A SUPERCONDUCTING BOLOMETER FOR INFRARED MEASUREMENTS[1]

ROBERT M. MILTON[2]

Department of Chemistry, The Johns Hopkins University, Baltimore 18, Maryland

A sensitive high-speed bolometer, operating at about 16°K., has been constructed which will give detectable signals from an impulse of radiation 1.2×10^{-4} sec. long, containing 2×10^{-6} ergs of energy, using a wide-band pass amplifier. The sensitive element is a ribbon of columbium nitride, 0.125 in. x 0.010 in. and 0.001 in. thick, which has a superconducting transition 0.07° wide at 15.8°K. The nitride, which serves as the receiver, is bakelited to a copper block which, by means of an electric heater and hydrogen at its triple point, is maintained at a constant temperature such that the columbium nitride is in the steepest portion of its resistance–temperature curve. At this point, values of dR/dt may run from 1 to 100 ohms deg.$^{-1}$ The bolometer is used in a bridge circuit with 10 milliamperes of current; the first stage of amplification is a transformer (1-ohm primary impedance, 1.1-megohms secondary impedance); the second stage is a conventional wide-band audio amplifier. The peak noise level of the apparatus is equivalent to 0.025 microvolt at the bolometer level. Frequency response curves for sine- and square-wave radiation inputs have been obtained. The energy source employed is an oxidized iron plate kept at 100°C.

I. INTRODUCTION

Infrared radiometry in the middle 1930's was in the position that the detectors then used had been perfected to the stage where the factor limiting their sensitivity was Brownian motion or a related effect (5). The most sensitive detectors had their limits of detection at a flux of about 10^{-3} ergs sec.$^{-1}$, and time constants ranging from 1 to 10 sec.

In 1938 (1) and 1939 (10) it was pointed out that superconductivity offered an excellent means for measuring very small quantities of energy. A superconductor being used as a bolometer, temperature coefficients of resistance could be increased by many orders of magnitude, thermal capacities would fall to very low values, and statistical fluctuations would be reduced with the absolute temperature.

The first results obtained with superconducting bolometers showed a minimum detectable flux of about 10^{-3} ergs sec.$^{-1}$ with a 10-sec. time constant (2, 3). The superconductor was a coil of tantalum wire refrigerated by a helium bath, boiling under reduced pressure at 3.22°K. The factor limiting the sensitivity of this instrument was the temperature fluctuation of the helium bath.

Soon after this there arose a need for an infrared detector of similar sensitivity at about 10 μ but with a time constant equal to or less than 0.001 sec., and with

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the emphasis on handling isolated short-duration energy pulses. It was toward this end that this work on the superconducting bolometer was directed.

In 1941 (4) and independently in 1942 (11) it was found that columbium nitride was a superconductor in the region above 14°K. This discovery opened the way to a solution to the temperature fluctuations of the refrigerating bath. By utilization of the triple-point mixture of hydrogen at 14°K., obtained by pumping on the vapor above boiling hydrogen, as a temperature sink for a superconducting bolometer of columbium nitride, the background temperature fluctuations could be very greatly reduced. The bolometer could be raised to the appropriate operating temperature by an electric heater placed between the bolometer and the sink. It was along these lines that the development proceeded.

II. PREPARATION OF COLUMBIUM NITRIDE

The first papers (4, 11) on the superconducting properties of columbium nitride did not agree on the position and width of the transition or on the method of preparation. These disagreements had to be cleared up, and in such a manner as to yield small-dimension, electrically conducting columbium nitride specimens with very sharp superconducting transitions.

A new nitriding method was chosen. It called for the heating of columbium metal by the passage of current through it while suspended in a stream of ammonia. It was hoped that if ammonia were used instead of nitrogen the temperature might be lower and the time shorter than otherwise. The method proved successful and will reproducibly yield columbium nitride with transitions at 15.9°K. ± 0.1° and 0.15 ± 0.04 degrees wide. A strip of columbium metal[3], 20 cm. long, 6 mm. wide, and either 0.0254 mm. or 0.0063 mm. thick, is suspended tautly in a slowly flowing stream of dry ammonia. Current is passed through the metal and it is maintained thus for 20 min. at temperatures between 1350°C. and 1500°C., as read with an optical pyrometer with no emissivity correction.

A second method, using a stationary atmosphere of purified nitrogen in place of the ammonia, has been tried. The temperature is kept at 1500°C. for 1 hr. The results are not strictly reproducible but the transitions usually lie between 14°K. and 15°K. and the transition widths vary from 0.03° up. A more complete report on this has appeared (14). Figure 1 is a plot of resistance against temperature for several specimens of columbium nitride. Curve a is for a typical preparation in ammonia, while curves b and c are for two different samples prepared in nitrogen.

