

## Microwave Surface Impedance of Superconductors of the Second Kind

GASTON FISCHER

*RCA Laboratories, Ltd., 8005 Zurich, Switzerland*

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A simplified model of the mixed state of a superconductor of the second kind is proposed. The generation and parallel alignment of "fluxoids" under the influence of an externally applied magnetic field results in a medium whose conductivity is position-dependent in all directions perpendicular to the applied field. The proposed model is that of a two-fluid superconductor with carrier concentrations sinusoidally space-modulated in only one direction. This model is found to account extremely well for the experimentally observed behavior. In particular, the large dependence of the absorption of energy on the relative angle between applied dc field and induced microwave current is satisfactorily explained. The ratio of absorbed energies in the perpendicular and parallel configurations is predicted to lie between 1 and 7, whereas recent experiments with various materials have yielded ratios between 1 and 15. Our model also predicts that this anisotropy is not very dependent on temperature and applied magnetic field, also in agreement with experimental findings.

### I. INTRODUCTION

THE study of superconductivity by the method of microwave surface impedance measurements is a very young science. Most investigations have so far been restricted to so-called "soft superconductors," or "superconductors of the first kind." Experiments performed in the absence of an applied dc magnetic field<sup>1,2</sup> have found satisfactory theoretical explanations.<sup>3-5</sup> But when a magnetic field is applied, results<sup>6,7</sup> are found which present day<sup>8</sup> theory has not been able to explain. "Hard superconductors," or "superconductors of the second kind" (in this paper we shall attribute the same meaning to both words), are still far less well known than their "soft" counterparts. Since microwave surface impedance measurements are themselves generally difficult to interpret, it would seem that such measurements performed with hard superconductors are unlikely at this stage of the art to yield useful information. Several factors, however, seem to contradict this pessimistic viewpoint. First of all, the few experiments that have been performed<sup>9</sup> with hard superconductors have revealed large, clearly defined, and reproducible effects. Secondly, hard superconductors are characterized by short mean free paths of their normal carriers, so that, in general, classical conditions prevail, and the surface impedance problem is accordingly simplified. Thirdly, we shall see in Sec. II that strong magnetic fields induce a very special

kind of directivity inside hard superconductors which is not of the usual tensorial nature. This directivity is of such strength and so characteristic of hard superconductors that very typical and strong effects are expected to result from it. It is therefore likely that an understanding of the striking effects observed in the surface impedance of hard superconductors may be arrived at before one understands the smaller, and perhaps more subtle effects, found with soft superconductors.

### II. SUPERCONDUCTORS OF THE SECOND KIND

The mixed state of a superconductor of the second kind is a good example of a medium where the conductivity is position-dependent. Magnetic fields of a certain strength can penetrate superconductors of the second kind without necessarily destroying superconductivity. According to the most current views,<sup>10</sup> this field penetration is in the form of quantized bundles of flux, so-called fluxoids, at the center of which the material is normal and the field obtains a maximum. As one moves from the center of the fluxoid, the material becomes superconducting, and the field decays essentially as it would at a normal superconducting interface. Since the equilibrium distribution of normal and superconducting electrons is a function of the local magnetic field, the conductivity  $\sigma$  becomes position-dependent. In the Abrikosov<sup>10</sup> theory the fluxoids run parallel to the applied field, and their intersection with a perpendicular plane indicates that they are disposed in a square array. Exceptionally, a triangular array may be more stable. In an actual hard superconductor this perfectly regular arrangement may not obtain, but it is reasonable to assume that the separation between nearest fluxoids will not differ very much from an average value  $d$ . This average value  $d$  is a function of the applied field  $H$ . At fields just above  $H_{c1}$ , the onset of *field penetration*, the separation of fluxoids is larger than the penetration depth  $\lambda$ . As the field increases, the average separation  $d$

<sup>1</sup> M. A. Biondi, M. P. Garfunkel, and A. O. McCoubrey, *Phys. Rev.* **108**, 495 (1957).

<sup>2</sup> M. A. Biondi and M. P. Garfunkel, *Phys. Rev.* **116**, 853 and 862 (1959).

<sup>3</sup> D. C. Mattis and J. Bardeen, *Phys. Rev.* **111**, 412 (1958).

<sup>4</sup> I. M. Khalatnikov and A. A. Abrikosov, *Advan. Phys.* **8**, 45 (1959).

<sup>5</sup> P. B. Miller, *Phys. Rev.* **118**, 928 (1960).

<sup>6</sup> M. Spiewak, *Phys. Rev. Letters* **1**, 136 (1958); *Phys. Rev.* **113**, 1479 (1959).

<sup>7</sup> P. L. Richards, *Phys. Rev.* **126**, 912 (1962).

<sup>8</sup> G. Dresselhaus and M. S. Dresselhaus, *Phys. Rev.* **118**, 77 (1960).

<sup>9</sup> M. Cardona, G. Fischer, and B. Rosenblum, *Phys. Rev. Letters* **12**, 101 (1964); M. Cardona and B. Rosenblum, *Phys. Letters* **8**, 308 (1964); see also B. Rosenblum and M. Cardona, *Phys. Letters* **9**, 220 (1964).

<sup>10</sup> A. A. Abrikosov, *Zh. Eksperim. i Teor. Fiz.* **32**, 1442 (1957) [English transl.: *Soviet Phys.—JETP* **5**, 1174 (1957)], see also Ref. 14.

between fluxoids decreases and, according to Abrikosov,<sup>10</sup> reaches a value of  $\lambda_0/\kappa$  just before the superconductor finally becomes normal. In the above quotient,  $\lambda_0$  is the actual weak-field penetration depth at the temperature  $T$  considered, and  $\kappa$  is the Ginzburg-Landau<sup>11</sup> parameter. Gor'kov<sup>12</sup> has shown that for pure metals  $\kappa=0.96\lambda_0/\xi_0$ , where  $\xi_0$  is Pippard's coherence distance.<sup>13</sup> Thus, at fields near the *quenching* field  $H_{c2}$  the average fluxoid separation  $d$  is about equal to the coherence distance  $\xi_0$ .

