THE INFLUENCE OF PHYSICAL STRAIN ON THE
PROPERTIES OF SUPERCONDUCTORS

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CHAPTER I

The Helium Liquefier

In order to provide liquid helium it was decided to construct a Kapitza-Collins type liquefier which would yield approximately $5\frac{1}{2}$ liters per hour. A discussion of the design, construction and operation of this liquefier follows.

The liquefier produces the necessary refrigeration by means of work performed adiabatically by the gas in a two-cylinder reciprocating engine, the energy being dissipated externally to the liquefier by a suitable dynamotor. The gas, which is cooled in the engines, is used to cool regeneratively the incoming gas by means of a counter-flow heat interchanger. A detailed discussion of this interchanger will appear later in this paper.

A gas-flow diagram of the liquefier is shown in Figure I. The helium gas of XX welding purity, supplied in cylinders by the Bureau of Mines, is allowed to flow at high pressure through a liquid nitrogen-cooled charcoal trap and thence into a low pressure storage tank

1. P. Kapitza, Nature 133, 7 (1934)
via a reducing valve. Using a pair of two-stage compressors the gas is then compressed to a working pressure of approximately 15 atmospheres. Between each stage of compression the gas is cooled to $10^\circ - 20^\circ C$ in water baths and also passes vertically through oil traps.

The gas is then further purified in the left-hand column of the liquefier which consists of a liquid nitrogen-cooled charcoal trap and a pre-cooler. This allows very pure helium gas to enter the main portion of the liquefier at $78^\circ K$. Figure V is a diagram of the flows inside the liquefier. The high pressure gas entering the right-hand column of the liquefier flows down a heat interchanger to the first engine where it divides, part of it going through the first charcoal pot and the first engine and part of it continuing down the interchanger to the second engine. That part which goes through the first engine is cooled by expansion and enters the low pressure side of the interchanger and flows upward to return to the gas holder. At the second engine the high pressure gas again divides, part going through the engine and part continuing on down the interchanger. The gas cooled in the second engine is also returned to the low pressure side of the interchanger. The final portion of
Figure I
Gas Flow Diagram of Helium Liquefier
the high pressure gas goes through a Linde heat interchanger and a Joule-Thompson valve into a vessel which collects the liquid helium. The flow is continuous and, since the heat exchange is regenerative, the gas at the top of the Linde interchanger eventually reaches a temperature of about 10 K and the Joule-Thompson effect then reduces the temperature to that of liquid helium.

Figure IX shows the liquefier, associated compressors and control panel. The right-hand column of the liquefier hangs inside a dewar the outside wall of which is an iron pipe 12 inches in diameter, 1/2 inch thick and 56 inches long. Its inner wall is 18 gauge monel with an inside diameter of 10 inches shown in Figure II. The iron pipe is lined with 18 gauge aluminum which has been highly polished to reduce radiation losses. Between the two walls, and thermally connected to the inner wall at the height of the first engine, is a liquid nitrogen-cooled radiation shield. This shield is made of .032 inch thick copper sheet formed into a cylinder and soldered along the seam. At the bottom of the shield, below the inner part of the dewar, is attached a brass cylindrical vessel one inch thick and having a capacity of a liter. Leading to and from this vessel in spirals tightly soldered to the shield are 1/4 inch copper tubes
through which liquid nitrogen may be forced. This insures a temperature of 78\textdegree K on the shield with the vessel at the bottom acting as a reservoir so that liquid nitrogen need not be added continuously.

The space between the walls of the dewar is pumped continuously by means of a D.P.I. MC 275.01 oil diffusion pump backed by a Welch Duo-seal pump, No. 1405. This maintains a vacuum of approximately $10^{-6}$ millimeters of mercury.

One of the most essential parts of the liquefier proved to be the main heat interchanger in the right-hand column, as shown in Figure I. Our specific requirements demanded a heat interchanger with maximum dimensions of 36 inches in length by 5 inches in width to operate between temperatures of 80\textdegree K and 8\textdegree K with gas flows up to 30 cubic feet per minute and an over-all efficiency of greater than 98 per cent. In this interchanger heat is transferred between the high pressure and low pressure streams of gas. A measure of the heat transfer in terms of experimentally observed quantities is given by the equation

$$U L = \frac{m_0 c_0 m_i c_i}{m_i c_i - m_o c_o} \ln \frac{\Delta c}{\Delta h} = \frac{m_0 c_0 m_i c_i}{m_i c_i - m_o c_o} \ln \frac{m_i c_i - E m_o c_o}{(1 - E) m_i c_i}$$  \hspace{1cm} (1)
Figure II
Diagram of Main Dewar of Helium Liquefier
where

\[ U = \text{heat transfer coefficient (joules/mole}^\circ\text{C cm)} \]

\[ L = \text{heat interchanger length in centimeters} \]

\[ m_0 = \text{moles per second of outgoing gas} \]

\[ m_i = \text{moles per second of incoming gas} \]

\[ C_0 = \text{molar specific heat at constant pressure} \]

\[ C_i = \text{molar specific heat at constant pressure} \]

\[ E = \text{efficiency} = \frac{\Theta - \Delta \Theta}{\Theta} \quad (2) \]

\( \Theta \) and \( \Delta \Theta \) are shown in Figure III.

The total heat transfer is given by

\[ m_0 C_0 (\Theta - \Delta \Theta) = m_i C_i (\Theta - \Delta \Theta) \quad (3) \]

for a heat interchanger which does not absorb energy from other sources.

