the theoretical standpoint, an especially important number to know for a superconductor. If current carriers of both

worth while to repeat the experiment, using a method that avoids this difficulty. In Sec. II we will discuss the early experiment more carefully, and the simpler aspects of the question of whether or not there ought to be a Hall effect.

### II. DISCUSSION OF THE KAMERLINGH ONNES-HOF EXPERIMENT, AND CURRENT MOBILITY

The arrangement used by Kamerlingh Onnes and Hof was the one ordinarily used for Hall effect measurements; a thin flat plate was oriented perpendicularly to the magnetic field, and pairs of current electrodes and Hall probes were in contact with the edge of the sample. We now know that such a flat plate cannot, except in very small fields, exclude the magnetic field in a real Meissner effect—this would lead to extremely high fields near the edges, which would destroy the superconductivity, and allow the magnetic field to penetrate

signs are present, their contributions to the Hall effect tend to cancel, leading to small Hall coefficients. For example, tin and lead have Hall coefficients about five times smaller than that of copper, and this can be attributed to this effect of their complex band structure. In these cases, one might expect the Hall coefficient in the superconducting state, if it existed, to tell us whether all bands go superconducting at once, or whether only one band actually superconducts. In the latter case, the Hall coefficient should jump as we go into the superconducting state. Unfortunately, the superconducting Hall effect seems not to exist.

the sample. The actual thickness of the sample was  $\lesssim 1$  mm, and its lateral dimensions  $\sim 1$  cm, so that even if it were in the optimum shape of an oblate spheroid, an applied field of 300 gauss would lead to fields at the edge of about 2000 gauss. In fact the sample was not an oblate spheroid, so that the fields must have been even higher, and we can be sure that the sample was in the intermediate state. What then has this to do with the Hall effect?

To see this, consider first a simple picture of the origin of the Hall effect, in the case of carriers of only one sign. Suppose we have a long rod of rectangular cross section aligned parallel to the  $z$  axis, with its faces determining the  $x$  and  $y$  axes. Suppose further that a current of density  $j$  is flowing in the  $z$  direction and a magnetic field  $H$  is applied in the  $y$  direction. Before the field is applied the charge density in the rod will be uniform according to the theorems of electrostatics. When the field is applied the charges will be accelerated and deflected in the  $x$  direction, thus producing a nonuniform charge distribution across the rod.<sup>3</sup> This will continue until the nonuniform charge distribution produces a transverse electric field  $E$ , sufficient to counteract the deflection forces of the magnetic field. This is the Hall field. This state of equilibrium is well known to occur when  $E=vH$ , where  $v$  is the drift velocity of the charges and everything is measured in electromagnetic units. In fact, this gives us a simple derivation of the value of the Hall coefficient  $R$ , which is defined by

$$R = E/jH, \quad (1)$$

since  $j = nev$ , where  $n$  is the number of carriers per unit volume, and  $e$  is their charge. Thus, from (1) we obtain

$$R = v/j = 1/ne, \quad (2)$$

which is the usual expression for the simple situation here described. In fact, here lies the importance of the Hall coefficient—it measures directly the number of carriers per unit volume. It cannot be too strongly emphasized, however, that this description is valid only in the simplest cases.

Why, now, this digression? It shows that if for any reason the currents filaments were not mobile in the metallic lattice, perpendicularly to their direction of motion, the electric field would not be set up to counterbalance the effects of the magnetic forces, and we would have no Hall effect. But this is the situation in the intermediate state, according to Kamerlingh Onnes and Tuyn,<sup>4</sup> so that we can easily believe that there ought not to be a Hall effect in the intermediate state.<sup>5</sup> This argu-

<sup>3</sup> In this particular geometry, the nonuniform charge distribution will consist of surface charge distributions on the faces determined by the  $y$ - $z$  plane.

<sup>4</sup> H. Kamerlingh Onnes and W. Tuyn, Proc. Acad. Sci. Amsterdam 25, 443 (1923).

<sup>5</sup> Another way of expressing this is to say that if in their transverse displacement the superconducting currents meet restraining forces which do not also affect normal electrons, equilibrium may

ment does not, however, apply to the superconducting state, as has been shown by several experiments,<sup>6</sup> so that the question of the existence of the Hall effect in the superconducting state must still, from this point of view, be considered open.

### III. METHOD AND RESULTS

The method used will be described in greater detail in a separate publication, since it is generally applicable to high-conductivity substances for which measurements of the Hall coefficient are normally most difficult. Consequently, we will be satisfied here with a description of its application to the superconductor used.

The sample was a prolate spheroid of pure, ductile, polycrystalline vanadium, originally from the Electro-Metallurgical Corp.,<sup>7</sup> and its claimed purity was 99.7 percent. Runs were made with the surface machined and then cleaned by soaking in hydrochloric acid, and then after electropolishing, all with the same results.

The spheroid was mounted in a Helmholtz coil, which was also immersed in the helium, and so arranged as to provide a longitudinal magnetic field. Contacts were made to the sample by pressure (provided by phosphor bronze springs) at two points on the equator of the sample, and at one pole.

