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Relative Absorption of 10 Mc/sec Longitudinal Sound Waves in a Superconducting Polycrystalline Tin Rod*

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The relative absorption of 10 Mc/sec sound pulses has been studied between 1.5°K and 3.73°K (the transition temperature) in superconducting polycrystalline tin and above 3.73°K to about 4.2°K in the normal metal. Above the transition the absorption was heavy, but below it, the absorption decreased considerably as the temperature was lowered. It was possible to estimate how the minimum value of the absorption coefficient (which differed from the true value by an undetermined constant equal to the absorption coefficient at the absolute zero of temperature) varied as a function of temperature but no success has yet been achieved in correlating this quantitatively with existing theories of superconductivity or of absorption of sound in metals at low temperatures.

I. INTRODUCTION

THE transition between the superconducting and normal phases was first shown to have an effect on the absorption of sound in a pure superconductor by Bömmel and Olsen,[1] who observed that the absorption at a frequency of 1 Mc/sec in lead changed while the transition was taking place in the presence of a magnetic field; that the absorption was in fact different in the two phases for a lead single crystal was later discovered by Bömmel,[2] who covered the frequency range 9–27 Mc/sec and showed that in the superconducting phase the absorption was substantially less than in the normal phase for the same temperature both for longitudinal and transverse waves. That a similar effect was observable in polycrystalline tin with 10 Mc/sec (longitudinal) sound was reported by the author[3] and it is the purpose of this paper to amplify the contents of that abstract. A number of other investigators[4–6] have also recently reported an essentially similar effect in tin.

II. EXPERIMENTAL METHOD

The experimental arrangement is illustrated by the block diagram (Fig. 1). Short (1–2 μsec) pulses of high frequency (10 Mc/sec) alternating voltage were fed to an X-cut quartz transducer attached to one end of the specimen. There was sufficient electrical "pickup" from this pulse to produce a deflection (after amplification, etc.) on the cathode-ray oscilloscope and also to provide a convenient triggering and synchronizing impulse for the sweep (of approximately 50 μsec duration). The transducer converted the electrical impulse into longitudinal sound waves which traveled down the rod and were reconverted by a second similar transducer into an electrical impulse at the other end. The envelope of this transmitted pulse was visible (after amplification and rectification) on the sweep of the oscilloscope as shown in the diagram (and also in Figs. 3 and 4).

The tin specimen was made from rods of 99.999% pure tin (Johnson, Matthey and Company, Laboratory No. 5606, Catalogue No. JM 530), and was cast in vacuo after degassing as a rod of about 2.2 cm diameter. The ends were turned flat in a lathe and then ground with No. 600 grind. The quartz plates were of $\frac{1}{2}$-in. diameter and unpolished. The bonding material between transducer and specimen was Dow Corning 200 fluid, viscosity 2.5×10^6 centistokes, as recommended by McSkimin[7] and the bond was made substantially as described by Squire[8] except that the electrodes probably pressed down rather harder on the specimen. The method of mounting the specimen is illustrated in Fig. 2; the tin rod was upright in the liquid helium bath, suspended by the electrical leads, and the cryostat was of conventional design. Temperatures were measured on the 1949 helium vapor pressure scale.

The electronic circuits were part of an apparatus described recently by Cedrone and Curran[9]; the oscilloscope was a Tektronix type 514D and the trace was photographically recorded with a Fairchild Polaroid Oscilloscope Camera. The amplifier was tested for

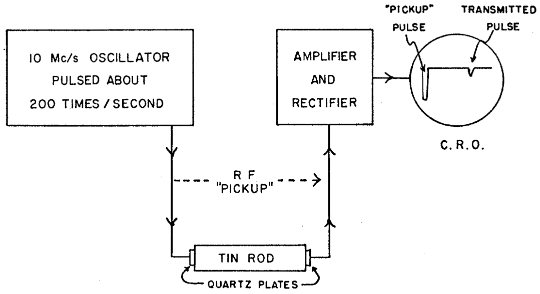

FIG. 1. Block diagram of the experimental arrangement.

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* Supported by the Office of Naval Research.

† On leave of absence from Charterhouse, Godalming, Surrey, England.

[1] H. E. Bömmel and J. L. Olsen, Phys. Rev. **91**, 1017 (1953).

[2] H. E. Bömmel, Phys. Rev. **96**, 220 (1954).

[3] L. Mackinnon, Phys. Rev. **98**, 1181(A) (1955).