The relaxation time  $\tau$  of normal electrons in superconductors of the second kind is generally short, so that for the microwave frequencies considered here (up to 100 Gc/sec), one has  $\omega\tau \ll 1$ . Under these conditions we can reasonably assume that the equilibrium state of the superconductor follows the microwave field, and the size of the skin depth  $\delta$  is then identical with the dc penetration depth  $\lambda$ . We therefore conclude that for fields just above  $H_{c1}$  the fluxoid separation  $d$  is larger than  $|\delta|$ , whereas at fields just below  $H_{c2}$ , this separation is only a fraction  $1/\kappa$  of  $|\delta|$ . At fields only moderately above the onset of the mixed state, Abrikosov<sup>10</sup> has shown that the field at the center of the fluxoid is only about twice the applied field. Since, at the same time, the average field inside the superconductor has already increased to a good fraction of the applied field, it is obvious that the average separation between fluxoids cannot be much different from the penetration depth  $\lambda$ . Consequently, once flux penetration occurs, a rather large number of fluxoids move into the superconductor, as exemplified by the vertical slope of the magnetization curve derived by Goodman<sup>14</sup> from Abrikosov's theory. The average fluxoid separation quickly becomes of order  $\lambda$ , at which separation fluxoids start to interact. As the field increases further the separation decreases much less rapidly, slowly reaching the value  $\lambda/\kappa$  as  $H$  approaches  $H_{c2}$ .

Let us assume as in Fig. 1 an external dc field  $\mathbf{H}$  to be applied parallel to the surface  $z=0$  and take the direction of  $\mathbf{H}$  as  $x$  axis. Because of the fluxoid alignment parallel to  $\mathbf{H}$ , we do not expect the equilibrium distribution of normal and superconducting electrons  $n_n$  and  $n_s$  to vary in that direction. In directions  $y$  and  $z$ , however, we do expect variations of  $n_n$ ,  $n_s$ , and consequently of  $\sigma$ , the conductivity. We have then to deal with two basic configurations, *parallel* when the microwave current is flowing parallel to the fluxoids, and *perpendicular* when the microwave current is flowing in directions perpendicular to the fluxoids.

It may be worth mentioning that we expect the two-field configurations to yield different surface imped-

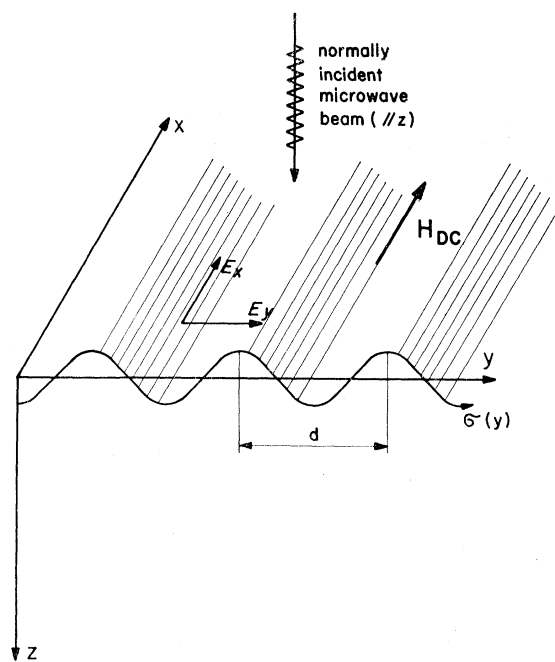


FIG. 1. Coordinate system to be used throughout this paper. The medium extends over all  $z>0$  and radiation is impinging parallel to the  $z$  axis. The cosine function symbolizes the periodic conductivity in the  $y$  direction.

ances. It is true that to the incident microwaves the metal acts like a short circuit with respect to a high-impedance source. A constant total current is therefore induced in the metal, irrespective of local variations of the conductivity. As a consequence the magnetic induction at the surface  $z=0$  is independent of coordinate  $y$ . For  $z>0$ , however,  $\mathbf{B}(y,z)$  does vary with  $y$ .  $\mathbf{E}(y,z)$ , on the other hand, is never independent of  $y$ , even when  $z=0$ . Since we cannot assume *a priori*  $\mathbf{E}(y,z)$  to be the same in the two configurations, we cannot expect *a priori* to find identical surface impedances.

### III. MICROWAVE SURFACE IMPEDANCE

Let us choose a Cartesian coordinate system as shown in Fig. 1, with a semi-infinite metal extending over the region  $z>0$ . A polarized microwave beam is assumed to fall vertically onto the metal from the vacuum ( $z \leq 0$ ). A system of electric and magnetic fields is set up in the metal near the surface, but because of skin effect these fields decay rapidly as one moves deeper into the metal. The surface impedance  $Z$  is then defined as the ratio of the electric field at the surface to the component parallel to the surface of the induced current density,  $j_{11}$ , integrated from  $z=0$  to  $z=\infty$ ,

$$Z = E(z=0) / \int_0^{\infty} j_{11}(z) dz. \quad (1)$$

The two main factors which determine the microwave

<sup>11</sup> V. L. Ginzburg and L. D. Landau, Zh. Eksperim. i Teor. Fiz. **20**, 1064 (1950).

<sup>12</sup> L. P. Gor'kov, Zh. Eksperim. i Teor. Fiz. **36**, 1918 (1959); **37**, 833 (1959); **37**, 1407 (1959) [English transl.: Soviet Phys.—JETP **9**, 1364 (1959); **10**, 593 (1960); **10**, 998 (1960)].

<sup>13</sup> A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 745 (1953).

