Pressure dependence of the thermoelectric power of sodium between 5 and 14 °K*

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The effect of pressure on the thermoelectric power of sodium has been measured between 5 and 14 °K where phonon drag is believed to play a prominent role. A superconducting quantum interference device (SQUID) was used to measure the tiny voltages involved. At 1 and 2 kbar no effect was observable, but at 3 kbar the thermoelectric power was observed to grow smaller in magnitude, but remained negative. The effect of pressure was most noticeable above 11 °K and was monotonically increasing with temperature above that point. The results have been compared with the predictions of a theory of phonon-drag thermoelectric power by Bailyn, which are in rather good qualitative agreement with the data. The results of this experiment therefore support his contention that a detailed understanding of the lattice spectrum, rather than Fermi-surface distortion, is necessary to understand the role of phonon drag in the alkali metals.

I. INTRODUCTION

While it is expected that the thermoelectric power (TEP) should be sensitive to the same characteristics of ordinary metals (the shape of the Fermi surface, the lattice spectrum, electrophonon interaction, etc.) as electrical and thermal conductivities, the TEP has not yielded to explanation by traditional theories nearly as well as these other transport properties. Limitations in theory are particularly evident at low temperatures $(T \ll \Theta_D)$ where for example; in the alkali and noble metals, pronounced oscillations and sign reversals often occur.

The thermoelectric power S is the only one of the three transport properties which is not restricted in sign. A negative value of S implies that electrons tend to diffuse down an applied temperature gradient, which is considered normal behavior. However, contrary to intuition, a tendency for electrons to diffuse from low to high temperatures (S>0) under the same circumstances is quite common.

This lack of restriction in sign is undoubtedly the cause of the inability of standard theories to adequately explain the behavior of the TEP. Even without a detailed analysis, one can imagine a relatively small TEP of either sign which is the result of two large contributions of nearly equal magnitude but opposite sign. Even a small shift in either contribution can produce a sign change in TEP as well as an enormous fractional change in its magnitude. Thus, different scattering processes can be viewed as acting in competition with each other in the case of the TEP. whereas in the cases of electrical and thermal resistivities the same scattering processes all act to increase them. In order to make accurate theoretical predictions of the TEP, it is obvious that individual

scattering processes must be understood with much greater precision than is necessary for the resistivities. An understanding of thermoelectric power, therefore, represents a severe test of any theory of electronic transport phenomena in metals.

Traditional theories of TEP generally assume that in the case of electron-phonon scattering, the collision integral in the electron Boltzmann equation can be adequately represented by setting the phonon distribution equal to its equilibrium value in the absence of a temperature gradient or an electric current. This assumption, which is justifiable when there are frequent collisions among lattice vibrations at high temperatures or between lattice vibrations and impurities, leads to the definition of the diffusion thermoelectric power.

Within the relaxation-time approximation the TEP, S, is given by the familiar relation¹

$$S = \frac{\pi^2 k_B^2 T}{3eE_F} \left(\frac{\partial \ln \sigma}{\partial \ln E} \right)_{E_F} , \qquad (1)$$

where σ is the electrical conductivity and *E* is some hypothetical Fermi energy. The derivative is to be evaluated at E_F , the actual Fermi energy of the material. T is the absolute temperature, k_B is Boltzmann's constant, and e(<0) is the electronic charge. If the electrical conductivity were dominated by normal electron-phonon scattering, this expression would generally predict a negative value for S since any increase in kinetic energy of the electrons usually reduces the effect of the scattering potential. Then $(\partial \ln \sigma / \partial \ln E)_{E_F}$ should always be greater than zero. However, the expansion of the Fermi surface toward the Brillouin-zone boundary in monovalent metals reduces the minimum phonon wave vector required for umklapp scattering, thereby increasing the number of phonons available for such a process. Whether $\partial \ln \sigma / \partial \ln E$ is positive or negative depends upon

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which trend dominates: the reduction in the electron-ion scattering cross section with increasing Fermi energy or the increased number of phonons available for umklapp scattering.

It is generally believed that the high-temperature $(T > \Theta_D)$ TEP can be explained within the context of traditional theories once details of the electron-phonon and electron-impurity interactions are understood well enough to predict quantities such as $\partial \ln l / \partial \ln E$, which figures prominently in the above expression for *S* and is generally more difficult to calculate accurately than *l* itself (*l* is the electron mean free path). However, the behavior at low temperature is quite incomprehensible within such a theoretical framework. A more complex model is clearly indicated.

A more complete treatment must dispense with the assumption that the phonon distribution has its equilibrium value N_0 in the Boltzmann equation for the steady-state distribution of electrons and that the electron distribution has its equilibrium value in the phonon transport equation. A departure from the equilibrium is certainly more reasonable since any temperature gradient gives rise to a phonon heat current, while an electric current, though carried by electrons, interacts with the lattice vibrations and cannot fail to drag some phonons along with it. In the calculation of transport properties it is necessary to suppose that both distributions deviate from their equilibrium values simultaneously in both Boltzmann equations; the nonequilibrium phonon distribution enters into the electron transport equation in the same way that the nonequilibrium electron distribution function enters into the phonon Boltzmann equation. The inclusion of these extra terms was first considered by Gurevich² and results in the theory of "phonon-drag thermoelectric power."

Qualitatively, the effect can be understood as follows: in the presence of a temperature gradient, lattice waves travel preferentially from hot to cold. This anisotropic distribution of phonons scatters electrons in such a way as to push them more often toward the cold end than the reverse. Zero current results only when the electrostatic field resulting from an excess of charge at the cold end counterbalances the combined effect of this phonon drag and the normal tendency of electrons to diffuse down a temperature gradient. The observed thermoelectric power S then should be expressible as the sum of a diffusion term S_d and a phonon-drag term S_g .³

An equivalent explanation can be formulated in terms of the Peltier coefficient, $\pi = TS$. In this case, phonon drag results in a much larger value of heat flow accompanying the flow of electricity in the absence of a temperature gradient. The presence of an electric current tends to scatter phonons preferentially in the direction of motion of the carriers and results in a lattice heat flux U_g , in addition to that normally carried by electrons.

Implicit in the above explanation is the assumption of conservation of crystal momentum in electron-phonon scattering. In such a normal N process the general tendency is for electrons to emit phonons opposite to the direction of the electrical current \mathbf{j} . Since $\mathbf{U}_g = \pi_g \mathbf{j}$, this contribution to the Peltier coefficient is negative.

But the reverse is often true in the case of an electron-phonon umklapp (U) process, which generally results in phonons emitted in the direction opposite to the average drift velocity of the electrons and, therefore, in the same directions as j. The phonon-drag contribution under these circumstances is positive.

Thus, the sign of S in the temperature region where S_g is of comparable or greater importance than S_d may be positive or negative depending upon which term dominates the collision term of the Boltzmann equation (U or N processes). Naturally, the proximity of the Fermi surface to the Brillouinzone boundaries is important in this respect since it determines the minimum wave vector which can participate in a U process.