[4] H. E. Bömmel, as reported by W. P. Mason, Phys. Rev. **97**, 557 (1955).

[5] Benjamin Welber, Phys. Rev. **98**, 1196(A) (1955).

[6] J. K. Landauer, Phys. Rev. **96**, 296 (1954).

[7] H. J. McSkimin, J. Appl. Phys. **29**, 988 (1953).

[8] C. F. Squire, Phys. Rev. **95**, 1126 (1954).

[9] N. P. Cedrone and D. R. Curran, J. Acoust. Soc. Am. **26**, 963 (1954).

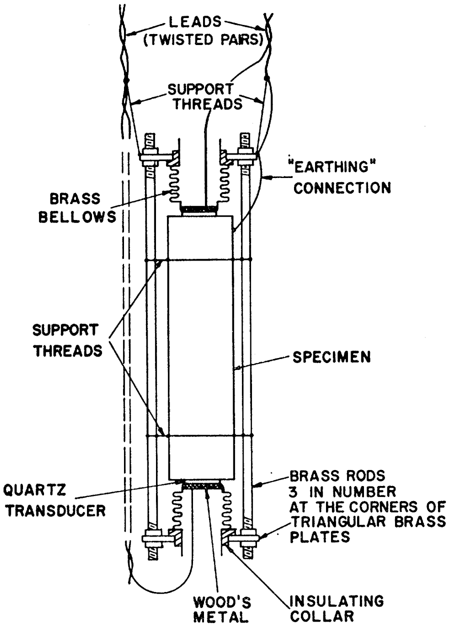

FIG. 2. Experimental arrangement for mounting the tin specimen.

linearity with the help of an input pulse fed from a source of constant amplitude through a calibrated attenuator; it was found to be as linear as the attenuator was good—adequately so for the purpose of the main part of this experiment. With the gain of the amplifier kept constant and with the input pulse to the specimen keeping constant amplitude, the height of the transmitted pulse—as seen on the oscilloscope—becomes a relative measure of the absorption of the sound in the rod; this height was measured on the photograph with the help of a traveling microscope.

III. EXPERIMENTAL RESULTS

The length of the specimen was originally 11.55 cm. It was found that the absorption in the temperature range 3.73–4.2°K was very heavy and the transmitted pulse was not very much greater than the noise level of the amplifier. This is shown in Fig. 3. However, below the superconducting transition (3.73°K) in the absence of a magnetic field (other than the earth's field) the amplitude of the transmitted signal increased considerably as the temperature was lowered. This is seen both in Fig. 3 and Fig. 4; in fact, by 1.52°K the pulse amplitude had increased to some 150 times the amplitude observed at 3.73°K.

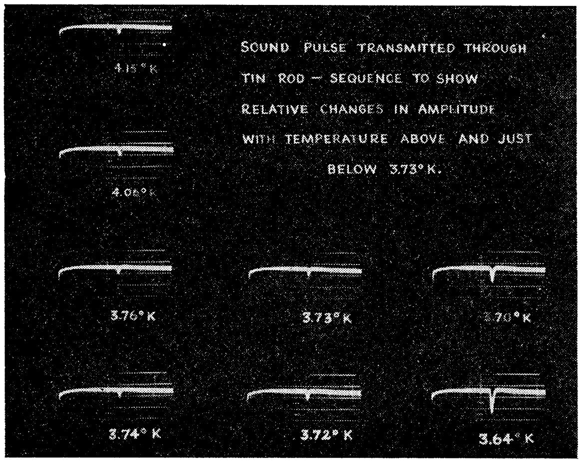

FIG. 3. Photographs of oscilloscope—3.64 to 4.15°K.

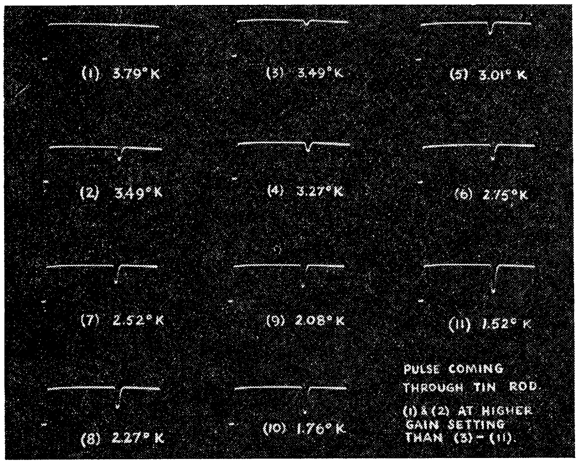

FIG. 4. Photographs of oscilloscope—1.52 to 3.79°K.