\( U \), the heat transfer coefficient, may be computed from empirical formulae based on experimental observations\(^3\). Thus

\[ \frac{1}{U} = \frac{1}{H_i} + \frac{1}{H_k} + \frac{1}{H_o} \quad (4) \]

where \( H_i \) is the heat transfer between the incoming gas

---

Figure III
Schematic Diagram of a Heat Interchanger
Figure III

Diagrammatic Heat Interchanger

- H.P. IN
- L.P. OUT
- T_{11}
- T_{12}
- T_{21}
- T_{22}

Relative Temperature Scale

ΔH → ΔC
and the wall, $H_0$, the heat transfer between the outgoing gas and the wall and $k/t$ the heat transfer through the wall. Due to the high thermal conductivity of the wall this latter term may be neglected. $H_1$, $H_0$ and the pressure drops are given by

$$H = 0.15 C \eta^{0.25} (M \rho / d)^{0.75} \text{ joules/sec cm}^2 \text{ per} \text{ K}$$

and

$$\delta P = 0.0277 \eta^{0.25} M^{0.75} \rho^{0.75} / \rho \text{ dynes/cm}^2$$

where

- $d$ = tube diameter in centimeters
- $C$ = specific heat in joules/gram K
- $m$ = moles/sec
- $M$ = molecular weight of the gas
- $P$ = pressure in atmospheres
- $\eta$ = viscosity in poise

An estimate of the heat transfer, $U_L$, may be obtained from the required heat interchanger efficiency and the gas flows. The simultaneous requirements of dimensions, pressure drops and turbulent flow to insure maximum heat transfer place stringent requirements upon the tube diameter "$d$." In the high pressure flows these requirements are easily met by merely using 1/4 inch tubing, but the low pressure flows required some 2,000 tubes of approximately 0.010 inch diameter. This was accomplished
by threading 1/4x0.030 inch copper tubing to a depth of 0.015 inch with a 1/4x28 die. When the threaded tube was wound in two layers on a 4 inch monel tube, each inch of high pressure channel provided 56 low pressure channels, the high pressure and low pressure flows being perpendicular to each other. Thus there are approximately 1600 low pressure channels for the return flow. Figure IV shows the general construction of this interchanger. Twine was put between windings to help insure turbulent flow. The brass shim stock fitted tightly against the threads and the cotton cloth between the second brass shim stock and the outer monel cover are used to prevent the low pressure flow from short circuiting part of the interchanger.

The interchanger was constructed in four parts: A, before the first engine; B, across the first engine; C, between the two engines; and D, across the second engine. See Figure V. The Dimensions and performances of each section are given in Table I and in Figure V.
Figure IV

Detail of Heat Interchanger
Figure V
Performance and Flow Diagram of Heat Interchanger
FIGURE V
Figure VI is two views of the completed unit as it appears in the liquefier.

During the construction of the liquefier the helium transfer tube was originally inserted into the helium collection pot through a 5/8 inch inconel tube. This tube, which was rigidly soldered to the helium pot and the top of the liquefier, merely acted as a sheath. The space at the top between the sheath and the transfer tube was closed by means of a piece of rubber tubing spanning the opening, as shown in A, Figure VII. Under this arrangement it was impossible to liquefy due to the heat leak down the sheath and the transfer tube caused by spontaneous vibrations in the column of helium gas extending from the helium pot up to the top, which was at

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room temperature. In order to stop this heat leak, the transfer tube was installed directly into the helium pot and a valve inserted in the tube immediately above the pot, as in B, Figure VII. This eliminated the enclosed column of helium gas and removed a heat leak.

There are three variables which may be adjusted during the operation of the liquefier: (1) the pressure of the incoming gas, (2) the relative period of the opened and closed phases of the intake valves of both engines, and (3) the Joule-Thompson valve.

Automatic control mechanisms and safety devices connected to the liquefier are as follows:

(1) A limit switch which turns off the compressors if the gas in the storage tank gets low

(2) A temperature control to turn off the compressors if the interstage water cooler gets too warm

(3) A speed control on the dynamotor which also turns off the compressors if the speed of the engines exceeds 500 rpm

(4) A pressure control to turn off the compressors if the pressure inside the dewar reaches 8 pounds per square inch.

(5) A 1/2 inch safety valve on the high pressure line which releases if the pressure reaches 275 pounds per
Figure VI

Two Views of Completed Heat Interchanger and Associated Engines
Figure VII
Two Diagrams of Transfer Tube
square inch.

The diffusion pump on the main dewar is protected by two methods: (1) a thermal switch turns the pump off if the cooling water is not flowing and the pump gets hot, and (2) a relay, connected to a D.P.I. vacuum gauge, turns off the diffusion pump if the pressure exceeds the limit of the range of the gauge.

Before operating the liquefier it is necessary to purge the system of all contaminations, including water vapor and other gases. The first step is to isolate the two charcoal traps (see Figure I) by means of the appropriate valves. The traps are then pumped out while they are gently heated. Then all the helium gas in the storage tank is released. After liquid nitrogen has been put on the first charcoal trap, clean helium is allowed to enter the storage tank. The compressors are started and this gas is circulated through the compressor system but not through the liquefier. At this time the oil collected in the oil traps is blown off, the remainder of the helium gas is released to the atmosphere, and fresh gas is again put into the gas holder.

The second step in the pre-operative cleaning process is to pump out the liquefier and flush with clean helium. The low pressure side of the liquefier system
is pumped through the helium transfer tube and the high pressure side through the blow-off line on the second engine charcoal trap. This is done with the Joule-Thompson valve open. Then clean gas is allowed to enter from the gas holder through the low pressure line. This is repeated five or six times with an occasional turning over of the engines in order to clean out the cylinders. Lastly, the trap and pre-cooler in the left-hand column are covered with liquid nitrogen. The liquefier is now ready for operation.

In order to observe the temperature at various points in the liquefier, seven copper-constantin thermocouples are attached at the points indicated in Figure VIII: (1) the inlet to the first engine, (2) the exhaust of the second engine, (3) the inlet of the second engine, (4) the helium pot, (5) the exhaust of the first engine, (6) the input to the liquefier and (7) the outlet of the liquefier. In addition to the thermocouples, two gas thermometers were employed; one on the helium pot and the other on the low pressure side of the Joule-Thompson valve.