III. BOLOMETER CONSIDERATIONS

If the signal from the bolometer is amplified without any distortions, the resulting signal, $\Delta\phi$, as observed on a cathode-ray screen or other instrument, will be

$$\Delta\phi = a\Delta iR = ai\Delta R = aiR\left(\frac{1}{R}\frac{dR}{d\theta}\right)\Delta\theta \tag{1}$$

[3] Obtained from the Fansteel Metallurgical Company, Chicago, Illinois. The impurities (mostly oxygen) = 0.2 per cent.

where a is the factor of amplifications, i the current through the bolometer, R the resistance of the superconductor when in operating condition, $\dfrac{1}{R}\dfrac{dR}{d\theta}$ or ρ the temperature coefficient of resistance, and $\Delta\theta$ the increase in temperature of the bolometer.
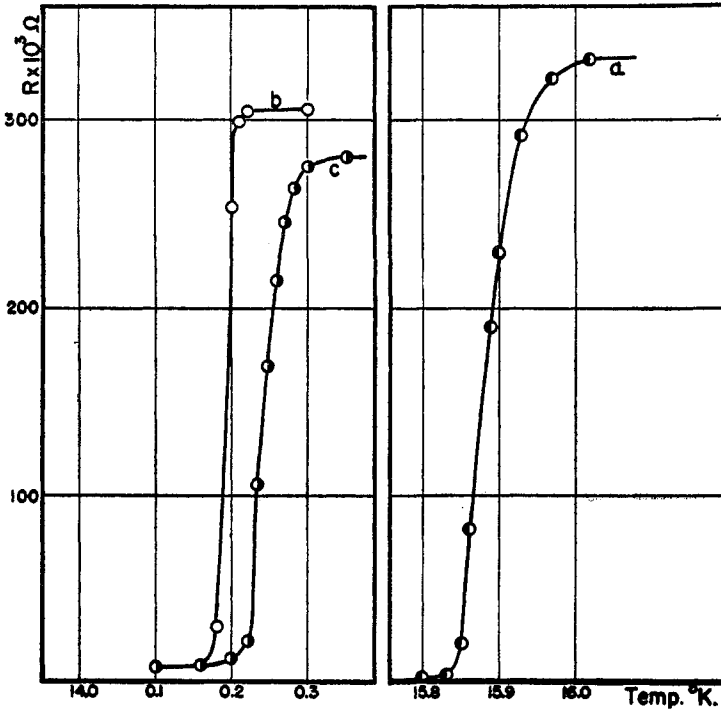

FIG. 1. Resistance *versus* temperature. Columbium nitride superconducting transitions. Curve a, sample prepared in ammonia; curves b and c, samples prepared in nitrogen.
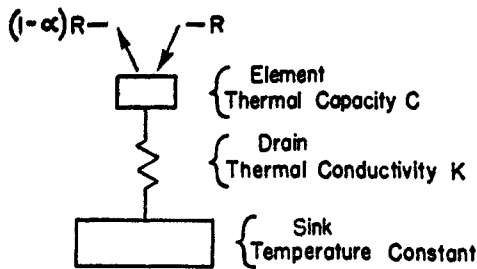

FIG. 2. Idealized thermal diagram

Consider first the temperature rise, $\Delta\theta$. Let us assume simply, as in figure 2, that radiation falls on an element with the heat capacity c, that fraction α of it is absorbed, that the conductivity of this element is such that there are no appreciable temperature gradients in it, that a thermal drain of conductivity k

and negligible thermal capacity connects the element to a constant temperature sink, and that there are no radiation losses. If θ represents the temperature of the element, at least part of which is the superconducting element, and $\theta_0 = 0$ the temperature of the sink, we can determine θ as a function of c and k and the characteristics of the radiation wave.

If radiation of intensity J falls on the detector, starting from $t = 0$ we have:

$$\theta = \frac{\alpha J}{k} \left(1 - e^{-\frac{k}{c}t} \right) \tag{2}$$

Figure 3 shows a plot of this equation and gives the $\Delta\theta$ for a short-duration energy pulse.

If the radiation has the following form:

$$R = I + I \sin\left(2\pi f t - \frac{\pi}{2} \right) \tag{3}$$

where f is the frequency of the sine wave, the equation for θ can be obtained. To simplify this equation we consider two extremes, one when

$$k \gg 2\pi f c$$

and

$$\theta = \frac{\alpha I}{k} \left(1 + \sin\left[2\pi f t - \frac{\pi}{2} \right] \right) \tag{4}$$

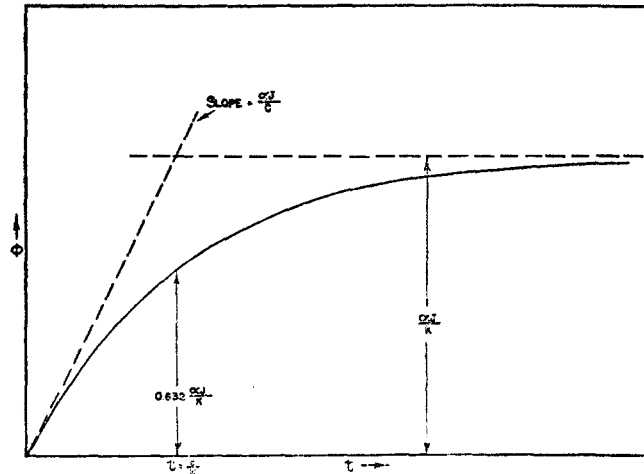and the other when

$$k \ll 2\pi f c$$

FIG. 3. Graphical representation (solid curve) of the equation

$$\theta = \frac{\alpha J}{k} \left(1 - e^{-\frac{k}{c}t} \right)$$

Broken lines are asymptotes.

and

$$\theta = \frac{\alpha I}{2k} - \frac{\alpha I}{2\pi f c} \cos\left[2\pi f t - \frac{\pi}{2}\right] \tag{5}$$

A log–log plot of the equation for which equations 4 and 5 are the asymptotes is represented by figure 4. For the heat system which we have described, the time constant is defined as $t_c = c/k$, and its importance for the two types of radiation signals described is made clear from figures 3 and 4.