A graph of pulse height (or amplitude) plotted against a function of $T/3.73$ (where T is the absolute temperature) approximating to $(T/3.73)^2$ produced a straight line (as shown by curve 1 of Fig. 5). The function of $T/3.73$ was that given by Lock, Pippard, and Shoenberg[10] for the temperature dependence of the critical magnetic field; this result may be coincidental as far as the function is concerned—it certainly was coincidental in that it appeared that the length of the specimen was accidentally chosen in such a way that a straight line resulted. It can readily be shown that if the normal law for sound absorption is obeyed, i.e., if

$$h_T = He^{-\alpha_T l}, \tag{1}$$

where h_T is the observed transmitted pulse height at temperature T, H the input pulse amplitude, α_T the amplitude absorption coefficient, in nepers/cm when l, the length of the specimen, is in cm, and if at some length l_1 the height h_{1T} is also given by

$$h_{1T} = h_{10}\phi(T)$$

where h_{10} is the transmitted pulse height at the absolute zero and $\phi(T)$ is some function of the absolute temperature, then at some other length l_2 the height h_{2T} will be given by

$$h_{2T} = h_{20}\psi(T),$$

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[10] Lock, Pippard, and Shoenberg, Proc. Cambridge Phil. Soc. **47**, 811 (1951).

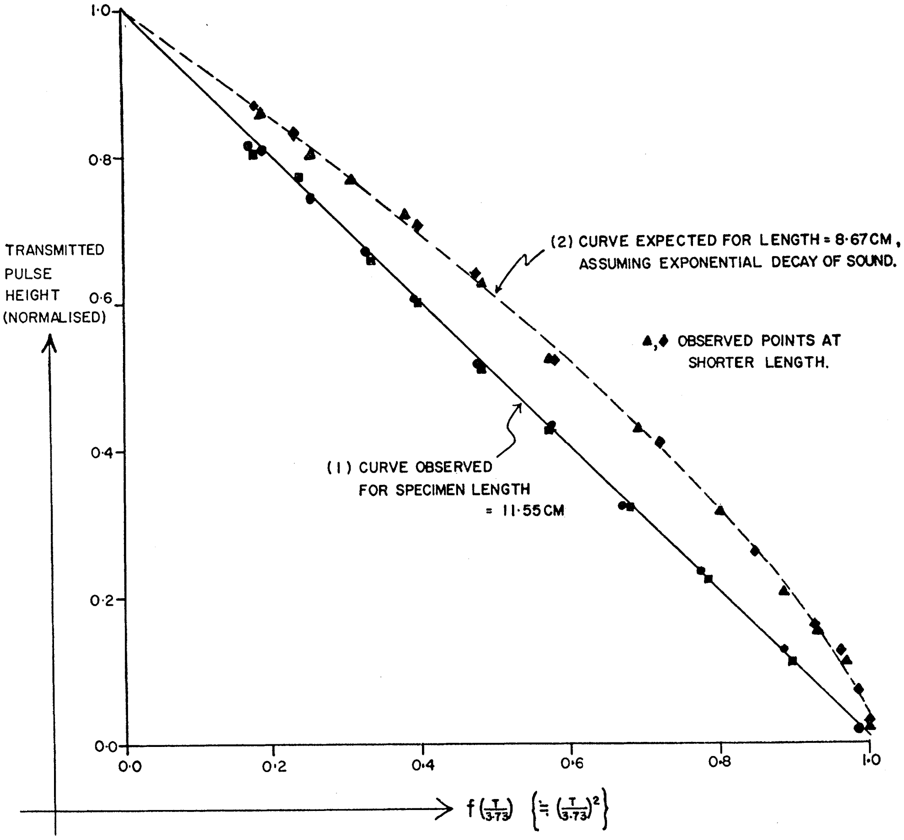

FIG. 5. Graphs of height of transmitted sound pulse (after normalization) plotted against $f(T/3.73)$ for both lengths of specimen.

where h_{20} is again the transmitted pulse height at the absolute zero and

$$\psi(T)=[\phi(T)]^{(l_2/l_1)}. \qquad (2)$$

(This result will hold whether or not there is absorption at the absolute zero of temperature.)

