same range. Figure 1 shows the results of the four separate measurements below $T^2 = 5.0$. If less weight is given to the first and less precise set of data represented by the open circles, then below $T^2 = 2.2$ ($T = 1.48\,^\circ\mathrm{K} = 0.163T_C$) the individual determinations fall along a straight line which passes through the origin. A possible interpretation would be that the electronic specific heat at this temperature is inconsiderable in comparison with the superconducting lattice specific heat and that the latter can be represented by a T^3 term with an altered value of Θ which may be evaluated from the data as 243°K.

We regard this interpretation as provisional since a number of small corrections must be made to these data to account for the thermal capacities of the heater wires wound around the sample, for the Allen-Bradley carbon resistor, and for the glyptal adhesive. These corrections, now being investigated, would all be subtracted and their influence, if significant, could only increase the discrepancy with the normal line. A detailed report of the measurements will be submitted in the near future.

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[1] International Conference on the Electronic Properties of Metals at Low Temperatures, Geneva, New York, August 25-29, 1958 (unpublished).

[2] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, Phys. Rev. 108, 1175 (1957).

[3] H. A. Boorse, Phys. Rev. Letters 2, 391 (1959).

[4] G. V. Chester, Phys. Rev. 104, 883 (1956).

[5] C. A. Bryant and P. H. Keesom, Phys. Rev. Letters 4, 460 (1960).

[6] W. B. Pearson and I. M. Templeton, Phys. Rev. 109, 1094 (1958).

CHANGES IN SUPERCONDUCTING CRITICAL TEMPERATURE PRODUCED BY ELECTROSTATIC CHARGING*

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In the process of charging a parallel plate condenser, electrons are added to one plate and removed from the other one. Using a film 100 A thick as one of the condenser plates, it is possible to add or subtract about one electron for each 10^4 atoms. The maximum charge that can be added is limited by the breakdown strength of dielectrics, typically on the order of 10^6 v/cm. The effect of electrostatic charging on the conductivity of a metal film has been investigated repeatedly over the last fifty years.[1-3] Recent measurements by Deubner and Rambke[4] and by Bonfiglioli, Coen, and Malvano[5,6] have shown that the normal-state conductivity of metals can be modified by electrostatic charging (field effect). Changes of relative conductivity on the order of one in 10^4 have been produced. The conductivity of the films can be increased or lowered depending on the sign of the added charge.

We have made measurements of the effect of charging on the normal-state conductivity of films of gold and have examined the effect on both the superconducting transition temperature and the normal-state conductivity of tin and indium. Charging resulted in a change in the normal-state conductivity of all metals tried. It caused a change in the transition temperature of the superconducting materials.

Ruby (muscovite) mica substrates about $5\ \mu$ thick were used for the experiments. A gold coating was evaporated onto the back side to serve as one plate of the condenser, and gold potential and current contact patches were placed on the front. The substrates were then placed in a vacuum system and the film to be studied was evaporated so as to form the second plate of the condenser. Charging voltages of 150 volts were applied giving a maximum electric field of 3×10^5 v/cm. The conductivity of the film was measured using a 1000-cycle bridge. Film thickness was estimated from the temperature-dependent part of the resistance.

Of the metals examined, gold would be expected to have the simplest conductivity mechanism. Our gold films were condensed at room temperature. Negative charging resulted in an increase in conductivity while positive charging caused a decrease. The relative change in conductivity was of the same order of magnitude as the ratio of added or subtracted electrons to the number of atoms in the film. Measurements made at room temperature and at 77°K gave essentially the same results. The magnitude of the change in conductivity was the same for positive and negative charging.

Tin and indium films were prepared by evaporation onto mica substrates held at liquid nitrogen temperature. The films were annealed to about 200°K. Measurements were made of the normal-state field effect as the films were cooled down to liquid helium temperature. The effect in both indium and tin was opposite in direction to that found for gold. Negative charging decreased the conductivity while positive charging increased it. For tin the effect was very much larger than for indium.

For the superconducting measurements the film temperature was slowly lowered through the transition region. Resistance vs temperature curves for an indium and a tin film are shown by the dashed curves in Figs. 1 and 2. The next step was to stabilize the temperature at various points in the transition region and measure the change of resistance caused by charging. The results are shown by the solid curves of Figs. 1 and 2. The displacement of the transition curve necessary to cause the observed resistance changes was calculated from the slope of the R vs T traces.

Qualitative measurements made in the superconducting transition region for five indium films showed in every case an increase in resistance with negative charging and a corresponding decrease with positive charging. This effect is the same in sign but much larger than that found for normally conducting indium. The measured resistance changes correspond to a decrease in transition temperature with negative charging. Quantitative measurements were made on three indium films. Thicknesses ranged from 60 to 120 A. The results of Fig. 1 are typical. A field of 2.6×10^5 v/cm produced a shift in transition temperature on the order of 10^{-4}°K. Approximately 3×10^{-5} electron were added for each atom of the film. The amount of added charge was obtained from capacity measurements and the charging voltage. The number of atoms was calculated from the thickness estimate using the normal density of indium. To an accuracy of 10% the decrease in transition temperature caused by negative charging was equal to the increase caused by adding positive charge.