From the above analysis it is seen that in order to obtain a maximum $\Delta\theta$, α should be as near 1 as possible, c as small as feasible, and k so chosen that c/k
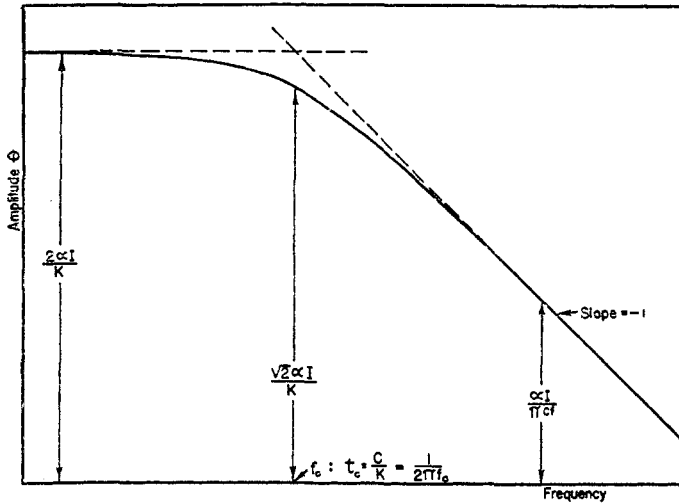

FIG. 4. Plot of the total amplitude of the temperature oscillation against frequency of sine-wave radiation on log–log paper.

is equal to the duration of the radiation pulse for which the instrument is designed, or so that $k = 2\pi c f_c$, where f_c is the frequency in which one is interested. Larger values for k will decrease the $\Delta\theta$ almost linearly; smaller values will not appreciably increase the temperature rise, except when the duration of flash is longer, a condition generally disadvantageous.

According to equation 1 the signal should be proportional to the current. However, there is a limit to the current that can be passed through the bolometer, because the i^2R heat must be conducted away by the drain. It is evident that if the maximum slope of the curve of i^2R against temperature for the bolometer is larger than k, thermal instability will result and it will not be possible to operate the bolometer at the point where $dR/d\theta$ is largest and the detector most sensitive. For a given bolometer then, the current should be adjusted until the following equation nearly holds:

$$k = i^2 R \rho_{\max}. \tag{6}$$

To use higher currents, k would have to be increased or R and $\rho_{\max}$. decreased, but since i appears as the square, these would lead to reduced signals.

The signal is directly proportional to ρ. The maximum value of ρ is determined by the width of the superconducting transition, assuming that the shape of this curve is similar for all samples. Thus sharper transitions are desirable, but the signal is not increased proportionally because equation 6 must hold. As ρ is increased, i^2 must be decreased and the effect on the signal is thus $(\rho_2/\rho_1)^{\frac{1}{2}}$.

Similar considerations hold for R, so that changes in the resistance of the element affect the signal as $(R_2/R_1)^{\frac{1}{2}}$. The value of R is changed by the physical dimensions of the superconductor.
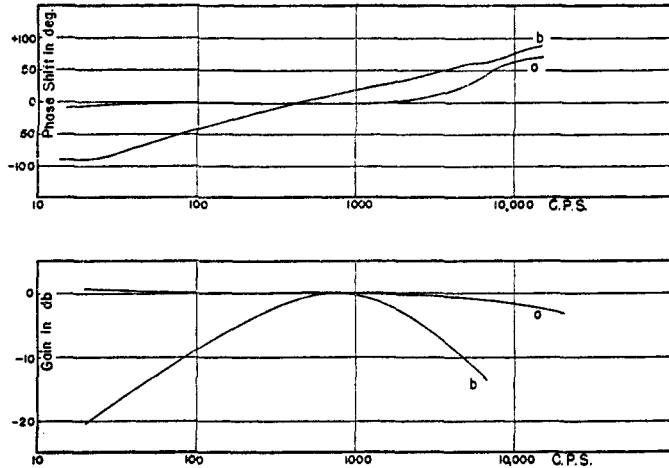

FIG. 5. Phase shift and relative gain of amplifier: (a) without transformer; (b) with transformer.

Equation 1 assumes that we can take any voltage change and amplify it by a factor a without any distortions. This can usually be done, but in general, amplification is only carried to the point where noise levels are seen. The average vacuum-tube amplifier with a band pass of 20 to 20,000 c.p.s. will have a noise level, due to shot and grid resistor noises, at the first tube of from 2 to 20 microvolts. As will be shown later, the thermal noise in the bolometer itself is about 2×10^{-3} microvolts. To make as much use of this low level of noise as possible, a specially built high-gain transformer was placed between bolometer and amplifier. The transformer had a split primary of 1-ohm impedance and a secondary of 1.1-megohms impedance. With this in the amplification circuit, equation 1 is no longer strictly valid. Figure 5 shows the extent of the frequency and phase distortion thus introduced. Figure 6 is the complete amplification circuit. The bolometer is placed in one arm of a bridge, opposite an equal resistance dummy, and the connections to the primary are such that extraneous disturbances cancel out.