The length of the specimen was therefore reduced to 8.67 cm and, assuming the straight-line result for the longer length, the expected pulse height-temperature curve for the shorter specimen was calculated using Eq. (2) and has been incorporated in Fig. 5 as curve 2. Experimental points have been added to this figure and it can be seen that they lie reasonably close to this curve, thus confirming the negative exponential nature of the absorption and the earlier coincidence of the straight line.

It should be emphasized that all measurements were relative and that each set of experimental points required independent normalization before incorporation in the graph (Fig. 5).

The absolute value of the absorption at the absolute zero of temperature—or at any temperature—cannot be estimated from these results but, assuming that the extrapolation to the absolute zero is valid, then we can write that, for pure superconducting polycrystalline tin, the equation

$$\alpha_{T\,\min}=\frac{1}{11.55}\ln\left(\frac{1}{1-f(T/3.73)}\right), \qquad (3)$$

where

$$f\left(\frac{T}{3.73}\right)\doteqdot\left(\frac{T}{3.73}\right)^2,$$

and $\alpha_{T\,\min}$ is a minimum value for the absorption coefficient α_T [as defined by Eq. (1)], will be reasonably valid for all temperatures below but not very close to 3.73°K. Furthermore, $\alpha_{T\,\min}$ may differ from α_T by a constant undetermined quantity (equal to the value of α_T at 0°K) throughout this temperature range.

Equation (3) would predict an infinite absorption at the transition temperature. However, the observed value of $\alpha_{T\,\min}$ at this temperature was about 1.0 ± 0.4 nepers/cm and, using this, we can construct an $\alpha_{T\,\min}$-temperature graph as shown in Fig. 6.

The relatively high uncertainty in the value of $\alpha_{T\,\min}$ at the transition temperature arises from a discrepancy which appears when $\alpha_{T\,\min}$ is estimated from the different lengths of tin rod; the longer length gives a higher value than the shorter length. This may be due to slight nonlinearity of the amplifier which becomes important only when very small pulses are involved and is not important with larger pulses. The error involved here does not affect the general conclusions or the values for $\alpha_{T\,\min}$ below the transition—merely the point at which the absorption coefficient-temperature curve for tin above the transition temperature will break away from the very steep part of the curve of Fig. 6.

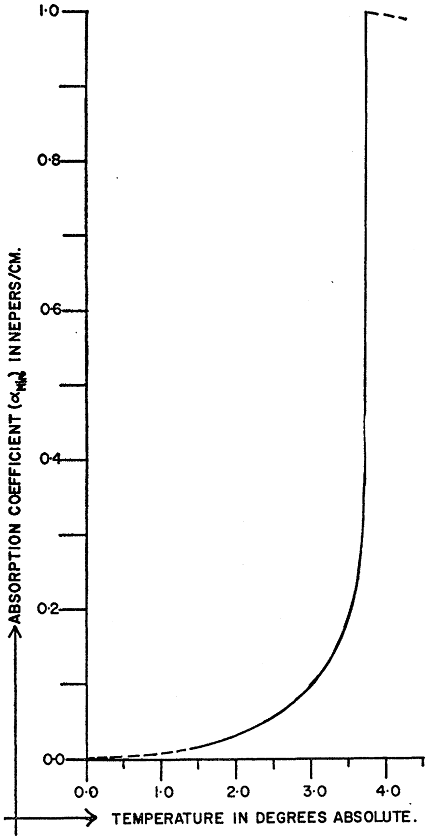

FIG. 6. Graph of the electronic absorption coefficient ($\alpha_{T\,\min}$) plotted against absolute temperature.

IV. DISCUSSION AND CONCLUSIONS

It is clear that if superconductivity is a consequence of electron-lattice interaction, this change in absorption of sound must be in some way related, and reasonable qualitative explanations of the effect have already been published.[11,12] Theory so far[11–13] has only succeeded in accounting in a quantitative manner for the heavy absorption in the normal metal and has made no explicit predictions as to the variation with temperature of the absorption coefficient in the superconducting state—although there has been a prediction by Landau and Khalatnikov[14]; this however does not seem immediately applicable to these results as it discusses only the absorption to be expected in the superconducting state as a result of the disturbance by the sound wave of the equilibrium between superconducting and normal electrons; the experiments would seem to indicate that absorption by the normal electrons alone is perhaps the more important process. While the theories of absorption in the normal metal differ slightly in their approach, they all agree that for the frequency used in these experiments, the absorption coefficient is proportional to the electrical conductivity. (They show also that this result would not hold for an infinite conductivity but will hold for the usual experimentally observed conductivities.) Morse[13] and Kittel[12] both treat the normal absorption as a consequence of a relaxation of the Fermi surface in momentum space and Morse[13] has pointed out that the experimental results indicate that this relaxation must be very much speeded up by the presence of even a small number of superconducting electrons. This would certainly seem to be the case; if one assumes Morse's value for α in the normal metal, namely,

