SUPERCONDUCTING TRANSITION TEMPERATURE
OF SUPERIMPOSED FILMS OF TIN AND SILVER*

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(Received July 5, 1962)

Recent experimental results by Smith, Shapiro, Miles, and Nicol[1] have shown that a film of a normal metal in contact with a film of a superconducting metal lowers the transition temperature below that of the superconducting film. They demonstrated that superconductivity is a property of the combined film system and that the depression of the transition temperature increases as the thickness of the normal metal increases. Cooper[2] has offered a simplified model to explain this effect. This work was undertaken to determine quantitatively the relationship between the transition temperature and the thicknesses of the two superimposed films.

The combination Ag-Sn was chosen so that the characteristics near the transition temperature of the superconducting metal could be observed and also so that a comparison could be made with the measurements on the Ag-Pb combination.[1] The thermodynamic solubilities of Ag in Sn and Sn in Ag at 50°C are estimated to be less than 0.1 and 6.0 atomic percent, respectively.[3] Also, measurements of Allen[4] indicate no change in the transition temperature of Sn when Ag is present in solid solution in reasonable amounts. It is, of course, the diffusion rate that determines the ratio of the constituents, but the thermodynamic solubilities give an upper limit. In order to minimize or at least keep constant the diffusion and oxidation effects, an effort was made to prepare all specimens under the same conditions.

It was decided to make the thicknesses of the films less than the coherence length and penetration depth in the hope that this would facilitate comparison of results with theory. The specimens were prepared in the following way. A thin film of Sn 1 mm wide, 20 mm long, and of mean thickness 303 ± 15 Å was prepared by evaporating to completion a known mass of Sn onto a glass microscope slide at a pressure of less than 2×10^{-5} mm Hg. Immediately after evaporation of the Sn and with no change in the pressure, a Ag film was evaporated which covered the entire central portion of the Sn. The thickness of the Ag film was determined and varied also by evaporation to completion. Each specimen was exposed to the heated boat for the same length of time (2 min) with the

temperature of the substrate not exceeding 50°C. After fabrication they were stored from 12 to 16 hours in a desiccator. The specimens were then cooled and the transition temperatures were determined by measuring the resistance. A sharp decrease (approximately 50 percent) in the resistance of all specimens occurred at approximately 3.8°K which corresponded to the temperature at which the ends of the Sn film became superconducting. The transition temperature of the Sn-Ag central region occurred at a lower temperature, at which point the resistance dropped very abruptly ($\Delta T \sim 0.02$°K) to values too small to measure. The transition temperature was independent of measuring current. The thicknesses of the thicker films were determined directly at a later time by means of an optical multiple-beam technique.[5] The thicknesses of the thinner films were calculated from the thicker ones by scaling in the ratio of the masses of material evaporated.

Figure 1 shows the depression of the transition temperature as a function of Ag thickness for a mean Sn thickness of 303 ± 15 Å. The transition temperature drops continuously with little scatter from that of pure Sn down to the lowest temperature that we could attain (0.9°K). A straight-line
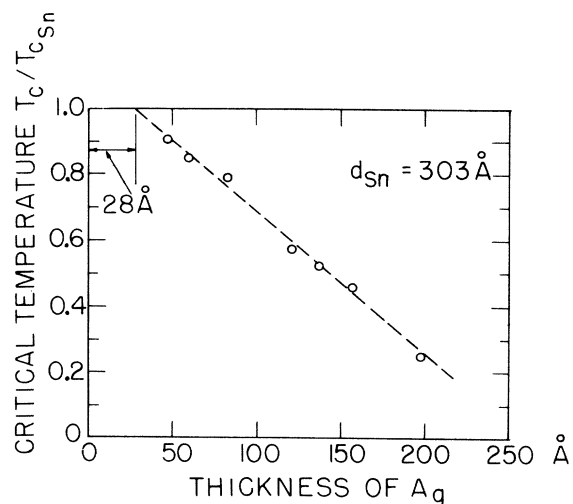

FIG. 1. Critical temperature of superimposed films of Ag and Sn vs thickness of Ag. (Sn thickness, 303 ±15 Å.)