IV. BOLOMETER CONSTRUCTION

For three reasons it seemed wise to make the superconducting element itself the receiver: (1) heat capacity was kept at a minimum; (2) it was difficult to obtain an adhering blackening agent at these low temperatures without short

circuiting the element; and (3) the highly granular surface of the columbium nitride indicated that it might be not too poor an absorber of infrared radiation. The element was made as thin and narrow as was feasible, considering the difficulty that was encountered in handling the brittle nitride.

Since the temperature at every point on the superconducting detector must be the same if the maximum $dR/d\theta$ is to be realized, the i^2R heat generated in the detector and the radiant energy it absorbs must be conducted away from
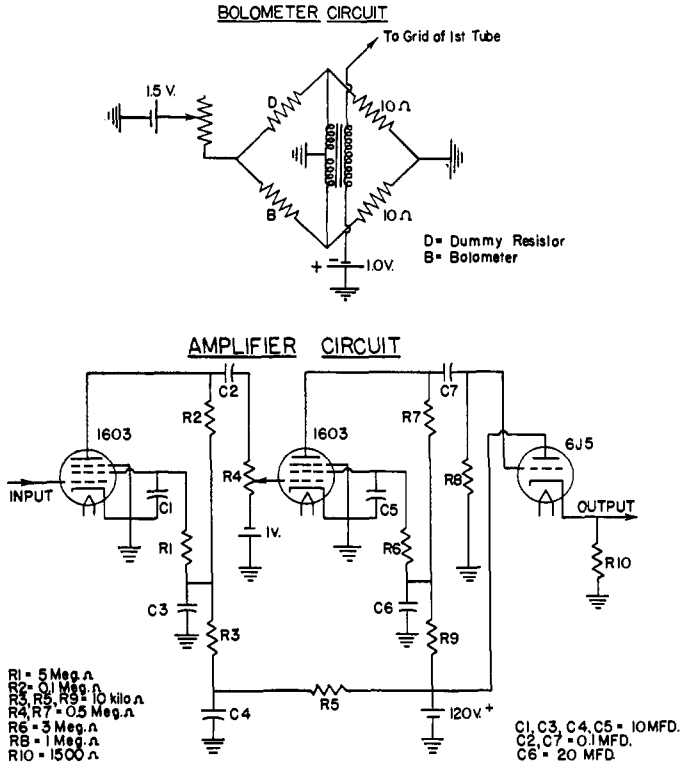

FIG. 6. Bolometer and amplifier circuits

every unit section of the element with equal facility. This, plus the fact that to obtain such a small time constant would require a large thermal conductivity, led to the binding of the entire lower surface of the superconducting element to a massive copper bar, whose end was immersed in the hydrogen. A thin layer of an electrically insulating adhesive was used for this purpose. Although several adhesives were tried, bakelite lacquer[4] was finally chosen because of its ease of application and its ability to withstand the differential expansions and hold securely at very low temperatures.

In its final form, the element was a piece of columbium nitride, 6.35 mm. long, 0.254 mm. wide, and either 0.0254 mm. or 0.0063 mm. thick, that had been cut from the nitrided foil. Each end was copper plated for a length of 1.6 mm.,

[4] Bakelite lacquer BL 3128 from the Bakelite Corporation, Bound Brook, New Jersey.

using an acid copper-plating solution and very low current densities to obtain an adherent plate. These ends were wet with a zinc chloride–hydrochloric acid flux and immersed in a molten bead of solder,[5] care being taken not to heat the solder much above its melting point, as extreme heat tends to loosen the copper plate.

The bolometer base was a 6.35-mm. square copper bar, surrounded by a protecting cup. Two 36 B. and S. gauge copper wires, bakelited to this cup, made electrical connection with the element. The top of the copper bar was smoothed with crocus cloth and a thin layer of bakelite lacquer applied. This was air dried for 4 hr. and then baked at 140°C. for 5 hr. This process was repeated (usually once or twice) until the desired thickness of insulator was obtained.
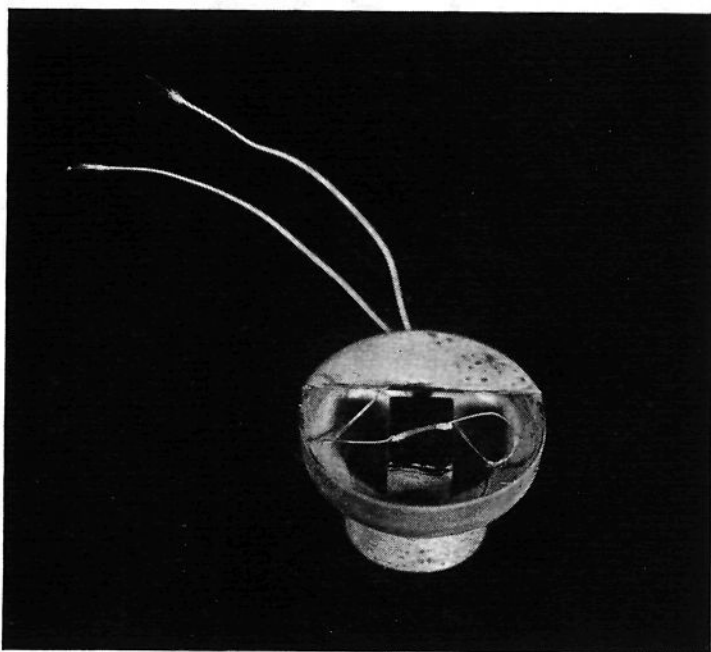

