(straight line and peak-to-valley) showed that these errors only slightly affected the final determination of the normalized peak height, as shown by the error bars in Fig. 6. Therefore, we can be confident that the intensity profile of the interrogating pulse train is quite reproducible. Experimental studies have shown that this reproducibility was absent if a "diffuser" was not used. A histogram of normalized intensity as a function of segment position under conditions that resulted in a favorable signal-to-noise ratio is shown in Fig. 6. A slight decrease in intensity of transmitted segments at later times may be indicated.

It is important to realize that the measurements described in this article were made with only a single picosecond pulse. Because the bleaching of the bacteriochlorophyll band at 865 nm (P 865) has a millisecond recovery time, the use of the whole laser pulse train would have shown only that all of the echelon segments could be transmitted when the sample was excited. Therefore no kinetic information could have been obtained. In studies in which an entire laser train is used to excite a sample and subsequent fluorescence in the picosecond range is monitored, great care must be taken to ensure that long-lived intermediates do not contribute artificial results.

This work has enabled us to observe the very first steps in photosynthesis. What was found was that photooxidation of the reaction center is not an instantaneous process when it is excited with green light. Rather an incubation period of a few picoseconds is needed to transfer the energy to P 865. If the bleaching of P 865 is concomitant with the electron ejection, then this work is a direct measure of the rate of photooxidation. However, the strong interactions between the bacteriopheophytins and the bacteriochlorophyll (P 865) are clearly demonstrated. This confirms a general belief that could not be directly substantiated with previous experimental techniques.

Current experiments are oriented toward directly measuring the rate of photooxidation itself by studying the kinetics of the 1250-nm band of these reaction centers. These results in conjunction with those in this article and previously reported quantum yield measurements (*13*) are expected to definitely answer the important question as to whether or not the triplet state of bacteriochlorophyll (P 865) plays an active role in photosynthesis.

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Millikelvin Temperatures Measured with a Noise Thermometer

Brownian motion in electrical circuits has been used to measure temperatures as low as 2 millikelvins.

John C. Wheatley and R. A. Webb

The temperature region below a few thousandths of a degree absolute is distinguished as much by its inaccessibility as by the abundance of important scientific problems present there. Here in particular we refer to the recent observations (*1*) that liquid ^{3}He transforms into new and remarkably different phases over a broad range of pressures at temperatures below 0.0026 K (2.6 mK). These discoveries have emphasized the need for a thermometer capable of accurate measurement of absolute or thermodynamic temperature in this temperature regime. We describe here one approach to the thermometry problem.

There are few thermometers for which the absolute temperature may be obtained from the empirical temperature with confidence and simplicity in the millidegree range. Neither "ideal gas" nor vapor-pressure thermometry is possible since all gases have condensed with negligible vapor pressure at much higher temperatures. Analogs of these methods are possible in principle either by measurement of the osmotic pressure of solutions of ^{3}He in superfluid ^{4}He or by measurement of the melting pressure of ^{3}He, but discussion of these techniques is beyond the scope of this article. Magnetic thermometers, for which the thermometric parameter is the magnetic susceptibility, χ, are used quite commonly. If χ obeys Curie's law, $\chi = C/T$, where C is the Curie constant and T is the absolute temperature, then not only is T determined directly by C/χ but also the sensitivity increases as T decreases. Nuclear magnetism in some metals ought to obey Curie's law in the millidegree range, but nuclear susceptibilities are not as easily measured as electronic susceptibilities, for which the strength of the magnetism is much greater. Measurement of nuclear magnetism usually requires a substantial externally applied magnetic field

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either to enhance the thermometer signal or to saturate electronic impurity magnetism. This is undesirable when low temperatures are achieved by adiabatic demagnetization of paramagnetic salts. On the other hand, for electronic magnetic materials low magnetic fields can be used, but the quantity C/χ departs from T in the millidegree range, even for the most weakly interacting materials now in use. Nevertheless, a magnetic temperature T^* can be defined by $T^* \equiv C/\chi$. It is a very useful empirical thermometer, but then the relation between T^* and T must be established. In the past this has been done for some important cases by means of thermodynamic measurements (*2*). However, for a given T, T^* usually depends on sample geometry and preparation, so that transferring the T^*-T relation from one experiment to another is usually inaccurate. In this article we show that an important practical alternative is the measurement of the mean square noise currents in a series electrical circuit consisting of a resistance and a superconducting coil.

Lawson and Long (*3*) suggested over 25 years ago that the random noise voltage or Johnson noise (*4*) generated in a resistor by the Brownian motion of the electrons might be a possible absolute thermometer for the millidegree range. Their suggestion is based on Nyquist's theorem (*5*), which states that the mean square open circuit voltage across a passive two-terminal network at temperature T is

$$d\langle e^2\rangle = 4\,kT\,R(f)\,df \qquad (1)$$

where $R(f)$ is the real part of the impedance across the terminals, f is the frequency, and k is Boltzmann's constant. If a resistor R and self-inductance L are connected in a series circuit, then noise currents flow, the mean square noise currents $d\langle i^2\rangle$ being equal to the mean square voltage given above divided by $(R^2+\omega^2L^2)$, the square of the circuit impedance:

$$d\langle i^2\rangle = \frac{4\,kT/R}{1+\omega^2\tau^2}\,df \qquad (2)$$

where $\omega = 2\,\pi f$ and $\tau = L/R$. The content of this expression is illuminated by integrating with respect to frequency to find the total mean square current,

$$\langle i^2\rangle = \int_0^\infty \frac{4\,kT/R}{1+\omega^2\tau^2}\,df = \frac{kT}{L} \qquad (3)$$

By rearranging this equation we find that the average value of the fluctuating magnetic energy $\frac{1}{2}\,Li^2$ in a coil whose terminals are connected across a resistor R in contact with a thermal reservoir at absolute temperature T is $\frac{1}{2}\,kT$. This is exactly the value expected from the equipartition-of-energy theorem for a system with one degree of freedom, and corresponds to the random center-of-mass motion of the electrons as a whole. There will be no quantum effects in the present temperature range for our experiments since the relevant frequencies are less than a few hertz. The above result emphasizes the analogy between a thermometer measuring mean square noise currents in an L-R circuit and a thermometer measuring pressure in an ideal gas at constant volume.

