

# Surface Energy Effects at the Boundary between a Superconductor and a Normal Conductor\*

**Abstract:** Films of tin ranging from 500 to 1400 Å in thickness have been prepared in pairs by vacuum deposition onto rotating cylindrical glass and metal substrates. The temperature dependence of the critical fields has been measured. The critical temperatures of the films on metal substrates are all depressed. Their critical fields at absolute zero, however, are usually not depressed but can be higher than those of the corresponding films on glass. This increase can be explained by a negative surface energy arising from a short mean free path of the superconducting electrons in an incidental oxide layer at the surface of the metal. Most of the films on glass had an abnormally small value of the critical field at absolute zero.

## Introduction

The experiments were originally started with the aim of obtaining further evidence that the superconductivity of thin films on bulk normal metal can be inhibited by the normal electrons.<sup>1</sup> Very soon it became apparent that copper carries an oxide layer thick enough to prevent this effect.<sup>2</sup> The critical temperatures of the films on metal were only somewhat depressed but their critical field curves seemed to cross those of the films on glass. The actual crossing could not be observed initially, since the necessary high fields could not be reached with the copper field coils used.

The experiments were repeated with niobium field coils capable of producing 3500 amp/cm at the lowest temperatures. The crossover could now be clearly observed. Later runs with other substrates did not yield a crossover, presumably because the intervening oxide layers were not well enough controlled. Since, in addition, the films on glass showed abnormally low critical fields which so far are unexplained, the results here must still be considered of a preliminary nature.

## Experimental arrangement

The glass substrates were chemically cleaned and for a few seconds exposed to hydrofluoric acid vapor to provide nucleation centers. The metal substrates were electrolytically polished. After insertion of the samples the vacuum system was usually baked for 12 hrs at 120°C. (All rubber seals were prebaked separately to remove volatile substances, notably sulfur compounds.)

The system has two MCF 60 pumps in series and after return to room temperature attained a pressure of  $10^{-7}$  mm Hg. During evaporation, however, the pressure

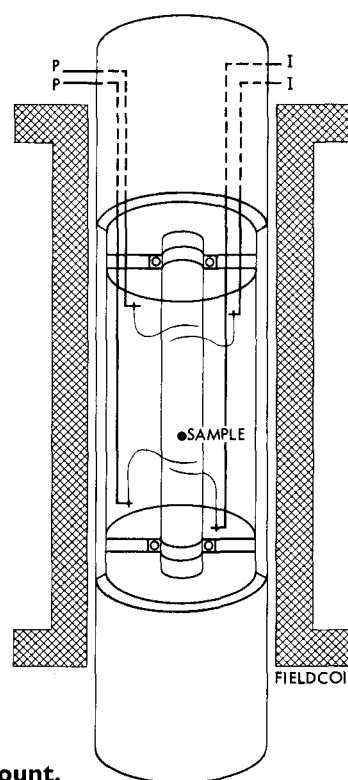


Figure 1 Sample mount.

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rose to about  $10^{-5}$  mm Hg. The heaters were operated at a temperature high enough to deposit the film in less than a minute.

The thickness of the films was determined both from the volume of the charge and the difference between the room-temperature resistance and residual resistance. Both values agreed to about 20%.

The samples were mounted in a holder shown in Fig. 1, which fitted tightly into the field coil. Current and potential leads were attached with silver paint. The field coil had overwound ends to increase the uniformity of the field.

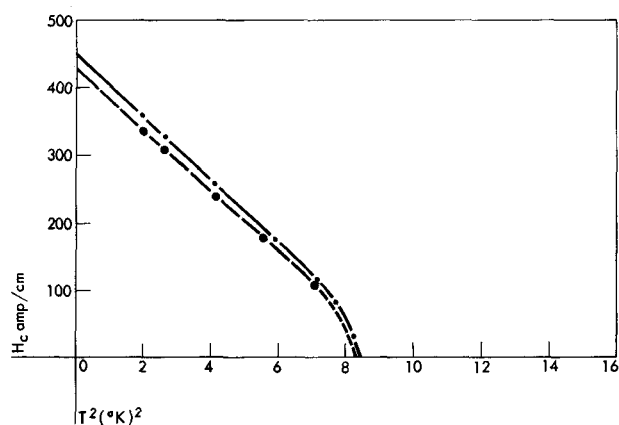
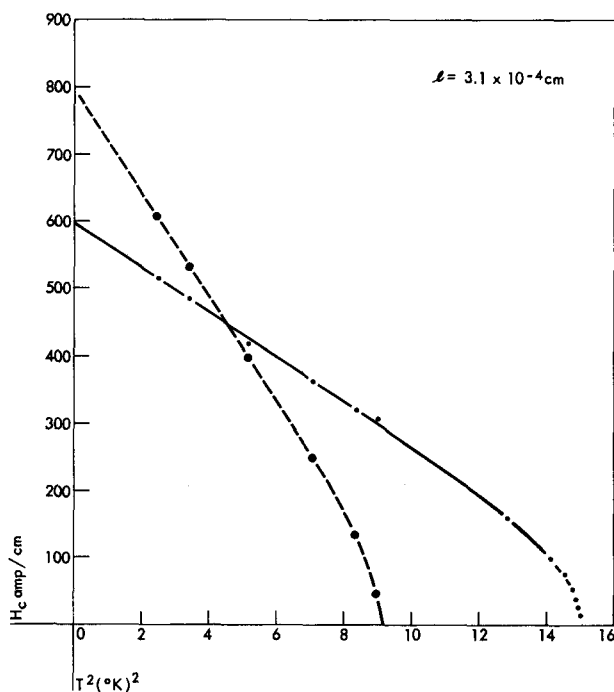
The resistance of the films was recorded as a function of the magnetic field with an *X-Y* recorder and pre-amplifier or galvanometer with photoelectric readout. It was possible to use currents small enough to be independent of the current.