An audiofrequency current (frequencies of 80 cycles and 800 cycles were used) was then passed through the coil, providing an alternating longitudinal magnetic field. Special precautions were taken to insure that the field wave form was pure. This field then induced the diamagnetic currents in the sample that were necessary to exclude it from the interior of the sample, and we will now be concerned only with the situation in the penetration region of some 500A, since it is only there that we have the magnetic field and current required to produce a Hall effect.

Call the penetration depth  $\lambda$ , the current density  $j$ , the magnetic field  $H$ , and the Hall electric field  $E$ . Then

$$\mathbf{E} = -R(\mathbf{J} \times \mathbf{H}) \quad (3)$$

where  $R$  is the Hall constant. This is the more precise form of Eq. (1). Now, in the skin,

$$\text{curl} \mathbf{H} = 4\pi \mathbf{J}, \quad (4)$$

since we can certainly neglect the displacement current, so that

$$\mathbf{E} = \frac{R}{4\pi} (\mathbf{H} \times \text{curl} \mathbf{H}). \quad (5)$$

However, there is a vector identity to the effect that

$$\frac{1}{2} \nabla (H^2) = \mathbf{H} \times \text{curl} \mathbf{H} + (\mathbf{H} \cdot \nabla) \mathbf{H}, \quad (6)$$

be set up without a Hall field. If, on the other hand, they meet mainly forces that act on all electrons alike, whether electrical or not, we will observe a Hall effect.

<sup>6</sup> E. U. Condon and E. Maxwell, Phys. Rev. 76, 578 (1949); W. V. Houston and N. Muench, Phys. Rev. 79, 967 (1950).

<sup>7</sup> I am indebted to Mr. D. H. Wenny of these Laboratories for supplying the vanadium, and to Mr. R. A. Ehrhardt, also of these Laboratories, for electropolishing it.

in which the last term on the right-hand side is of order  $\lambda/a$  with respect to the first, where  $a$  is a dimension of the sample. This follows from the fact that the magnetic field at the surface of the sample is almost exactly parallel to the surface, and changes appreciably in a distance  $\lambda$  going into the material, as compared with a distance of order  $a$  along the surface.

Consequently,

$$\mathbf{E} = \frac{R}{8\pi} \nabla (H^2), \quad (7)$$

and the Hall potential  $e$  between the surface of the sample and its interior, obtained by integrating (7), is

$$e = RH_0^2/8\pi, \quad (8)$$

where  $H_0$  is the value of the magnetic field at that point on the surface of the sample with which contact is being made.

It should be noted that (8) is an instantaneous, or dc equation in the case of a superconductor. If, now,  $H_0$  is varying sinusoidally with time, we notice that  $e$  will have a dc and a second harmonic component, but no fundamental. This makes it possible to use tuned amplifiers for detection, and in this way to eliminate all difficulties with pickup and therefore neutralization of the fundamental signal.

If we confine ourselves to rms values, and only to the second harmonic part  $e_2$  of the Hall signal, (8) reads

$$e_{2(\text{rms})} = RH_{0(\text{rms})}^2/16\pi\sqrt{2}, \quad (8')$$

which is the practical form to use. If, for example,  $R$  has a typical value of  $700 \times 10^{-6}$  emu, and  $H_0$  is 1000 gauss, then  $e_2$  will be 10 emu, or 0.1  $\mu\text{v}$ , which,

in view of the low output impedance of the Hall signal, can be easily and accurately measured. If one were not concerned about staying under the critical field of the specimen, the fact that the signal goes up quadratically with field could be exploited to give really large signals.

The detection system used in this experiment began with a step-up transformer with a gain of 140, to take advantage of the low impedance mentioned above. This was followed by a low-noise amplifier with a gain of 100, and finally by a General Radio type 736-A Wave Analyzer, which is a tuned vacuum-tube voltmeter, with a 4-cycle bandwidth. The combination provided a full scale sensitivity of about 0.02  $\mu\text{v}$ , with a 4-cycle bandwidth.

The procedure was to search for a signal between one of the equatorial electrodes and the polar electrode, and to monitor by looking at the two equatorial electrodes between which there ought not to be a Hall signal. This was done at various magnetic fields up to the critical field as peak, and at temperatures from 1.5°K to 4.2°K. The transition temperature in zero field for vanadium is about 5.1°K.

No observable Hall signal was found, and an upper limit on  $R$  of  $150 \times 10^{-6}$  emu can be set. This upper limit is to be compared with the normal value for vanadium at room temperature of  $800 \times 10^{-6}$  emu.<sup>8</sup>

In a separate theoretical paper, we will try to get some insight into this result, and to make more precise its implications for the molecular and phenomenological theories of superconductivity.

In conclusion, I would like to thank Dr. B. T. Matthias for the use of his cryostat for this experiment.

<sup>8</sup> Recently measured by Dr. S. Foner, to whom I am indebted for communicating his result prior to publication.