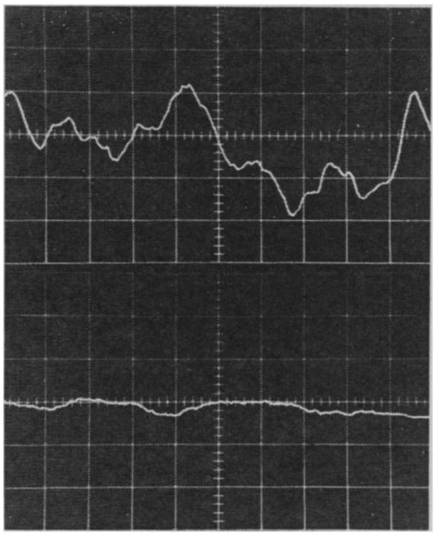

Fig. 1. Oscilloscope traces showing amplified noise currents from a 3-micro-ohm resistor at 12 mK and effective device noise currents for the same sensitivity. The noise currents have been filtered by means of a low-pass filter with a time constant of 2 seconds. The horizontal sweep is 2 seconds per main division or 20 seconds in overall width. The upper trace is a plot of noise currents coupled to a superconducting device at 4.2 K via a superconducting coil for the 3-micro-ohm resistor at 12 mK. The lower trace is for the same arrangement but with a zero resistance circuit.

Regarding the latter, a single gas atom of mass m and velocity v executes a random motion under the action of collisions with the other atoms, which constitute a thermal reservoir at temperature T. The mean square kinetic energy $(\frac{1}{2}\,mv^2)$ is equal to $\frac{3}{2}\,kT$. The pressure P, which is the thermometric parameter in this case, is two-thirds of the number density of atoms times $\langle\frac{1}{2}\,mv^2\rangle$, giving the ideal gas law. The resistance R does not appear in the integrated expression (Eq. 3) for the mean square noise currents, nor do parameters describing the collisions appear in the above expressions for an ideal gas. But they are essential to the attainment of equilibrium at temperature T. Without resistance, the current would be constant; and without collisions in a gas, the velocity would be constant. Both thermometers measuring mean square noise currents and those measuring pressure in a low-density gas reflect the same basic statistical law, that of equipartition of energy. Thus in a very real sense thermometry based on fluctuating noise currents in an electrical circuit and that based on pressure measurements at constant volume for an ideal gas are conceptually similar. Indeed, the concept is sufficiently simple, yet basic, that our confidence in its application to the measurement of thermodynamic temperatures is strengthened, even though we freely admit its difference from the direct application of the laws of thermodynamics as in (*2*).

The temperature measurements discussed here imply a very high power sensitivity. The current fluctuations in the macroscopic L-R noise circuit at our lowest temperature of 2 mK reflect an average magnetic energy which is one-third the average kinetic energy of a single gas atom at this temperature, or about 10^{-26} joule. For a typical circuit time constant of 10^{-1} second the corresponding dissipation rate is 10^{-25} watt.

If electrical noise from Brownian motion is such a good thermometer, why has it not been used more in the past? The answer is that the noise currents (or voltages) had to be amplified by electronic circuits which themselves introduced noise into the measurements. Ingenious schemes intercomparing noise-generating resistors (*6*) or using identical amplifiers with the same noise source and then subsequent correlation to eliminate amplifier voltage noise (*7*) have been employed. But the basic problem is that these electronic circuits all are characterized by "temperatures" enormously large as compared with the millidegree temperatures to be measured here. With the introduction of superconducting devices based on the Josephson effect (*8*), the characteristic device temperature may be reduced to the microdegree region. This is why noise thermometry is now being used successfully in the millidegree region. An example given by Giffard *et al.* (*9*) of the exceedingly small noise introduced by the detecting device itself is shown in the oscilloscope traces of Fig. 1. The overall width of both traces is 20 seconds, and each measures vertically with the same sensitivity the effective input current to a cryogenic "ammeter" based on the Josephson effect. In the upper trace the noise source is a 3-micro-ohm resistor at 12 mK which is coupled to the ammeter by a superconducting coil with superconducting leads. The noise has been treated by a low-pass filter having a 2-second time constant. In the lower trace there is a similar circuit arrangement but no noise-generating resistance—the input circuit is completely superconducting. In this case the noise shown reflects the device temperature T_D. Since the mean *square* fluctuations are proportional to T, it is clear that T_D is very much less than the 12 mK ambient temperature of the resistor.

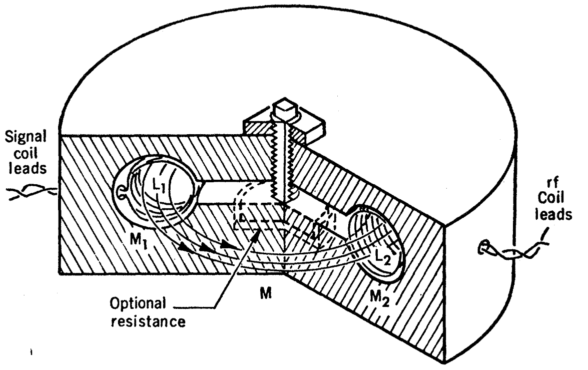

Fig. 2. Schematic section of a superconducting niobium point contact device having toroidal geometry. The signal coil and rf coil have self-inductances L_1 and L_2, respectively, and mutual inductances M_1 and M_2, respectively, to circuits through the point contact made with the sharpened niobium screw. The two coils are flux-coupled as shown with mutual inductance M. For voltage sensing a resistive section may be included, as indicated by the dashed lines, to interrupt the superconducting path. For current sensing no resistive section is present.