FIG. 7. The bolometer

The columbium nitride element was finally placed on top of a freshly applied coating of lacquer and gently pressed down to insure wetting of the entire lower surface. This was air dried for 1 day and then baked at 140°C. for another.

If any bakelite ran over the top surface it was removed after baking by scraping gently with a sharp instrument. The lead wires, tinned and fluxed, were brought into position and soldered to the element with a touch of the soldering iron. Figure 7 is a photograph of a bolometer.

The resistance of an element 0.0254 mm. thick is about 0.4 Ω just above the superconducting transition. The resistance of the thinner element is four times this value.

V. BOLOMETER TESTING

The source of radiation was a wrought-iron plate, whose front surface had been oxidized by heating to red heat in the air and on whose back surface was cemented a nichrome heater. The temperature was read by a chromel–alumel thermocouple. The form of the radiation curve was determined by the chopping

[5] One part of lead to one part of tin.

wheel placed directly in front of the source and the shutter placed immediately in front of the wheel. The light paths were so designed that the only variable radiation that was impinging on the bolometer came through the shutter. All the energy that hit the bolometer through the shutter came either from the aluminum chopping wheel or from the heated iron plate. Two wave forms were used: a sine wave, and a square pulsed wave with the radiation off forty-eight times as long as it was on.
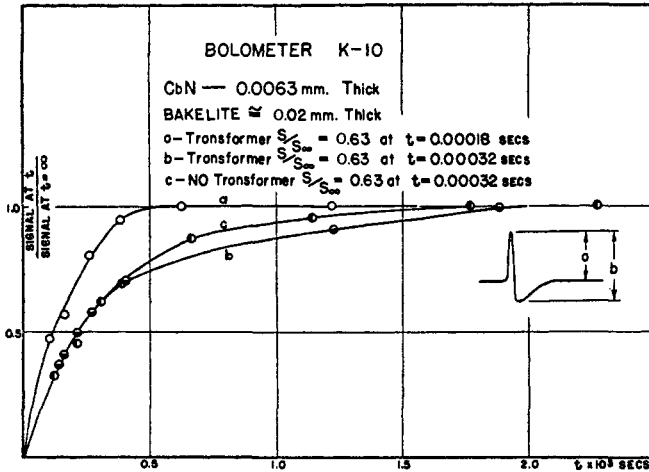

FIG. 8. Response of bolometer K-10 to square-wave input as a function of duration of flash.

In this last type of wave the equation for the change in radiation hitting the bolometer is:

$$Q/t = \frac{A_1 A_2 \sigma(\alpha_1 \beta_1 T_1^4 - \alpha_2 \beta_2 T_2^4)}{\pi d^2} \tag{7}$$

where A_1 is the area of the shutter, A_2 the area of the bolometer, σ the radiation constant, α_1 the black-body coefficient for the oxidized iron surface, β_1 the fraction of the thermal radiation from T_1 passing the rock salt window in the cryostat, T_1 the temperature of the heated source, α_2, β_2, T_2 the same quantities for the aluminum wheel, and d the distance between bolometer and shutter.

The most sensitive bolometer used in these studies, K-10, was made with a columbium nitride thickness of 0.0063 mm., a bakelite thickness of approximately 0.02 mm., and a transition width of about 0.08°K. A peak signal voltage of 0.4 microvolt as against a peak noise level of 0.025 microvolt, SNR = 16, was obtained with this bolometer when $T_1 = 373$°K., $T_2 = 300$°K., $A_1 = 0.39$ cm.², $d = 60.8$ cm., and $t = 0.001$ sec. The sensitive area of the bolometer, neglecting the solder-covered ends, is 0.008 cm.² For the oxidized iron surface α_1 is taken as 0.79, and α_2 for the aluminum surface as 0.10. Integration of the radiation

curves, assuming rock salt transparency below 15 μ and opaqueness above 15 μ to be complete, gives $\beta_1 = 0.70$ and $\beta_2 = 0.56$. Substituting and solving yields
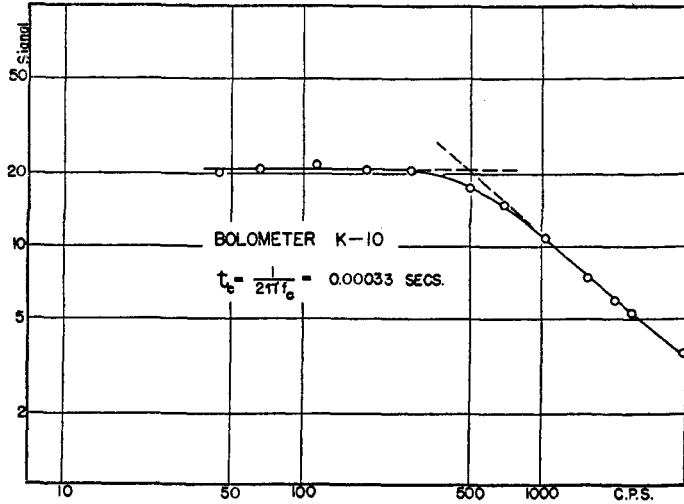
$$Q/t = 0.159 \text{ erg sec.}^{-1}$$