<sup>14</sup> B. B. Goodman, IBM Res. Develop. J. **6**, 63 (1962).

surface impedance of a metal are the conditions at the boundary  $z=0$ , and the relation between current density  $\mathbf{j}$ , and the electromagnetic fields  $\mathbf{E}$  and  $\mathbf{B}$ . One relation between  $\mathbf{j}$  and  $\mathbf{B}$  is contained in Maxwell's equations. Neglecting displacement currents<sup>15</sup> and assuming a time dependence of the form  $\exp(i\omega t)$ , these equations read

$$\nabla \times \mathbf{B} = (4\pi/c)\mathbf{j}, \quad (2)$$

$$\nabla \times \mathbf{E} = -(i\omega/c)\mathbf{B}. \quad (3)$$

Elimination of  $\mathbf{B}$  gives a differential equation for  $\mathbf{E}$ ,

$$\nabla \times \nabla \times \mathbf{E} = -(4\pi i\omega/c^2)\mathbf{j}, \quad (4)$$

which is basic to all microwave surface impedance problems of metals. This differential equation can be solved only once the boundary conditions are specified, and if a second relation between  $\mathbf{j}$  and  $\mathbf{E}$  is given. A great deal of attention has been devoted to such situations where the ( $\mathbf{j}-\mathbf{E}$ ) relation is *nonlocal*,<sup>16,17</sup> that is, of the form

$$\mathbf{j}(\mathbf{r}) = \int \sigma \cdot K(\mathbf{r}-\mathbf{r}') \cdot \mathbf{E}(\mathbf{r}') \cdot d^3r'. \quad (5)$$

In addition, the more general problem when the product  $\sigma K(\mathbf{r}-\mathbf{r}')$  is of tensorial nature has also been investigated.<sup>18</sup> All theories, however, have assumed  $\sigma$  to be independent of position and  $K$ -dependent only on  $\mathbf{r}-\mathbf{r}'$ , and not on  $\mathbf{r}$  and  $\mathbf{r}'$ , separately. The problem of a position-dependent  $\sigma$  has not received any attention. In a paper about to appear elsewhere,<sup>19</sup> we have investigated the microwave surface impedance of a semi-infinite medium in which a scalar but complex conductivity  $\sigma$  is periodic in a direction parallel to the surface  $z=0$ . The calculation has been carried out in detail in the special case when the conductivity is of the form

$$\sigma(y) = \sigma_0 + 2\sigma_1 \cos(ky), \quad (6)$$

with a period  $d$ ,

$$d = 2\pi/k, \quad (7)$$

and when the ( $\mathbf{j}-\mathbf{E}$ ) relation is strictly local.

The problem with a conductivity  $\sigma(y)$  periodic in one direction is, of course, not equivalent to the situation obtaining in the mixed state of a hard superconductor, where the conductivity  $\sigma(y,z)$  is periodic in the two directions  $y$  and  $z$ . However, the first and simpler one of these two problems has in common with

the more complex second one that two basically different configurations may be defined with respect to the polarization of the microwave beam. We shall speak of a *parallel* configuration when the induced microwave current is flowing parallel to the conductivity pattern (i.e., parallel to the  $x$  axis) and of a *perpendicular* configuration when the microwave current is flowing perpendicularly to the conductivity pattern (i.e., parallel to the  $y$  axis). In spite of neglecting the variation of  $\sigma$  with coordinate  $z$ , the formulas derived in Ref. 19 reproduce some of the essential features observed in recent measurements of the microwave surface impedance of hard superconductors.<sup>9</sup> We shall therefore present and discuss these results here.

#### IV. CONDUCTIVITY OF HARD SUPERCONDUCTORS

In order to appreciate the conclusions reached in Ref. 19 we have to obtain an estimate of the relative magnitude of the position-dependent part of the conductivity. Since we only need an estimate, it will be sufficient to derive it in terms of a two-fluid model, for which the high-frequency conductivity is

$$\sigma = \frac{n_n e^2 \tau}{m(1+i\omega\tau)} - \frac{n_s e^2}{m\omega} = \frac{e^2}{m\omega} \frac{(n_n + n_s)\omega\tau - in_s}{1+i\omega\tau}. \quad (8)$$

In (8) we have taken identical masses for normal and superconducting electrons, the concentrations of which have been labeled  $n_n$  and  $n_s$ , respectively. In a hard superconductor,  $n_n$  and  $n_s$  vary with position while, of course, their sum remains constant. At the center of fluxoids, obviously,  $n_s=0$ .

Let us decompose  $n_n$  and  $n_s$  into a constant and a variable part. With obvious meanings of the symbols, we write

$$n_0 = n_n + n_s = (n_{n0} + n_{\pm}) + (n_{s0} - n_{\pm}). \quad (9)$$

For the constant part  $\sigma_0$  and the variable part  $\sigma_{\pm}$  of the conductivity we then have

$$\sigma_0 = \frac{e^2}{m\omega(1+i\omega\tau)} (n_0\omega\tau - in_{s0}), \quad (10)$$

$$\sigma_{\pm} = \frac{e^2}{m\omega(1+i\omega\tau)} (+in_{\pm}). \quad (11)$$

Calling  $n_1$  and  $2\sigma_1$  the extremal values of  $n_{\pm}$  and  $\sigma_{\pm}$  in order to be consistent with our particular form (6) of  $\sigma$ , we have also

$$\sigma_1 = \frac{e^2}{2m\omega(1+i\omega\tau)} (+in_1). \quad (12)$$

Since both  $n_n$  and  $n_s$  are never allowed to become negative, the largest permissible  $|n_1|$  can only equal the smaller one of the two parameters  $n_{n0}$  and  $n_{s0}$ .

We seek to determine, now, the range of complex

<sup>15</sup> Displacement currents can be neglected up to frequencies of 100 Gc/sec when the magnitude of the conductivity  $|\sigma|$  is always larger than about one  $(\Omega \text{ cm})^{-1}$ .