Noise Detector

A device employing the Josephson effect may be used to measure thermal noise by sensing either noise currents (an "I-device," for short) or noise voltages (a "V-device"). The V-device was proposed and originally studied by Kamper and Zimmerman (*10*) and then applied to rather low temperatures by Kamper *et al.* (*11*) and by Soulen and Marshak (*12*). The I-device was introduced and demonstrated by Giffard *et al.* (*9*) and later treated more completely by Webb *et al.* (*13*). To avoid repeating details found elsewhere (*8–10*), we will confine our discussion here to a strictly operational view of a superconducting device. A possible example is shown in cutaway view in Fig. 2. A toroidal cavity in a superconducting niobium block has a thin open slot in its central plane which is bridged by a sharpened niobium screw making a point contact adjusted to give a "critical current" i_c of a few microamperes. For currents in excess of i_c a voltage appears across the point contact. Two coils are located in the toroidal cavity. The radio-frequency (rf) coil serves as a means to sense the average flux state of the device. The signal coil, usually of superconducting niobium wire, serves to couple currents into the device from outside sources. The device functions stably and satisfactorily at 4 K, in thermal contact with a liquid helium bath boiling at atmospheric pressure. As shown, Fig. 2 is an I-device. However, it can be turned into a V-device, like that described by Kamper *et al.* (*11*), if the superconducting niobium circuit is interrupted in the region below the point by a thin section of resistive material, for example, silicon bronze, as shown by the dashed lines in Fig. 2. A d-c voltage may then be introduced into circuits through the point if, for example, the ground return of the rf coil is spot-welded to the niobium disk below the point so that a small d-c current i through the rf coil will cause an iR drop across the resistive section. Practical devices need not have the above geometry, but it serves our purpose in explaining their general operation.

The operation of the device when properly sensed electronically is as follows. When a current is introduced into the signal coil, the output voltage of the electronics is a periodic function of the resulting input magnetic flux φ, referred to any circuit in the niobium through the point, with a period equal to the flux quantum, $\varphi_0 = h/2e = 2.07 \times 10^{-7}$ gauss-square centimeter $= 2.07 \times 10^{-15}$ weber (where h is Planck's constant and e is the charge on the electron). If the input flux, again referred to any circuit through the point, increases linearly with time at a rate $\dot{\varphi}$, then the output voltage will oscillate at a frequency $f = \dot{\varphi}/\varphi_0$. Using Faraday's law to replace $\dot{\varphi}$ by V immediately suggests the correct result that in a V-device a voltage V in series with the point leads to a periodically varying output voltage with frequency $f = V/\varphi_0$. Stated succinctly, the output voltage is periodic with the above periodicity; and, when it is nearly sinusoidal, its phase is given by

$$2\pi(\varphi + \int V dt)\ /\varphi_0$$

where φ is proportional to the input current and V is the voltage across the point. A noise current introduced via the signal coil leads to a random fluctuation of output phase about some steady value. On the other hand, when the resistive section has been included and biased with d-c constant current I_0 to produce a d-c voltage $V_0 = I_0 R$, there will be a random frequency modulation produced by the random noise voltage about the average frequency V_0/φ_0.

We now turn to a more detailed discussion of the I-device and its application to noise thermometry. In addition to the noise introduced by the source whose temperature is to be measured, there is also unwanted noise generated both in the device itself and in its associated electronics. The noise generated in the device itself has been studied theoretically by Kurkijärvi and W. Webb (*14*) and experimentally by Giffard *et al.* (*9*) and by Jackel *et al.* (*15*) for the rf-biasing detection method (*16*). The result derived by Kurkijärvi and Webb is quite complicated, owing to the nonlinearity of the system and its complex behavior. At frequencies low by comparison with the rf-bias frequency f_0 they find a white power spectrum for the noise flux. The mean square noise flux $\langle \varphi_N^2/\varphi_0^2 \rangle$, referred to the flux quantum, is given approximately by

$$\left\langle \frac{\varphi_N^2}{\varphi_0^2} \right\rangle \approx \left(\frac{kT}{\varphi_0^2/L_S} \right)^{4/3} \left(\frac{2.5\,B}{f_0} \right) \quad (4)$$

where L_S is the self-inductance of the device for circuits through the point and B is postdetection bandwidth. In a typical case we may have $L_S = 10^{-9}$ henry, $f_0 = 20$ megahertz, $T = 4.2$ K, and $\langle \varphi_N^2/\varphi_0^2 \rangle^{1/2} \simeq 2 \times 10^{-5} B^{1/2}$ hertz$^{-1/2}$. Actual measurements by Giffard *et al.* (*9*) gave values for $\langle \varphi_N^2/\varphi_0^2 \rangle^{1/2} B^{-1/2}$ of the order of 10^{-4} hertz$^{-1/2}$ with about an equal contribution of amplifier voltage noise. They also found the root-mean-square effective flux noise per square root of the postdetection bandwidth to be frequency independent at low frequencies with no evidence for