The bath temperature was electronically regulated and was determined from the vapor pressure using the 1958 vapor pressure scale.

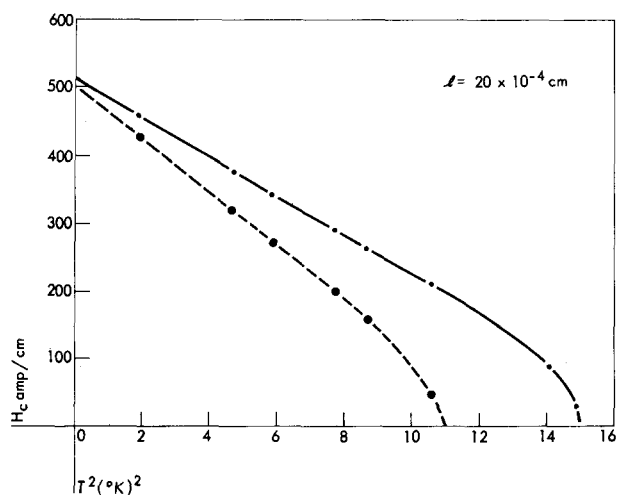
### Experimental results

Figure 2 shows critical field curves (defined as the field necessary to restore 50% of the normal resistance) for a 657 Å film on glass and copper (refrigeration tubing) substrates. The critical temperature of the film on copper is decreased, but the critical field at absolute zero is increased compared to that of the film on glass.

**Figure 2** Critical field curve for a tin film of 657 Å on glass (solid line) and on copper (broken line) substrates. The mean free path indicated refers to the film on glass.



**Figure 3** Critical field curve for a film of 500 Å copper and 1000 Å tin on glass (solid curve) and copper (broken curve) substrates.



**Figure 4** Critical field curve for a tin film of 667 Å on glass (solid line) and on No. 40 copper wire (broken line) substrate. The mean free path indicated refers to the film on glass.

Figure 3 shows a similar set of data for films of 500 Å copper plus 1000 Å tin on glass and copper substrates. Both curves are closely parallel, with almost the same transition temperature, indicating that the substrate influences the films but little. Neither one of the films shows an abnormally high critical field at absolute zero, which was not to be expected, since the boundary between the copper film and the tin film is free from oxide and does not cause an abrupt change in the energy gap.

Since the copper refrigeration tubing was not quite pure (mean free path  $0.28 \times 10^{-4}$  cm) a No. 40 copper wire (mean free path  $3.5 \times 10^{-3}$  cm) was tried as a substrate. The small depression of the critical temperature shown in Fig. 4 indicates the presence of a

rather thick oxide film, and the critical field curves do not cross over.

Subsequently a very impure substrate metal was tried to determine whether it would favor high critical fields. As Fig. 5 shows, the oxide layer was again too thick and the curves do not cross over.

Figure 6 shows the transition width as a function of temperature and is typical of the transitions observed.

## Discussion

Figure 7 shows a sketch of the spatial variation of the magnetic field and the energy gap across a film of tin on a glass substrate and on a copper substrate with intervening CuO layer.

A calculation of the critical fields has to consider both<sup>3-6</sup> the spatial variation of the field and the energy gap. All the films presented here have second-order transitions and the energy gap goes to zero at the critical field.<sup>7</sup> It appears that only for quite limited combinations of normal substrates and oxide layer is an increase of the critical field found. This was to be expected, since there should be no effect in the absence of the oxide film (spread out *n-s* boundary) or for very thick oxide layers (very sharp boundary).

Attention should be drawn to an anomalous behavior of the critical fields of the films on glass substrates: In almost all cases the critical fields at absolute zero are much smaller than those found by other investigators.<sup>8</sup> Impurities, variable thickness of the films and other defects usually lead to abnormally high fields.<sup>9</sup> Together with the low residual resistances the low critical fields were initially taken as proof of the good quality of the films until a detailed calculation of the penetration depths leads to values much smaller than commonly accepted.