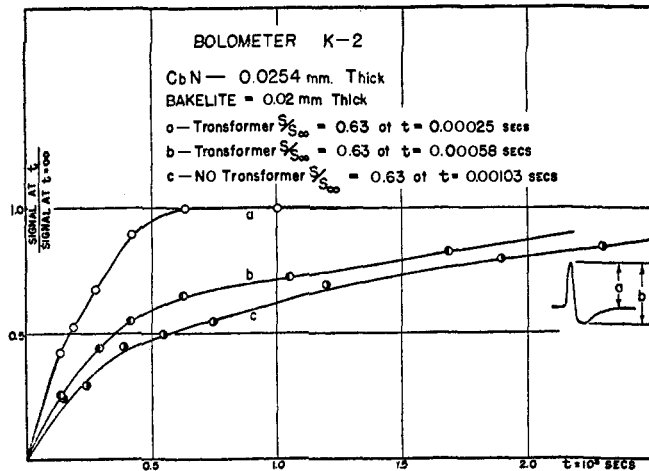FIG. 9. Response of bolometer K-10 to sine-wave radiation input as a function of frequency.

FIG. 10. Response of bolometer K-2 to square-wave input as a function of duration of flash.

Thus the minimum detectable signal, SNR = 1, is for a flux of 1×10^{-2} ergs sec.$^{-1}$ Figure 8 shows the response of this bolometer to the square pulse. The shortest duration pulse tested was for 1.2×10^{-4} sec. At this point the signal is down 48 per cent from the value at 1×10^{-3} sec., so that for a flash of 1.2 $\times$

10^{-4} sec. the minimum detectable flux is 1.92×10^{-2} ergs sec.$^{-1}$ The energy in this pulse is 2.3×10^{-3} ergs.
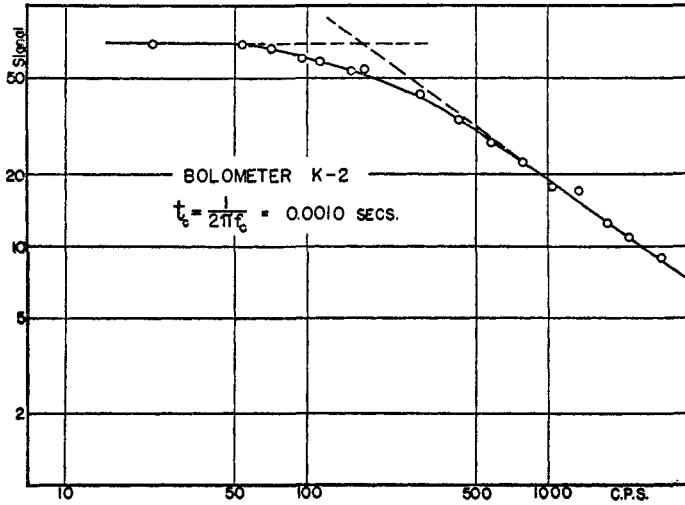

FIG. 11. Response of bolometer K-2 to sine-wave radiation input as a function of frequency.
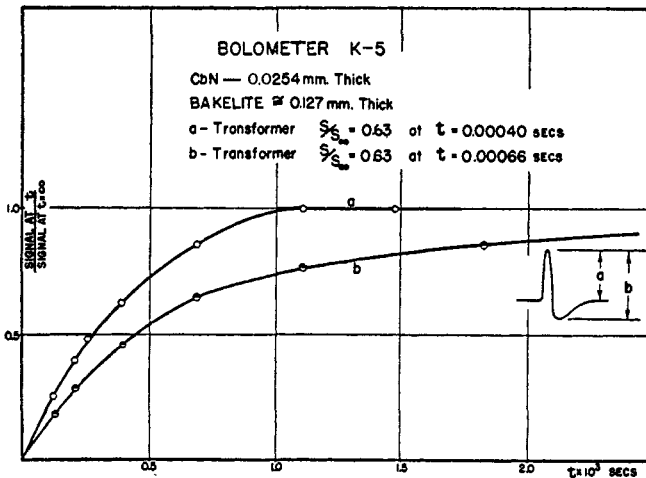
FIG. 12. Response of bolometer K-5 to square-wave input as a function of duration of flash.

Figures 8, 10, and 12 for bolometers K-10, K-2, and K-5, respectively, show the bolometer response to the square-wave input as a function of duration of flash. Figures 9, 11, and 13 show the responses for the same bolometers to sine-wave radiation input. In the latter case either the transformer has been removed or the signal corrected for the attenuation of the transformer, so that the signal is a direct measure of the temperature oscillation. In the square-

wave plots, three curves appear. The one taken without the transformer represents the temperature change accurately. Two are taken with the transformer in. One of these is a measure only of that portion of the signal above the center line, while the second is a measure of the total amplitude. It is only the former that is sharp like the radiation wave, and since it is directly proportional to the intensity of radiation and current in the bolometer, it is only the signal and noise above the mean line that are used in sensitivity measurements.