Other scattering mechanisms, in addition to the strength of the electron-phonon interaction, also determine the phonon-drag contribution to the thermoelectric power. Phonons streaming down a temperature gradient generally collide with impurities, grain boundaries, and other phonons, so that only a fraction of their momentum is transferred to the electrons. Anharmonic coupling and phonon-impurity scattering grow stronger with increasing temperature and thus tend to damp out phonon drag. Above the Debye temperature, they have reduced it to negligible proportions, while at extremely low temperatures very few phonons exist at all. The maximum effect, then, would occur at some intermediate temperature, as MacDonald's data indicate.³

Starting with the work of Gurevich, a number of theories have been proposed to explain the low-temperature behavior of the TEP (Klemens,⁴ Hanna and Sondheimer,⁵ Ziman,^{6,7} Bailyn,⁸ and MacDonald⁹), particularly in the alkali metals where the assumption of a nearly spherical Fermi surface is reasonable. It is only when umklapp processes are neglected that a relatively simple analytic expression is possible for S_{g} . Under this restriction all the models lead to essentially the same result;

$$S_{g} = \frac{1}{3Ne} \sum_{j} \int_{0}^{\omega_{j} \max} C(\omega_{j}) \frac{\tau_{p}(\omega_{j}) d\omega_{j}}{\tau_{pe}(\omega_{j}) + \tau_{p}(\omega_{j})} , \quad (2)$$

where $C(\omega_j)$ is the contribution to the lattice specific heat from phonons with frequency ω and polarization j, N is the number of conduction electrons per unit volume, τ_p is the total phonon-relaxation time for collisions with electrons, phonons, and impurities, and τ_{pe} is its relaxation time for collisions with electrons alone. This expression predicts that ideally, the phonon-drag thermoelectric power can be as large as -6691 $\times (T/\Theta_D)^3 \mu V/^{\circ}$ K, where Θ_D is the Debye temperature of the material. When collisions between phonons and impurities or phonons and other phonons are frequent enough to maintain equilibrium in the phonon distribution, $\tau_p \rightarrow 0$ and $S_e \rightarrow 0$, as expected.

A complete elucidation of phonon-drag thermoelectric power including the effects of U processes is a much more involved theoretical enterprise, even for the case of an isotropic Fermi surface and lattice spectrum. Nevertheless, Ziman^{6,7} and Bailyn⁸ have succeeded in reproducing the main qualitative features for the alkali metals, particularly the positive humps and sign changes. Their theories, however, emphasize different aspects of the problem.

Ziman's theory, based on a variational solution to the Boltzmann equation, is largely concerned with the role played by Fermi-surface distortion in phonon-drag thermoelectric power, since in addition to reducing the minimum phonon wave vector required for an umklapp process, its effect is compounded by a resulting upturn in the electronphonon matrix element itself in the umklapp region.¹⁰ The entire effect of Fermi-surface distortion is embodied in a variable U(110), a quantity proportional to the energy gap at the center of the (110) face of the first Brillouin zone.

While differences between longitudinal and transverse-sound velocities are accounted for, each set of vibrational modes is represented by its own average Debye temperature $(\overline{\Theta}_T \text{ or } \overline{\Theta}_L)$ and deviations from a purely longitudinal or transverse character are neglected. Thus, lattice-spectrum anisotropy is completely ignored in this theory.

Since most models of the electron-phonon interaction predict that transverse waves can participate only in umklapp processes, the quantity $\overline{\Theta}_T / \overline{\Theta}_L$ as well as U(110) is of critical importance in determining the sign of S_{g} .

Ziman's model may be used to predict a value for S_g in a metal-like sodium with its spherical Fermi surface by setting U(110) equal to zero; $\overline{\Theta}_T/\overline{\Theta}_L$ can be approximated by a weighted average of $\overline{\Theta}_T$ and $\overline{\Theta}_L$ over the three symmetry directions, [110], [100], and [111], of the unit cell:

$$\frac{\overline{\Theta}_T}{\overline{\Theta}_L} = \frac{[1/(2\times13)][3\Theta_{T_1}(100) + 3\Theta_{T_2}(100) + 6\Theta_{T_1}(110) + 6\Theta_{T_2}(110) + 4\Theta_{T_1}(111) + 4\Theta_{T_2}(111)]}{\frac{1}{13}[3\Theta_L(100) + 6\Theta_L(110) + 4\Theta_L(111)]}$$

Relating the Debye temperatures to the appropriate elastic constants,

$$\begin{split} \Theta_{T_1}(100) &= \Theta_{T_2}(100) = \Theta_{T_1}(110) \sim C_{44}^{1/2} ,\\ \Theta_{T_2}(110) \sim \left[\frac{1}{2}(C_{11} - C_{12})\right]^{1/2} ,\\ \Theta_{T_1} &= \Theta_{T_2}(111) \sim \left[\frac{1}{3}(C_{11} - C_{12} + C_{44})\right]^{1/2} ; \end{split}$$

and using Daniel's data¹¹ for sodium

$$\begin{split} &C_{44} = 4.19 \times 10^{10} \text{ dyn/cm}^2 ,\\ &\frac{1}{2}(C_{11} - C_{12}) = 0.585 \text{ dyn/cm}^2 ,\\ &B_S \equiv \frac{1}{3}(C_{11} + 2C_{12}) = 6.61 \text{ dyn/cm}^2 ; \end{split}$$

we find $\overline{\Theta}_T / \overline{\Theta}_L \approx 0.44$.

In Ziman's model,⁷ a graph of S_g vs $T/\overline{\Theta}_L$ shows an enormous positive swing in S_g before it becomes negative for this value of $\overline{\Theta}_T/\overline{\Theta}_L$. To conform to the experimental data for sodium, $\overline{\Theta}_T/\overline{\Theta}_L$ would have to be about 1 and even then the computed values for S_g would be too large by a factor of about 3. While an improved variational function and the use of a more realistic phonon spectrum might improve the results, as it stands the model appears inadequate to explain even the zero pressure of behavior of S. Bailyn^{8,12} has formulated a theory which takes detailed account of the variation of sound velocity with direction as well as deviations of phonon polarization from perfect longitudinal or transverse character. In this model, the source of the increasingly positive character of the low-temperature thermopower of the alkalis is the variation in their lattice spectra, while the shape of their Fermi surfaces is relegated to a secondary role. A point-by-point calculation is used to avoid the approximation inherent in using average Debye temperatures which may underestimate the low-temperature umklapp contributions.

Bailyn's expression for S_{g} is

$$S_{g} = -\frac{1}{3N|e|} \sum_{j,\bar{\mathbf{q}}} \sum_{\vec{\mathbf{k}}} \sum_{\vec{\mathbf{k}}}^{(j,\bar{\mathbf{q}})} \alpha(j\bar{\mathbf{q}}; \vec{\mathbf{q}} + \vec{\mathbf{k}}) h(\vec{\mathbf{q}} + \vec{\mathbf{k}}) \cdot \vec{\nabla}_{q} \omega \frac{\partial N_{0}}{\partial T}$$
(3)

where N is the total number of free electrons per unit volume, $\partial N_0 / \partial T$ is the temperature derivative of the equilibrium distribution of phonons, q is a phonon wave vector of branch j and frequency ω , and \vec{K} is a reciprocal lattice vector. The notation $\sum_{\vec{K}} (j, \vec{q})$ means a sum over all umklapp processes in which phonon (j, \bar{q}) can participate, including $\vec{K} = 0$. The quantity $\alpha(j\bar{q}; \bar{q} + \vec{K})$ is the probability that a phonon (j, \bar{q}) will be destroyed by means of an electron-phonon *U* process involving \vec{K} relative to the probability of destruction by all processes, which include all possible umklapp processes as well as collisions not involving electrons, such as impurities and other phonons. This last term reduces α and phonon drag at high temperatures. However, it was neglected in this calculation.