In order to cool the entire liquefier down to liquid nitrogen temperature quickly helium gas, which has been pre-cooled in the left-hand column, is allowed to enter the interchanger at 180 pounds per square inch pressure,
Figure VIII
Diagram of Liquefier Showing Positions of Thermocouples and Gas Thermometers
Figure VIII
is blown down through the high pressure side, and is by-passed through the second engine charcoal trap blow-off tube and the helium transfer tube directly back to the low pressure side of the compressors. This continues without the engines running until thermocouple No. 3 indicates approximately $110^\circ K$. Then the by-pass through the charcoal trap is closed, the engines are started by means of the dynamotor and 3.5 cubic feet of gas per minute is still allowed to by-pass through the transfer tube. This quantity is adjusted by means of the Joule-Thompson valve. The input pressure is kept at 110 pounds per square inch.

When thermocouple No. 2 indicates the lowest temperature in the system, the Joule-Thompson valve is closed completely, but the transfer tube valve is kept open so that 3.5 cubic feet of gas per minute continues to flow through it. This process cools the helium pot by forcing the cold, low pressure gas from the second engine down through the low pressure side of the Linde heat interchanger and out the transfer tube. Except for conduction this is the only method to cool the helium pot before the Joule-Thompson valve reaches the inversion temperature. When the temperature at the helium pot reaches about $30^\circ K$ the input pressure will fall to ap-
proximately 160 pounds per square inch. At this time the engines are stopped and the inlet cams set to a minimum time opening. This prevents the engines from taking too large a portion of the gas and greatly reducing the pressure at the Joule-Thompson valve.

On restarting, the by-pass flow is again adjusted to 3 cubic feet per minute by means of the transfer tube valve. When the helium pot reaches a temperature of $20^\circ$K, as indicated by its gas thermometer, the inside of the dewar is evacuated. When the gas thermometer on the Joule-Thompson valve indicates $10^\circ$K, the valve is opened very slightly keeping the pressure at the valve up to 130 pounds per square inch. The transfer tube by-pass should be readjusted to about $1/2$ cubic foot per minute and completely closed when the Joule-Thompson thermometer indicates liquefaction has begun. For best liquefaction rate the valve pressure should be 90 pounds per square inch, the flow 23 - 25 cubic feet per minute and the pressure in the helium pot 3.5 pounds per square inch. The liquefaction rate can be observed by timing the rate at which the gas storage tank falls.

After 125 cubic feet of gas has been liquefied (approximately 5 liters), the compressor is turned off, the dynamotor stopped, the Joule-Thompson valve closed,
the high pressure input and the low pressure return valves closed, and the transfer tube valve opened. Then, if a pressure of 1.5 - 2 pounds per square inch is maintained in the helium pot by means of the input valve, the liquid helium will be blown through the transfer tube into a dewar.
Figure IX
View of Liquefier, Associated Compressors and Control Panel
CHAPTER II

Magnetic Cooling

In 1926 Giauque and Debye independently suggested the adiabatic demagnetization of a paramagnetic salt as a method for easily obtaining temperatures below 1°K. This method is analogous to the process of compressing a gas isothermally then allowing it to expand adiabatically with a resultant drop in temperature. Thermodynamic considerations of a magnetic material follow.

The first law of thermodynamics for a magnetic sample subjected to a magnetic field is

\[ \text{d}Q = \text{d}U - H \text{d}M \]

(7)

where \( \text{d}Q \) is the heat added to the sample, \( \text{d}U \) the change in its internal energy, \( H \text{d}M \) the work done by the source of the field, \( H \) the applied field, and \( M \) the magnetic moment of the sample. During a reversible process,

\[ \text{d}Q = T \text{d}S = \text{d}U - H \text{d}M \]

(8)

where \( \text{d}S \) is the change in entropy. Then using Maxwell’s relation from the enthalpy function \( H = U + MH \), and taking \( T \) and \( H \) as the independent thermodynamic

5. J. Giauque, Am. Chem. Soc. 49, 1864 (1927)
variables, one may write
\[
\left( \frac{\partial U}{\partial H} \right)_T = T \left( \frac{\partial M}{\partial T} \right)_H + H \left( \frac{\partial M}{\partial H} \right)_T \tag{9}
\]
Thus the second law may be written in the form
\[
T dS = \left[ \left( \frac{\partial U}{\partial T} \right)_H - H \left( \frac{\partial M}{\partial T} \right)_H \right] dT + T \left( \frac{\partial M}{\partial T} \right)_H dH \tag{10}
\]
In equation (10) \( \frac{\partial U}{\partial T} \left( \frac{\partial M}{\partial T} \right)_H \) is the specific heat in constant magnetic field and is positive. For an isentropic process, i.e. \( dS = 0 \),
\[
\left[ \left( \frac{\partial U}{\partial T} \right)_H - H \left( \frac{\partial M}{\partial T} \right)_H \right] dT = -T \left( \frac{\partial M}{\partial T} \right)_H dH \tag{11}
\]
Now if \( \frac{\partial M}{\partial T} \left( \frac{\partial M}{\partial T} \right)_H \) is negative, an adiabatic decrease in field results in a decrease in temperature. This is the first requirement for a material which is to be used as the working substance in a magnetic cooling cycle.