Figure 5 Critical field curve for a tin film of 474 Å on glass (solid line) and super-nickel (30% Ni, 70% Cu, broken line) substrates. The mean free path indicated refers to the film on glass.

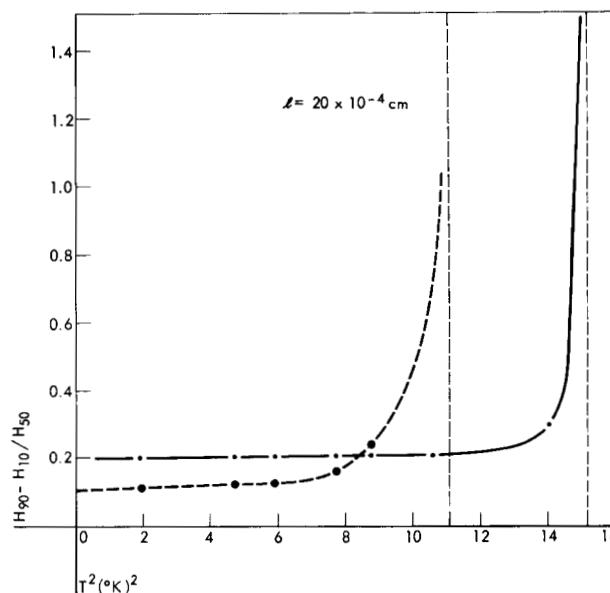
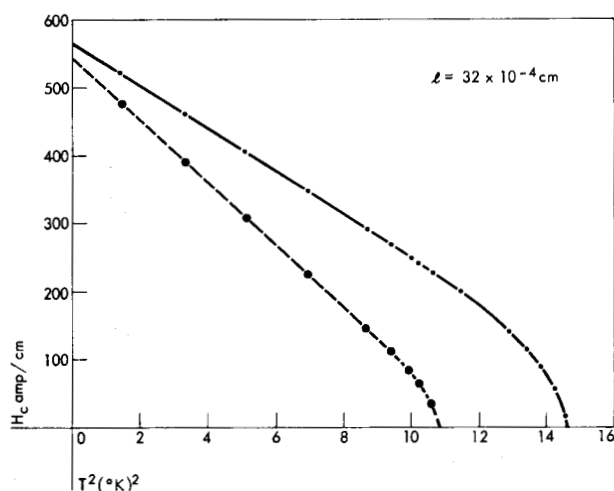


Figure 6 Width of the transition of the films used for Fig. 4.

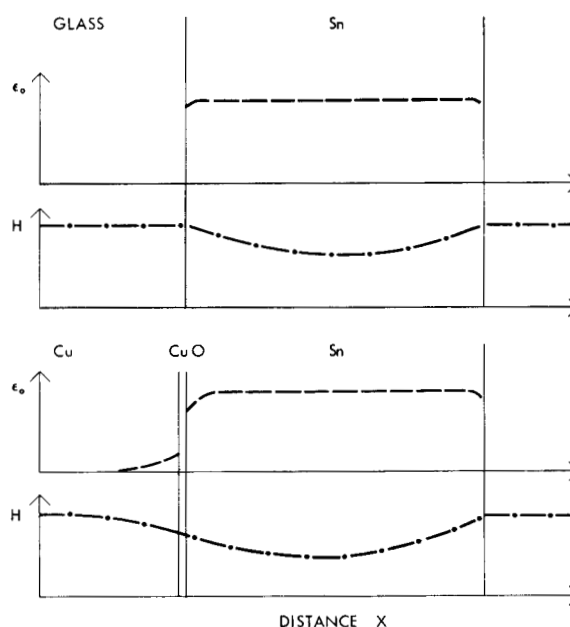


Figure 7 Spatial dependence of the energy gap and the magnetic field for tin films on glass and copper substrates (schematically).

The reason for this behavior is not at all clear. Calibration mistakes, misalignment and circular symmetry have been ruled out as a cause. Some of the films seem to have a preferred crystal orientation. This is evidenced by a decrease of the normal resistance by about 5% when the current density is raised from  $10^2$

to  $10^6$  amp/cm<sup>2</sup>. Such decrease can occur in oriented films if the drift velocity is high enough to change the surface area of the Fermi surface: This changes  $\sigma_0/l$  and therefore the resistance. It is possible that preferred crystal orientation also affects the critical fields.

The uncertainty of the cause of the anomalously low critical fields, of course, also affects the conclusions drawn from the behavior of the films on metal substrates. Nevertheless the experiments here give support to the idea that a negative surface energy at the interface between superconducting and normal domains is responsible for high critical fields observed in some metals.<sup>10</sup> B. B. Goodman reached independently the same conclusion.<sup>11</sup>

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### References and footnotes

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