Bailyn's formulation has a simple structure in that S_g is expressible as a sum of two terms, one representing the contribution from N processes and the other from U processes, while in Ziman's treatment no such separation is possible. The two terms are in opposition since $\mathbf{\bar{q}} \cdot \mathbf{\bar{\nabla}}_{q} \omega = q |v_q| > 0$ and $(\mathbf{\bar{q}} + \mathbf{\bar{K}}) \cdot \mathbf{\bar{\nabla}}_{q} \omega = \mathbf{\bar{v}}_q \cdot (\mathbf{\bar{q}} + \mathbf{\bar{K}})$, which is generally negative. The net effect is a difference between two large and nearly equal quantities. By ignoring the scattering of phonons by anything but electrons we see that the first term, due to N processes, is just the specific heat; that is,

$$S_{g} = -\frac{1}{3N|e|} \sum_{j,\vec{q}} h\vec{q} \cdot \nabla_{q} \omega \frac{\partial N_{0}}{\partial T}$$
$$= -\frac{1}{3N|e|} \frac{\partial E}{\partial T} = -\frac{C_{v}}{3N|e|} ;$$
$$\sum_{\vec{k}}^{(j\vec{q})} \alpha(j\vec{q};\vec{q}+\vec{k}) = 1 .$$

Bailyn concludes that the longitudinal modes contribute negligibly to the thermopower compared to the transverse modes because the longitudinal velocities are large and have small α 's. If longitudinal phonons were the only ones contributing to umklapp-phonon drag, Fermi-surface distortion would be of indisputable importance, but the much larger contributions from the transverse modes come from directions where the wave vector is not that small; q is smallest where it, the electron-scattering vector, and the reciprocal lattice vector are all lined up. Along these symmetry directions transverse waves are rigorously transverse so the polarization factor in the electron-phonon transition probability is zero. Away from this direction the polarization factor increases, but so does the quantity qv, thereby exponentially diminishing the number of available phonons. A peak in the contribution to S_{e} should be reached some distance away. A surprising result of Bailyn's calculations is that one of the transverse modes contains phonons which individually contribute more than any phonons in any other mode, and these are well above twice the minimum size needed for participation in a Uprocess. The results of Bailyn's calculations are shown in Fig. 1, together with MacDonald's experimental data.²⁴

While Bailyn was able to achieve fairly good quantitative agreement with experiment, as will be discussed later, his numerical computations involved some approximations to Eq. (3) and several adjustable parameters. Under these circumstances one cannot help but question the physical significance of his results. The present study was undertaken to provide a more rigorous test of Bailyn's theory since it would permit a comparison of his predictions of the changes in thermoelectric power with experiment under small reductions in lattice parameter. Measurements were made of the effect of hydrostatic pressure up to 3 kbar on the TEP of sodium at temperatures below about 14 °K, where the effect of phonon drag is believed to be most evident.

Sodium is a relatively compressible material undergoing a change in volume of almost 4% under a pressure of only 3 kbar. As will be discussed in Sec. III, its anisotropy parameter $(C_{11} - C_{12})/2C_{44}$ does not change under such compression which makes it reasonable to assume that its spherical Fermi surface remains undistorted at this pressure and that the pressure dependence of the polarization of the phonon modes can be ignored. Thus, only changes in the electron-ion interaction and the frequencies of the lattice vibrations need be considered in analyzing the data.



FIG. 1. Comparison of theoretical calculation of Bailyn with experiment for low-temperature TEP of alkali metals.

II. EXPERIMENTAL METHOD

A. Voltage measurement

In order to specify the pressure dependence of the thermoelectric power of sodium with as much accuracy as possible, a direct differential method was used rather than differentiating a leastsquares fit of thermoelectric voltage versus temperature. Since traditional voltmeters, which have a range above 1 nV, were considered inadequate for this purpose, the tiny signals were measured with a [superconducting quantum interference device (SQUID)] which is designed to work at liquid-helium temperatures, and under favorable circumstances can measure signals in the subpicovolt range. Details regarding the theoretical basis for the operation of the SQUID system can be found in the instruction manual published by the (S.H.E.) Superconducting Helium Electronics Manufacturing Corp.¹³ and in a paper by Gifford, Webb, and Wheatley.¹⁴ In this experiment, the SQUID and associated circuits were connected as a self-balancing potentiometer with a loop gain of 10⁸, with the output displayed on a digital voltmeter.

The over-all experimental arrangement is shown in Fig. 2. Leading from either end of the sodium wire was a ribbon, 0.09 in. wide $\times 0.003$ in. thick, consisting of a thin layer of niobium-tin, having a transition temperature of about 17 °K, sandwiched between two layers of copper. It was brought out to the liquid helium where it eventually made contact to niobium wires leading directly to the SQUID probe. (See Nos. 13, 14, and 21 of Fig. 2.) Since all external connections leading from the sample to the SQUID system were superconducting, no corrections to the measured output were needed to deduce the actual thermoelectric emf produced by the sample in the temperature range of this study ($T \le 14$ °K).

Unfortunately, picovolt sensitivity was not achieved in this experiment as a result of noise, despite rather elaborate precautions. To eliminate the problem of high-frequency stray fields, the entire cryostat was surrounded by a continuous copper shield consisting of $\frac{1}{32}$ -in. copper sheet. All leads entering the region of the input circuit to the SQUID were shielded and equipped with *L*section rf filters consisting of $10-\mu$ H inductors and 1000-pF capacitors to ground. Noise due to changing stray magnetic fields was eliminated by surrounding the lower end of the cryostat insert and the SQUID probe with a superconducting lead bag which was made by soldering together strips of lead foil 0.0015 in. thick.

Even after the elimination of stray electromagnetic fields, the presence of microphonic noise was still enough to prevent the SQUID system from locking. (There is a maximum rate at which changing input flux to the SQUID can be nulled out. Beyond that maximum slewing rate, the system will not lock.) To obviate this problem, vibrations of the helium Dewar inside the nitrogen Dewar were eliminated by means of oil that was poured into the bottom 1.5-in. annular space between them. This froze the two Dewars together when the liquid nitrogen was poured in.

Surprisingly, microphonics were still a problem. However, it was later realized that while the lead bag expels stray magnetic flux from its interior, it does trap whatever flux is present at the instant it goes superconducting. The size of the pressure vessel made it impossible to reduce the cross-sectional area of the loop formed by



FIG. 2. Overview of experimental setup (not drawn to scale): (1) Brass flanges, (2) outer copper shield $(\frac{1}{32}$ -in. sheet, 52 in. high × 22 in. across), (3) liquid nitrogen, (4) frozen oil, (5) frozen nitrogen, (6) liquid helium, (7) brass baffles (4.95-in. diameter), (8) helium level detector, (9) superconducting lead bag, (10) vacuum can (8 in. long × 3.5-in. diameter), (11) bath germanium resistor, (12) Stycast epoxy vacuum feedthrough, (13) niobium-tin-copper superconducting leads, (14) SQUD probe, (15) nitrogen-level resistor, (16) helium depth probe hole, (17) kovar electrical feedthrough for electrical leads, (19) aluminum shield for rf traps, (20) helium inlet port, (21) niobium leads.

the sodium sample and connecting leads to the SQUID below several square inches. Vibrations of the vacuum can, in which this large loop sits relative to the lead bag, can result in considerable microphonic noise. This source of noise was finally eliminated by pouring liquid nitrogen into the helium Dewar to a level an inch or so above the bottom of the vacuum can. At liquid-helium temperatures the nitrogen froze the whole assembly rigidly to the inner Dewar.

The presence of the liquid nitrogen in the helium cryostat solved the microphonics problem, but proved to be a cryogenic disaster. It more than doubled the amount of helium required to cool the cryostat from 77 to $4.2 \,^{\circ}$ K (from 20 to 50 liter), and resulted in transfer times of several hours.

The other source of noise was thermal noise associated with the sample resistance (all other leads were superconducting) which was unusually high (to be discussed later). The combination of this noise and residual microphonics produced about 40-pV noise rather than the ideal figure of 1 pV.

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To measure the thermoelectric power the bomb was first heated to the desired temperature T; then, with one end controlled at that temperature, the temperature of the other end was controlled at various points between T - 0.1 °K and T + 0.1 °K. The temperature controller was capable of controlling to about 0.1 Ω which represents a temperature uncertainty of 0.1 mK below 5 °K and about 7 mK at 13 °K.¹⁵ The error signal from the controller and the SQUID output were monitored on a chart recorder to make it obvious when a steady state was reached after a step in temperature was made. A visual average was taken of the digital voltmeter output to determine the thermoelectric voltage. Eight such temperature settings were



FIG. 3. Detail of pressure cell.

usually made for each measurement of the thermoelectric power.

