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transverse vibration, of energy proportional to $\omega_{\min}$, would finally be left. Thus, the physical model, assuming it could be constructed in the laboratory, would simulate the atom even in its quantal aspects. This phenomenon, however, is *not* contained in the differential equations of motion of the string and does not follow from the mathematical analysis presented above. This specifically quantal aspect of the radiation probably would suppress the double-frequency radiation mentioned above; emission of grains of radiation carrying energy equivalent to $(\omega_0 + \omega_1)$, in contrast to $(\omega_0 - \omega_1)$, would be precluded on the basis of insufficient energy in a microscopic version of the elastic-string model.

APPENDIX

The abbreviations used for certain matrix

elements employed in this paper are tabulated below.

$\int u_k' u_l'' dx = M_{kl}$	odd	negative,
$\int u_n u_k'' dx = P_{nk}$	even	negative,
$\int u_n u_k'' x dx = N_{nk}$	odd	negative,
$\int u_n u_k' dx = Q_{nk}$	odd	positive.

The parity and intrinsic sign of these elements are also indicated.

* Present address: 2643 12th Ave. N.W., Calgary, Alberta, Canada.

¹ P. Ehrenfest, *Ann. Physik* **33**, 1571 (1910).

² N. Minorsky, *Introduction to Non-Linear Mechanics* (Edwards Brothers, Inc., Ann Arbor, Mich., 1947).

³ The well-known double-frequency radiation is assumed to be suppressed.

Thermoelectric Power Experiment for the Advanced Laboratory

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Apparatus suitable for measurements of the thermoelectric power of wires in the temperature region from 77 to 300 K is described. An outline of the theoretical treatment of thermoelectric power is presented and typical results are given for aluminum, gold, and iron. This experiment has been used in the undergraduate advanced laboratory.

I. INTRODUCTION

This experiment was developed to introduce the student to the phenomenon of thermoelectricity, while at the same time teaching him potentiometric techniques. A need was felt for an experiment more sophisticated than the ordinary thermocouple calibration experiment which is often done on the elementary level and which places emphasis on thermoelectricity as a tool for measuring temperatures. Recent changes in the philosophy of advanced laboratories have eliminated older experiments concerned merely with learning to use the potentiometer. This experiment is designed to introduce the student to precision potential measurements in the process of studying the thermoelectric power of various interesting metals

The techniques used in this experiment were adapted from those used in current research.

II. THEORY

Measurements of the electrical and thermal conductivities of metals yield information about the processes by which electrons and phonons interact with each other, and with fixed scatters such as boundaries, vacancies, and other defects. Thermoelectric power measurements can also be interpreted to give information about the various scattering mechanisms which are present in the metallic specimen as the consequence of its impurities, surfaces, and past thermal and mechanical histories.

Consider a wire with current density $\mathbf{J}$ which

has an electric field $\mathbf{E}$ and a temperature gradient ∇T existing in it at the point where $\mathbf{J}$ is observed. If the wire is reasonably long and thin, all of the vectors will be parallel and one can write

$$\mathbf{J} = \alpha \mathbf{E} + \beta \nabla T. \quad (1)$$

The coefficient α can be identified as the electrical conductivity if ∇T is set to zero in Eq. (1).

If the wire is open circuited ($\mathbf{J}=0$), then

$$\mathbf{E} = -(\beta/\alpha) \nabla T = -S \nabla T. \quad (2)$$

The quantity S is called the absolute thermoelectric power of the metal.

The wire (of material a) is now connected to the potentiometer by two leads of material b . The temperature of the junctions between the leads of material b and the potentiometer is T_0 and the junctions between materials a and b are at temperatures T_1 and T_2 , as shown in Fig. 1(a). Assume that T_2 is larger than T_1 . The potentiometer measures the potential ΔV developed between the two junctions:

$$\begin{aligned} \Delta V &= -\int \mathbf{E} \cdot d\mathbf{l} = \int S \nabla T \cdot d\mathbf{l} \\ &= \int S dT \\ &= S_b(T_2 - T_0) + S_a(T_1 - T_2) + S_b(T_0 - T_1) \\ &= (S_b - S_a)(T_2 - T_1). \end{aligned} \quad (3)$$

In the last step the assumption is made that the thermoelectric powers S_a and S_b are varying so slowly with temperature that these factors may be taken out of the integrals with small error. The error decreases as the temperature difference between the junctions is reduced. Equation (3) shows that the details of the temperature dis-

FIG. 1. Two thermoelectric circuits which may be formed from materials a and b . For given temperatures T_1 and T_2 , both circuits produce the same emf.

FIG. 2. The thermoelectric power of an idealized metal.

tribution are unimportant; the temperatures of the junctions uniquely determine the thermal potential ΔV .

