

The two microwave points, those at the left in the figure, were obtained by using a *K*-band klystron with a crystal harmonic generator kindly supplied by Han-Ying Ku. The accuracy is limited by stray reflections and by standing waves. For the infrared points, a mercury arc was utilized together with a Golay detector. The *f*/1.5 grating spectrometer used to separate the various frequencies is similar to several described in the literature.^{6,7} A moderately wide band of radiation had to be taken to obtain a measurable signal. The accuracy is limited by the available energy and running time, up to one hour per point.

* Supported in part by the U. S. Office of Naval Research; the Signal Corps; and the Office of Scientific Research, U. S. Air Force.

† National Science Foundation Postdoctoral fellow.

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Energy Gap Interpretation of Experiments on Infrared Transmission through Superconducting Films*

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(Received September 4, 1956)

THE transmission and reflection properties of a film which is thin compared to a skin depth and in transverse dimensions large compared to a wavelength are determined completely by the complex admittance per square of the film. If we have a film of admittance *Y* laid on a substrate of index of refraction *n*, the ratio of the power transmission with film to that with no film is

$$T = |1 + Z_0 Y / (n + 1)|^{-2}, \quad (1)$$

where *Z*₀ is the impedance of free space (4π/*c*, cgs; 377 ohms, mks). For normal metals, *Y* is simply 1/*R_N*, where *R_N* is the dc resistance per square of the film. The relation (1) has been verified with the films used in our experiments.¹ Note that these ~20 Å films give a transmission of only ~¼, independent of ω, despite the fact that the skin depth is ~1000 Å and depends on ω. We are dealing with an impedance mismatch problem rather than a penetration depth problem.²

In the superconducting state, *Y* becomes complex and frequency-dependent. If we use Eq. (1), the experimentally measured ratio of the transmission *T_S* is the superconducting state to that of the normal state is

$$\frac{T_S}{T_N} = \left\{ \left[T_N^{\frac{1}{2}} + (1 - T_N^{\frac{1}{2}}) \frac{\sigma_1}{\sigma_N} \right]^2 + \left[(1 - T_N^{\frac{1}{2}}) \frac{\sigma_2}{\sigma_N} \right]^2 \right\}^{-1}, \quad (2)$$

where we have introduced a complex conductivity for the superconducting state: σ₁(ω) - *i*σ₂(ω) = σ_N*R_N**Y*(ω). Thus the interpretation of the transmission results is reduced to a discussion of the complex conductivity. While measurement of only the transmitted power is insufficient to fix both σ₁ and σ₂ at a given frequency, the Kramers-Kronig (K-K) relations³ allow such a separation if measurements are available over the entire relevant frequency range. Care is required because of the pole of σ(ω) at the origin, associated with the lossless conduction.

The K-K relations are satisfied by the London-type conductivities:

$$\sigma_1^L = \frac{c^2}{8\lambda^2} \delta(\omega - 0), \quad \sigma_2^L = \frac{c^2}{4\pi\lambda^2\omega}.$$

These are equivalent to a lossless inductive admittance of the film. If this term alone were present in the superconducting state, the transmission through the film would rise continually with increasing frequency, reaching complete transmission, *T_S* = 1, at high frequencies. Since in fact *T_S* → *T_N* at high frequencies, one might simply assume that the normal conductivity was also present in both states. This would give the correct high-frequency limit, but would fail to give the observed peak in transmission at intermediate frequencies. We shall now indicate how an energy-gap model provides a natural explanation of this peak.

We consider a model of a superconductor at absolute zero⁴ in which a gap of width ħω_g ≈ 3*kT_c* appears in the spectrum of one-electron energy states. This width is suggested by specific heat data.⁵ The lossy conductivity σ₁ will be zero for photon energies ħω < ħω_g. For ω > ω_g, σ₁ will rise gradually with ω as an increasing fraction of the states originally within ħω of the occupied states below the Fermi level are still available for excitation. If the gap merely excluded the states within ħω_g, leaving all else unchanged, this simple picture would suggest a rise as σ₁ = σ_N(1 - ω_g/ω). The experimental rise seems to be faster, cutting off at least as fast as (1 - ω_g²/ω²). This might correspond to the states displaced from the gap just "piling up" on either side, so that the change averages to zero more rapidly for ω ≫ ω_g.

Given any assumed cut-off form for σ₁(ω), the K-K relations determine the corresponding σ₂'(ω) which must be added to σ₂^L(ω). For any reasonable cutoff, σ₂'(ω) is negative, has a maximum magnitude of the order of σ_N near ω_g and falls as ω/ω_g at low frequencies and as ω_g/ω at high frequencies. (See Fig. 1.) Since only 4π $\mathbf{J} + \partial\mathbf{D}/\partial t = (4\pi\sigma + i\omega\epsilon)\mathbf{E}$ enters the relevant Maxwell equation, this imaginary term in the conductivity is equivalent to a real dielectric constant ε(ω) = -4πσ₂'(ω).