The effect of charging on the transition temperature of tin was opposite to that found for indium. Qualitative measurements on seven films all showed an increase in transition temperature with negative charging. Quantitative results were obtained with four tin films having thicknesses from 70 to 110 A. Results typical of three of these are shown in Fig. 2. Here again the mag-

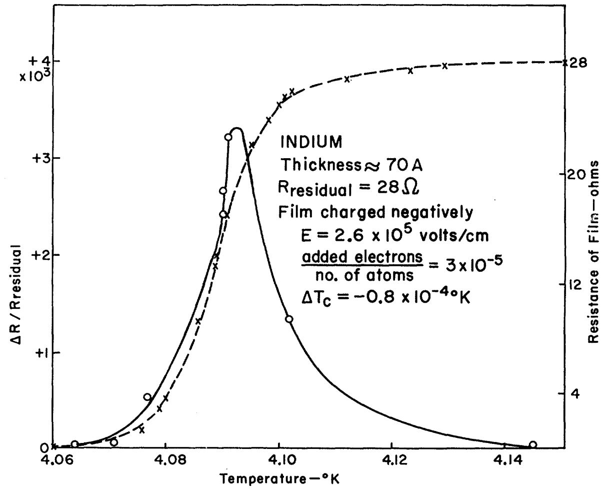

FIG. 1. Transition curve and change of resistance caused by negative charging of an indium film. Positive charging causes a change in resistance of the same size but in the opposite direction.

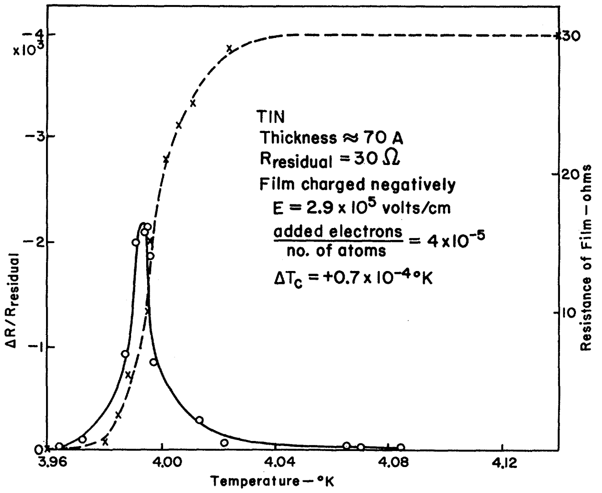

FIG. 2. Transition curve and change of resistance caused by negative charging of a tin film. Positive charging produces a change in resistance of the same size but in the opposite direction.

nitudes of the shifts of transition temperature with positive and negative charging were equal. It should be noted that the effect of charging on the resistance of tin films is opposite in sign in the superconducting transition region to that found for normally conducting material. The fourth tin film showed a shift in transition temperature an order of magnitude larger. For this film, the size of the effect was not symmetrical with respect to charge, the increase in transition temperature being about six times larger than the decrease. However, the width of the transition region was also an order of magnitude larger than for the other films, perhaps indicating a lack of uniformity.

After the first experiments on tin had been made but before measurements on indium were started, Donald Seraphim pointed out to us that an effect similar to the one observed might result if the substrate were piezoelectric. Strains which would depend on the sign of the applied charge could cause changes in transition temperature. The space group $C_{2h}(2/m)$ usually quoted for muscovite[7] has a center of symmetry, a property that rules out the possibility of piezoelectric behavior. Unfortunately, a closer look at the literature indicates that the details of the muscovite structure are still in doubt since the proposed structure does not account for all of the x-ray diffraction lines.[8] Accordingly, experiments were made to try and detect piezoelectric behavior in muscovite. None was found. Strips of mica 3 mm by 19 mm were cut from material similar to that used for the field-effect measurements. Thin gold films were evaporated onto both sides of the strips. The specimens were then clamped at one end in a special vise which also made electrical contact to the gold films. The free end of the mica was observed in a microscope as fields of 3×10^5 v/cm were applied first in one direction and then in the other. A piezoelectric behavior capable of causing a charge-dependent raising and lowering of the superconducting transition temperature would have shown up as a deflection dependent on the direction of the applied field. No such effect was observed. Any such strain $(\Delta l/l)$ was less than 1×10^{-8}. Measurements of the effect of pressure on the transition temperature of tin give $\Delta T_c = 30.0\,\Delta V/V$.[9] Assuming $3\Delta l/l \approx \Delta V/V$, the change in transition temperature that could be produced by a still undetected piezoelectric effect would be less than 1×10^{-6} °K. This is two orders of magnitude smaller than the shifts in transition temperature reported here. A further reason for believing that the effects are not caused by strains in the substrate is that the shifts are in opposite directions for tin and indium. This is in contrast to measurements[9] which show that compression lowers the transition temperatures of both materials.

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[1] E. Bose, Physik. Z. 7, 373 (1906).

[2] R. W. Pohl, Physik. Z. 7, 500 (1906).

[3] H. Mayer, Physik Dünner Schichten (Wissenschaftliche Verlagsgesellschaft M. B. H., Stuttgart, 1955), Vol. II, Chap. 2, p. 272. (Discussion and further references.)

[4] A. Deubner and K. Rambke, Ann. Physik 17, 317 (1956).

[5] G. Bonfiglioli, E. Coen, and R. Malvano, Phys. Rev. 101, 1281 (1956).

[6] G. Bonfiglioli, E. Coen, and R. Malvano, Phys. Rev. 115, 330 (1959).

[7] W. W. Jackson and J. West, Z. Krist. 76, 211 (1930).

[8] S. B. Hendricks and M. E. Jefferson, Am. Mineralogist 24, 729 (1939).

[9] L. D. Jennings and C. A. Swenson, Phys. Rev. 112, 31 (1958).