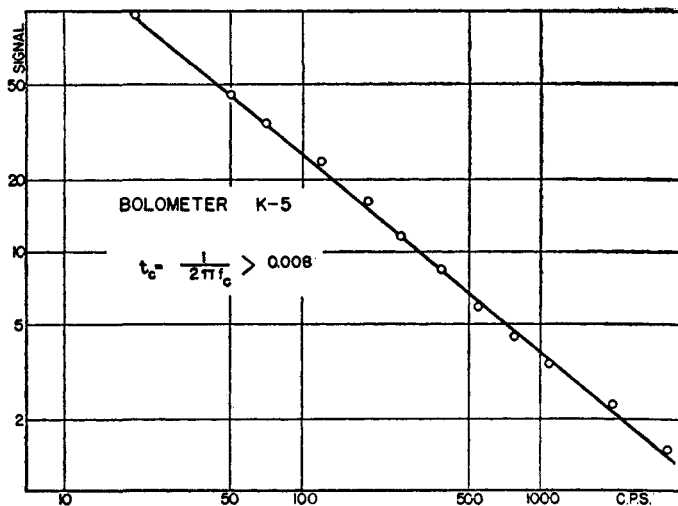FIG. 13. Response to bolometer K-5 to sine-wave radiation input as a function of frequency.

VI. DISCUSSION OF RESULTS

It is seen that the response curves look very similar to those that would be expected for the simple heat theory predicated earlier. The response times from sine-wave studies agree with those from the square-wave plot when the transformer is not used. The slopes of the high-frequency asymptotes are not -1 but nearer $-\frac{3}{4}$. This is a measure undoubtedly of the deviation from the simple assumptions. The reaction to a square wave when the transformer is in the circuit is such as to give an effective time constant considerably smaller than that determined with sine-wave inputs. Bolometer K-10 has an effective time constant of 1.8×10^{-4} sec. The figures show that by increasing the thickness of bakelite the time constant is increased, and by decreasing the columbium nitride thickness the time constant is decreased.

The heat capacity of columbium nitride has been measured at room temperature (13). If this heat can be broken down into heats of a columbium atomic lattice and a nitrogen atomic lattice, as done in this article, it is possible to assign Debye θ values to each if the relative contributions at room temperature are known. The authors give evidence to support their division of the heats between the two lattices. If their division is used, the Debye θ for columbium is

approximately 330 and that for nitrogen 810. This value for columbium falls halfway between those on either side of it in the Periodic Table. On this basis the heat capacity of columbium nitride at 15°K. is 0.19 joules deg.$^{-1}$ gram-mole.$^{-1}$ For the sensitive portion of a superconducting element 0.0254 mm. thick with a density of 8.4, the capacity is 3 ergs deg.$^{-1}$

No measurements have been made on the thermal conductivity of columbium nitride. The electrical resistance is almost constant between 300°K. and 15°K., so if the Wiedemann–Franz law held accurately the thermal conductivity should fall by a factor of 20 in going to 15°K. If we assume that $k = 0.5$ watt cm.$^{-1}$ deg.$^{-1}$ at 300°K., it would be approximately 2.5×10^{-2} watt cm.$^{-1}$ deg.$^{-1}$ at 15°K. The conductivity from the upper surface of the columbium nitride element to the lower would be 8×10^{5} ergs sec.$^{-1}$ deg.$^{-1}$

The value for the thermal conductivity of bakelite lacquer has been placed in the region of 5×10^{-5} watts cm.$^{-1}$ deg.$^{-1}$ at 15°K. by measurements made in this laboratory (7). The thermal conductivity of the bakelite directly beneath the sensitive element and 0.0254 mm. thick would be 1.6×10^{3} ergs sec.$^{-1}$ deg.$^{-1}$

The thermal conductivity of copper at 15°K. is 59.52 watts cm.$^{-1}$ deg.$^{-1}$ (6), and the heat capacity is 0.041 cal. deg.$^{-1}$ mole^{-1} (9). The cross-sectional area of the copper bar of length 26.8 cm. connecting the bolometer base with the hydrogen pot is 0.24 cm.^{2} The heat conductivity of this path is 5.3×10^{6} ergs sec.$^{-1}$ deg.$^{-1}$

Thus in comparing these three thermal conductivities it is seen that there is some justification for neglecting temperature gradients in the columbium nitride, assuming that the copper base is essentially the temperature sink, and placing the important thermal resistance in the bakelite.

There is no good way to estimate the heat capacity of bakelite at 15°K. If, however, the thermal capacity of the bakelite directly between the columbium nitride and the copper base is small with respect to that of the element, we can neglect it and estimate the time constant as

$$ t_c = \frac{c}{k} = \frac{3}{1.6 \times 10^3} = 0.002 \text{ sec.} $$

VII. NOISE LEVELS

The thermal fluctuations of conduction electrons produce a fluctuating voltage E across a resistance R according to the equation

$$ \overline{E^2} = 4kTR\Delta f \tag{8} $$

where T is the absolute temperature and Δf the band width. For a bolometer that in its transition has $R = 1$ used in conjunction with a band pass amplifier of 5000 c.p.s.

$$ E = 2 \times 10^{-9} \text{ v.r.m.s.} $$

The measured total noise level of the bolometer, transformer, and amplifier when the bolometer has current passing through it but is either completely normal or superconducting is 1.5×10^{-8} v.r.m.s., calculated at the bolometer level.