B. High-pressure system

The design of the pressure vessel presented several unique problems. Bringing any temperature sensor, such as a thermocouple or a semiconducting element, into the high-pressure cell would have entailed a calibration of their thermometric properties under pressure. Unfortunately, no prior measurements had ever been made of the pressure dependence of the TEP of any materials at helium temperatures, so no comparative basis for such a calibration was available. Therefore, temperature sensors had to be placed outside the pressurized region of the cell. It was thus necessary to design a seal, viable at cryogenic temperatures, which used the end plugs themselves both as electrodes and as gradientfree regions where temperatures could be measured. These had to be electrically insulated from each other (so as not to short out the sample) and designed in such a way as to minimize the temperature difference between the ends of the sample and the point where the temperature is measured and external leads contact the end plugs (in order to exclude the thermoelectric power of the end plug from the measurement). There appeared to be no precedent for such a seal, so the final configuration was the result of a long evolution of imperfect designs.

The body of the vessel was made of maraging steel which was heat-treated at 900 °F for 3 h and then air-cooled to room temperature. One of the pressure seals was a standard Bridgeman unsupported area seal with an indium packing ring and copper and brass antiextrusion rings (Fig. 3). The pressure seal at the other end of the bomb was a tapered end plug (half-angle $\approx 7\frac{10}{2}$) which fit into a tapered hole. The sealing action and the electrical isolation of this end plug from the rest of the vessel was provided by a Stycast¹⁶ epoxy conical shell (half-angle $= 7\frac{10}{2}$) having a wall thickness of $\frac{1}{16}$ in. and a length of 0.7 in. In order to provide an initial seal, the shaft of the end plug was threaded and, by means of a nut, was partially extracted.

The Stycast epoxy could not be machined; it consistently wore away tool bits. It had to be molded directly into the proper shapes. Because the uncured epoxy was so viscous, it was impossible to pour it directly into a cavity in the shape of an annulus only $\frac{1}{16}$ in. thick and 0.7 in. deep and avoid leaving voids. It was therefore necessary to pour the uncured epoxy into a wide tapered cavity having the same outer diameter as the shell, and then push out most of the material with a center piece

having exactly the same shape as the tapered end plug. This process left a thin cavity completely filled with epoxy. The epoxy was then cured at room temperature for 24 h. For ease of removal of the hardened shell, all surfaces of the mold (stainless steel) were initially coated with Eccoslip¹⁶ mold release.

Both pressure seals were quite reliable once they were seated at room temperature at a pressure between 20 000 and 25 000 $lb/in.^2$. The bomb was then cooled under this pressure to liquidnitrogen temperatures when the pressure was released for a zero-pressure run at helium temperature or increased for a higher-pressure run. The maximum obtainable pressure was not limited to the room-temperature prestress point. Occasionally, the seals did leak at lower temperatures, but could be reseated by warming back up to nitrogen temperature, or if necessary, to room temperature. However, the epoxy never cracked and never extruded very much. No run was ever aborted as a result of a leaky seal.

A third seal was made on the side of the bomb with a fill-line connection consisting of a $\frac{1}{2}$ in. long $\times \frac{1}{8}$ -in.-o.d. length of stainless-steel tubing¹⁷ which was coned and threaded to form a standard cone seal. This stud, originally 0.024-in i.d., was drilled out, slipped over, and brazed into a much smaller, $\frac{1}{32}$ -in.-o.d. ×0.006-in.-i.d., stainlesssteel fill-line capillary, supplied by the Superior Tube Co. It ran through one of the vacuum lines along the entire length of the cryostat to room temperature. A similar adaptor was made at that point to connect to the external pressure system. The tiny capillary was used because of the relatively small heat leak it introduced. A $350-\Omega$ heater was wrapped around the entire length of the fill line to ensure its being open during pressurization.

The maximum obtainable pressure was limited by the strength of the tapered end plug. While both end plugs were made primarily of maraging steel, the low thermal conductivity of this material (probably about 0.001 W/cm² at 4.2 °K) made it impossible to satisfy the second design requirement that there be negligible temperature difference between the thermometer and the end of the sample. To obviate this problem, an end plug of pure copper was tested first. Unfortunately, it blew out at about 32 000 lb/in.². Since no material was found that was strong and yet highly thermally conducting, a compromise was reached whereby copper inserts were brazed into both end plugs as shown in Fig. 3. Two holes $\frac{1}{8}$ in. in diameter, were drilled, one for the thermometer and one for external leads, to a point within the copper insert and 0.15 in. from the bottom of the hole in

which the sample assembly screws into each plug. A test of this composite demonstrated its ability to withstand a pressure of over 3 kbar with very little outward motion of the tapered end plug. Undoubtedly it could have contained higher pressures, but in the interest of safety was limited to 3 kbar.

The high-pressure pumping station consisted of an air-driven two-stage diaphragm pump¹⁸ which took helium gas at 3500 lb/in.² from a storage bottle and raised it to 30 000 lb/in.². At 15:1 Harwood intensifier was used to raise the pressure to any desired point above this.

C. Sample preparation

The sodium samples (originally supplied in ampoules by Leico Industries¹⁹) were extruded wires $(20 \times 0.1 \text{ cm})$ wrapped around a nylon rod $(\frac{1}{2}$ -in. diameter ×1.35 in. long) threaded with a square groove 0.05 in. wide $\times 0.05$ in. deep. The sample fit loosely in the groove to avoid strain by any differential thermal contraction. On each end of the nylon rod was glued a copper disk (0.4-in. diameter $\times 0.05$ in thick) with a groove 0.03 in. long running across its flat surface in which each end of the sodium wire was laid. Since the thickness of the wire was 0.04 in., part of it extended above the surface of the copper disk. In addition, a 0.3-in.-long stub of sodium was pressed on top of the portion already sticking out, so a considerable amount of the material extended above the surface of the copper.

A rigid copper connector $(\frac{1}{2}$ -in. diameter) was screwed into one end of the rod, pressing tightly to the copper disk, thus mashing the sodium between the two copper surfaces. It was hoped that this mashing would produce a good electrical and thermal contact between the sodium and the copper. The other end of the copper connector was screwed (5-40 screw) tightly into a tapped hole drilled in the copper insert of the tapered plug. It was hoped that this action would produce excellent thermal contact between the surface of the connector and the insert.

Because the tapered end seals pressure by moving out slightly, the connection from the other end of the nylon rod to the Bridgeman seal had to be flexible and still be highly thermally conducting. For this purpose, a flexible connector was made consisting of two square copper plates ($0.5 \times 0.5 \times 0.05$ in.) attached to each other by means of rectangular pieces of copper foil ($0.35 \times 0.5 \times 0.003$ in.) nominally 99.9999% pure, as opposed to the electrolytic tough-pitch copper used everywhere else. Three layers were clamped on all four sides of each disk and were flexed somewhat. It was hoped that the reduction in crosssectional area would be compensated by the higher conductivity of the high-purity copper foil. The two plates were screwed into the nylon rod and the other end plug exactly as at the other end.

In order to minimize the amount of solid helium in the sample chamber and, therefore, any parallel conduction heat, a nylon sheath was slipped over the threaded rod, thus filling up almost all the remaining space in the bomb. The two end plugs and sample assembly were then slipped as a single unit into the bomb and the initial pressure seals made. All of this assembly work was done inside a glove bag filled with dry helium. A cutaway view of the sample mounted inside the bomb is shown in Fig. 4.