extrapolation suggests that the transition tempera-
ture would be reduced to zero at approximately
250 Å of Ag. An extrapolation of the curve to the
transition temperature of pure Sn indicates that
approximately 28 Å of the Ag layer is not effec-
tive. It is known[6] that Ag will adsorb a surface
layer of oxygen and that the process is nearly
complete at 12 to 16 hours. This oxygen then
presumably reacts with the silver to form silver
oxide, which, of course, would not be conducting.
Thus it is plausible that the silver has an oxide
layer of ~28 Å which must be subtracted from the
measured thickness. The specimen with $t = 0.46$
was measured again after aging for one week at
room temperature with the result that t had in-
creased by 0.03, which indicates that diffusion
effects are small. Also, this small change can
be accounted for by assuming that the silver-
oxide layer has increased by 7 Å. The assump-
tion has been made that there is an oxide layer
of 28 Å and the data have been replotted in Fig. 2
by using the corrected Ag thickness (d_{Ag}').

The expression for the depression of the transi-
tion temperature given by Cooper[2] is

$$T_c = T_{c_{Sn}} \exp\{-\beta d_{Ag}/[N(0)V]_{Sn} d_{Sn}\}, \quad \beta \leqslant 1, \quad (1)$$

which, for small exponent, becomes

$$T_c \cong T_{c_{Sn}} \{1 - \beta d_{Ag}/[N(0)V]_{Sn} d_{Sn}\}. \quad (2)$$

Here, $[N(0)V]_{Sn}$ is the interaction constant for Sn
and β is a factor to take into account any poten-

FIG. 2. Critical temperature of superimposed films
of Ag and Sn vs ratio of the corrected Ag thickness to
Sn thickness.

tial barrier arising from a hypothetical chemi-
sorbed oxygen layer between the metals.

Douglass[7] has formulated a phenomenological
theory in which an expression for the reduction
in the transition temperature is derived which is
valid when the thicknesses are less than the pene-
tration depth and coherence length:

$$T_c = T_{c_{Sn}} \left(\frac{1 - \alpha d_{Ag}'/d_{Sn}}{1 + \alpha d_{Ag}'/d_{Sn}} \right)^{1/2}, \quad (3)$$

which, for small d_{Ag}'/d_{Sn}, becomes

$$T_c \simeq T_{c_{Sn}} (1 - \alpha d_{Ag}'/d_{Sn}). \quad (4)$$

The quantity α is

$$\alpha = \frac{\left(-H_{c_{Ag}}^2\right)/N_{Ag}}{H_{c_{Sn}}^2(0)/N(0)_{Sn}}, \quad (5)$$

where $H_{c_{Sn}}(0)$ and $N(0)_{Sn}$ are the critical field
and the number of superconducting electrons per
cubic centimeter, respectively, for Sn at $T = 0$,
and $H_{c_{Ag}}$ and N_{Ag} are the corresponding quanti-
ties for Ag. The quantity $H_{c_{Ag}}$ has the following
meaning. It is assumed for Ag that the free en-
ergy of the superconducting state is positive and
can be described by a "critical field" $\Delta F = -H_{c_{Ag}}^2/$
8π. Since ΔF is positive, then $H_{c_{Ag}}$ has to be im-
aginary, which makes α positive. Equation (3)
predicts that the transition temperature goes to
zero at $d_{Ag}/d_{Sn} = 1/\alpha$, whereas for Eq. (1) the
transition temperature is always finite. It is to
be noticed that (2) and (4) have the same functional
form, with the difference occurring in the coeffi-
cient. The initial linear decrease in the transition
temperature was determined from the data of
Fig. 2 to be of the form