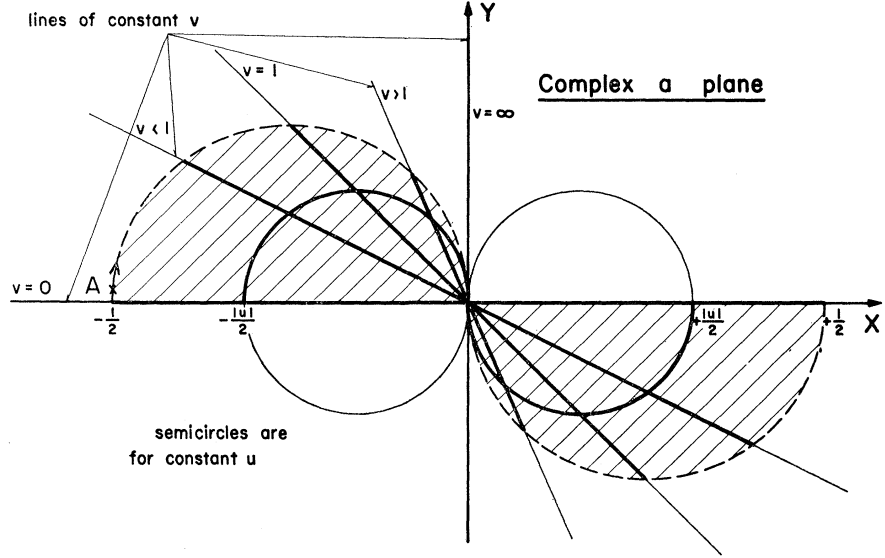
<sup>16</sup> G. E. H. Reuter and E. H. Sondheimer, Proc. Roy. Soc. (London) **A195**, 336 (1948).

<sup>17</sup> R. B. Dingle, Physica **19**, 311 (1953).

<sup>18</sup> A. B. Pippard, Proc. Roy. Soc. (London) **A203**, 98 (1950); and **A224**, 273 (1954); E. H. Sondheimer, Proc. Roy. Soc. (London) **A224**, 260 (1954); G. E. Smith, Phys. Rev. **115**, 1561 (1959).

<sup>19</sup> G. Fischer, J. Math. Phys. **5**, 944 (1964).

FIG. 2. Complex  $a = \sigma_1/\sigma_0$  plane. The only possible values of  $a$  are those within the two hatched semicircles.



values which the ratio  $a = \sigma_1/\sigma_0$  may obtain when the other parameters assume any of the values that they are allowed to take. We have

$$a = \frac{\sigma_1}{\sigma_0} = \frac{1}{2} \frac{in_1}{n_0\omega\tau - in_{s0}} = \frac{1}{2} \frac{-n_1n_{s0} + in_1n_0\omega\tau}{(n_0\omega\tau)^2 + n_{s0}^2}. \quad (13)$$

Let us introduce two parameters  $u$  and  $v$ .

$$u = n_1/n_{s0}, \quad \text{and} \quad v = n_0\omega\tau/n_{s0}. \quad (14)$$

$v$  can assume any real positive value, whereas  $u$  is restricted to real values between  $-1$  and  $+1$ .

$$v \geq 0, \quad (15a)$$

$$-1 \leq u \leq +1. \quad (15b)$$

$a$  then becomes

$$a = X + iY = \frac{1}{2}u[(-1 + iv)/(1 + v^2)], \quad (16)$$

which defines  $X$  and  $Y$ ,

$$X = -\frac{1}{2}u[1/(1 + v^2)], \quad (17)$$

$$Y = +\frac{1}{2}u[v/(1 + v^2)]. \quad (18)$$

In the complex  $a$  plane, Eqs. (15) to (18) define pairs of semicircles or segments of straight lines, depending whether one considers  $v$  or  $u$  to be a variable parameter. If  $v$  is taken as parameter, its elimination from (17) and (18) yields the equations of a pair of circles,

$$(X \pm \frac{1}{4}u)^2 + Y^2 = (\frac{1}{4}u)^2, \quad (19a)$$

whereas the elimination of  $u$  gives the straight line

$$Y = -vX. \quad (19b)$$

Only semicircles of the kind marked with a heavy line in Fig. 2 are allowed, since the other half circles violate (15a). Likewise, only the heavily marked

straight line segments satisfy (15b) and (19b). For a given  $u$ , all permitted values of  $a$  lie on the two semicircles drawn with a full line in Fig. 2. The largest semicircles are obtained when  $u = \pm 1$ , and are indicated with dashed lines. All permitted values of  $a$  are therefore comprised within the hatched areas of Fig. 2, and we can conclude that under all circumstances one has

$$|a| \leq \frac{1}{2}. \quad (20)$$

An interesting special limit occurs when  $\tau \equiv 0$  and thus also  $v \equiv 0$ , and  $Y \equiv 0$ .  $a$  is then purely real and comprised in the range

$$-\frac{1}{2} \leq a \leq +\frac{1}{2}, \quad \text{i.e.,} \quad a^2 \leq \frac{1}{4}. \quad (21)$$

If, in that same limit, we look at (10) and (12), we see that

$$\sigma_0(\tau \equiv 0) = -i(n_{s0}e^2/m\omega), \quad (22)$$

$$\sigma_{\pm}(\tau \equiv 0) = +i(n_{\pm}e^2/m\omega), \quad (23)$$

and in terms of  $n_1$  and  $\sigma_1$ ,

$$\sigma_1(\tau \equiv 0) = +i(n_1e^2/2m\omega). \quad (24)$$

In this limit, then,  $\sigma(y, z)$  is purely imaginary negative. This leads to a purely imaginary surface impedance, meaning that there is no absorption of incident radiation. This result is not surprising since power can be dissipated only via normal electrons, and  $\tau \equiv 0$  means that these electrons are completely immobile, incapable of absorbing energy from any field. To secure the possibility of energy absorption,  $\omega\tau$  cannot be neglected altogether, but with  $\omega\tau \ll 1$ , expansion to linear terms will usually suffice.