D. Temperature measurement

In order that as much of the measured temperature gradient as possible appear across the sample



FIG. 4. View of sample mounted inside pressure cell: (1) Pressure vessel, (2) niobium-tin-copper ribbon, (3) germanium thermometers wrapped with enamel coated copper leads, (4) nylon sheath, (5) sample, (6) threaded nylon mandrel, (7) flexible copper connector (square), (8) copper disk (glued to mandrel), (9) rigid copper connector, (10) end of sample, mashed between the copper disk and connector, (11) capillary fill line $(\frac{1}{32}$ -in. o.d., 0.008-in. i.d.), (12) fill-line heater (wrapped noninductively so as not to couple magnetic flux into squp circuit), (13) flexible copper connector, (14) rigid copper connector. itself, it was necessary to maximize the thermal resistance between the two ends of the sample and minimize it between the ends and the thermometers. In this regard, the mounting procedure included the following features: (i) the sample was wound on a nylon rod; (ii) almost all the dead space in the sample chamber was filled with nylon. Thus any parallel conduction of heat through the solid helium was sharply reduced. The nylon itself has a thermal conductivity in the neighborhood of 10^{-4} W/cm² at 4.2° K²⁰ and, therefore, provides good thermal insulation; (iii) all material between the ends of the sample and the thermometers was copper (annealed at 600°C for several hours); (iv) the thermometers and leads were placed in the bottoms of deep holes drilled into the end plugs where they would be as close to the ends of the sample as possible; and (v) the sodium sample was made reasonably long and thin (20 cm long \times 0.1-cm diameter) to minimize its conductance. A calculation performed using reasonable values for the conductivities of the walls of the bomb, the copper, the solid helium and the nylon indicated that even if the thermal conducitivity of the sodium were 20 W/cm², 99% of the temperature difference between the two thermometers should appear across the sample itself.

The two thermometers were calibrated ²¹ germanium resistors encapsulated in cylindrically shaped metal containers (about $\frac{1}{8}$ -in. diameter $\times \frac{3}{8}$ in long) filled with helium exchange gas.²² Since most of the heat conduction to the germanium itself is through the leads and not the exchange gas,²³ lengths of No. 36 gauge formvarcoated copper wires were soldered onto the platinum stubs sticking out of the capsule, were wrapped tightly around it, and then varnished, with GE 7031 varnish, onto the surface of the container. It was hoped that this process would thermally ground the thermometer to the bottom of the copper hole, where it would be sensing the temperature of a point as close to the end of the sample as possible. In addition, the thermometers were isolated from heat leaks down the electrical leads which eventually led out of the cryostat by means of 18-in. lengths of resistance wire (19.48 56/ft) which were soldered between those leads and the copper grounding wires. Temperatures were measured by an ac bridge.¹⁵

A number of 0.015-in. gold wires attached to both ends of the bomb and leading directly to the liquid helium through the epoxy vacuum seal served as thermal links between the bomb and the helium bath.





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			TABLE I. Th	ermoelectr	ic power of so	odium at variou	s temperature	s and press	sures.		
			Pressure				Pressure				Pressure
$T (^{\circ}K)$	$S(\mu V/^{\circ}K)$	$\sigma_{S}(\mu V/^{\circ}K)$	(kbar)	$T (^{\circ}K)$	$S(\mu V/^{\circ}K)$	$\sigma_{S}(\mu V/^{\circ}K)$	(kbar)	$T(^{\circ}\mathrm{K})$	$S(\mu V/^{\circ}K)$	$\sigma_{S}(\mu V/^{\circ}K)$	(kbar)
	Sample 1										
7.50	-0.243	0.001	0	7.50	-0.238	0.001	73	12.50	-0.535	0.004	က
8.00	-0.278	0.002		8.00	-0.272	0.001		13.00	-0.551	0.004	
8.50	-0.302	0.002		8.50	-0.307	0.002		13.50	-0.564	0.004	
7.04	-0.186	0.002		9.00	-0.342	0.002		13.80	-0.582	0.005	
9.00	-0.337	0.002		9.50	-0.374	0.001		13.00	-0.554	0.004	
9.50	-0.365	0.003		10.00	-0.418	0.004					
10.00	-0.394	0.014		10.50	-0.443	0.004			Sample 2		
10.50	-0.438	0.002		11.00	-0.471	0.005		00 0	667 U		c
11.00	-0.468	0.002		11.50	-0.508	0.004		0.00	0.440	0.015	D
11.50	-0.518	0.004		12.00	-0.549	0.005		9.00 0	-0.402	600 0	
12.00	-0.541	0.006		12.50	-0.561	0.012		9.00	0.401	200.0	
12.50	-0.588	0.009		13.00	-0.617	0.011		11.00	-0.500	010.0	
13.00	-0.612	0.005		7.04	-0.217	0.001		00.11	-0.033	CIU.U	
9.00	-0.343	0.001		8.00	-0.277	0.002		40 1	-0.313	200.0	
6.50	-0.190	0.004		6.50	-0.190	0.001		00.01	057.0-	200.0	
6.00	-0.150	0.003		6.00	-0.159	0.001		12.00	-0,032	910.0	
5.62	-0.140	0.004		5.50	-0.137	0.001		5.50	-0.311	0.002	က
5.62 ^a	-0.132	0.007		13.00	-0.616	0.004		7.04	-0.326	0.016	
5.62 ^a	-0.132	0.001		5.30	-0.128	0.001		9.00	-0.416	0.008	
5.36	-0.130	0.001		000	100 0	100 0	c	10.00	-0.470	0.020	
9.25	-0.353	0.004		8.00 0.00	0100	100.0	Ċ	11.00	-0.585	0.005	
11.50	-0.494	0.006		9.00	0.000	0.001		8.00	-0.450	0.001	
			·	8.5U	-0.298	100.0					
06.7	-0.238	0.001	T	9.50	-0.373	0.004					
8.00	-0.269	0.001		10.00	-0.403	0.009					
8.50	-0.305	0.001		10.50	-0.421	0.001					
9.00	-0.340	0.002		11.00	-0.449	0.003					
9.50	-0.376	0.002		11.50	-0.468	0.004					
7.04	-0.218	0.001		12.00	-0.508	0.004					
10.00	-0.413	0.002		12.50	-0.539	0.007					
10.50	-0.465	0.006		13.00	-0.558	0.003					
11.00	-0.487	0.004		7.50	-0.231	0.002					
11.50	-0.505	0.005		7.04	-0.209	0.001					
12.00	-0.538	0.007		6.50	-0.181	0.002					
12.50	-0.586	0.008		6.25	-0.150	0.001					
13.00	-0.619	0.009		13.50	-0.563	0.005					
6.50	-0.178	0.001		13.80	-0.579	0.005					
6.00	-0.155	0.001		13.00	-0.556	0.010					
5.50	-0.128	0.005		12.50	-0.515	0.003					
5.30	-0.119	0.002		12.00	-0.504	0.004					
				11.50	-0.481	0.002					
^a With a s	small amount	of exchange gas					^b With meas	surable exc	hange gas del	iberately added	(see text).

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A. Presentation of data

The raw data for each temperature T was a series consisting, on the average, of eight resistance and voltage readings approximately equally spaced in the range T - 0.1°K to T + 0.1°K. In order to extract a value for the thermoelectric power a least-squares fit was made for the calibration data of the germanium resistor at the variable end of the bomb.

Graphs of thermoelectric voltage E_i versus ΔT_i are illustrated for points taken at 8 and at 10°K in Figs. 5(a) and 5(b), respectively. These two graphs are representative of the two extremes in the quality of the data.

The values of all the thermoelectric powers and their standard deviations are listed in Table I. The zero-pressure points are plotted in Fig. 6(a),



FIG. 6. Zero-pressure results: (a) present experiment; (b) MacDonald's data (Ref. 24).

while MacDonald's data²⁴ are shown in Fig. 6(b) for comparison. The high-pressure points are plotted in Fig. 7.

In Fig. 8, the fractional changes in S, $(S_p - S_0)/S_0$ for sample 1 are plotted as a function of temperature for the three pressures used in this experiment. The error bars were calculated from the formula

$$\delta \left(\frac{S_{p} - S_{0}}{S_{0}} \right) = \frac{S_{p} - S_{0}}{S_{0}} \left(\frac{\delta (S_{p} - S_{0})}{S_{p} - S_{0}} + \frac{\delta S_{0}}{S_{0}} \right) ,$$

where $\delta(A)$ is the error in A, and $\delta(S_p - S_0) = \delta S_p + \delta S_0$. As a result of large uncertainties due to the necessity of using exchange gas, the data for sample 2 were not considered reliable enough to warrant such a plot. This point will be discussed later.