The usual definition for the thermoelectric power,

$$S_b - S_a = \lim_{\Delta T \rightarrow 0} (\Delta V / \Delta T) \quad (4)$$

is thus obtained. Usually this definition is presented directly; the advantage of using Eq. (2) as the defining equation is that it is possible to analyze the second thermoelectric circuit which is shown in Fig. 1(b) and show that one does indeed get Eq. (4) in this case also. The advantage of using Eq. (4) as the defining equation is that one does not, in fact, measure the absolute thermoelectric power S_a , but instead the difference in the thermoelectric powers of the two materials, $S_b - S_a$.

To obtain the absolute thermoelectric power of an unknown material, its relative thermoelectric power must be measured with respect to a known standard material. A commonly used standard material is lead, the thermoelectric power of which has been measured by Christian *et al.*¹ Up to 18 K the thermoelectric power was measured against the superconductor Nb_3Sn , taking advantage of the fact that the thermoelectric power of superconductors is known to be zero.² At higher temperatures the thermoelectric power was obtained from measurements of the Thomson coefficient.³

FIG. 3. Typical plot of thermal emf as a function of temperature for gold. The thermoelectric power of gold relative to the lead standard is the slope of this line.

The nonmagnetic conductor has two contributions to its thermoelectric power, one from the redistribution of conduction electrons down the sample (the diffusion thermoelectric power) and the other from the interaction between the conduction electrons and the nonequilibrium phonon distribution produced by the temperature gradient (the phonon-drag thermoelectric power).

The expression for the diffusion thermoelectric power S_e is obtained by solving the Boltzmann equation with the electric field and the temperature gradient acting on the electrons. The result is⁴

$$S_e = -(\pi^2 k^2 T / 3eE_F) (\partial \ln \sigma / \partial \ln E)_{E=E_F}, \quad (5)$$

where E_F is the Fermi energy at which the derivative is evaluated, e is the electronic charge, and σ is the electric conductivity. For free electrons, the derivative is equal to three, which gives

$$S_e = -(\pi^2 k^2 T / eE_F). \quad (6)$$

This result can be obtained using the same sort of plausibility argument which is often used for rough calculations of the electronic specific heat and the electronic spin paramagnetism.⁵ Consider an electron traveling down the wire toward the cooler end. On the average it will lose energy $k\Delta T$

as it passes from a location where the temperature is $T + \Delta T$ to one where the temperature is T . Because the electrons obey Fermi-Dirac statistics, only a fraction $(kT)/E_F$ of the electrons is available to carry energy down the wire, provided that the temperature T is much lower than the Fermi temperature. The net energy carried per electron is thus of the order of $k^2 T \Delta T / E_F$. If ΔV is the thermal potential difference which is thereby set up, then

$$e\Delta V \cong k^2 T \Delta T / E_F$$

or

$$|S_e| = \Delta V / \Delta T \cong k^2 T / eE_F. \quad (7)$$

As is the usual case with arguments of this sort, the correct result is obtained apart from a numerical coefficient.

If appropriate numbers are put into Eq. (6) with the assumption that the charge carriers are electrons, one gets $S_e \cong -10^{-8} T$ V/K. Aluminum and lead, for example, do indeed have such a negative term, linear in T and of the right magnitude, in their total thermoelectric power.⁶ On the other hand, the noble metals (copper, gold, and silver) have a positive linear term. This indicates that the factor $(\partial \ln \sigma / \partial \ln E)_{E=E_F}$ is negative, the reasons for which are complex.⁷

The phonon drag component of the thermoelectric power, S_g , arises from the flux of phonons in the lattice which is set up in response to the temperature gradient. The resulting phonon-electron collisions tend to transfer electrons to one end of the sample, thereby setting up an electrical potential difference across it.

The temperature dependence of S_g can be calculated by assuming that the phonons lose some fraction of their energy to the electrons in passing down the temperature gradient. If the specific heat per atom in the lattice is c_g , then $e\Delta V \cong c_g \Delta T$, or

$$|S_g| = \Delta V / \Delta T \cong c_g / e. \quad (8)$$

For temperatures below approximately $\frac{1}{10}\Theta_D$, where Θ_D is the Debye temperature, the specific heat of the lattice is proportional to T^3 , which gives a total low-temperature thermoelectric power of

$$S = AT + BT^3. \quad (9)$$

At temperatures approaching the Debye temperature, the specific heat is a constant. The fraction of the phonons scattered by electrons

decreases as phonon-phonon scattering becomes more probable, with the result that S_p falls off with increasing temperature. For aluminum and lead S_p goes as $1/T$; for other metals it falls off faster.

Between the high and low temperature regions, S_p passes through a maximum, typically, in a pure metal, at a temperature of approximately $\frac{1}{2}\Theta_D$. The resulting phonon-drag peak is superimposed on the linear diffusion thermoelectric power, giving a curve like that shown in Fig. 2 if both S_e and S_p are negative.