Consider a system of \( N \) ions in a magnetic field. Assume no interaction between ions and no effect on the ions due to a crystalline field. Then if \( \mu_i \) is the magnetic moment of the \( i \)th ion and \( H_i \) is the magnetic field acting on that ion, the Hamiltonian for the system is
\[
\mathcal{H} = \sum \mu_i \cdot H_i \tag{12}
\]
If the total angular momentum of the ion is \( J \), then
\[
\mu = gJ\beta \quad \text{where } g \text{ is the Lande } "g" \text{ factor and } \beta \text{ is the Bohr magneton.}
\]
Then in a magnetic field the magnetic quantum number \( m \) is quantized to the values
\(-J, -J+1, \ldots, J\) parallel to the field and the separation between energy levels is \(-mg\beta H\). Assuming a Boltzmann distribution, the partition function can be written as

\[
Z = \sum_{-J}^{J} \exp \left(-\frac{mg\beta H}{kT} \right) \tag{13}
\]

The magnetic moment for the system of ions is

\[
M = \frac{N \sum_{-J}^{J} g m \beta \exp \left(-\frac{mg\beta H}{kT} \right)}{\sum_{-J}^{J} \exp \left(-\frac{mg\beta H}{kT} \right)} = NkT \frac{\partial}{\partial H} \left( \frac{1}{2} \right) \tag{14}
\]

If the ion is in the S state, or if the orbital momentum has been quenched, then \(J = s\), \(g = 2\) and the system is one of spins only. Then equations (13) and (14) become

\[
Z = \sum_{-a}^{a} \exp \left(-2m\beta H/kT \right) \tag{13a}
\]

and

\[
M = \frac{N \sum_{-a}^{a} m \beta \exp \left(-2m\beta H/kT \right)}{\sum_{-a}^{a} \exp \left(-2m\beta H/kT \right)} = NkT \frac{\partial}{\partial H} \left( \frac{1}{2} \right) \tag{14a}
\]

Thus for a spin system

\[
\frac{M}{R} = \frac{1}{k} \left[ (a+1) \text{coth}(a+1)y - \text{coth} y \right] = \frac{1}{k} B(a) \tag{15}
\]

where \(y = \frac{\beta H}{kT}\) and \(B(s)\) is the Brillouin function.

For small values of \(y\), i.e. \(\beta H \ll kT\), equation (15) reduces to

\[
\frac{M}{R} = \frac{y}{3} \frac{1}{k} a(a+1)y = \frac{CH}{RT} \tag{16}
\]

which is Curie's law for a paramagnetic material.
The entropy is given by \( ^7 \)
\[
S = R \frac{\partial}{\partial T}(T \ln Z) \tag{17}
\]
or
\[
\frac{S}{R} = y \coth y - (2a+1) y \coth (2a+1) y \]
\[
- \ln \sinh (2a+1) y - \ln \sinh y \tag{18}
\]

If \( y = 0 \), i.e. \( H = 0 \)
\[
\frac{S}{R} = \ln (2a+1), \tag{19}
\]
and for small values of \( y \)
\[
\frac{S}{R} = \ln (2a+1) - \frac{2}{3} a(a+1) y^2, \tag{20}
\]
or
\[
S = S_0 - \frac{1}{2} C \frac{H^2}{T^2} \tag{21}
\]
where
\[
C = \frac{y}{3} \frac{e^{2/\beta}}{k} a(a+1) R \tag{22}
\]
is the Curie constant from equation (16).

If a paramagnetic sample is magnetized isothermally to a field \( H \) at a temperature \( T_i \), the entropy change is
\[
S(H, T_i) - S(0, T_i) = \int_0^H \frac{\partial M}{\partial T} dT \tag{23}
\]

Now, if the sample is demagnetized adiabatically to a final temperature \( T_f \),
\[
S(H, T_i) - S(0, T_f) = 0 \tag{24}
\]

where $C_0$ is the specific heat in zero field. Thus from equations (23), (24) and (25)

$$S(0, T_f) - S(0, T_c) = \int_{T_f}^{T_c} \frac{C_0}{T} dT \quad (25)$$

Since the specific heat is given by 8

$$C = R \frac{d}{dT} \left[ T^2 \frac{d}{dT} (ln \frac{Z}{\beta}) \right] \quad (27)$$

the above ideal case has zero entropy in zero field which implies the attainment of the absolute zero of temperature by adiabatic demagnetization from an infinitely small field.

At low temperatures deviations from Curie's law occur due to magnetic interactions between the ions and the interaction of the crystalline field with the ions. The crystalline field removes part of the degeneracy of the lowest level and when $kT$ is of the order of this splitting, an anomaly in the magnetic behavior of the sample occurs which is similar to the Schotky specific heat anomaly. The choice of a suitable salt for a magnetic cooling process requires that it obey Curie's law at the higher temperature and have its magnetic

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8. Ibid.
anomaly at a very low temperature. The ground state of the chromium ion \( \text{Cr}^{+*+} \) in potassium chrome alum, \( \text{K Cr(SO}_4\) \cdot 12 \text{H}_2\text{O} \), is \( 4F_{3/2} \) but the orbital angular momentum is quenched\(^9\) and the spins free. The crystalline field acts on the spins only through the spin-orbit coupling\(^{10}\). The lowest state of the \( \text{Cr}^{+*+} \) ion is four-fold degenerate in a cubic field, but in addition to the cubic field there also exists a small trigonal field which reduces the four-fold degeneracy to two two-fold states. According to Kramers\(^{11}\) no further splitting due to the crystalline field is possible. This separates the lowest level into two levels with moments \( \pm 3/2 \) and \( \pm 1/2 \) with the \( +3/2 \) state lying lower. If \( \delta \) represents the energy difference between the two levels, the partition function per ion is 

\[
Z = 2 \left[ 1 + \exp\left( -\frac{\delta}{kT} \right) \right]
\] (28)

Hebb and Purcell\(^{12}\) deduce a specific heat of the form 

\[
\frac{C_0}{R} = \frac{a}{T^2} = \left( 2.40 \frac{T^2}{\gamma} + \frac{1}{\gamma} \frac{T}{\delta^2} \right) / T^2
\] (29)

where the first term on the right side of the equation

---

is due to the magnetic interactions of the ions and the second term is due to the crystalline field. The experimental values of $\tilde{\tau}$ and $\delta$ from Hebb and Purcell\textsuperscript{13} and Bleaney\textsuperscript{14} are

$$
\tilde{\tau} = 0.0204^\circ K \quad \text{and} \quad \delta = 0.245^\circ K.
$$

Figure X shows the variation of entropy at various magnetic fields for potassium chrome alum. A cooling cycle is indicated by the line ABC. If the salt is magnetized isothermally at a temperature of $1.3^\circ K$ to a field of 10,000 gauss, the entropy reduction is indicated by AB; then an adiabatic demagnetization to zero field, BC, indicates a final temperature of about $0.10^\circ K$.