B. Discussion of results and comparison with theory

The only reasonable conclusion that can be drawn from the graphs of $(S_p - S_0)/S_0$ at 1 and 2 kbar is that the effect of pressure is essentially zero within the experimental error. On the other hand, there is a noticeable effect at 3 kbar which indicates that (ignoring the possible crossover at 9.5°K, which may be spurious) the fractional change of the thermoelectric power is negative and is increasing in magnitude above 11°K. With-in the context of the existing theories of phonon



FIG. 7. Comparison of zero-pressure and high-pressure data.

drag it seems reasonable to assume that both the positive contribution to S (due to U-processes) and the negative contribution (due to N-processes) should decrease in magnitude simply because pressure generally increases sound velocities and therefore decreases the number of phonons available for any electron-phonon interaction. What determines the net change in thermoelectric power is the term that decreases faster. The data for sodium indicate that, since S is growing less negative with pressure, the contribution from Nprocesses is diminishing in magnitude more rapidly than that due to U processes.

In order to compare the results of this experiment with the predictions of Bailyn's theory, the pressure dependencies of the following quantities must be considered: (a) The speed of sound (This should affect the normal and umklapp contributions to S differently. The former, since it depends more or less on the specific heat of the lattice, involves only an average Debye temperature. The latter is more sensitive to certain directions of phonon propagation.); (b) the phonon-polarization vectors; (c) the electron-phonon interaction; (d) the shape of the Fermi surface.

Fortunately, the spherical Fermi surface of sodium seems not to be distorted under moderate compression. While direct observations of this effect have not been made, this conclusion is consistent with Daniels's finding that the anisotropy parameter, $(C_{11} - C_{12})/2C_{44}$ is not pressure dependent in sodium up to 2 kbar,¹¹ and with the theoretical models of Fuchs²⁵ and Ham.²⁶ Thus, it seems reasonable that band-structure effects can be ignored.

Bailyn's explicit expression for a pure material can be written as a sum of positive and negative contributions, S_+ and S_- , due to U and N processes, respectively;

$$S = S_{+} + S_{-},$$

$$S_{-} = -\frac{1}{N|e|2\pi^{3}} C_{v} = -6691 \left(\frac{T}{\Theta}\right)^{3} \frac{\mu V}{\circ K},$$

$$S_{+} = -\frac{1}{N|e|2\pi^{3}} \sum_{j} \vec{K} \cdot \int \alpha(j \vec{q}; \vec{q} + \vec{K}) \qquad (4)$$

$$\times (\vec{\nabla}_{q} h \omega) \frac{\partial N_{0}}{\partial t} d^{3}q.$$

N is the total number of conduction electrons per unit volume; |e| is the magnitude of the electronic charge, and K is any one of the 12 equivalent reciprocal-lattice vectors of the bcc Brillouin zone. The heat capacity per unit volume of the lattice, C_V , is approximated by a T^3 dependence, where Θ is a slowly varying function of temperature. Bailyn's expression for α is

$$\alpha(j\vec{\mathbf{q}};\vec{\mathbf{q}}+\vec{\mathbf{K}}_n) = \left(1 + \sum_{K \neq K_n} \beta(\vec{\mathbf{q}}\vec{\mathbf{K}}_n,K)\right)^{-1}.$$

where the sum is over all the reciprocal-lattice vectors $K \neq K_n$ in which a phonon $(j\bar{q})$ can participate. In the rigid-ion approximation



FIG. 8. Pressure variation of TEP.

$$\beta\left(\mathbf{\vec{q}} \ \mathbf{\vec{K}}_{n}, \mathbf{\vec{K}}\right) = \frac{\left|\mathbf{\hat{\xi}} \cdot (\mathbf{q} + \mathbf{\vec{K}})\right|^{2}}{\left|\mathbf{\hat{\xi}} \cdot (\mathbf{\vec{q}} + \mathbf{\vec{K}}_{n})\right|^{2}} \frac{\left|V\left(\mathbf{\vec{q}} + \mathbf{\vec{K}}\right)\right|^{2}}{\left|V\left(\mathbf{\vec{q}} + \mathbf{\vec{K}}_{n}\right)\right|^{2}},$$

where ξ is the polarization vector for phonon $(j\vec{q})$ and $V(\vec{k})$ is the electron-ion matrix element. Since crystal momentum is conserved $\vec{q} + \vec{K} = \vec{k'} - \vec{k}$, the electron scattering vector β is, in effect, the ratio of the probability that phonon $(j\vec{q})$ will interact with an electron via a U process involving \vec{K} to that involving \vec{K}_n . Under pressure $\vec{q} + \vec{K}_n$ does not change direction,

Under pressure $\mathbf{\tilde{q}} + \mathbf{\tilde{K}}_n$ does not change direction, but increases in magnitude as a^{-1} , where *a* is the lattice constant. Thus $|\mathbf{\tilde{q}} + \mathbf{\tilde{K}}|^2/|\mathbf{q} + \mathbf{\tilde{K}}_n|^2$ is not pressure dependent.

Since the polarization vector $\hat{\xi}(j\vec{q})$ depends on the elastic constants, C_{ij} , its direction should be a function of the lattice parameter. While the functional dependence of $\hat{\xi}$ on C_{ij} at a general point in the Brillouin zone is complex, near the three symmetry directions its components can be expressed in terms of a combination of elastic constants which depend very strongly on the anisotropy parameter, $(C_{11} - C_{12})/2C_{44}$,²⁷ which is not a function of pressure. It is therefore reasonable to assume, particularly in light of other approximations made by Bailyn, that $|\hat{\xi} \cdot (\hat{q} + \hat{K})/\hat{\xi} \cdot (\hat{q} + \hat{K}_n)|^2$ is not pressure dependent.

The ratio of the V's will change only if the fractional change of $V(\vec{k})$ with pressure is a function of \vec{k} . A simple Thomas-Fermi model of the electron-ion interaction predicts that this fractional change is strictly independent of \vec{k} .²⁸ That is,

$$V(\mathbf{r}) \sim (1/\mathbf{r})e^{-\mathbf{r}/\lambda}$$
, $V(\mathbf{k}) \sim (1/k^2 + \lambda^{-2})$.

where \mathbf{k} (the electron scattering vector) = $2k_F \sin \frac{1}{2}\theta$ (k_F is the Fermi wave vector and θ is the scattering angle) and $\lambda \sim r_S$, the mean atomic radius. Since r_S^{-1} and k_F are inversely proportional to the lattice parameter, $|V(k')/V(k)|^2$ is obviously independent of it. A more realistic model would undoubtedly predict some dependence of this ratio on the lattice parameter, but its pressure dependence is probably considerably smaller than that of $V(\mathbf{k})$ itself. It thus seems reasonable to assume



FIG. 9. Theoretical positive and negative contributions to TEP for various pressures.

that α is not a function of pressure.

This approximation is consistent with the fact that the actual expression Bailyn used to make his calculation of S_+ was, in fact, only an approximation to Eq. (4). In particular, he assumed that for each polarization, j, α could be removed from the sum over \bar{q} and had some effective value α_j . He also made use of another parameter, γ_j , a geometrical factor for each polarization. The product $A_j \equiv \alpha_j \gamma_j$ was treated as a constant adjusted to fit experiment. Since this constant was not rigorously derived from first principles, it hardly seems worthwhile to try to calculate subtle changes in α_i due to pressure.

The actual expression used to calculate $\boldsymbol{S}_{\!\!\!+}$ was

$$S_{+} = 367.3 \sum_{j=1,2} A_{j}F(\Phi_{j}/T) \quad \mu V/^{\circ} K$$
$$A_{1} = 0.07, \quad A_{2} = 0.035,$$
$$F(z) = (z/e^{z} - 1) - \ln(1 - e^{-z}).$$

 $k_B \Phi_j$ represents an average phonon energy over those modes that contribute significantly to S_+ , as opposed to an average over all the vibrational modes of a solid. The use of an average Φ_j represents another approximation to Eq. (4). Bailyn was able to obtain good results for all the alkali metals by assuming that $\Phi_1 = (0.35hk_F/k_B)(C_{44}/\rho)^{1/2}$ and $\Phi_{II} = (0.25hk_F/k_B)(C_{44}/\rho)^{1/2}$, where ρ is the mass density and $(hk_F/k_B)(C_{44}/\rho) = 172$ K for sodium.⁸ Since the numbers 0.35 and 0.25 were not derived from a first-principles calculation, one can only assume that they are pressure independent.

