

contribution to the current from the holes when either the field or frequency is varied. This is permissible since other measurements suggest that the hole mass is much larger than the electron mass.<sup>2</sup>

A measurement of the absolute power reflection coefficient at a frequency  $>\omega_A$  gives  $R=0.25$ . In this region the charge carriers make a negligible contribution to the complex conductivity, and the reflection coefficient is determined simply by the dielectric constant of the lattice,  $\epsilon$ . From the standard formula for this ( $R = |\epsilon^{\frac{1}{2}} - 1|^2 / |\epsilon^{\frac{1}{2}} + 1|^2$ ) we find  $\epsilon=9$ . From these data and the above value for  $\epsilon$ , we find the number of electrons in pure bismuth to be approximately  $5 \times 10^{16}/\text{cc}$ .

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<sup>4</sup> J. E. Aubrey and R. G. Chambers, J. Phys. Chem. Solids **3**, 128 (1957).

<sup>5</sup> P. W. Anderson, Phys. Rev. **100**, 749 (1955). Equation (1) is slightly different in this reference because  $e^{-i\omega t}$  time dependence was assumed.

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## Conductivity of Superconducting Films: A Sum Rule

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GLOVER and Tinkham<sup>1</sup> have studied the transmission of superconducting films over a wide range of infrared frequencies. Their measurements of the real part of the conductivity,  $\sigma_1(\omega)$ , where  $\omega$  is the angular frequency, can be interpreted in terms of a universal function  $s_1(x) = \sigma_1(\omega)/\sigma_N$ .  $\sigma_N$  is the conductivity of the metallic film in its normal state, while the reduced frequency  $x$  is defined in terms of the transition temperature  $T_c$ , and the Planck and Boltzmann constants:  $x = \hbar\omega/kT_c$ . In addition to these measurements Glover and Tinkham investigated the transmission of thin films for microwaves and found that the conductivity  $\sigma_2^L(\omega)$  in this "low"-frequency region, could again be expressed in terms of a universal function  $s_2^L(x) = \sigma_2^L(\omega)/\sigma_N$ . It was further found that  $s_2^L(x)$  had

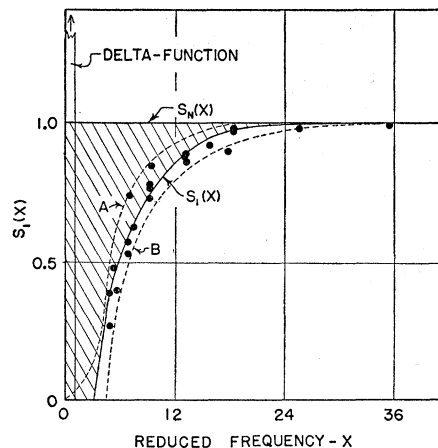


FIG. 1. Real part of the conductivity of a superconductor as a function of frequency from infrared measurements of Glover and Tinkham.<sup>1</sup> The ordinate gives  $s_1(x) = \sigma_1(\omega)/\sigma_N$ , the real part of the conductivity of the superconductor divided by that in the normal state. The abscissa is given in reduced frequency units,  $x = \hbar\omega/kT_c$ . The shaded area, "lost" in the superconducting transition, is required by the sum rule to be exactly compensated by the delta-function distribution occurring at zero frequency. The strength of the delta function in turn determines the magnitude of the London-type lossless inductance. Modifications (A) and (B) give approximate limits to indicate how far the curve  $s_1(x)$  could be displaced while still remaining consistent with the experimental values.

the lossless inductance type of frequency dependence:

$$s_2^L(x) = (1/a)/x. \quad (1)$$

This functional dependence on frequency was predicted by the London theory, but the constant  $a$ , introduced by Pippard,<sup>2,3</sup> was found to be much smaller than predicted by this theory and to have the universal value of  $a = 0.27 \pm 0.05$ . According to the Kramers-Kronig relations (Appendix B of reference 1), such a frequency dependence in the imaginary part of the conductivity requires a delta-function behavior in the real part at zero frequency. Thus establishing Eq. (1) is equivalent to detecting a term<sup>4</sup>  $\pi\delta_+(x)/2a$  in  $s_1(x)$ . Conversely, if the delta-function contribution can be measured, the London-type conductivity will be known. (The subscript on the delta function indicates an infinitesimal shift toward positive  $x$ .)

The Glover-Tinkham measurements can be regarded as independent determinations of, on the one hand, the London imaginary conductivity  $s_2^L(x)$ , and on the other hand, the variation of the real part of the conductivity  $s_1(x)$  for nonzero values of its argument. In the present note we would like to point out that, because of a sum rule, there is an *a priori* relationship between these two types of measurements. As soon as the function  $s_1(x)$  is known for all nonzero values of its argument, the strength of the London term  $s_2^L(x)$  can immediately be inferred. Thus the sum rule provides a consistency check not only on experimental data but also on any theory of the frequency-dependent conductivity for a superconductor.

The derivation of the sum rule follows familiar lines and is very simple. At high frequencies, such that  $\hbar\omega$  is much greater than any of the binding energies of the electrons in the metal, the absorptive or real part of the conductivity vanishes and the imaginary part becomes [Eq. (B-1) of reference 1]

$$\sigma_2(\omega) = -\frac{2\omega}{\pi} \int_0^{+\infty} \frac{\sigma_1(\omega_1)d\omega_1}{\omega_1^2 - \omega^2} \sim \frac{2}{\pi\omega} \int_0^{+\infty} \sigma_1(\omega_1)d\omega_1. \quad (2)$$

The sum rule now results from requiring that the electrons and ions all behave as free at these high frequencies, and consequently that  $\sigma_2(\omega)$  be the same regardless of whether the metal is in its normal or superconducting state. Introducing  $s_1(x)$  and designating the change brought about by the superconducting transition by  $\Delta$ , we have the sum rule<sup>5</sup>

$$\Delta \int_0^{+\infty} s_1(x)dx = 0. \quad (3)$$

At a given frequency the value of the real part of the conductivity can, of course, be different in the superconducting and normal states. The integral, however, of conductivity over frequency is the same for both.