The sign of the phonon-drag thermoelectric power depends on the details of the phonon-electron interaction. If the collisions are normal ones, in which the wave vectors of the phonon and the electron before collision add to give the wave vector of the electron after collision, the electron is scattered forward toward the cold end of the sample. The sign of S_p is consequently negative.

If, on the other hand, the electron is scattered in an umklapp process (in which the electron also undergoes a Bragg reflection), the electron may be scattered backward toward the warm end of the sample. This results in a positive contribution to S_p . The noble metals, for example, have a positive phonon-drag peak presumably due to umklapp scattering, so that their S -vs- T curves are approximately the negative of that shown in Fig. 2

III. METHODS OF MEASUREMENT

Thermoelectric power measurements may be made by using either a differential or an integral technique. The differential technique consists of heating up both junctions to the average temperature required, and then establishing a small temperature difference ΔT between them. The corresponding thermal potential ΔV is then measured and the thermoelectric power is calculated from $S_a - S_b = \Delta V / \Delta T$. The advantage here is that any spurious emf's can be bucked out before the temperature difference is set up. Hopefully the measurement is made quickly enough so that the spurious emf's do not change while the measurement is being made. One disadvantage is that the temperature difference must be kept small if the thermoelectric power is changing rapidly with temperature, with the result that the thermal potential is small. Another dis-

FIG. 4. Details of the cryostat. A, brass plate; B, Dewar; C, liquid nitrogen; D, constantan wire; E, copper wire; F, reference wire; G, sample wire; and H, copper block. A vent in the brass top plate is not shown. The copper block to which the hot junctions are soldered is normally wrapped in Styrofoam.

advantage is the problem of keeping both junctions at constant temperatures, since both the hot and cold junctions are above the temperature of the reference bath, which also serves as a heat sink.

When using the integral method, the cold junction is kept in a bath of constant temperature T_0 . The hot junction is heated to a temperature T and the resulting thermal potential V is noted. A plot of V as a function of T is made and the thermoelectric power at a given temperature is found by taking the slope of the curve. If the spurious emf's change over the period of time during which the measurements are made, the slope of the graph, and hence the thermoelectric power, will be in error. Unless some method of zero offset is used, the potentiometer must be of wide range as well as being capable of being read to fractions of a microvolt.

In this experiment a modification of the integral method is used. The thermal potential, which is measured with an electronic microvoltmeter, is bucked out at the beginning of a series of measurements, and the hot junction is allowed to heat up slowly (approximately 0.5 K/min). At intervals of about 0.4 K the temperature and the thermal potential are recorded. The data are plotted as in Fig. 3 and the thermoelectric power obtained from the slope of the line. Since the thermoelectric power of most samples above 77 K (the lowest

TABLE I. (a) Thermoelectric power of lead as a function of temperature, after Christian *et al.* (Ref. 1); (b) thermoelectric power of the noble metals as a function of temperature, after Cusack and Kendall (Ref. 10).

(a)		(b)			
T	S	T	S ($\mu\text{V/K}$)		
(K)	($\mu\text{V/K}$)	(K)	Cu	Ag	Au
70	-0.78 ₄	100	1.19	0.73	0.82
80	-0.79 ₄	150	1.12	0.85	1.02
90	-0.82 ₄	200	1.29	1.05	1.34
100	-0.86 ₅	273	1.70	1.38	1.79
113.2	-0.91	300	1.83	1.51	1.94
133.2	-0.96				
153.2	-1.02				
173.2	-1.06				
193.2	-1.10 ₅				
213.2	-1.15				
233.2	-1.18				
253.2	-1.21				
273.2	-1.25				
293.2	-1.27 ₅				

temperature used in this experiment) changes fairly slowly with temperature, straight lines are fitted to the data points.

IV. APPARATUS

The measurements are made with an apparatus (Fig. 4) of a design modified from that of Henry and Schroeder.⁸ The sample and reference wires are twisted tightly together and soldered with indium to a $\frac{3}{4} \times \frac{3}{4} \times \frac{3}{8}$ in. copper block to form the hot junction. The block is soft soldered to a length of $\frac{3}{8}$ -in. i.d. thin-walled copper-nickel or stainless-steel tubing about 18 in. from the bottom of the tubing. The lower ends of the two wires are soldered to #30 copper wires (Leeds and Northrup thermocouple grade) which run up the center of the tube to the potential measuring device.

A copper-constantan thermocouple for measuring the temperature of the hot junction is indium soldered to the copper block as closely to the sample junction as possible. The cold junction of the thermocouple is at the lower end of the tube.

The copper block is enclosed in a layer of Styrofoam which serves to insulate the hot junction against sudden changes in the temperature of the surrounding atmosphere. The massive copper block also contributes to the temperature

stabilization because of its mass and good thermal conductivity.