The foregoing analysis has allowed us to put upper bounds to the amplitude of the variable part of the conductivity of a superconductor of the second kind. We have not, however, derived any information relative

to the shape of the function  $\sigma(y, z)$ . The actual shape of  $\sigma(y, z)$  would have to be derived from a theory of hard superconductors; this could probably be done starting from the theory of Abrikosov,<sup>10</sup> but will not be attempted here. The knowledge of  $\sigma(y, z)$  has to be gained in the form of knowledge in function of temperature  $T$ , applied dc magnetic field  $H$ , and material constants of the superconductor of the following parameters:

$$n_{s0} = n_{s0}(T, H), \quad (25)$$

$$n_{\pm} = n_{\pm}(T, H), \quad (26)$$

$$k = k(T, H). \quad (27)$$

(26) also implies knowledge of  $n_1$  and  $\sigma_1$ , and we recall that  $d = 2\pi/k$  is the spatial period of  $n_{\pm}$ . From (26) and (27) one should therefore be able to derive a relation between  $\sigma_1$  and  $d$ . Following the discussion of Sec. II, we can say that when  $H$  is only slightly above  $H_{c1}$ ,  $k$  will be near the small end of its range, whereas  $\sigma_1/\sigma_0$  will be large. As  $H$  increases,  $k$  will increase, and  $\sigma_1/\sigma_0$  decrease, although  $\sigma_1/\sigma_0$  may at first remain more or less constant until the density of fluxoids has reached the point where they start to interact appreciably.

In the absence of any detailed knowledge about  $\sigma(y, z)$ , we shall then choose a conductivity of the form given by (6), but where  $\sigma_1$  and  $k$  have the meanings and properties attributed to them in this section.

#### V. SURFACE IMPEDANCE OF THE PERIODIC MODEL

Let us assume a semi-infinite metal and a vertically incident microwave beam as represented schematically in Fig. 1 with a conductivity as given by (6). We have shown in Ref. 19 that two independent field configurations result with generally different surface impedances. Following the definitions of Sec. III, we call  $Z_{11}$  and  $Z_1$  the impedances obtaining when  $E_y = 0$  or  $E_x = 0$ , respectively. According to Ref. 19, the average surface impedances  $Z_{011}$  and  $Z_{01}$  can be expressed by a common formula with slightly different meanings of the symbols which have all been listed in Table I.

$$Z_0 = Z_{00} \frac{(\Gamma + B - 1)(\Gamma + B)^{1/2} - (\Gamma - B - 1)(\Gamma - B)^{1/2}}{2B(\Gamma^2 - B^2)^{1/2}}. \quad (28)$$

TABLE I. Meaning of the symbols appearing in formulas (28), etc.

	For $Z_{11}$	For $Z_1$
$Z_{00}$	$4\pi i \omega \delta_0 / c^2 = (4\pi i \omega / c^2 \sigma_0)^{1/2}$	idem
$\Gamma$	$1 + \frac{1}{2}b$	idem
$B$	$(\frac{1}{4}b^2 + 2a^2)^{1/2}$	$[\frac{1}{4}b^2 + 2a^2(1+b)]^{1/2}$
$b$	$\delta_0^2 k^2 = 4\pi^2 (\delta_0^2 / d^2)$	idem
$a$	$\sigma_1 / \sigma_0 = \delta_0^2 / \delta_1^2$	idem
$1/\delta_0^2$	$4\pi i \omega \sigma_0 / c^2$	idem
$1/\delta_1^2$	$4\pi i \omega \sigma_1 / c^2$	idem
$k$	$2\pi/d$	idem

The entire difference between the two configurations is concentrated in parameter  $B$ .

The spatial variation of  $Z_{11}$  and  $Z_1$  is given by another common formula

$$Z(y) = Z_0 + 2Z_1 \cos(ky), \quad (29)$$

where

$$Z_{111} = -Z_{00} a \frac{(\Gamma + B_{11})^{1/2} - (\Gamma - B_{11})^{1/2}}{2B_{11}(\Gamma^2 - B_{11}^2)^{1/2}}, \quad (30)$$

and

$$Z_{11} = -Z_{00} a (1+b) \frac{(\Gamma + B_1)^{1/2} - (\Gamma - B_1)^{1/2}}{2B_1(\Gamma^2 - B_1^2)^{1/2}}. \quad (31)$$

The parameters of these formulas are also contained in Table I.

Formulas (28) to (31) are valid provided the following condition is true (cf. Ref. 19):

$$d^2 / |\delta_0^2| \ll (4\pi)^2 |\sigma_0 / \sigma_1| \approx 160 |\sigma_0 / \sigma_1|. \quad (32)$$

We know that  $|\sigma_0 / \sigma_1| \geq 2$ , and since  $\delta_0$  is simply the average skin depth, (32) receives a simple interpretation; for the largest possible variation of the conductivity (28) to (31) are valid as soon as  $d$  becomes smaller than about five skin depths. But when  $d$  is larger than  $|\delta_0|$ , both configurations give practically identical results, the surface impedance  $Z(y)$  being then uniquely determined by the *local* value  $\sigma(y)$  of the conductivity

$$Z(y) = \left( \frac{4\pi i \omega}{c^2 (\sigma_0 + 2\sigma_1 \cos(ky))} \right)^{1/2}. \quad (33)$$

The average impedance  $Z_0$  is then given by the integral over one period of  $Z(y)/d$ . When  $|\sigma_1 / \sigma_0| \ll 1$  this average tends toward  $Z_{00}$ , whereas for larger ratios one is led to complex Legendre integrals.