Thus, the only two quantities whose pressure dependence need be considered are Θ in S_{-} and



FIG. 10. Theoretical TEP for various pressures.

 $(hk_F/k_B)(C_{44}/\rho)^{1/2} \equiv \Gamma$ in S_+ . These can readily be calculated to first order in the pressure ΔP :

$$\Theta(P) = \Theta(0) + (d\Theta/dP)_{P=0}\Delta P$$
$$= \Theta(0) + \frac{d\Theta}{\Theta dV/V} \cdot \left(\frac{\Theta dV}{V dP}\right)_{P=0}\Delta P$$
$$= \Theta(0) (1 + \gamma \beta_0 \Delta P),$$

where γ is the Grüneisen constant, which equals 1.25 for sodium,²⁹ and β_0 is the compressibility at zero pressure, measured by Swenson to be 1.3×10^{-2} kbar⁻¹.³⁰ Therefore,

$$\Theta(P) = \Theta(0)(1 + 0.01625 \Delta P),$$

where ΔP is the pressure in kbar. Similarly,

$$\Gamma(P) = \Gamma(0) + \left(\frac{d\Gamma}{dP}\right)_{P=0} \Delta P.$$

The other parameters are assigned the values $C_{44} = 0.56 \times 10^{11} \text{ dyn/cm}^2$, $dC_{44}/dP = 1.63$, $\rho = 0.927$ g/cm³, $d\rho/dP = \rho\beta_0 = 1.205$ g dyn/cm, $k_F = 0.90 \times 10^8 \text{ cm}^{-1}$, and $dk_F/dP = \frac{1}{3}k_F\beta_0 = 0.39 \times 10^{-3} \text{ cm/dyn}$. Putting these values into the expression for $d\Gamma/dP$ leads to $\Gamma(P) = 172(1+2.03 \Delta P)^\circ \text{K}$. Therefore $\Phi_1 = 60(1+0.710 \Delta P)^\circ \text{K}$ and $\Phi_2 = 43(1+.508 \Delta P)^\circ \text{K}$

In Figs. 9–11 are shown the results of the calculation for S_+ , S_- , S_- , and $(S_p - S_0)/S_0$ in the temperature range from 12°K to 16°K for pressures of 0, 1, 2, and 3 kbar. It is immediately obvious from Fig. 9 that S really is the result of two very large contributions of nearly equal magnitude and opposite sign. For example, at 16°K and P = 0, $S_+ \approx 6.36 \ \mu V/^{\circ} K$ and $S_- = -7.2 \ \mu V/^{\circ} K$. Only a 10% error in S_- can make almost a 100% error in S itself.



FIG. 11. Theoretical pressure variation of TEP.

The calculation predicts that the tendency for the thermoelectric power of sodium to increase in magnitude with temperature is less pronounced under pressure. In particular, at 3 kbar S has already started to drop in size at 12°K. While the data do not indicate an upturn in S at this temperature, they do indicate a flattening out and suggest the start of an upturn, perhaps at 14° K. In addition, the calculated values of $(S_{p} - S_{0})/S_{0}$ are qualitatively consistent with the experimental results at 3 kbar even though they are too large by a factor of about 3. Considering the sensitivity of S to very small errors in S_+ and S_- , the agreement is surprisingly good. These discrepancies can probably be reduced by a more careful determination of $\alpha(j\vec{q};\vec{q}+\vec{K})$ and $\Phi_j(\vec{q})$.

C. Discussion of errors

While the accuracy with which the thermoelectric power was measured was reasonably high (several percent uncertainty) its rather small pressure dependence has reduced the amount of detailed information that can be obtained from this experiment. This is particularly true at 1 and 2 kbar where the only reasonable conclusion that can be drawn is that $(S_p - S_0)/S_0$ is zero within the experimental error. At 3 kbar a trend is definitely observable, but even there large uncertainties are evident. It would be desirable to reduce the experimental errors by at least one order of magnitude to be able to specify the pressure dependence with reasonable precision. The worst uncertainties in the present experiment are due to random errors which have the effect of increasing the error limits in a particular measurement without affecting its average value, as opposed to systematic errors which presumably affect all measurements, regardless of pressure, in the same manner and therefore have little influence on the measured pressure coefficient $(S_{p} - S_{0})/S_{0}$.

The most serious random error resulted from imperfect temperature control at both ends of the sample. The controller was unable to maintain the resistance of the germanium thermometers constant to much better than 0.1 Ω at any temperature. This value of 0.1 Ω was also the smallest increment by which the resistance could be changed. Near 4.2°K this change represents a temperature change of only about 0.0001°K, while at 11°K the same 0.1 Ω represents 0.003°K. This diminished thermometric sensitivity together with a relatively large thermoelectric power conspired to make it impossible at the upper end of the temperature range to achieve the voltage stability of 40 pV mentioned earlier in connection with the SQUID. At 11°K the measured value of S was approximately 0.5 μ V/°K. At this temperature a fluctuation of 0.003°K would produce a change in the SQUID output of 1.5 nV. While the observed oscillations were somewhat smaller (about 1 nV), it was still necessary to average over rather large voltage fluctuations. On the other hand, at 6°K where $S \approx 0.2 \ \mu$ V/°K, a temperature fluctuation of 0.001°K would produce a shift in the voltage output of only 20 pV. Consequently, the output, as observed on the chart recorder, was very steady for long periods of time at the lower end of the temperature range.

The major problem arose from the phase shifts due to the time delay between the application of heater power and the response of the resistor. Near 5°K about 2 min were required to reach a steady state after the control point was suddenly shifted by a few hundredths of a degree. At 12°K it sometimes took 8-10 min to stabilize after a similar transient was introduced. Such an increase is inevitable at higher temperatures because the thermal time constant is proportional to C_{ν}/κ , where C_{ν} is the specific heat and κ is the thermal conductivity. Now C_v varies as T^3 , while κ is more or less proportional to T. In stainless steel $\kappa \approx 0.003 \text{ W/cm}^2$ at 5°K, while at 12°K $\kappa \approx 0.01$ W/cm^2 , over three times larger. At the same time C_v increases by a factor of $(\frac{12}{5})^3 \approx 13.8$. Thus $(C_{\nu}/\kappa)_{12}/(C_{\nu}/\kappa)_{5}\approx 4.2$. In light of this ratio, the 8:2 ratio for settling times is not surprising. However, it should be possible to scale both time delays down by placing the heater coils closer to the sensing resistor than they were in this experiment and by reducing the mass of the bon b. In retrospect, the vessel was definitely overdesigned for containing a pressure of 3 kbar. (Our original intentions, abandoned in the interest of safety, was to attempt measurements at 6-7 kbar.) It should be possible to reduce the ratio of o.d. to i.d. from the present 2.5 to less than 2.0 without introducing a safety hazard.

Apparently the manner in which the heater coils are wrapped is also important. Greater care should have been taken to wrap them in a single layer so that no time delay is introduced by the necessity of heat penetrating through one layer to the next.

The presence of exchange gas in the vacuum can can also result in thermometry errors since it thermally couples the resistor to the helium bath. Under these circumstances the resistor does not sense the temperature exactly at the bottom of the hole, but some distance away because of the existence of an extra conducting path through the exchange gas. Despite the fact that a vacuum gauge above the cryostat consistently read pressures of 10^{-6} mm, the equilibration temperature of the bomb with no heater current varied from day to day between 5.7°K and about 6°K. Since the gold links could not have changed, these fluctuations must have been due to the presence of small amounts of exchange gas resulting from intermittent leaks into the vacuum can either through the indium seal or the epoxy feedthrough.