$$T_c = T_{c_{Sn}} (1 - 1.60 d_{Ag}'/d_{Sn}). \quad (6)$$

Comparing (6) with (2), one obtains $\beta = 0.47$ by
using $N(0)V = 0.29$. The comparison of (6) with (4)
gives $H_{c_{Ag}} = 246i$ gauss (which of course means
that $-H_{c_{Ag}}^2/8\pi$ is positive) by using $H_{c_{Sn}}(0) = 308$
gauss, $N(0)_{Sn} = 0.246 N_0$ electrons/cc, and N_{Ag}
$= 0.098 N_0$ electrons/cc. By using the determined
constant 1.60, the full expressions (1) and (3)
were plotted and are shown in Fig. 2. The data
points appear to fall faster than the exponential
given by (1), and Eq. (3) appears to be a better
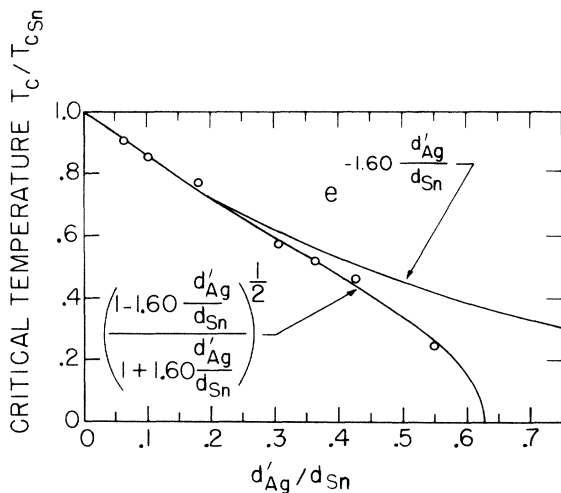fit to the data.

One would expect that Eq. (3) would be more descriptive of the facts because it contains parameters that are characteristic of the normal metal, whereas Eq. (1) was derived under the assumption that the role of the normal metal was to dilute the interaction constant of the superconductor by means of a spatial average. [It was explicitly assumed that the interaction constant of the normal metal equaled zero, whereas a more realistic assumption would have allowed the interaction constant $N(0)V$ to be of the opposite sign (repulsive interaction) and to be different for different normal metals.] Several additional bits of supporting evidence are as follows:

(1) By using a "reasonable" extrapolation of the data of Smith et al.[1] on Pb-Ag, the initial linear decrease was found to be given by $T_c = T_{c_{Pb}}$ $\times[1 - 0.16 d_{Ag}/d_{Pb}]$. To fit Eq. (1) would require that $\beta = 0.062$, which is eight times smaller than the β obtained in this experiment. On the other hand, fitting this expression to Eq. (3) gives a value for the "critical field" of the Ag of $220\,i$ gauss. This is only ten percent different from the value determined by this experiment.

(2) We have made similar, but less accurate, measurements on the depression of the transition temperature of Sn by films of Co. We find that the initial decrease is $T_c = T_{c_{Sn}}[1 - (25 \pm 6)d_{Co}/d_{Sn}]$. To fit Eq. (1) requires that $\beta \sim 7.3$, whereas, according to Cooper, β should not be greater than 1. On the other hand, fitting this expression to Eq. (3) gives $H_{c_{Co}} \approx 1400\,i$ gauss, which agrees with the observation of Meissner[8] that Co is much more effective in reducing the transition temperature of superconductors than metals that are not ferromagnetic.

In summary, we have measured the depression of the transition temperature of thin films of Sn by thin films of Ag and Co. We find that the data can best be explained by a phenomenological theory that allows the normal metal to have a superconducting state of a higher free energy than the normal state. In the language of the Bardeen, Cooper, and Schrieffer theory,[9] for nonmagnetic metals the repulsive screened Coulomb interaction is larger than the attractive electron-phonon interaction term and gives a negative interaction constant. For ferromagnetic metals the exchange interaction gives a term that is also repulsive and would make the interaction constant more negative. We further suggest that the postulated potential barrier between the metals caused by "dirty experimental conditions" does not exist.

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[6]R. G. Meisenheimer, Proceedings of the Second International Congress on Surface Activity (Academic Press, Inc., New York, and Butterworths Scientific Publications, Ltd., London, 1957), Vol. 2, p. 299.

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PHENOMENOLOGICAL THEORY OF SUPERIMPOSED FILMS OF NORMAL AND SUPERCONDUCTING METALS*

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Cooper[1] has recently proposed a simplified model to explain the properties of superimposed films of superconducting and normal metals. His essential idea is that the two-film combination is superconducting with an interaction parameter $N(0)V$ that is characterized by the superconductive metal but is diluted in strength by a spatial average over both metals. This leads naturally to an exponential dependence of the transition temperature on the ratio of the thicknesses. There are two defects with this model: (1) The normal metal does not influence the properties of the combination other than by its thickness, whereas one would expect that different normal metals of the