From Eq. (33), we see that in the range  $d > |\delta_0|$ , a local relationship between  $z$  and  $\sigma$  results. This is in contrast to what obtains in the range described by (32), that is, when  $|\delta_0| > d$ , where formulas (28) to (31) apply. In spite of assuming a local "current-field" ( $\mathbf{j} - \mathbf{E}$ ) relation, one does not end up with a local ( $Z - \sigma$ ) relation. There is a smearing-out effect which results here not from a long mean free path  $l$ , but because of field penetration effects. The fields cannot vary much in space over distances smaller than a skin depth. With this in mind, one can give a very pertinent interpretation to the range of validity (32) of our treatment. When  $|d/\delta_0|$  is very large, a Fourier expansion of the fields  $\mathbf{E}$  and  $\mathbf{B}$ , and consequently also of  $Z(y)$ , restricted to only one oscillatory term, will be satisfactory only when  $|\sigma_1 / \sigma_0| = |a|$  is sufficiently small. It is then possible to expand any function  $f(\sigma)$ . Thus,

$$f(\sigma) = f(\sigma_0) + (df/d\sigma) 2\sigma_1 \cos(ky), \quad (34)$$

and one can easily check that under these circumstances, formulas (28) to (31) give identical results to formula (33) expanded according to (34). On the other

hand, if  $|d/\delta_0|$  is not very large, the smearing-out effect on  $Z(y)$  insures that, even when the conductivity varies very much, (i.e.,  $|a| \cong \frac{1}{2}$ ),  $\mathbf{E}$ ,  $\mathbf{B}$ , and  $Z(y)$  do not vary very much, and a Fourier expansion with but one oscillatory term is again satisfactory. The conditions under which formulas (28) to (31) are the least satisfactory are such, therefore, that  $|a|$  approaches  $\frac{1}{2}$ , and  $|d/\delta_0|$  is very much larger than unity. If we apply these considerations to superconductors of the second kind, we find that conditions under which our treatment is valid are practically always realized.  $|a|$  is largest at low-magnetic field  $H$  above  $H_{c1}$ ; but we have seen in Sec. II that for fields little larger than  $H_{c1}$ , the fluxoid separation  $d$  is approximately of the same size as penetration depth and skin depth

$$d \approx |\delta_0| \cong \lambda. \quad (35)$$

With increasing field  $H$ , the separation  $d$  decreases, and while  $|a|$  may, at first, remain constant, it will eventually also decrease when  $H$  approaches  $H_{c2}$ .

Expressions (28) to (31) are sufficiently complex that comparison in general terms of the two configurations is very difficult. However, if we limit ourselves to such conditions as apply to superconductors of the second kind, these expressions take on very simple forms. With (35) we find

$$|b| = k^2 |\delta_0^2| = 4\pi^2 (|\delta_0^2|/d^2) \approx 40 \gg 1, \quad (36)$$

and, therefore, also

$$|b| \gg |a| \quad \text{or} \quad |a^2|. \quad (37)$$

Under these conditions (28) reduces to

$$Z_{011} \cong Z_{00} = (4\pi i \omega / c^2 \sigma_0)^{1/2}, \quad (38)$$

and

$$Z_{01} \cong Z_{00} (1 - 2a^2)^{-1/2}. \quad (39)$$

It is interesting to note that every explicit dependence on the period  $d$  has disappeared from (38) and (39). In spite of their apparent simplicity, we should like to point out, however, that these formulas contain a dependence on field  $H$ , frequency  $\omega$ , and temperature  $T$ , since  $\sigma_0$  is itself dependent on these variables.

#### IV. RESULTS AND DISCUSSION

Although our model only reproduces "some" of the characteristics of superconductors of the second kind, it is of interest to see what behavior formulas (38) and (39) predict with respect to frequency  $\omega$ , magnetic field  $H$ , and temperature  $T$ . Since the two sets of available experimental results<sup>9</sup> have both been obtained with material for which  $\omega\tau \ll 1$ , we shall limit our analysis to this case. In the lower part of the mixed state (i.e.,  $H > H_{c1}$ , but appreciably  $< H_{c2}$ ),  $n_0$ ,  $n_{s0}$ , and  $n_1$  are commensurable. It is therefore appropriate to expand  $\sigma(y)$  with respect to  $\omega\tau$  up to linear terms. We

start with (10) and (12).

$$\sigma_0 = -i(n_{s0}e^2/m\omega)\{1 + i\omega\tau(n_0/n_{s0} - 1)\}, \quad (40)$$

$$\sigma_1 = +i(n_1e^2/2m\omega)(1 - i\omega\tau). \quad (41)$$

If our hypothetical metal is to resemble as best as possible a superconductor of the second kind in the mixed state, we must require that it should become normal for isolated values of  $y = y_0$ . Planes  $y = y_0$  correspond to the centers of fluxoids. We have then to require

$$y_0 = (2n+1)\pi/k = (n + \frac{1}{2})d, \quad (42)$$

and

$$n_1 = n_{s0} \leq \frac{1}{2}n_0. \quad (43)$$

The equality sign in (43) holds at temperatures near zero and fields little above  $H_{c1}$ . As  $H$  and  $T$  increase,  $n_{s0}$  will decrease, becoming zero as  $H = H_{c2}$ . In the complex  $a$  plane of Fig. 2, the low  $H$  and low  $T$  limit corresponds to a point  $A$  on the largest semicircle near the real axis. As  $H$  and  $T$  increase, one moves toward the origin of the coordinate system along the semicircle as indicated by the arrow.

In order to have a suitable reference, we derive first the complex surface impedance  $Z_n = R_n + iX_n$  of the corresponding normal metal, setting, therefore,  $n_1 = n_{s0} \equiv 0$ . We find

$$Z_n = R_n + iX_n = (1+i)(\omega/ec)(2\pi m/n_0\omega\tau)^{1/2}, \quad (44)$$

and obviously  $R_n = X_n$ .