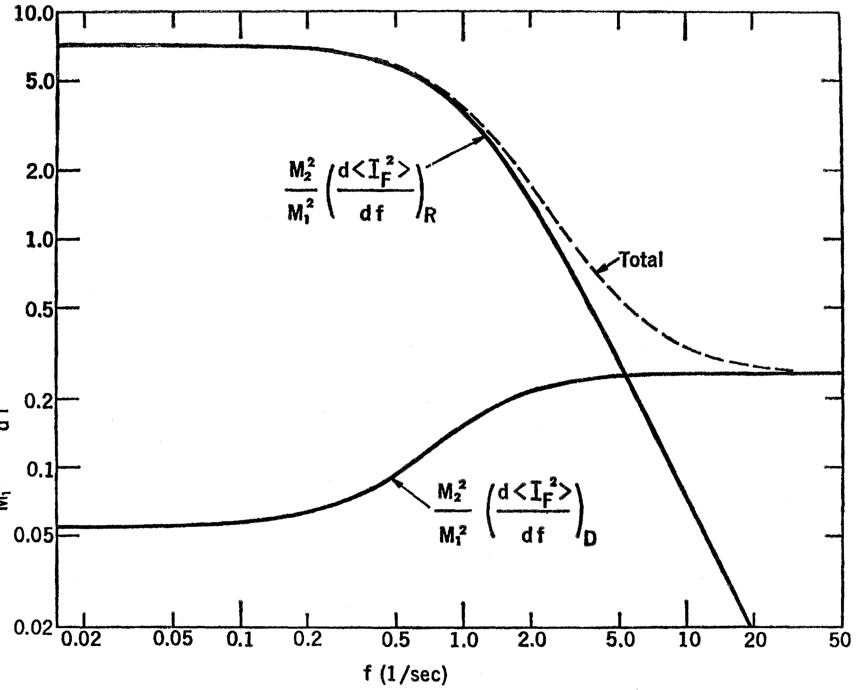

Fig. 3. Power spectrum of feedback currents for an actual current-sensitive noise thermometer arrangement according to Eqs. 5 and 6 in the text; $\langle I_F^2\rangle$ has been multiplied by M_2^2/M_1^2 to refer it to the input circuit. Here $T = 2$ mK, $R = 15.4$ microohms, $M_1 = 2.51 \times 10^{-8}$ henry, $M_2 = 2.15 \times 10^{-9}$ henry, $\tau = 0.154$ second, $\gamma = 0.336$ second, and $\epsilon = 0.9 \times 10^{-4}$ hertz$^{-1/2}$ are measured quantities. For noise measurements the upper cutoff frequency of the active band-pass filter was set at 1.04 hertz and the lower at 0.016 hertz.

an upturn at subhertz frequencies. This experimental result is essential to the success of the present noise temperature measurements.

In practice, in order to achieve a wide dynamic range negative feedback is employed in conjunction with phase-sensitive detection to maintain a constant flux state of the superconducting device, current being fed back into the rf coil to compensate for any flux changes introduced by the signal coil. The temperature-sensing resistor R is connected to the superconducting signal coil leads by zero resistance contacts and located at the point where the temperature is to be measured. The superconducting device itself is held at 4 K, in thermal contact with the ^{4}He bath but not actually in the liquid. In spite of the temperature gradients there are no thermal electromotive forces in the leads since they are superconducting. What is actually measured is the feedback voltage, which drives current I_F into the rf coil through a suitably large resistance to keep the flux constant. The power spectrum $d\langle I_F^2\rangle/df$ of this current is shown in Fig. 3 for an actual sensor at 2 mK. That part contributed by R is given by (*13*)

$$\left(\frac{d\langle I_F^2\rangle}{df}\right)_R = \frac{M_1^2}{M_2^2}\,\frac{4\,kT/R}{1+\omega^2(L_1')^2/R^2} \tag{5}$$

where $L_1' = L_1 - M_1M/M_2$. The various inductances are indicated in Fig. 2. The quantities M_1 and M_2 are mutual inductances of the signal and rf coils to circuits in the device through the point. Owing to the flux-guiding effect of the superconducting body, the signal and rf coils are coupled by a mutual inductance M; L_1 is the self-inductance of the signal coil circuit without feedback. With feedback keeping the total flux in the torus constant, the effective self-inductance of the signal coil is modified to L_1', and the noise power spectrum is correspondingly modified. Both modifications are substantial in a practical device. That part of the power spectrum of I_F due to the device itself and its associated electronics is given by (*13*)

$$\left(\frac{d\langle I_F^2\rangle}{df}\right)_D = \frac{\epsilon^2\,\varphi_0^2}{M_2^2}\,\frac{1+\omega^2\gamma^2}{1+\omega^2\tau^2} \tag{6}$$

where $\epsilon\varphi_0$ is the experimentally measurable root-mean-square effective device flux noise per square root of the postdetection bandwidth (10^{-4} hertz$^{-1/2}$, typically), $\gamma = L_1/R$, and $\tau = L_1'/R$. At frequencies so low that $\omega L \ll R$ there is essentially no response in the signal coil circuit (via the mutual inductance M) to modify the total flux coupled to the device per unit feedback current. On the other hand, at frequencies so high that $\omega L \gg R$, feedback currents responding to the fluctuations of the white spectrum of device flux noise induce significant currents in the signal coil circuit via M which in turn reduce the total flux coupled to the device per unit feedback current. As a result the power spectrum of I_F responding to the white power spectrum of device flux noise changes from one frequency-independent value at low frequencies to a higher frequency-independent value at high frequencies, the transition region in frequency being similar to that where the noise power spectrum from R decreases. These effects are illustrated quantitatively in Fig. 3.

A precise band-pass filter and integrating mean square voltmeter are used by Webb *et al.* (*13*) after the electronics and feedback arrangement. The low frequency cutoff is set so that very little white noise power from the resistor is rejected. Inspection of Fig. 3 shows that if the upper frequency cutoff of the filter is varied, then eventually the mean square output will increase linearly with this frequency, the slope being proportional to ε^2. In this way ε^2 may be evaluated empirically, so that with a knowledge of circuit parameters the power spectrum of I_F due to the device may be found at all relevant frequencies. Webb *et al.* have shown (*13*) how the various circuit parameters may be measured and have demonstrated that the noise thermometer may be used as an absolute thermometer requiring no fixed point for calibration. In temperature measurement conditions the upper frequency cutoff Ω of the band-pass filter is set so that $\Omega\tau \approx 1$.