This value is the same whether the bolometer is in the circuit or not, showing, as indicated by the above calculation, that the noise level thus observed lies in the transformer or the first tube.

There is a second type of noise that must be considered. If we have a subsystem of thermal capacity C_v that is in equilibrium with a temperature sink, it can be shown that there are statistical fluctuations of the actual energy from the mean value of the energy of the subsystem (8 or 12). The same is true for the temperature of the subsystem and the equations for these fluctuations are

$$\overline{(E - \bar{E}_0)^2} = C_v k T^2 \tag{9}$$

$$\overline{(T - \bar{T}_0)^2} = \frac{kT^2}{C_v} \tag{10}$$

where k is the Boltzmann constant and $\bar{E}_0$ and $\bar{T}_0$ are the mean values of the energy and temperature of the subsystem.

A calculation of these fluctuations for the bolometer with $C_v = 3$ ergs deg.$^{-1}$ gives root-mean-square fluctuations of:

$$\Delta E = 3 \times 10^{-7} \text{ ergs}$$

$$\Delta T = 1 \times 10^{-7} \text{ degree}$$

Since we cannot be sure of the energy to better than 3×10^{-7} ergs, we might not expect to be able to detect energies smaller than this with the present model bolometer. However, with radiation signals that have definite frequency characteristics and with an amplifier passing only a limited band, as in the present case, the interfering temperature fluctuations should be considerably reduced and one should expect to have a limit of detection smaller than 3×10^{-7} ergs. The limit of detection at the present stage of development is 2.3×10^{-6} ergs. Even considering the fact that only a portion of this is absorbed by the detector, it appears to be considerably larger than the limit imposed by statistical fluctuations.

One asks whether this type of noise has ever been observed. As previously mentioned fairly large currents, 0.100 ampere, can be passed through the bolometer when it is completely normal or superconducting without raising the noise level above that from the first tube and transformer. If the columbium nitride has its temperature adjusted so that it is in the steep portion of its transition, the noise will increase. This increased noise is roughly proportional to the current passing through the bolometer and appears to have a random frequency distribution. This type of noise was not observed in the earlier work on this development but only appeared when bolometers approached sensitivities of the order 10^{-5} to 10^{-6} ergs. Thus it has many of the characteristics one would expect of the statistical type of fluctuation we have discussed. In ordinary operation the current in the bolometer was kept such that this noise was just appearing and the peak-to-peak voltage of the noise was 5×10^{-8} volts.

In some bolometers another type of noise was noted. This appeared whether

current was passing through the bolometer or not, and only when the element was in a certain portion of its superconducting transition. It consisted of many short-duration 10^{-4} sec. pulses with peak voltages of 0.15×10^{-6} volts.

REFERENCES

(1) ANDREWS, D. H.: Am. Phil. Soc. Yearbook **1938**, 132.

(2) ANDREWS, D. H., BRUCKSCH, W. F., JR., ZIEGLER, W. T., AND BLANCHARD, E. R.: Phys. Rev. **59**, 1045 (1941).

(3) ANDREWS, D. H., BRUCKSCH, W. F., JR., ZIEGLER, W. T., AND BLANCHARD, E .R.: Rev. Sci. Instruments **13**, 281 (1942).

(4) ASCHERMANN, G., FRIEDERICH, E., JUSTI, E., AND KRAMER, J.: Physik. Z. **42**, 349 (1941).

(5) BARNES, R. B., AND SILVERMAN, S.: Rev. Modern Phys. **6**, 162 (1934).

(6) BREMER, H., AND DE HAAS, W. J.: Commun. Kamerlingh Onnes Lab. Univ. Leiden No. **243a** (1935).

(7) DESORBO, W.: Unpublished work, The Johns Hopkins University, Baltimore, Maryland.

(8) FOWLER, R. H.: *Statistical Mechanics*, Chap. XX. University Press, Cambridge (1936).

(9) GIAUQUE, W. F., AND MEADS, P. F.: J. Am. Chem. Soc. **63**, 1897 (1941).

(10) GOETZ, A.: Phys. Rev. **55**, 1270 (1939).

(11) HORN, F. H., BRUCKSCH, W. F. JR., ZIEGLER, W. T., AND ANDREWS, D. H.: Phys. Rev. **61**, 738 (1942).

(12) LANDAU, L., AND LIFSHITZ, E.: *Statistical Physics*, p. 40. University Press, Oxford (1938).

(13) SATOH, S., AND SOGABE, T.: Sci. Papers Inst. Phys. Chem. Research (Tokyo) **38**, 174 (1941).

(14) SOCOLAR, S. J.: "New preparations and superconductivity studies on columbium nitride," presented at the 109th Meeting of the American Chemical Society, Atlantic City, New Jersey, April, 1946.