To obtain a corresponding expression for  $Z_{011} = R_{011} + iX_{011}$ , we introduce (40) into (38),

$$Z_{011} = Z_{00} = \frac{2\omega(\pi m)^{1/2}}{ec} \left\{ i + \frac{\omega\tau}{2} \left( \frac{n_0}{n_{s0}} - 1 \right) \right\}, \quad (45)$$

and have also

$$R_{011} = R_{00} = [(\pi m)^{1/2}/ec](\omega^2\tau/n_{s0}^{3/2})(n_0 - n_{s0}), \quad (46)$$

$$X_{011} = X_{00} = 2(\pi m)^{1/2}\omega/ecn_{s0}^{1/2}. \quad (47)$$

In terms of  $R_n = X_n$ , we get

$$\frac{R_{011}}{R_n} = \frac{R_{00}}{R_n} = \frac{1}{\sqrt{2}} (\omega\tau)^{3/2} \frac{(n_0 - n_{s0})n_0^{1/2}}{n_{s0}^{3/2}}, \quad (48)$$

$$\frac{X_{011}}{X_n} = \frac{X_{00}}{X_n} = \left( \frac{2n_0\omega\tau}{n_{s0}} \right)^{1/2}. \quad (49)$$

We recall that the condition that  $n_{s0}$  and  $n_0$  should be commensurable restricts the range of validity of formulas (45) to (49) to fields  $H_{c1} < H < H_{c2}$ , such that

$$n_0\omega\tau \ll n_{s0}. \quad (50)$$

But since  $\omega\tau \ll 1$ , conditions (50) may well allow  $H$  to come fairly close to  $H_{c2}$ . In addition, one also finds the inequalities

$$R_{011}/R_n \ll X_{011}/R_n < 1. \quad (50')$$

At low  $H$  and  $T$ , such that the equality sign prevails in (43), formulas (48) and (49) reduce to

$$R_{011}/R_n = (\omega\tau)^{3/2}, \quad (51)$$

$$X_{011}/R_n = 2(\omega\tau)^{1/2}. \quad (52)$$

Before attempting discussion of these results, we shall derive corresponding expressions for the perpendicular configuration. With (10) and (12) we find first

$$a = \sigma_1/\sigma_0 = in_1/2(n_0\omega\tau - in_{s0}), \quad (53)$$

and then, with  $\omega\tau \ll 1$  and (43) and (50), expanding to linear terms in  $\omega\tau$ :

$$(1 - 2a^2)^{-1/2} = \sqrt{2}\{1 - i(n_0/n_{s0})\omega\tau\}. \quad (54)$$

Combining (54), (39), and (45), we find

$$Z_{01} = -\frac{2\omega}{ec} \left( \frac{2\pi m}{n_{s0}} \right)^{1/2} \left\{ \frac{\omega\tau}{2} \left( \frac{3n_0}{n_{s0}} - 1 \right) + i \right\}, \quad (55)$$

and therefore

$$R_{01} = -\frac{1}{ec} \left( \frac{2\pi m}{n_{s0}} \right)^{1/2} \omega^2\tau \left( \frac{3n_0}{n_{s0}} - 1 \right), \quad (56)$$

$$X_{01} = (2\omega/ec) (2\pi m/n_{s0})^{1/2}. \quad (57)$$

In terms of  $R_n = X_n$ ,

$$\frac{R_{01}}{R_n} = (\omega\tau)^{3/2} \left( \frac{n_0}{n_{s0}} \right)^{1/2} \left( \frac{3n_0}{n_{s0}} - 1 \right) \ll 1 \quad (58)$$

and

$$X_{01}/R_n = (4n_0\omega\tau/n_{s0})^{1/2} < 1. \quad (59)$$

Inequalities similar to (50') are thus also valid in the perpendicular configuration. Comparing the two configurations, we see that

$$\frac{R_{01}}{R_{011}} = \sqrt{2} \frac{3n_0 - n_{s0}}{n_0 - n_{s0}} > 1, \quad (60)$$

and

$$X_{01}/X_{011} = \sqrt{2} > 1. \quad (61)$$

If we look again at the limit of low  $T$  and  $H$ , when the equality sign obtains in (43), we find

$$R_{01}/R_n = 5\sqrt{2}(\omega\tau)^{3/2}, \quad (62)$$

$$X_{01}/R_n = 2\sqrt{2}(\omega\tau)^{1/2}, \quad (63)$$

and

$$R_{01}/R_{011} = 5\sqrt{2} \approx 7. \quad (64)$$

This ratio of  $R_{01}$  to  $R_{011}$ , the largest possible one in the mixed state of our superconductor model, is in surprisingly good agreement with the measurements of Cardona *et al.*<sup>9</sup> if we consider the great simplicity of the model.

Looking at (60) we find also that the ratio  $R_{01}/R_{011}$  is not very dependent on temperature and magnetic

field in the whole range (50) of applicability of (60). When  $n_{s0} \ll n_0$ , one still finds

$$R_{01}/R_{011} = 3\sqrt{2} \approx 4. \quad (65)$$

The relative insensitivity of the above ratio against variations of  $T$  and  $H$  is also in agreement with experimental observations.<sup>9</sup>

Our model, as was emphasized in Sec. IV, does not provide any information as to the detailed dependence on temperature and field of  $n_{s0}$ , but our results nevertheless clearly show that there is very little absorption at low fields and temperature. As  $T$  and  $H$  increase,  $n_{s0}$  decreases, and in both configurations  $R$  and  $X$  increase. We also believe that the predicted frequency dependences of  $R \propto \omega^2$  and  $X \propto \omega$  are probably correct as long as excitation absorption across the energy gap can be neglected.