\textsuperscript{13} Ibid.
Figure X
Variation of Entropy with Temperature at Various Magnetic Fields for Chromium Potassium Alum
$\text{Figure X}$

$\ln 4 - S_R$

$T$

$0.0$ $0.5$ $1.0$

$H = 10000$ gauss

$H = 5000$ gauss

$H = 8000$ gauss
CHAPTER III

Apparatus

The Cryostat

Figure XI shows the cryostat used in the magnetic cooling process. The various parts are as follows:

$C_1$ - Filler tube through which the inner dewar is filled with liquid helium

$C_2$ - 5/8 inch inconel tube through which the sample chamber is evacuated by a VMF 20 diffusion pump

$C_3$ - 1/4 inch inconel tube which connects to a manometer system to measure the vapor pressure of the helium bath

$C_4$ - Stupacoff seal through which enter the electrical leads to the measuring coil

$C_5$ - Stopcock between sample chamber and helium pumping line

$C_6$ - 2 inch copper line leading to a Welch pump No. 1397 which is used to reduce the vapor pressure over the helium bath

$C_7$ - Stopcock through which vacuum space of the helium dewar may be flushed with air and pumped out between experiments

$C_8$ - Vacuum space of helium dewar

$C_9$ - Vacuum space of nitrogen dewar

$C_{10}$ - Main sample chamber (brass)

$C_{11}$ - 5/8 inch brass tube with .020 inch wall

$C_{12}$ - Measuring coil

$C_{13}$ - Mica spacers

$C_{14}$ - Potassium chrome alum ellipsoid
Figure XI
Diagram of Cryostat
Figure XI shows the cryostat and magnet. The magnet is the Weiss type with a rectangularly-shaped cast iron yoke the short sides of which are perpendicular to the core. The yoke is 2\(\frac{1}{8}\) inches thick by 8\(\frac{1}{2}\) inches wide. The short sides of the rectangle are 36 inches long and the long sides, parallel to the core, are 54 inches long. Along the horizontal median of the yoke are solid cylindrical armatures of Armco iron 6 inches in diameter. The inner caps on the armatures are tapered to 2 inch pole faces. These tapered ends are screwed into the armatures by a threaded screw 4 inches long which is part of the cap. The gap between the pole pieces is regulated by moving the armatures horizontally by means of heavy screws on their yoke ends.

The windings about each armature, insulated by two layers of friction tape, are divided into 10 sections, each having 147 turns of 5/16 inch copper tubing. The sections are connected in series electrically but in parallel hydraulically for the cooling water. Insulating fiber separates the coils from the armatures and brass end plates, which constitute the spool on which
the coils are wound.

Current is supplied to the coils by a 15 KW motor-generator which operates from a 440 volt a.c. line. The total resistance of the magnet circuit is about 1.5 ohms. The coils are cooled by a flow of water which is supplied by a special 3 inch pipe and is fed to the magnet through a heavy rubber hose. A similar rubber hose carries the waste water to the sewer. At the head of the sewer pipe is a visible flapper valve which permits one to see if the water is flowing.

During a cooling cycle the following steps are employed: With the valve on the VMF 20 diffusion pump closed helium gas is allowed to flow through the stop-cock $C_5$ into the sample chamber until a pressure of about 25 microns is reached. Then $C_5$ is closed and the cryostat placed so that the sample is between the poles of the magnet. The magnet is turned on and the heat of magnetization is carried by the exchange gas to the helium bath. The helium bath is kept at 1.3°C by reducing the vapor pressure with the Welch pump No. 1397. When equilibrium has been reached, the valve on the VMF 20 pump is opened and the pressure in the sample chamber reduced to about $10^{-5}$ millimeters of mercury. Then the magnet is turned off and the cryostat removed from be-
Figure XII

View of Cryostat and Magnet
tween its poles. At this time the temperature of the sample has been reduced according to Figure X.

The number and disposition of radiation shields indicated as C_{16} of Figure XI is critical in determining the warm-up time. As shown, only one copper radiation shield, fitted at the bottom of C_{2}, was used during most of the experiments. Under this arrangement the heat leak to the sample was about 750 ergs per minute, which resulted in a convenient warm-up time of the order of an hour. When an experiment was attempted with no radiation shields in the tube above the sample, it was found that the heat leak was 18,000 ergs per minute. This influx was so great it was impossible to observe the warm-up. Within a few minutes after demagnetization the sample was found to be at a temperature well above that of the helium bath. In one particular case the temperature of the sample changed from 0.2 K to 7.5 K within thirty minutes.

If much greater thermal isolation is desired, a system of radiation shields, as shown in Figure XIII, may be used. Using this shield it was found that the heat leak was reduced to 150 ergs per minute and a warm-up time of about five hours. For the particular problem being investigated an extremely long warm-up proved disadvantage-
Figure XIII

Diagram of Radiation Shield
FIGURE XDL
Temperature Measurement

Temperature measurements were made by the ballistic mutual inductance method. A diagram of the circuit is shown in Figure XIV. The sample is hung inside one-half of a secondary. The other half is wound in series opposition and acts as a compensator. Each half contains 8,000 turns of No. 44 copper wire. The primary is one layer of No. 44 copper wire containing 180 turns per centimeter. The coils are fitted around the sample chamber inside the helium bath. See Figure XI. M consists of two mutual inductors, a Leeds and Northrup, No. 722480, millihenry and a General Radio Company, type 107K, microhenry, which are used to balance any inequalities in the two halves of the secondary. S is a 3,000 ohm Ayrton universal shunt, G a Leeds and Northrup galvanometer, Model No. 2284, with a sensitivity of 0.050 microvolts per millimeter, C.D.R.X. of 8 ohms, and a period of 6.2 seconds, R is a decade resistance used to control the primary current, and A is a Weston Electric millammeter, model No. 931. The source of current is two 6 volt storage batteries.