$$\alpha=\frac{4}{15}\frac{\omega^2 m E_0\sigma}{\rho_0 c_0{}^3 e^2}$$

where ω is the angular frequency of the sound, c_0 its velocity, ρ_0 is the density of the metal, and σ is its conductivity, e and m are the charge and mass of the electron, respectively, and E_0 is the Fermi level, and further if one assumes this result to hold for the superconducting metal, the variation in the product $E_0\sigma$ (the σ involving the relaxation time) needed to account for the observed variation of α is too great to be correlated with existing two-fluid models of superconductivity on a "proportion of normal electrons" basis, (even allowing that one does not really know how E_0 and σ will vary). It is perhaps easy to see that collisions between normal and superconducting electrons might very well shorten the relaxation time (as they might involve momentum distributional changes for the normal electrons without energy changes), but no simple model has been found to which will fit the observations. The picture does however seem to suggest that the value of the electronic sound absorption coefficient (previously called $\alpha_{T\,\min}$) in the superconducting state, being dependent on some different mechanism (possibly of an electron-electron interaction type, but not necessarily so and not necessarily involving a "two-fluid" concept), may be almost independent of its value in the normal state where the relaxation mechanism is very likely to be affected by those impurities (including lattice imperfections) which affect electrical conductivity values. However, further experimental work is needed to establish this plausible but uncertain point; it could not be expected to hold true when the value of normal electrical conductivity is low.

The discussion of these experiments has ignored absorption due to the lattice only, which has presumably to be added to the electronic absorption to obtain the total absorption. However, the variation with temperature of lattice absorption can reasonably be taken as small in the temperature range covered.

Experiments have been carried out on the effect of a magnetic field on the absorption; the results obtained will be the subject of a separate report, but it can be

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[11] W. P. Mason, Phys. Rev. **97**, 557 (1955).

[12] C. Kittel, Phys. Rev. **98**, 1181(A) (1955).

[13] R. W. Morse, Phys. Rev. **97**, 1716 (1955).

[14] L. D. Landau and I. M. Khalatnikov, Doklady Akad. Nauk. S.S.S.R. **96**, 469 (1954). I am indebted to Dr. R. T. Beyer for drawing my attention to this paper and for preparing a translation; a few copies of this translation have been mimeographed and are available to those interested.

stated at this stage that existence of a hysteresis effect, as discovered by Bömmel,[2] has been confirmed and that in the normal metal, the absorption does depend strongly on magnetic field (so far applied only along the specimen). This effect was also originally found by Bömmel[15]; in the specimen described here, at the shorter length and at 3.9°K, about 200 oersted will double the amplitude of the transmitted pulse.

The author is very grateful for advice given by Dr. H. J. McSkimin of the Bell Telephone Laboratories in the making of the transducer-specimen bond and also to Dr. H. E. Bömmel for early information about his work. (This investigation was started independently without the knowledge that other work was being done, but the discovery of the effect is due to Dr. Bömmel.) He also acknowledges with thanks assistance given during the measurements by graduate students and others at Brown University.

He would also like especially to thank Dean R. B. Lindsay for his encouragement throughout this work and for making possible his visit to Brown University. He is also grateful to the Headmaster and Governing Body of Charterhouse School for an extended leave of absence.

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[15] H. E. Bömmel (verbal communication).

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Properties of Germanium Doped with Manganese

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The temperature dependence of the electrical resistivity and Hall coefficient in *p*- and *n*-type manganese-doped germanium crystals indicates that manganese introduces two acceptor levels in germanium at 0.16±0.01 ev from the valence band and 0.37±0.02 ev from the conduction band. The distribution coefficient for manganese in germanium is $(1.0\pm0.2)\times10^{-6}$. Comparison is made with other fourth-row metals (V, Fe, Co, and Ni) as impurities in germanium.