The support tube passes through a quick coupler in a brass plate which serves to support the apparatus from the top of the Dewar vessel into which it is inserted. The lower end of the tube with the cold junctions attached is dipped into liquid nitrogen contained in the Dewar. The temperature of the hot junctions may be varied roughly by sliding the tube up and down, thus changing the length of the tube which is immersed in the liquid. Once the proper temperature range has been found the hot junction is allowed to warm up slowly and steadily as the nitrogen level falls. A slightly soft Dewar is of advantage here; a hard Dewar does not let the nitrogen level fall fast enough to take data in a reasonable length of time. In this case a heater may be glued to the copper block to warm up the hot junction. A 100- Ω carbon resistor connected directly to the output of an auto-transformer has worked well.

The output of the copper-constantan thermocouple is measured to the nearest microvolt with a Leeds and Northrup type K-3 potentiometer and a Leeds and Northrup DC null detector. The

FIG. 5. Thermoelectric power of gold as a function of temperature. The squares are from the data presented by Cusack and Kendall (Ref. 10); circles are the present work.

temperature is obtained from the potential values using the tables of Powell, Caywood, and Bunch.⁹

The thermal potential can be measured in two ways. The less satisfactory method is to use the same potentiometer for both the temperature and thermal potential measurements. To allow for the temperature drift, the output of the copper-constantan thermocouple is measured before and after the thermal potential is noted, and the readings averaged. The scatter in the potential in a V -vs- T plot is of the order of $\pm 0.3 \mu\text{V}$.

The thermal potential data on Fig. 3 were taken with a Keithley model 148 nanovoltmeter, used on the $10\text{-}\mu\text{V}$ range. Less expensive instruments, such as the Fluke model 845A microvoltmeter, or a second potentiometer, could also be used for measuring the thermal potential. With a second instrument the potential and temperature measurements may be made almost simultaneously, even if the experimenter is working alone.

V. TYPICAL RESULTS

It is desirable to study the thermoelectric power of a number of samples during the same run. Wires of aluminum, gold, copper, iron, and lead (all 99.999% pure and 10-mil diam) are soldered together at the copper block to form a variety of hot junctions. Gold, aluminum, and iron are

FIG. 6. Thermoelectric power of aluminum as a function of temperature.

FIG. 7. ST vs T^2 for aluminum showing the region in which $S = AT + C/T$.

chosen as the unknowns because of the interesting behavior of the thermoelectric power of each material.

Gold

Gold is studied because it is almost linear over the region 150–300 K. Copper is also linear over this region and is perhaps a better choice since its linearity continues to higher temperatures. The linear region may be interpreted as indicating that the electron diffusion component to the thermoelectric power is dominant; see Fig. 2. To give a large thermal emf the gold sample, which has a positive thermoelectric power, is measured relative to lead, which is negative. The thermoelectric power of lead is taken from the data shown in Table I(a); these measurements constitute a widely used standard. Table I(b) gives the thermoelectric power of the noble metals: gold, silver, and copper.¹⁰

Typical data for gold taken in this experiment are plotted in Fig. 5 along with the data from Table I(b). Any points for which the thermal

FIG. 8. Thermoelectric power of 99.999% pure iron showing the magnon-drag peak.

emf-vs-temperature plots are nonlinear are not used in plotting Fig. 5. Curvature in these plots is taken to mean that the sample hot junction is not warming at the same rate as the thermocouple hot junction.

Aluminum

Aluminum is of interest because its thermoelectric power falls off as $1/T$ on the high-temperature side of the phonon-drag peak. The thermal emf is measured relative to gold, since aluminum has a negative thermoelectric power and gold is positive. Figure 6 shows the variation of the thermoelectric power with temperature, and Fig. 7 is a graph of ST as a function of T^2 . This combination of variables will produce a straight line if the thermoelectric power can be written as

$$|S| = AT + C/T. \quad (10)$$

From the graph, one can see that this behavior appears at temperatures of about 300 K and higher. The coefficients are $A = 1.99 \times 10^{-3} \mu\text{V}/\text{K}^2$

and $C = 290 \mu\text{V}$. By comparison, Gripsover *et al.*⁶ got $A = 2.34 \times 10^{-3} \mu\text{V}/\text{K}^2$ and $C = 284 \mu\text{V}$ in the temperature region 200–300K.

Iron

The thermoelectric power of iron has a peak at about 200K which has been interpreted by Blatt *et al.*¹¹ as arising from a magnon-drag effect. This interaction between the electrons and the magnons or quantized spin waves can be regarded as an analog of phonon drag. The peak is shown in the data presented in Fig. 8. Lead is used as the standard material, although the choice of a standard material is not crucial in the temperature range 100–300K because of the large magnitude of the thermoelectric power of iron.

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