The effective mean square feedback current reflected through the band-pass filter to the output may be written, from Eqs. 5 and 6, in the form

$$\langle I_F^2\rangle = \frac{M_1^2}{M_2^2}\,\frac{4\,kT}{R}\,B_R + \frac{\epsilon^2\varphi_0^2}{M_2^2}\,B_D \tag{7}$$

where B_R and B_D are effective passbands according to the different frequency spectra of the resistance sensor noise and the device noise. This equation may be rewritten

$$\langle I_F^2\rangle = \frac{M_1^2}{M_2^2}\,\frac{4\,k}{R}\,B_R(T + T_D) \tag{8}$$

where

$$T_D = \frac{\epsilon^2\varphi_0^2 L_1'}{4\,kM_1^2\,\tau}\,\frac{B_D}{B_R} \tag{9}$$

is the effective device temperature, and where we have expressed R in terms of $\tau = L_1'/R$. For high accuracy it is desirable to make $T_D/T \ll 1$ at the lowest temperature anticipated for measurement. This suggests the use of a large τ—reflecting the R^{-1} intensity of the white part of the sensor noise power spectrum. However, the precision of the measurement is given by (*13*)

$$\frac{\sigma_T}{T} = \alpha \left(\frac{2\tau}{t} \right)^{1/2} \qquad (10)$$

where σ_T is the standard deviation in the measurement of T (T_D is assumed to be negligible) from its ensemble-averaged value, t is the time over which the noise is averaged, and α is a factor greater than but of the order of 1 which depends on the actual band pass. Hence for high precision for a given t it is desirable to make τ small. For a precision of 1 percent it is necessary to average for at least $2 \times 10^4\ \tau$. In our work at millidegree temperatures (*13*) we used $T_D = (0.052 \pm 0.008)$ mK and $\tau = 0.154$ second. A rather large τ was employed to make sure that T_D would be particularly small. An averaging time of 2000 seconds was required to obtain a 2 percent precision (Eq. 10), for the bandwidth actually used.

Application to Millidegree Thermometry

Accurate thermometry is essential for the interpretation of most experiments at low temperatures. However, in our opinion, the two problems currently most important in millidegree thermometry are the measurement of the pressure versus the absolute temperature phase boundary between the normal and extraordinary phases of liquid ^{3}He and the measurement of the relationship between magnetic temperature and absolute temperature for powdered specimens of cerous magnesium nitrate, $Ce_2Mg_3(NO_3)_{12} \cdot 24\ H_2O$ (CMN). The phase boundary problem has not yet received much attention, but, once the coordinates of the phase boundary between normal and extraordinary ^{3}He have been measured, pressure will serve as a secondary thermometer for ^{3}He measurements over a significant range of absolute temperature below about 2.6 mK (*17*). Liquid ^{3}He also plays a major role in the CMN temperature scale, which has been given serious attention.

Most measurements of ^{3}He properties at millidegree temperatures have been made on a T^* scale defined for powdered CMN in the form of a right-circular cylinder with the diameter equal to the height (*18*). The ^{3}He is not only the principal object of the measurement but also the indispensable means by which thermal equilibrium is achieved. It is esential that the ^{3}He be in intimate contact with the CMN (or any other thermometer) since the thermal boundary resistance (*19*) between two substances, one immersed in the other, can lead to dramatically large fractional temperature differences.

The concept of a thermal boundary resistance is particularly important when two substances, each of which can rapidly achieve internal thermal equilibrium, are weakly coupled thermally to one another. An important example is the contact between rather pure, strain-free copper and liquid ^{3}He at low pressure. The copper might have a thermal conductivity $\kappa_{Cu} = 10$ ($T/1$ mK) ergs per second per centimeter per millikelvin and the liquid ^{3}He a conductivity $\kappa_3 = 30$ (1 mK/T) ergs per second per centimeter per millikelvin. At 1 mK the thermal conductivity of ^{3}He is greater than that of copper at the same temperature. This is a very important property for low temperature experiments. The copper and the ^{3}He come into thermal equilibrium by exchanging phonons, the quanta of elastic waves. The rate of transfer of energy $\dot{Q}$ from copper at T_{Cu} to ^{3}He at T_3 has a form similar to that for blackbody radiation:

$$\dot{Q} = \sigma A (T_{Cu}{}^4 - T_3{}^4)$$

where σ is a parameter depending on the materials and A is the surface area. For small temperature differences ΔT between the two substances, the heat flow is

$$\dot{Q} = 4\ \sigma A T^3 \Delta T$$

so the effective surface conductance varies as T^3. The resistance to heat flow varies as $A^{-1}T^{-3}$. It is this resistance which is one of the principal sources of difficulty in very low temperature experiments. Except when it can be used advantageously for thermal isolation, a high boundary resistance should be avoided if possible. This can be done in some cases, again with liquid ^{3}He. The ^{3}He atom has a spin of ½ and a magnetic moment, and liquid ^{3}He is a Fermi liquid (*20*). The thermal contact between liquid ^{3}He and a magnetic substrate having a susceptibility which obeys Curie's law may be magnetic, rather than sonic, and similar physically to the contact first discussed by Korringa (*21*) between the Fermi fluid of electrons and the magnetic moments of nuclei in a metal. The electron-nucleon thermal resistance in metals is linear in T. Experimentally a linear T dependance, rather than one depending on T^{-3}, also describes the low temperature thermal contact between CMN and liquid ^{3}He (*22*), although at the lowest temperatures there is evidence for a series internal resistance in the CMN. The magnetic coupling of energy to ^{3}He is an essential ingredient to the success of our work in thermometry. Unfortunately, an isotopic ^{4}He impurity (nonmagnetic) in the ^{3}He at a sufficient concentration to cover the CMN surface with at least one monolayer will drastically reduce the magnetic coupling and thus increase the thermal boundary resistance (*23*). This effect seriously impairs the ability both to cool ^{3}He and other substances and to perform equilibrium experiments with solutions of ^{3}He in superfluid ^{4}He.