I. INTRODUCTION

SINGLE crystal germanium has been doped with manganese in a manner similar to the doping of germanium with Fe,[1] Co,[2] and Ni.[3] This paper will present the pertinent data related to the properties of manganese-doped germanium followed by a short comparison of the known properties of the fourth-row transition elements as impurities in germanium.

II. CRYSTAL PREPARATION

The details of the preparation of doped single-crystal germanium and the cryostat and assorted equipment used to take the measurements reported below are described in reference 1. In what follows the words crystal and sample will always refer to manganese-doped single crystal germanium unless noted.

Zone-melted manganese prepared by F. H. Horn of this laboratory, manganese obtained from Johnson-Matthey Company and manganese from Electro-Manganese Corporation, Knoxville, Tennessee, were all used with essentially the same results from each source.

In order to control the position of the Fermi level, the germanium melts were counterdoped by adding specific amounts of a single crystal Ge-As alloy. When used below, counterdoping will refer specifically to the addition of the Ge-As alloy either to compensate low-ionization energy acceptor impurities or to fill the levels introduced by the manganese.

III. EXPERIMENTAL RESULTS

A. Crystal Growing

It was found that when the pulling rate of the growing crystal was reduced from approximately 6 cm/hr to approximately 1.5 cm/hr, roughly 10 times as much Mn could be incorporated into the single crystal before the abrupt onset of lineage markings occurred.[1] These markings are apparently the result of small pockets of Mn or of a different Mn-Ge phase being incorporated in the growing crystal. With the growing rate equal to 1.5 cm/hr and a manganese concentration of 10^{19} to 10^{20} atoms/cc in the melt, the distribution coefficient (k_0) was $(1.0\pm0.2)\times10^{-6}$. The maximum solubility under the above conditions was approximately 10^{15} manganese atoms per cc. All crystals were grown in the (100) direction.

B. Electrical Properties

When manganese alone was used to dope the germanium melt, the crystals were always *p*-type. By counterdoping with a small amount of donor material, a low-lying level at 0.05 ev from the valence band and a second level at 0.16 ev from the valence band could be

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[1] W. W. Tyler and H. H. Woodbury, Phys. Rev. **96**, 874 (1954); R. Newman and W. W. Tyler, Phys. Rev. **96**, 882 (1954).

[2] Tyler, Newman, and Woodbury, Phys. Rev. **97**, 669 (1955).

[3] Tyler, Newman, and Woodbury, Phys. Rev. **98**, 461 (1955).

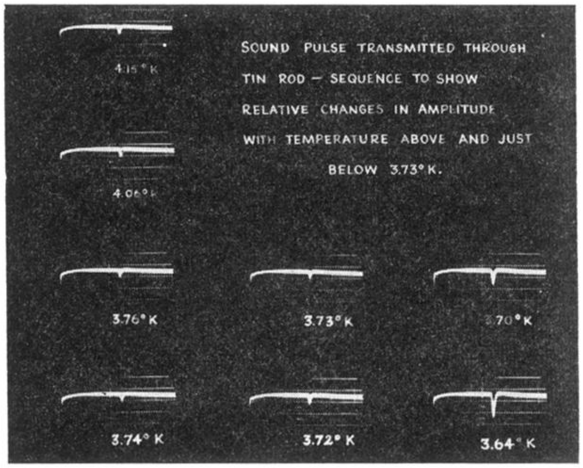

FIG. 3. Photographs of oscilloscope—3.64 to 4.15°K.

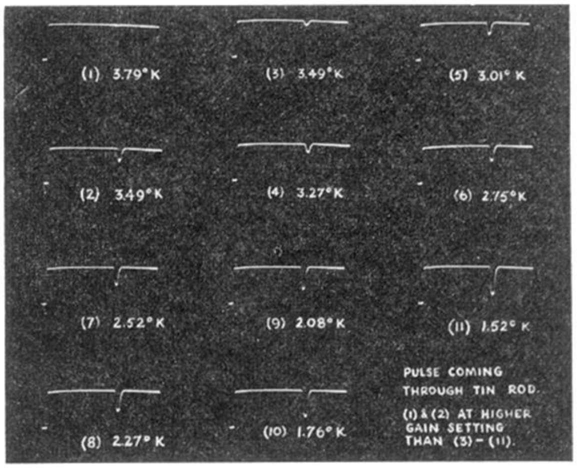

FIG. 4. Photographs of oscilloscope—1.52 to 3.79°K.