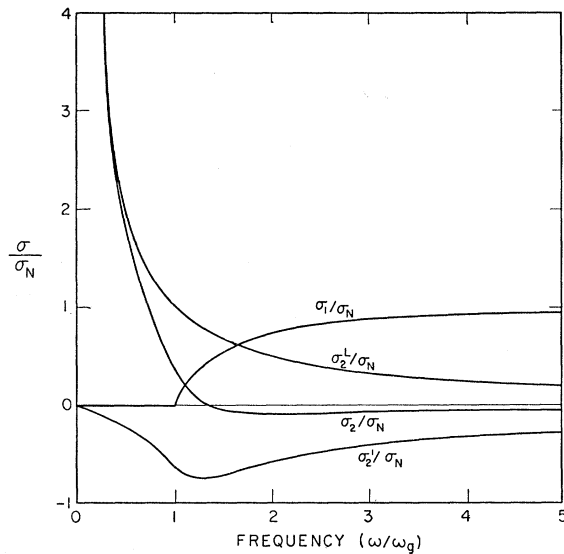


FIG. 1. Frequency dependence of conductivity for an energy-gap model at $T=0$ under the assumption $\sigma_1/\sigma_N = 1 - \omega_g^2/\omega^2$ and $\sigma_2^L/\sigma_N = \omega_g/\omega$.

For $\omega \ll \omega_g$, this has a constant value of the order of magnitude 10^5 ($\sim 4\pi\sigma_N/\omega_g$), and resembles the ϵ_0 predicted in the theory of Ginzburg and Landau.⁶ We note that the appearance of this term is a direct consequence of the cutoff of normal conductivity for $\omega < \omega_g$. Though this σ_2' term is important near $\omega = \omega_g$, it is completely swamped by σ_2^L for $\omega \ll \omega_g$. Thus σ_2^L alone can be determined directly from the microwave points.

To the limited accuracy of these data, both microwave points yield $\nu\sigma_2/\sigma_N = 11 \pm 2 \text{ cm}^{-1}$. With σ_N estimated to be roughly the value for bulk lead at room temperature (the residual resistance of the film is half its room temperature resistance), this corresponds to a value of the London λ increased from that of pure bulk lead by a factor of 7. This increase in λ appears to be related closely to the increase of λ with reduction of electron mean free path by impurities observed by Pippard⁷ and Chambers.⁸ For $\omega > \omega_g$ this reduced σ_2^L is nearly cancelled by the σ_2' term, leaving $\sigma_2 \ll \sigma_1$. Since σ_2 enters (2) only quadratically, T_S/T_N for $\omega > \omega_g$ is largely determined by σ_1 alone. This allows the form of decrease of $\sigma_1(\omega)$ in the superconducting state to be obtained directly from the excess of T_S over T_N for $\omega > \omega_g$.

The situation is summarized in the figure for the specific assumptions $\sigma_1/\sigma_N = 1 - \omega_g^2/\omega^2$ and $\sigma_2^L/\sigma_N = \omega_g/\omega$. The K-K relations then give

$$\sigma_2'/\sigma_N = -(1/\pi) \left\{ (1 - \omega_g^2/\omega^2) \ln |\omega_g + \omega| / |\omega_g - \omega| + 2\omega_g/\omega \right\}.$$

The sharp peak in transmission (see Fig. 1 of preceding Letter) near $\omega = \omega_g \approx 3kT_o/\hbar$ occurs because both σ_1 and σ_2 are very small there. For $T > 0$, it is expected that $\sigma_1 > 0$, even for $\omega < \omega_g$ and that the rise in σ_1 starts at a lower frequency and is more gradual. This would result

in a lower peak in the calculated transmission curve, as observed. Despite the reasonable agreement with experiment which can be achieved in this way, it should be emphasized that the specific forms proposed here are not meant to be exact or unique. They simply formalize an approach which seems promising for the interpretation of these and future experiments.

* Supported in part by the U. S. Office of Naval Research; the Signal Corps; and the Office of Scientific Research, U. S. Air Force.
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⁴ For $0 < T < T_c$, presumably the gap will be partially smeared out, and it may be only a region of sharply diminished density of states. These modifications would round off some features of our theoretical curves but leave the general principles intact.

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Paramagnetic Resonance of Hydrogen Atoms Trapped at Liquid Helium Temperature*

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(Received September 14, 1956)

HYDROGEN and deuterium atoms produced by electrical discharges have been successfully deposited and stored in their respective molecular matrices at liquid helium temperature. The identity of each atom has been established by the characteristic hyperfine splitting of its microwave electron-spin resonance spectrum.

The atoms were produced by an electric discharge in pure hydrogen or deuterium at a pressure of about 0.1 mm Hg. The discharge was of the electrodeless type operating at a frequency of 4 Mc/sec and a power of 100 w. The discharge products were pumped at a speed of about 1500 cm/sec past a short side-tube connected to a low-temperature cell. The side-tube was terminated by a glass slit $\frac{1}{2}$ mm wide by 10 mm long which served as the source slit for a simple molecular beam system. The molecular beam was condensed on a sapphire rod at a distance of 3.1 cm from the glass slit. The sapphire rod which was soldered to the bottom of a liquid helium reservoir was 2 mm in diameter and 22 mm long. With this system a 5-minute deposition generally provided an adequate sample. During sample deposition a good vacuum ($\sim 10^{-6}$ mm Hg) was maintained in the cell by the pumping action of the liquid-