Although it is easy to achieve excellent thermal equilibrium between pure ^{3}He and grains of CMN powder immersed in it, the metallic resistor we use as a noise sensor probably suffers from a T^{-3} thermal boundary resistance. In contrast, an ideal resistor would have a surface promoting magnetic thermal contact and a corresponding thermal boundary resistance which decreases with decreasing temperature.

An example of an experimental arrangement (*13, 24*) for the calibration of a CMN magnetic thermometer by a noise thermometer is shown schematically in Fig. 4. The interior of the epoxy cell is filled with pure liquid ^{3}He to ensure thermal equilibrium. A large mass of powdered CMN provides for magnetic cooling. The cell is precooled to a temperature below 20 mK by means of a ^{3}He-^{4}He dilution refrigerator with heat being conducted through a superconducting heat switch actuated by the fringing magnetic field of the solenoid used for magnetic cooling. With a starting field of 1000 gauss, final temperatures of the order of 2 mK are readily obtained. Both the noise thermometer and the CMN thermometer are located some distance from the CMN refrigerant with thermal contact being provided by the column of liquid ^{3}He. The noise sensor was a copper foil (4 by 15 by 0.025 millimeters) with ends connected with a minimum amount of soft solder to leads consisting of multifilament niobium-titanium in a copper matrix. This provided an essentially zero resistance contact to the superconducting niobium signal coil leads, which were spot-welded to the niobium-titanium filaments. The signal coil leads in turn were placed in a superconducting lead-plated and grease-filled cupronickel tube which was thermally grounded at various temperatures on its way to the superconducting device at 4 K. The resistance of the sensor was constant in the temperature range of the measurements. As the magnetic thermometer we used 16 milligrams of CMN powder (grain size less than 37 micrometers) packed into the shape of a right-circular cylinder with the diameter equal to the height. The CMN susceptibility was sensed by a miniature a-c mutual inductance bridge with a superconducting device as null detector as described by Giffard *et al.* (*9*). The leads to these coils were also carefully shielded, in much the same way as for the noise thermometer. Further shielding against external field disturbances was provided by a cylindrical niobium tube as shown. With this level of shielding measurements could be made even while the solenoid field was being changed.

The results of the measurements (*24*) for two different tests with the same thermometer are shown in Fig. 5 where log T_J is plotted against log T^* so that fractional errors will be emphasized. The quantity T_J is the Johnson noise temperature of the sensor; it is the measured noise temperature less the 0.05-mK device temperature. The noise thermometer was calibrated at a single point: 4.2 K. We used an averaging time of 2000 seconds for $T^* <$ 11 mK and an averaging time of 4000 seconds for $T^* > 11$ mK. The temperature drift rate may be estimated from these times and the density of points. At the lowest temperature the thermal time constant of the noise thermometer was 800 seconds. This is over 10^2 times larger than the value expected for relaxation of the electronic heat capacity through the thermal boundary resistance, an indication of the presence of another source of heat capacity. At zero field the nuclear heat capacity is too small to account for this thermal time constant, but electronic magnetic impurities may be the source of the problem. Although 800 seconds is a long time, the rate of change of temperature was slow enough that no important inaccuracy can be traced to thermal relaxation.

At higher temperatures, T^* for many magnetic thermometers is related to the absolute temperature T by a relation of the form $T = T^* + \Delta$. This approximate relation may be understood (*18*) in terms of thermometer shape and preparation as well as in terms of basic crystal properties. We fitted our data between 8 and 20 mK to an equation $T_J = T^* + \Delta$ and found $\Delta = (0 \pm 0.12$ mK). Within the imprecision of the measurements, shown (*13*) to result primarily from the natural scatter due to the finite averaging times, the noise temperature and the magnetic temperature are the same. In other experiments with another noise thermometer (*13*) we found that T_J was numerically the same as T^* within averaging time imprecision from 20 mK to 4.2 K. In those measurements no fixed point for calibration was used, although the agreement with known thermometers was better than we had expected on the basis of the accuracy of measurement of the parameters in the expression (Eq. 7) for mean square current. The results of all the above measurements together with our detailed understanding of the small device temperature give us confidence that we can accurately sense the absolute temperature of the noise thermometer itself. The major uncertainty lies then in the equilibrium between the noise thermometer and the surrounding ^{3}He.

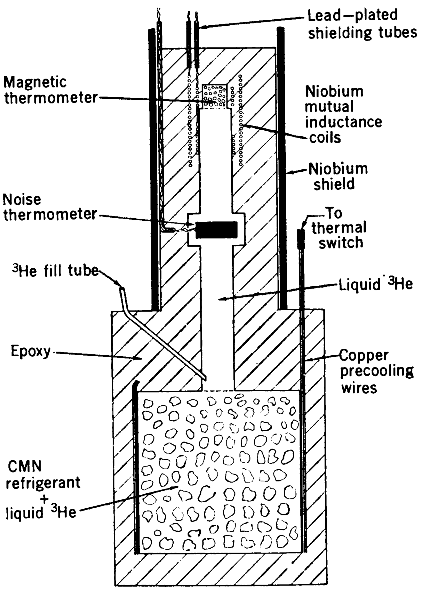

Fig. 4. Schematic drawing of a demagnetization cell in which CMN is used as the refrigerant and liquid ^{3}He is used as the thermal contact agent for the intercomparison of noise and magnetic thermometers. A typical cell might contain 10 grams of CMN as refrigerant and several cubic centimeters of liquid ^{3}He.