Figure XIV

Diagram of Temperature Measuring Circuit
Calibration was achieved by observing the deflection of the galvanometer as a function of the temperature when a small current was sent through the primary. The temperature was taken from the 1949 vapor pressure table. The mutual inductance $M$ was adjusted so that the deflection was zero at 4.2°K. The galvanometer deflections resulting, as the temperature was reduced, were plotted as a function of $1/T$. From this curve an equation relating the temperature and the deflections was written. The curve was then extrapolated to include the magnetic temperatures $T^*$, obtained after demagnetization. The shape of the sample was also considered, giving a temperature correction

$$\Delta = c f \left( \frac{n^{1/3}}{3} - N \right) = T^*_S - T^*$$

where $c$ is the Curie constant per cubic centimeter, $f$ is the filling factor, namely the ratio of the density of the compressed salt to the crystalline density, and $N$ is the demagnetization factor for the shape of the sample.

is then used to calculate $T^*_S$, the extrapolated Curie temperature based on a spherical specimen. The work of Cooke shows that the difference between $T^*_S$ and the absolute temperature at 0.2°K is of the order of 0.015°.

Since the specific heat of potassium chrome alum

17. N. Kurti and F. Simon, Phil. Mag., 26, 549 (1938).
is rather large, $c_0 = aR/T^2$, at low temperatures, it may be used as a refrigerant to cool other materials. The electronic specific heat of a metal is of the order of $10^{-4}T$ calories per mole, and the lattice specific heat is negligible at these temperatures. Taking the above data and the value of "a" from equation (29), it can be shown that 0.5 grams of the salt in warming up from 0.2°K to 0.3°K will cool approximately a mole of metal from 1.3°K down to 0.3°K.

**Preparation of Samples**

In order to study some properties of superconductors at low temperatures, it was necessary to imbed a piece of the metal in question inside a pill of powdered potassium chrome alum and cool it by demagnetization. The sample was constructed by placing the powdered salt and the metal inside a mold and then compressing the two together. The mold consisted of a split, rectangularly-shaped solid 4 inches long with a 3 inch square cross section and a 1 inch cylindrical cavity. During a pressing the mold was held together with four bolts. Inside the cavity was fitted a split cylinder with a 1 centimeter inside diameter. This in turn was lined with .001 inch steel shim stock which prevented the resulting sample
from sticking to the mold. Into one end of the mold was inserted a steel piston 1 inch long. On top of this was poured about 3 grams of the powdered salt, then the piece of metal to be tested, and, finally, 3 more grams of the salt. On top of the salt was inserted a steel cylinder three inches long which was forced in with a hydraulic press to a pressure of about 5,000 pounds per square inch. This pressure produced a hard cylinder of salt with a density about 0.90 that of the crystal and insured good thermal contact between the metal and the salt. The resulting cylinder was chucked in the lathe and shaped to an ellipsoid.
CHAPTER IV

Procedure and Results

If, for superconductors, the transition from a superconducting state to a normal state is considered as a phase transition, then some conclusions can be drawn from a thermodynamic treatment of the phenomenon. If, from the results of Meissner and Ochsenfeld, the magnetic induction B must always be zero inside a superconductor, then the volume susceptibility is \(-4\pi/3\).

Since the paramagnetic susceptibility of the potassium chrome alum, as indicated by the deflections of a galvanometer, is used to observe the temperature, a superconductor with its negative susceptibility will reduce the deflections. When a temperature is reached such that the superconductor makes a transition to the normal state, this diamagnetism disappears and an apparent increase in the paramagnetic susceptibility, as evidenced by the increased deflections, is observed. A warm-up curve of this type is shown in Figure XV. Curve A is a warm-up in zero magnetic field while B is in a small field. The points a and b are used to determine the transition temperatures for the two cases.

Figure XV

Warm-up Curves Showing Superconducting Transitions
The magnetic threshold field curves for some superconductors are shown in Figures XVI and XVII. To the left and below the curves the metal is in the super state and to the right and above, in the normal state. If the transition is reversible, we may write a Gibbs free energy function for each of the two phases which can exist in equilibrium

\[ G_n = G_s + \frac{VH^2}{g\pi} \]  

where \( n \) refers to the normal state and \( s \) to the super state and \( V \) is the atomic volume. Gorter and Casimir\(^{22}\) show that these results are general for any shaped specimen. Rewriting equation 31

\[ \Delta G = G_n - G_s = \frac{VH^2}{g\pi} \]  

Then

\[ \Delta S = S_n - S_s = -\frac{\partial(\Delta G)}{\partial T} = -\frac{VH}{4\pi} \frac{\partial\bar{H}}{\partial T} \]  

Since \( \frac{\partial\bar{H}}{\partial T} \) is always negative, we see that the entropy of the super state is less than the entropy of the normal state.

The difference in specific heats of the two phases is obtained by differentiating equation (33),

\[ \Delta C = C_n - C_s = T \frac{\partial(\Delta S)}{\partial T} = -\frac{VT}{4\pi} \left[ \left( \frac{\partial H}{\partial T} \right)^2 + H \frac{\partial^2 H}{\partial T^2} \right] \]  

22. See reference 19.
From a plot of $\Delta S$ as a function of temperature it is possible to determine the specific heat of the normal electrons as suggested by Daunt and Mendelssohn. At sufficiently low temperatures $\Delta S$ will be proportional to $T$. If, as according to Sommerfeld, the specific heat of the normal electron gas is given by $C_n = \frac{1}{2}T$, and if a threshold field of the form

$$H = H_0 \left[1 - \left(\frac{T}{T_c}\right)^2\right]$$

is assumed, then

$$\mathcal{J} = \left[\frac{\partial (\Delta S)}{\partial T}\right]_{T=0} = \frac{\sqrt{H_0^2 - \frac{1}{2}H_c^2}}{2\pi T_c^2} = \frac{1}{8\pi} \left(\frac{\partial H}{\partial T}\right)_{T=T_c}$$

Results

Cadmium

The cadmium used was from a bar supplied by Johnson, Matthey Laboratory, No. 2572, catalog No. 170, having a purity greater than 99.99%. The specimen, shaped to an ellipsoid, was pressed to a pressure of 5,000 pounds per square inch inside another ellipsoid of chrome potassium alum. The sample was hung inside the cryostat and cooled to temperature of about 0.2º by the magnetic method described in Chapter III. Observations were made at regul-

lar time intervals as the sample warmed up. After the transition in zero magnetic field was obtained, the procedure was repeated allowing the warm-up to occur in various applied fields. The field was produced by a solenoid fitted around the outside of the dewar. Current for the solenoid was provided by two storage batteries. Using a Grassot flux meter, No. 0-193311, and a Weston Ammeter, model 430 No. 1167, the magnetic field was determined to an accuracy of 1%.