## VII. CONCLUSIONS

Our theory shows in a quantitative way that a metal with a periodic conductivity pattern in a direction parallel to the metal surface has an anisotropic surface impedance. This theory applies in a semiquantitative way to hard superconductors, where the concentrations of normal and superconducting carriers vary in the two independent directions perpendicular to a strong dc magnetic field. In contrast to the present theory, Dresselhaus and Dresselhaus<sup>8</sup> have calculated the microwave surface impedance of superconductors in a magnetic field, and derived an anisotropy on the basis of the influence of the field on the kinetic properties of the normal carriers rather than on the spatial variation of their number. The Dresselhaus theory is aimed primarily at superconductors of the first kind, but Richards<sup>7</sup> has shown that this theory disagrees with his and Spiewak's<sup>6</sup> experimental results. Richards<sup>7</sup> also suggested that the changes in carrier concentration as a function of total applied field, dc and microwave magnetic field, may afford a better explanation of his results. The source of the carrier concentration variation postulated in the present paper and the one suggested by Richards<sup>7</sup> and others<sup>11,20</sup> have different origins, and effects of different magnitude are expected from these two sources. A difference between longitudinal and transverse situations occurs in a homogeneous metal because of the vector addition of dc and microwave fields,  $\mathbf{B}_{dc}$  and  $\mathbf{B}_{mw}$ . Since  $\mathbf{B}_{mw}$  is very small against  $\mathbf{B}_{dc}$  the resulting total  $\mathbf{B}$  field will not vary in size in the transverse configuration, whereas it will oscillate in time between  $B_{dc} - B_{mw}$  and  $B_{dc} + B_{mw}$  in the longitudinal configuration. Assuming a superconductor with field-dependent carrier concentration capable of responding to the oscillations of the total field at microwave frequencies, it is easy to conceive that the two configurations may result in different average surface impedances. The absolute size of the effect will be small,

<sup>20</sup> A. B. Pippard, *Advan. Electron. Electron Phys.* **6**, 1 (1954).

however, on account of the small ratio  $B_{mw}/B_{dc}$ . The effect described in the present paper arises not because of oscillations in time of the charge carrier concentrations, but because of their spatial dependence resulting from the penetration of quantized bundles of flux. Since the variations of  $B_{dc}$  inside hard superconductors are very large, an effect of a different order of magnitude is expected, as we have succeeded in showing in the present investigation, and as was observed by Cardona

*et al.*<sup>9</sup> The two effects may, of course, occur simultaneously, but with the very hard material used in the above mentioned experiments, the one effect is completely hidden by the other.

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## Quadrupole Antishielding Factors for Rare-Earth and Some Other Heavy Ions

R. E. WATSON

*Bell Telephone Laboratories, Murray Hill, New Jersey*

AND

A. J. FREEMAN

*National Magnet Laboratory,\* Massachusetts Institute of Technology, Cambridge, Massachusetts*

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Sternheimer quadrupole antishielding factors ( $\gamma_\infty$ ) are reported for several rare-earth ions and for several ions isoelectronic with  $I^-$  and  $Br^-$ . Radial excitations were obtained using the self-consistent-field unrestricted Hartree-Fock method ("orbitally polarized" H-F method) described previously. Comparisons with perturbation-theory estimates of Sternheimer are presented. It is concluded that a roughly constant value of  $\gamma_\infty \approx -80$  is appropriate for the trivalent rare-earth ions. The relation to experiment of theoretical estimates of  $\gamma_\infty$  for positive and negative ions is discussed.

### I. INTRODUCTION

THE distortion of an ion's closed shells by an external crystalline field and the contributions of such distortions to the electric-field gradient (EFG) at the nucleus of an ion were first investigated by Sternheimer and Foley.<sup>1</sup> The importance of such contributions (called antishielding), which are appreciable in large ions, has been emphasized by recent Mössbauer effect measurements of quadrupole interactions in rare earths.<sup>2</sup> Antishielding effects induced in closed shells by an external crystalline field are incorporated in the Sternheimer antishielding factor  $\gamma_\infty$ , such that the total EFG is  $q_{latt}(1 - \gamma_\infty)$ , where  $q_{latt}$  is the gradient due to the *external* environment. Neglecting refinements, two ways have been commonly used to estimate  $\gamma_\infty$ : (1) by numerical integration of the perturbation equations as is done by Sternheimer and collaborators<sup>1</sup>;

(2) by an analytic variational perturbation technique.<sup>3</sup>

In recent papers<sup>4,5</sup> we described a method, based on the unrestricted Hartree-Fock (UHF) formalism, for calculating these antishielding factors, and it was shown that some of the difficulties associated with the perturbation approach, such as orthogonality, exchange, and self-consistency, were resolved. Since these methods<sup>6</sup> do not yield equivalent results, one purpose of the present paper is to further calibrate and attempt to understand the inconsistencies which arise. Apart from these inconsistencies, the methods all suffer several severe shortcomings when one endeavors to relate results with experiment. A  $\gamma_\infty$  is, by definition, obtained by assuming that the crystalline charge distribution causing  $q_{latt}$  is completely external to the ion. This is an inadequate description of the ion's environment, and there arises the question of how a  $\gamma$  appropriate to experiment differs from a  $\gamma_\infty$ .

In the present paper we report UHF estimates of the antishielding appropriate to rare earths and to several

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<sup>1</sup> R. M. Sternheimer and H. M. Foley, *Phys. Rev.* **92**, 1460 (1953); H. M. Foley, R. M. Sternheimer, and D. Tycko, *ibid.* **93**, 734 (1954); R. M. Sternheimer, *ibid.* **96**, 951 (1954); **80**, 102 (1950); **84**, 244 (1954); **86**, 316 (1952); **95**, 736 (1954); **105**, 158 (1957); R. M. Sternheimer and H. M. Foley, *ibid.* **102**, 731 (1956).

<sup>2</sup> E.g., see S. Hüfner, M. Kalvius, P. Kienle, W. Wiedemann, and H. Eicher, *Z. Physik* **175**, 416 (1963); R. G. Barnes, E. Kankleit, R. L. Mössbauer, and J. M. Poindexter, *Phys. Rev. Letters* **11**, 253 (1963); R. L. Cohen (to be published); P. Kienle (to be published); R. Bauminger, L. Grodzins, and A. J. Freeman (to be published).

<sup>3</sup> T. P. Das and R. Bersohn, *Phys. Rev.* **109**, 360 (1958).

<sup>4</sup> R. E. Watson and A. J. Freeman, *Phys. Rev.* **131**, 250 (1963), designated as I.

<sup>5</sup> A. J. Freeman and R. E. Watson, *Phys. Rev.* **132**, 706 (1963), designated as II.

<sup>6</sup> See also A. Dalgarno, *Proc. Roy. Soc. (London)* **A251**, 282 (1959); *Advan. Phys.* **11**, 281 (1962).