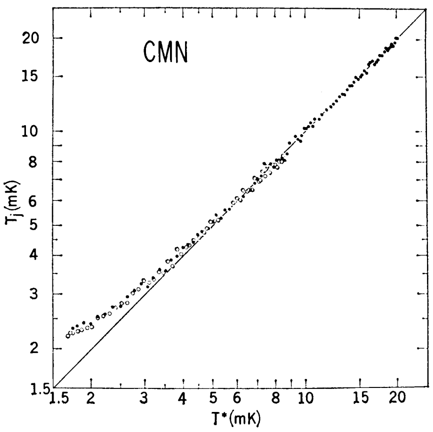

Fig. 5. Relationship of the Johnson noise temperature T_J of a copper resistor to the magnetic temperature T^* of powdered CMN in the form of a right-circular cylinder with the diameter equal to the height. The straight line corresponds to the equation $T_J = T^*$. On the log-log plot the filled and open circles correspond to two different measurements.

In principle, it is possible to check the correctness of the T_J-T^* scale (*13*) by means of absolute thermodynamic temperature measurements for CMN. Giauque and his collaborators (*2*) have measured the relationship between enthalpy and absolute temperature for a large single crystal of CMN. The specific heat of low pressure liquid ^{3}He is also known (*18*) with some confidence, particularly since the present noise temperature measurements became available. Hence, if the assumption is made that powdered CMN has the same relation between enthalpy and T as a large single crystal, it is possible to compute from CMN and ^{3}He data the relation between enthalpy and T for the cell in Fig. 4. Now suppose that the cell warms up from the lowest temperature under the action of a constant residual heat leak. Then in the region where the relationship between T and T^* is known (for example, $T = T^*$ in the present case) this heat leak $\dot{Q}$ may be evaluated from the computed cell heat capacity. The time t at which a magnetic temperature T^* is observed then becomes a thermometric parameter from which T is computed from the equation

$$\dot{Q}\,(t_0 - t) = \int_{T}^{T_0} C(T')dT' \qquad (11)$$

where T_0 is the absolute temperature in a region where the relation between T and T^* is known, t_0 is the time at which this temperature was observed, and C is the cell heat capacity computed as above. Our confidence in this approach was increased both by its consistency at higher temperatures and by the results. We found that for temperatures T so computed the difference

$T_J{}^4 - T^4$ was constant at 6 (mK)^4 within experimental error from $T_J =$ 5.3 mK down to $T_J = 2.3$ mK, nearly the lowest temperature. This result would be explained by a constant heat leak of the order of 10^{-7} erg per second to the noise thermometer if it had a normal copper-^{3}He thermal boundary resistance varying as T^{-3}. At the lowest sensor noise temperature of 2.2 mK this analysis would suggest that the actual temperature of the ^{3}He in which the sensor was immersed was 0.16 mK lower.

In our opinion the principal inaccuracy in millidegree noise thermometry lies in the thermal contact problem. If the thermal boundary resistance between a noise thermometer and ^{3}He can be substantially reduced, then accurate noise thermometry should be possible down to 1 mK.

Intercomparison of Noise Thermometers

Both the current- and voltage-actuated noise thermometers, the I- and V-devices, are capable in principle of measuring noise temperatures at 1 mK. Historically, the V-device was the first (*10*) to be used at low temperatures, but we believe that the I-device can be more readily applied to measurement. In this section we compare the two. In the approximation of a sinusoidal shape for the output voltage the relationship of output voltage phase θ to a voltage V across the point contact of the superconducting device is given by

$$\theta_V = \frac{2\pi}{\varphi_0} \int V dt \qquad (12)$$

and the relationship to a flux φ coupled to the device is

$$\theta\varphi = \frac{2\pi}{\varphi_0} \varphi \qquad (13)$$

A constant voltage V causes θ to increase linearly with time, whereas a constant φ leads to a constant θ. If V reflects a frequency-independent power spectrum of noise, then a component of V at frequency f will lead to a f^{-2} power spectrum in θ_V. On the other hand, a frequency-independent power spectrum of input flux (with flux proportional to current) will lead to a frequency-independent power spectrum $\theta\varphi$. Hence there is a greater sensitivity in the V-device to spurious very low frequency noise.

If the voltage applied across the point consists of a constant voltage V_0 plus a noise voltage with power spectrum 4 kTR per unit frequency, then the ensemble-averaged mean square phase change, expressed in cycles, relative to the average phase change after a time interval τ_V is (*10*)

$$\langle (f\tau_V - f_0\tau_V)^2 \rangle = \frac{2\ kTR}{\varphi_0{}^2} \tau_V \qquad (14)$$

where $f_0\tau_V = V_0\tau_V / \varphi_0$ is the average phase change after time τ_V. The ensemble-averaged mean square fluctuations in phase in an I-device, also expressed in cycles, are given by

$$\left\langle \left(\frac{\theta\varphi}{2\pi} \right)^2 \right\rangle = \frac{4\ kTM_1{}^2B}{\varphi_0{}^2\ R} \qquad (15)$$

where M_1 is a mutual inductance as in Fig. 2 and B is an appropriate bandwidth of order $R/4L_1'$. To both Eqs. 14 and 15 must be added an additional term due to device noise. The V-devices have been read (*10–12*) by measuring complete cycles in a fixed gate time τ_V rather than by attempting to measure the actual phase shift down to a fraction of a cycle. This introduces, according to Kamper and Zimmerman (*10*), a calculable "device noise" of (1/6) cycles squared which must be added to the right side of Eq. 14. This amount is no doubt in excess of the true device noise, but the use of such a value is regarded as preferable since it is known and calculable. It is not clear how to measure in situ the true device noise in the V-device, but this is possible in the I-device as we have explained above. To obtain the actual output, T should thus be replaced by $(T + T_D)$ in Eqs. 14 and 15 where

$$T_D = \frac{\varphi_0{}^2}{12\ kR\tau_V} \qquad (16)$$

in Eq. 14 and where T_D is given by Eq. 9 in Eq. 15. Putting in $R = 7 \times 10^{-6}$ ohm and $\tau = 1$ second used in the most advanced voltage-actuated instrument, we find $T_D = 3.7$ mK, which is to be compared with the device temperature of 0.05 mK measured for the current-actuated thermometer.