A magnetic threshold curve was obtained after the sample had been annealed in vacuo at 150°C for 1.5 hours. The results are shown in Table II and Figure XVI. Curve 25 was obtained from an unannealed sample of purity 26 99.5%, curve B is the Goodman and Mendoza results from an annealed sample, of estimated purity 99.996%, obtained from the New Jersey Zinc Company and curve C is the present results.

The present results are of order 5 gauss higher than the results of Goodman and Mendoza. This may be due to physical strains introduced in the sample as it was pressed into the salt pill, whereas their method avoided this possibility. Daunt's results from an unannealed

Figure XVI

Threshold Field Curves for Cadmium
sample show a transition temperature in zero field which agrees exactly with Kurti and Simon\textsuperscript{27}, but a plot of $H$ versus $T^*$ shows the transition curve not parabolic. Physical strains and impurities may possibly be responsible for this difference.

\textbf{Table II}

\textbf{Data for Magnetic Threshold Curves for Cadmium}

\begin{center}
\begin{tabular}{|c|c|c|c|}
\hline
 & Unannealed\textsuperscript{28} & Annealed \\
\hline
Axes of Cd. & 19x6 mm. & \\
Axes of Alum & 36x13 mm. & \\
$\theta$ & 0.81 & \\
$\Delta$ & 0.022° & \\
\hline
$H$ (gauss) & $T^*$ & $H$ (gauss) & $T^*$ \\
\hline
0 & .542 & 0 & .602 \\
7.95 & .440 & 6.03 & .560 \\
10.1 & .412 & 9.95 & .502 \\
10.3 & .413 & 11.0 & .490 \\
10.8 & .402 & 16.5 & .428 \\
21.4 & .279 & 16.7 & .408 \\
23.4 & .244 & 22.0 & .359 \\
23.6 & .243 & 23.1 & .326 \\
27.5 & & 27.5 & .264 \\
\hline
\end{tabular}
\end{center}

Curve C fits the equation

\[ H = H_0 \left[ 1 - \left( \frac{T}{T_c} \right)^2 \right] \quad (37) \]

with $H_0 = 35.8$ gauss and $T_c = 0.602^\circ$. (See Figure XVIII.)


\textsuperscript{28} See reference \textsuperscript{25}.
Goodman and Mendoza's results are also parabolic with $H_0 = 28.8$ gauss and $T_c = 0.560^\circ$. Kurti and Simon reported a transition temperature in zero field of $0.54^\circ$ and an initial slope of the transition curve approximately 100 gauss per degree.

The entropy differences between the normal and superconducting states, calculated from equation (33), are shown in Figure XIX. From equation (36) the value of $\gamma$ is $1.54 \times 10^{-4}$ calories per mole per degree squared. This value is compared with $1.28 \times 10^{-4}$ calories per mole per degree squared obtained by Goodman and Mendoza.

Zirconium

A piece of zirconium, in crystal bar form of purity greater than 99.8%, containing 0.04% hafnium by weight, loaned to us by the Oak Ridge National Laboratory, was investigated in the manner described above. First, a transition curve was obtained for the metal as it was received (the metal was refined by deposition from the iodide), and, secondly, it was annealed in vacuo at $800^\circ$C for $2^{1/2}$ hours and then reexamined. The results are shown in Table III and Figure XVII.
Table III
Data for Magnetic Threshold Curves for Zirconium

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<thead>
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<th>H(gauss)</th>
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<tr>
<td>146</td>
<td>.224</td>
<td>33.0</td>
<td>.314</td>
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</tbody>
</table>

Before annealing, the transition curve is not a parabola, but after annealing, it is of the form of equation (37) with \( H_c = 46.6 \) gauss and \( T_c = 0.546^\circ \). (See Figure XVIII).

From equation (36) the value of \( \tau \) is \( 3.92 \times 10^{-4} \) calories per mole per degree squared. This value is compared with the value \( 6.92 \times 10^{-4} \) calories per mole per degree squared obtained by Estermann and Friedborg by calorimetric methods on an unannealed sample.

29. Ibid.
Figure XVII

Threshold Field Curves for Zirconium
Figure XVII
Figure XVIII
Variation of H with \((T_\theta)^2\) for Cadmium and Zirconium
Figure XIX

Curves of Entropy Difference between the Super and Normal States of Cadmium and Zirconium
Kurti and Simon reported a transition temperature in zero field of 0.70° and an initial slope of 400 gauss per degree. The present results show zirconium to have an initial slope of 170 gauss per degree and suggest that the transition curve obtained after annealing to be an approach to a reversible transition.

The value of \( g/V \) is \( 2.76 \times 10^{-5} \) calories per cubic centimeter per degree squared and falls rather near the "hard" superconductor curve as suggested by Daunt.  
(See Figure XXIV).

Titanium

An attempt was made to anneal in vacuo at 800° C for 2.5 hours the same sample of titanium, of purity 99.95%, obtained from the Batelle Memorial Institute, used by Daunt and Heer. The transition temperature in zero field was found to be 0.558° with an initial slope of the transition curve equal to 450 gauss per degree. This is comparable to their results of 0.53° and 470 gauss per degree.

