moved from the samples; it does not appear to have a differential effect. For a sample of 1,3,5-trifluorobenzene containing oxygen, T_{1H} and T_{1F} were 1.85 and 1.82 sec at 20 Mc/sec. Further work is in progress on the problem and also on the chemical shift anisotropy. We wish to thank A. Saika and G. A. Williams for several helpful discussions and E. O. Stejskal for assistance with the measurements.

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Transmission of Superconducting Films at Millimeter-Microwave and Far Infrared Frequencies*

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MEASUREMENTS of the surface resistance of superconductors at microwave frequencies having photon energy comparable with kT_c have recently been announced. For tin[1] these measurements have been carried up to a frequency corresponding to $h\nu=1.9kT_c$ and for aluminum[2] to $2.3kT_c$. At these frequencies and at the lowest temperatures tried, both materials lost part but not all of their resistance in the superconducting state. At considerably higher frequencies, the absorption coefficient of tin has been studied.[3] For $\lambda=0.014$ mm, corresponding to $275kT_c$, no change in the absorption between normal and super conducting states was found, indicating no change in the resistance. We have made measurements of the transmission through superconducting lead and tin films. The frequencies used cover a good part of the previously unexplored intermediate region.

The quantity measured experimentally is the ratio of power transmitted through the film in the superconducting state to that in the normal. In Fig. 1 this is plotted against frequency for a typical lead film. Both the low-energy points, which indicate a reduction of the transmission corresponding to a partial loss of resistance in the superconducting state, and those at high energies for which there is no change, are in qualitative agreement with the previous experiments on bulk material. The high-energy data now make it possible to fix the maximum frequency for which there is a difference between the normal and superconducting states at about $20kT_c/h$. The most striking aspect of the results is that over a considerable region of frequencies the superconducting film has a higher transmission, corresponding roughly to *higher* resistance, than the normal film. The frequency dependence of Sn films has been measured only approximately. The existence of a maximum also in the transmission for Sn has been verified. If the frequency scale is reduced in the ratio of the transition temperatures ($3.7/7.2\sim0.5$), the results seem consistent with those for Pb. A suggested interpretation of the data is given by one of us in a separate letter.[4] Our results appear to support the energy-gap model of superconductors.

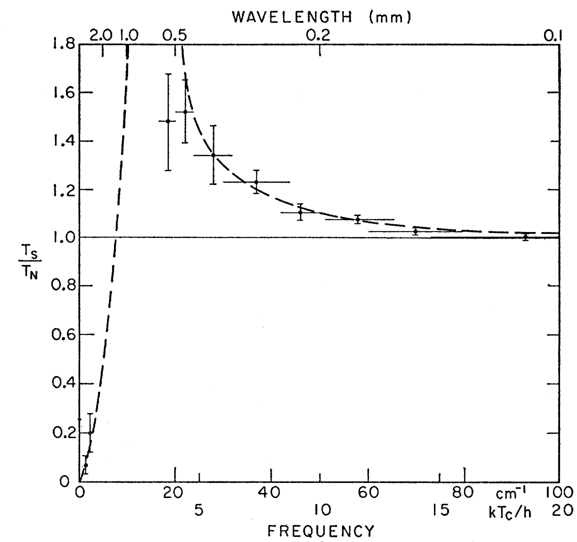

FIG. 1. Experimental transmission ratios of superconducting and normal states of a typical lead film (dc residual resistance 117 ohms; transmission in normal state$=\frac{1}{4}$) at $T/T_c=0.67\pm0.03$. The frequency uncertainty on each infrared point is the half-power width of the continuous spectrum used. The vertical error limits on these points are derived statistically from the data. The dashed curve is one proposed for $T=0$ and an energy gap of $3kT_c$, as described in the following Letter.

Films were produced *in situ* by evaporation in high vacuum onto a crystal quartz substrate held at 77°K and were annealed at room temperature. Current and potential contacts made it possible to monitor the dc resistance. Superconductivity could be destroyed by exceeding a critical value of the current. Estimates made both from the temperature-dependent part of the resistance and from the Fuchs[5] theory, assuming diffuse surface scattering, indicate that the thickness of the Pb film used was ~20 A. (Sn films up to five times as thick were also tried; all showed the increase in transmission.) The critical temperature was 0.12°K lower than for bulk material. The width of the transition region was less than 0.1°K.

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.

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

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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

$$T=|1+Z_0Y/(n+1)|^{-2}, \quad (1)$$

where Z_0 is the impedance of free space ($4\pi/c$, 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 $\sim$20 A films give a transmission of only $\sim\frac{1}{4}$, independent of ω, despite the fact that the skin depth is $\sim$1000 A 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: $\sigma_1(\omega)-i\sigma_2(\omega)=\sigma_N R_N Y(\omega)$. 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 σ_1 and σ_2 at a given frequency, the Kramers-Kronig (K-K) relations[3] allow such a separation if measurements are available over the entire relevant frequency range. Care is required because of the pole of $\sigma(\omega)$ 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 $T_S\rightarrow T_N$ 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 zero[4] in which a gap of width $\hbar\omega_g\approx 3kT_c$ appears in the spectrum of one-electron energy states. This width is suggested by specific heat data.[5] The lossy conductivity σ_1 will be zero for photon energies $\hbar\omega<\hbar\omega_g$. For $\omega>\omega_g$, σ_1 will rise gradually with ω as an increasing fraction of the states originally within $\hbar\omega$ of the occupied states below the Fermi level are still available for excitation. If the gap merely excluded the states within $\hbar\omega_g$, leaving all else unchanged, this simple picture would suggest a rise as $\sigma_1=\sigma_N(1-\omega_g/\omega)$. The experimental rise seems to be faster, cutting off at least as fast as $(1-\omega_g{}^2/\omega^2)$. 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 $\omega\gg\omega_g$.

Given any assumed cut-off form for $\sigma_1(\omega)$, the K-K relations determine the corresponding $\sigma_2'(\omega)$ which must be added to $\sigma_2{}^L(\omega)$. For any reasonable cutoff, $\sigma_2'(\omega)$ 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 $4\pi\mathbf{J}+\partial\mathbf{D}/\partial t=(4\pi\sigma+i\omega\epsilon)\mathbf{E}$ enters the relevant Maxwell equation, this imaginary term in the conductivity is equivalent to a real dielectric constant $\epsilon(\omega)=-4\pi\sigma_2'/\omega$.