The precision of measurement of $(T + T_D)$ for the V-device is given (*10*) by Eq. 10 with $\alpha = 1$, $\tau = \tau_V$, and $t = n\tau_V$, n being the number of counting periods. Thus essentially equal precision in $(T + T_D)$ in a measuring time t is obtained by both methods if the counting time τ_V in the V-device is about the same as the input circuit time constant τ in the I-device. Thus both τ_V and τ must be as short as possible to increase precision in a given averaging time.

Although τ_V must be kept short to increase precision in the available averaging time, the product $R\tau_V$ in the V-device ought to be made as large as possible to decrease device temperature (Eq. 16) and hence improve accuracy. How large R can be made is still an experimental question. Soulen and Marshak (*12*) have demonstrated the sensitivity of the effective R to the level of rf-bias and thereby have emphasized that in operation the point contact does act as a resistive shunt which must be taken into account and which will introduce noise.

Both the V- and I-devices have been shown to be "absolute" thermometers. After measurement of the circuit parameters indicated in Eqs. 14 and 15 the resultant noise temperatures for both types of thermometers were found to agree within measurement inaccuracy and imprecision with temperatures based on the ^{4}He vapor-pressure scale. However, an essential practical difference is that the I-device may be operated without the external leads to the noise-sensing circuit needed to measure in situ the relevant circuit parameters. In this case it must be calibrated at a fixed point, for example, 4.2 K. This is not really a disadvantage in most applications. The absence of external leads to the noise-sensing circuit is a great help in eliminating spurious noise sources and may well be crucial to the success of measurements reported here. It may be instructive in this connection to extend the experiments of Harding and Zimmerman (*25*) on resistive devices without external leads. Another practical advantage of the I-device is that the resistive sensor may be physically small and remotely located with respect to the more bulky superconducting detector, which is at 4.2 K. Furthermore, at least with present designs, the resistor in the I-device may be put in thermal contact with the sample to be measured more readily than the resistor in the V-device which is located in the interior of a superconducting block of niobium.

Conclusions

We find that the current-sensitive noise thermometer is a satisfactory sensor of absolute temperature down to 2 mK and possibly below. Its field of application is primarily to magnetically and electrically quiet situations where accuracy is important and high precision is not required. For example, the noise thermometer is an ideal instrument for calibrating a secondary thermometer, such as a pressure thermometer, whose calibration can readily and accurately be transferred from one laboratory to another. Further instrumental development for millidegree applications seems unnecessary at present. Rather the major problems in millikelvin noise thermometry that require attention in the immediate future involve establishing thermal contact to the thermometer and reducing its thermal response time.

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Air Pollution Monitoring by Advanced Spectroscopic Techniques

A variety of spectroscopic methods are being used to detect air pollutants in the gas phase.

J. A. Hodgeson, W. A. McClenny, P. L. Hanst

Pursuant to the Clean Air Act of 1970, the Environmental Protection Agency (EPA) published national ambient air quality standards which established maximum acceptable concentrations of certain air pollutants in the various states and regions (*1*). Table 1 lists the primary ambient air quality standards for gaseous pollutants (*1*). Implementation plans to meet the air quality standards are required of the various states. Measurements to determine ambient pollutant concentrations are inherently required in this scheme for achieving air quality. Air pollution measurements are also required in determining the effectiveness of control technology to limit pollutant emissions, for the determination of long-term trends in pollutant concentrations, in studies of the effects of pollutants on health, and in studies of pollutant transformations in the atmosphere. In this article we survey the current and future role of spectroscopic methods in meeting the requirements for the measurement of air pollutants. Detection methods must be sufficiently sensitive and interference-free to permit the investigator to determine whether these standards are met.

Before 1970, requirements for the measurement of gaseous pollutants were largely met by the use of instruments which were automated versions of standard wet chemical procedures. Such instruments were complex and were characterized by high maintenance requirements and marginal sensitivity and specificity. Spectroscopic techniques, whether in emission or absorption, offer means for the direct and continuous detection of the pollutant in the gas phase. The absorption or emission characteristics can serve to identify a pollutant and to measure its ambient concentrations. Furthermore, spectroscopy offers means for the direct observation of pollutants at a point or over an extended path without the need for any intervening sampling apparatus.

Spectroscopic techniques were used quite early to identify molecular pollutants in the atmosphere. The earliest studies were of the transmission spectra of solar radiation through the earth's atmosphere (*2*). Characteristic spectra of molecules in the atmosphere appear as absorption bands in the solar spectrum. Infrared absorption, in combination with a multipass cell, was used in early laboratory studies to identify compounds present during the photochemical irradiation of auto exhaust (*3*). The same technique applied by Scott *et al.* (*4*) yielded the first spectroscopic confirmation of ozone (O_3) and the first evidence of peroxyacetyl nitrate (PAN) in the Los Angeles atmosphere.

These early studies were qualitative rather than quantitative in nature and were carried out by researchers using rather complex equipment. Yet they amply demonstrated the power of spectroscopic techniques for the study of polluted atmospheres. Although the potential of spectroscopic techniques was recognized during the 1950's and

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