In addition to errors in temperature measurement, exchange gas also introduces errors in the measured temperature gradient. Since the gas represents another parallel conducting path between the ends of the sample, it decreases the ratio of the total conductance between thermometer and sample to that between the ends of the sample. Therefore, a smaller fraction of the temperature gradient, as measured by the two thermometers, actually appears across the specimen. The net result is a smaller measured thermoelectric power. If the actual amount of exchange gas could be kept constant it would introduce a systematic error and therefore not affect the pressure coefficient. However, it apparently varied somewhat from day to day despite continuous pumping.

On one particular day S was measured at 11.50°K as $(-0.518 \pm 0.006) \ \mu V / ^{\circ} K$. The heater current to the two heaters was 2.85 and 4.00 mA; the total power required to maintain the bomb at this temperature was about 24.1 mW. On another day Swas measured at the same temperature as (-0.494 \pm 0.006) μ V/°K. The two heater currents were 3.2 and 4.75 ma, so the heater power was 32.8 mW, giving evidence that some exchange gas was present. This was a rather extreme case, however. Somewhat more typical is a set of two measurements made at 9°K. In one case $S = (-0.337 \pm 0.002) \mu V/^{\circ} K$ with the two heater currents at 1.8 and 2.75 mA. The measurement was made with the heater currents at 1.5 and 2.9 mA. In this instance $S = (-0.343 \pm 0.001) \mu V/^{\circ} K$. The ratio of the two sets of power inputs is 1.013.

Another probable effect of exchange gas is to prevent the bomb from ever achieving a steadystate condition, at least for very long. Ever present convection currents tend to keep the bomb in a constant state of thermal oscillation which results in the necessity of a visual average being taken over larger voltage fluctuations. The net effect is a larger uncertainty in the measured thermoelectric power.

Sample 2 had to be run with some exchange gas. For some inexplicable reason the germanium resistor at the Bridgeman seal end of the bomb lost almost complete thermal contact with its end plug. In order to restore some coupling, exchange gas, along with its attendant problems, had to be introduced. These are reflected by the fact that the uncertainties in S are rather large compared to those found for sample 1 and that the shape of the curve was not quite as smooth as that of sample 1. (See Fig. 7) In addition, high-pressure data for this sample are so erratic that not too much significance can be attached to them.

There can be little doubt, however, that the larger measured value for the thermoelectric power of sample 2 is real. In light of the above comments, its measured value would have been even larger if it were possible to avoid using exchange gas. MacDonald²⁴ also found that the size of the thermoelectric power of sodium can vary from sample to sample of comparable purity, although the general shape of the curve of S vs. T was the same in all cases. At 9°K, for example, his result for "sample I" is about $-0.41 \ \mu V/^{\circ} K$, while at the same temperature, $S \approx -0.475 \ \mu V/^{\circ} K$ for his "sample II". This represents a change of about 15%.

These discrepancies may very well be due to the martensitic transformation which is known to occur in sodium starting at about 35° K as the temperature is lowered.³¹ While the fraction of the material that has transformed to the hcp phase seems to be independent of temperature below about 13° K, this fraction will almost certainly vary from sample to sample depending on its state of strain and the degree to which it is cold worked. Dugdale²⁹ estimates that about 25% of the material may transform.

It is difficult to estimate how the thermoelectric power of the low-temperature phase behaves. The Fermi surface remains spherical in going from the bcc to the hexagonal phase, but it is considerably closer to the six rectangular phases of the Brillouin zone than it is to the (110) face of the bcc zone. The greater proximity to the zone face suggests that umklapp processes are probably more frequent in the low-temperature phase, which alone indicates that the thermoelectric power of sodium is more positive than it would be if no martensitic transformation ever occurred. But this effect might be offset by large phonon velocities in certain critical directions. Since data on the elastic constants of the hexagonal phase do not exist, this possibility cannot be assessed.

In addition to any intrinsic dependence of S in the low-temperature phase, the pressure dependence of the thermoelectric power of sodium is also influenced by how pressure affects the amount of low-temperature phase present. Since the volume of the hexagonal phase is larger than that of the bcc phase by about 0.3%,³¹ pressure should tend to inhibit its formation.

Since Bailyn's original formulation and the above

calculations based on it do not account for the possible complications introduced by the martensitic transformation, they should be viewed with a certain amount of reservation.

The major systematic error in this experiment involved measuring the temperature difference between the two ends of the sample. The actual temperature gradient across the specimen was, of necessity, only a fraction of the measured gradient between the two thermometers because of the lack of perfect thermal conductance between the thermometer and sample. However, if this error is truly independent of pressure, it should not affect $(S_p - S_0)/S_0$. The use of a poor thermal conductor like nylon to fill almost all the dead space in the sample chamber helped to insure this by reducing parallel conduction through the solid helium to negligible proportions.

As was mentioned in Sec. II, a calculation based on reasonable values of the thermal conductivities of the walls of the bomb, the nylon, etc., indicates that even if the thermal conductivity of the sodium were 20 W/cm², 99% of the measured gradient actually appears across the sample. Unfortunately, a problem arose in the course of the experiment which calls this conclusion into question. The room-temperature resistance of samples 1 and 2 was about 14.5 m Ω . This value is consistent with that expected for a sodium wire of length 20 cm and diameter 0.1 cm. However, the resistance of the two samples actually rose at 4.2°K to 0.100 and 0.04 Ω , respectively! It was the Johnson noise resulting from these high resistances that was a major factor in reducing the ideal sensitivity of the SQUID from 1 to 40 pV.

When the residual resistance ratio was measured using a standard four-wire technique on other sodium wires prepared from the same source, its value was 700. It is quite probable that the resistance ratio would have been considerably higher if the samples were cooled more gradually.³² Therefore, the anomalous behavior of the resistance had nothing to do with the bulk properties of the sodium used.

A priori, one possible cause of this phenomenon may have been deterioration of the sodium surface between the time the wires were extruded and the time they were cooled sufficiently to the point where oxidation is negligible. This interval was several hours. Such deterioration would have reduced the cross-sectional area or the contact area with the copper connectors, or both. However, such extensive deterioration was unlikely. A practice sample was placed in the bomb and, at room temperature, its resistance increased overnight by only about 10%.

Undoubtedly the sodium did at least partially pull away from the copper disk, but the resulting contact resistance probably depended critically on the state of oxidation of the sodium and copper surfaces. These, of course, are unknown factors. However, the data indicate that while such a surface layer may have produced a large electrical barrier, it was not thick enough to produce much of a thermal barrier.

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FIG. 2. Overview of experimental setup (not drawn to scale): (1) Brass flanges, (2) outer copper shield $(\frac{1}{32}$ -in. sheet, 52 in. high × 22 in. across), (3) liquid nitrogen, (4) frozen oil, (5) frozen nitrogen, (6) liquid helium, (7) brass baffles (4.95-in. diameter), (8) helium level detector, (9) superconducting lead bag, (10) vacuum can (8 in. long × 3.5-in. diameter), (11) bath germanium resistor, (12) Stycast epoxy vacuum feedthrough, (13) niobiumtin-copper superconducting leads, (14) sQUID probe, (15) nitrogen-level resistor, (16) helium depth probe hole, (17) kovar electrical feedthrough for electrical leads, (19) aluminum shield for rf traps, (20) helium inlet port, (21) niobium leads.





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FIG. 4. View of sample mounted inside pressure cell: (1) Pressure vessel, (2) niobium-tin-copper ribbon, (3) germanium thermometers wrapped with enamel coated copper leads, (4) nylon sheath, (5) sample, (6) threaded nylon mandrel, (7) flexible copper connector (square), (8) copper disk (glued to mandrel), (9) rigid copper connector, (10) end of sample, mashed between the copper disk and connector, (11) capillary fill line $(\frac{1}{32}$ -in. o.d., 0.008-in. i.d.), (12) fill-line heater (wrapped noninductively so as not to couple magnetic flux into squp circuit), (13) flexible copper connector, (14) rigid copper connector.