Hafnium

Four series of measurements to obtain a transition

were made on three different samples of hafnium. The first specimen was 2.229 grams in a regular shape, 4.2x5.6x8.4 millimeters, obtained from the Materials Laboratory of the Isotope Research and Production Division, Y-12 Plant, at the Oak Ridge National Laboratory. This sample, containing 3 to 4% by weight of zirconium, was tested as it was received and also after having been annealed in vacuo at 825°C for 3 hours.

The second specimen consisted of 3 and a half grams of shavings, each approximately 0.3x0.5x2-15 millimeters, from a crystal bar containing 5.3% by weight of zirconium. These shavings were annealed in vacuo at 750°C for one hour.

The last sample consisted of a bar 0.34 centimeters in diameter by 5.05 centimeters long weighing 6.2 grams. This specimen, designated as "783" of purity 99.042%, was loaned to us by the Air Force at Wright-Patterson Field. It also was annealed in vacuo at 800°C for 2 hours.

In each case the metal was pressed at 5,000 pounds per square inch into a pill of about 5 grams of potassium chrome alum. The specimen was cooled to 0.2°C by the magnetic method and allowed to warm up as its suscepti-

bility was observed. In no case was a definite transition found, although Kurti and Simon reported a transition in zero field at 0.35°.

Subsequent tests on the hardness of the first sample of hafnium indicate that it had never been annealed. These tests show a hardness of 31 on the Rockwell C scale. According to Litton, hafnium recrystallizes at 800°C and, thereafter, has a hardness of 88 on the Rockwell B scale. Since all our annealing was done in the same vacuum furnace and the temperature observed by an optical pyrometer, it seems that the hafnium and titanium, which anneal at 800°C, were, in fact, not annealed, while zirconium, which anneals at 700°C, was effectively annealed.

Rhenium

Using a resistance method to obtain superconducting transition temperatures, Aschermann and Justi reported rhenium of purity 99.8% to be a superconductor with a zero field transition temperature of 0.85°. It was decided to try to obtain a transition curve for this element.

In the first instance the sample of rhenium was put

34. See reference 27.
35. See reference 33.
into a cryostat designed to examine materials for superconductivity in the liquid helium range of temperatures. The sample was placed inside a probe coil which could be moved one inch relative to the sample. The motion was accomplished by using an electromagnet to lift a piece of iron rod which was fastened to the 8 millimeter German silver tube, shown in Figure XX. The coil, of approximately 5,000 turns of No. 44 copper wire, was connected to an external ballistic galvanometer. As the sample was cooled in a small magnetic field deflections on the galvanometer were recorded as a function of the temperature. If the specimen were to make a transition to the superconducting state, the diamagnetic moment would cause a change in the magnetic flux linking the coil and, consequently, a change in deflection on the galvanometer as the coil was moved.

A sample of rhenium powder, of estimated purity 99.8%, prepared from ammonium perrhenate by hydrogen reduction, was obtained from the Chemistry Department of the University of Tennessee. This specimen was also annealed in vacuo to 800°C for 2½ hours.

In order to observe temperatures in the range where the vapor pressure over the helium bath is so small as to make reading a manometer rather difficult, a cali-
Figure XX

Diagram of Apparatus Used to Measure Superconducting Transition of Rhenium
Rhenium Apparatus

\( \frac{1}{4} \)" Inconel tube

\( 8 \)mm German Silver tube used to move coil

Brass rod spiders

Sample

Teflon

Figure XX
A transition for rhenium was obtained by cooling the sample to less than 2.0 K and then switching on and off a small magnetic field of 13.2 gauss. This procedure produced persistent super currents in the sample which altered the flux linking the probe coil. Frequent observations of deflections of the galvanometer were made as the sample was allowed to warm up. The persistent currents died out as the temperature increased and the deflections became constant when the transition temperature was reached, as shown in Figure XXI. The process was then repeated with the field kept on as the sample was allowed to warm up (also shown in Figure XXI). In this manner the two points, $T = 2.57^0K$, $H = 0$ and $T = 2.34^0K$, $H = 13.2$ gauss, were obtained and are shown in Figure XXII.

Meissner and Voigt show by the resistance method that rhenium is not superconducting down to $1.36^0K$.

37. See reference 16.
Figure XXI

Warm-up Curves Showing Superconducting Transitions of Rhenium
Rhenium

\[ H = 0 \]

\[ H = 13.2 \text{ gauss} \]

2.34° 2.57°
Figure XXII
Threshold Field Curve for Rhenium
Figure XXIII

Calibration Curve of Phosphor-Bronze Thermometer
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Appendix A (continued)

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e. B. B. Goodman, Nature 167, 111 (1951)


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r. S. A. Friedborg, I. Estermann and J. E. Goldman, Phys. Rev. 85, 375 (1952)


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x. A. Wexler and W. Corak, Westinghouse Research Laboratories, Scientific Paper 1610, 1951
Figure XXIV

Variation of $\gamma/V$ with $T_c$, Showing the Division into "Hard" and "Soft" Superconductors
Figure XXIV

\[ \frac{\gamma}{\nu} \times 10^{-5} \text{Gal/cc/degree}^2 \]
### APPENDIX B

**Elements Found Not to be Superconductors**

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<td>N. Kurti and F. Simon, Proc. Roy. Soc. A151, 610 (1935)</td>
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I, Thomas Stevenson Smith, was born in Hubbard, Ohio, February 8, 1921. After graduating from Hubbard High School in 1940, I entered Kenyon College. I withdrew from college in 1943 to accept a teaching position in the Army Air Force Pre-Meteorology Program. I returned to Kenyon College in 1946 and received the A.B. degree in June, 1947. In the autumn of 1947 I entered the Graduate School at The Ohio State University where I was appointed Graduate Assistant in the Department of Physics and Astronomy. In 1950 I received an appointment as Research Fellow and in 1951 as Research Assistant. I held the latter position for a year while completing the requirements for the degree Doctor of Philosophy.