The sum rule (3) will now be used to determine  $s_2^L(x)$  from Glover and Tinkham's values for  $s_1(x)$  shown in Fig. 1. At low frequencies the real part of the conductivity is lower in the superconducting than in the normal state while at high frequencies the two are equal. The sum rule, however, requires that the areas under the two curves  $s_1(x)$  and  $s_N(x)$  be equal. As indicated schematically in the figure, the necessary additional area is contained in the delta function at the origin associated with the London imaginary conductivity  $s_2^L(x)$ . The formal requirement of the sum rule (3) is that

$$\frac{\pi}{2a} = \int_0^{\infty} [1 - s_1(x)]dx. \quad (4)$$

The integral has been evaluated by using the three curves shown in Fig. 1.<sup>6</sup> The center of the three is taken from the original paper<sup>1</sup> while the two outer ones roughly determine maximum and minimum areas which would be compatible with the measurements. The errors given are therefore limits and not probable errors. The resulting value of the Pippard parameter is  $a = 0.21 \pm 0.05$ . This is to be compared with the value independently determined by Glover and Tinkham from the microwave transmission measurements,  $a = 0.27 \pm 0.05$ . The agreement is modest but must be considered satisfactory in view of the errors. Two other values of the parameter  $a$  are available. Faber and Pippard<sup>3</sup> found the value  $a = 0.15$  from measurements of the surface resistance of wires. Bardeen, Cooper, and Schrieffer<sup>7</sup> deduce from their theory  $a = 0.18$ . Both of these are closer to the film value obtained with the help

of the sum rule from the infrared measurements than to the microwave value. Because of the difficulty encountered in averaging over standing waves in the microwave experiments, there is perhaps also some reason for favoring the infrared value from an experimental point of view.

<sup>1</sup>R. E. Glover, III and M. Tinkham, Phys. Rev. **104**, 844 (1956); **108**, 243 (1957).

<sup>2</sup>A. B. Pippard, Proc. Roy. Soc. (London) **A216**, 547 (1953).

<sup>3</sup>T. E. Faber and A. B. Pippard, Proc. Roy. Soc. (London) **A231**, 336 (1955).

<sup>4</sup>The factor  $\frac{1}{2}$  enters because only positive values of  $\omega$  are considered.

<sup>5</sup>This is essentially the historical Thomas-Reiche-Kuhn sum rule and is well known in many branches of atomic and nuclear physics. It breaks down in cases where relativistic effects are important. For further discussion see J. S. Toll, Ph.D. thesis, Princeton, 1952 (unpublished), and Gell-Mann, Goldberger, and Thirring, Phys. Rev. **95**, 1612 (1954).

<sup>6</sup>A function suggested by Tinkham [M. Tinkham, Phys. Rev. **104**, 845 (1956)], later discarded<sup>1</sup> but now back in good standing, which fits the data reasonably well is  $s_1(x) = 1 - \gamma^2/x^2$  where  $\gamma$  is the reduced frequency corresponding to the intercept of the curve with the abscissa. On an energy gap picture it corresponds to the width of the gap. Upon using this particular form of  $s_1(x)$ , the sum rule leads to the result  $a = \pi/4\gamma$ . The fit to the points in Fig. 1 is moderately good for  $\gamma = 4$ , giving  $a = 0.20$ . This illustrates the point that on a gap picture the strength of the London-type conductivity is connected with the width of the gap. Specific heat measurements made on bulk material suggest a gap of about the same size as that found for thin films. This in turn would require that the  $s_2^L(x)$  terms be of about the same size, a somewhat surprising result.

<sup>7</sup>Bardeen, Cooper, and Schrieffer, Phys. Rev. **106**, 162 (1957); **108**, 1175 (1957).

## Maser Action in Ruby\*

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A THREE-LEVEL maser was proposed by Bloembergen,<sup>1</sup> and first operated by Scovil, Feher, and Seidel.<sup>2</sup> In our endeavor to find paramagnetic materials suitable for maser applications, we have investigated the electron-spin resonance properties of ruby ( $\text{Al}_2\text{O}_3:\text{Cr}$ ). This note reports briefly the results of our studies.

According to several investigators<sup>3-5</sup> the zero-field splitting in ruby is  $0.38 \text{ cm}^{-1}$ . The ground state of the trivalent chromium ion,  $\text{Cr}^{+++}$ , which is responsible for the coloring of ruby, behaves as  $S = \frac{3}{2}$ . The dependence of the energy levels of ruby on the magnetic field was calculated for the polar angle  $54^\circ 44'$ .<sup>6</sup> Experiment has indicated that the "forbidden" transition  $-\frac{3}{2} \rightarrow \frac{1}{2}$  is quite intense for this orientation. Calculations showed that for  $H = 4200$  gauss, the pumping frequency corresponding to this transition should be  $24 \text{ kMc/sec}$ , and the signal frequency corresponding to the  $-\frac{1}{2} \leftrightarrow \frac{1}{2}$  transition should be approximately  $9.3 \text{ kMc/sec}$ .

A cylindrical cavity was designed and built so as to excite the  $TE_{114}$  and  $TE_{011}$  modes, respectively, at the