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EFFECTS OF STRESS ON SUPERCONDUCTIVITY

by

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A THESIS
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DOCTOR OF PHILOSOPHY

Houston, Texas
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INTRODUCTION

This thesis is a study of the effects of stress on superconductivity in four metals. The magnetic property of a superconductor is that the induction, $B$, vanishes within the bulk metal. Therefore, the experiments investigated the effects of hydrostatic pressure on the magnetic critical field for the superconducting state. These remarks require a resume about superconductivity and some discussion about the motivation for this research. There is no clear understanding of superconductivity on a quantum or microscopic basis. Since the discovery by H. Kamerlingh Onnes of superconductivity in 1911, the formidable difficulties associated with performing research at temperatures near absolute zero have diminished due to technical advances, and a considerable quantity of data pertaining to various aspects of superconductivity has been obtained. These observations have led to a fairly complete understanding of the thermodynamics and electromagnetics of the superconducting state. However, understanding is limited to these bulk properties, and we do not have a satisfactory quantum mechanical theory that provides a description of the interactions between conduction electrons and the metal ions, and the manner in which these interactions lead to superconductivity. Of the several major attempts to construct such a theory, the most recent, that of Frohlich and Bardeen, has shown some promise. Their theory indicates that superconductivity arises from the interaction of electrons with the zero point lattice vibrations. If this is the
correct interaction, as it may well be irrespective of other faults of
the theory, then a study of the changes in the superconducting state
produced by a change in zero point lattice vibrations is of considerable
interest. The zero point lattice vibrations of a metal can be changed
by a change of isotopic mass or by a change in volume produced by
stress. The discovery by Serin\textsuperscript{9} and Maxwell\textsuperscript{10} in 1950 that different
isotopes of a metal have different temperatures of transition into the
superconducting state has given considerable support to the new theory.
The effect of stress has received somewhat less attention, probably
due to the greater experimental difficulties involved. Clearly it is
important because a shift of lattice vibration amplitude must result.
Accordingly, this thesis presents quantitative data on the stress effect
in four metals, with the stress system being that of hydrostatic
pressure. The data covers several aspects of the problem, but
probably the chief contribution is the temperature dependence of the
stress effect.

We need review only a few details of superconductivity, since
these have recently been fully collected in each of several books\textsuperscript{2, 11}
and in theses of the Low Temperature Laboratory, the Rice Institute.
By reference to the magnetic field versus temperature diagram \textit{given}
schematically in figure (5), one sees the phase boundary between the
"normal" and superconducting states. The superconducting state is
characterized by zero resistivity and zero magnetic induction B in
the bulk metal except for a small surface penetration depth of the
order of $10^{-5}$ cm. The phase boundary, or critical field curve, is approximately parabolic, and the experimental data for any superconductor can be accurately represented by an equation of form:

$$H_c(T) = H_0 \left[ 1 - (1+b) \left( \frac{T}{T_c} \right)^2 + b \left( \frac{T}{T_c} \right)^3 \right], \quad T \leq T_c$$

where $H_0$, $T_c$, and $b$ (small compared to unity) are characteristic of the particular metal and are defined by this equation, and where $H_c(T)$ is the magnetic field required to destroy superconductivity at temperature $T$. At temperatures $T > T_c$, the superconducting state does not exist.

The quantity $H_0$ is of particular significance in connection with the two-electron fluid model of superconductivity due to Casimir and Gorter.\(^{12}\) In this theory it is supposed that an energy gap $\gamma$ per unit volume exists between the normal electron state and the superelectron state. Further, the number $n_s(T)$ of superelectrons is 0 at $T_c$, maximum at $0^\circ K$, and a continuous function of $T$ between these limits.

Introducing the notation $\gamma = \frac{n_s(T)}{n_s(0^\circ K)}$, we can write the Gibbs Free Energy in the normal and superconducting states as:

$$G_n = U_o - V \frac{\gamma T^2}{2 \sqrt{\mu}} + G_{lHic}$$

$$G_s = U_o + V \left[ \gamma \left( \frac{\gamma^2}{2 \sqrt{\mu}} (1-\gamma)^{1/2} T^2 \right) + G_{lHic} \right]$$

where $\gamma$ is Sommerfeld's electronic specific heat constant and the exponent of $(1-\gamma)$ has been chosen to be 1/2 to give agreement with experiment. Clearly at $T = 0$ the difference in free energy is

$$\frac{(G_n - G_s)}{0^\circ K} = V \gamma$$

But this can only be the magnetic energy
density $\frac{M_{\text{ho}}^2}{2}$ multiplied by the volume. Thus we have $\beta = \frac{M_{\text{ho}}^2}{2}$.

The dependence of $\beta$ on lattice parameters can therefore be investigated by careful measurement of critical field as a function of temperature and lattice parameters. The only two parameters that can be varied are the isotopic mass and the volume. As we have indicated earlier, studies $^9, ^{10}$ on isotopes of various superconductors have shown that $H_0$ is changed by a change in isotopic mass $M$ in accordance with the relation $H_0 M^x = \text{constant}$, where $x$ is approximately $1/2$ and depends upon the metal studied. Early studies on stress effects have shown that $T_c$ is shifted by mechanical stress, but the shift in $H_0$, if any, was not determined. In the present work it is shown that $H_0$, and hence the energy gap $\beta$, is shifted by stress. The effects of stress follow no simple relation such as given for the isotope effect. Let us now review the previous studies on stress effects.

0.1 PREVIOUS STUDIES OF STRESS EFFECTS IN SUPERCONDUCTORS

In 1922 Sizzo and H. Kammerlingh Onnes$^{13}$ discovered that for tin, hydrostatic pressure lowered $T_c$ by $3 \cdot 10^{-5}$ degrees/atm., and tension raised $T_c$ by $2.8 \cdot 10^{-5}$ degrees/atm. The pressure was obtained by applying helium gas pressure to a closed cell, and the tension by stretching a tin wire. These early results are inaccurate due chiefly to anisotropic effects in the case of tension, and to the solidification of helium at the highest pressures used. It is precisely this solidification of helium under pressure which renders the present
research difficult. At pressures greater than the solidification pressure (80 atm. at 30 K), no fluids exist for transmitting hydrostatic pressure. For pressures below the solidification pressure, the total change in $T_C$ or $H_C$ is so small that precision determination of \( \frac{dT_C}{dP} \) is very difficult.

In 1944 Lazarew and Kan\textsuperscript{14} obtained pressures of an order of magnitude greater than the solidification pressure of helium by an ingenious ice bomb technique. Water was frozen in a constant volume cell, thus generating a pressure of about $2 \cdot 10^3$ atm. which could be measured by the strain in the walls of the cell. Since this is one of the techniques used in the present studies, a full description will be given in section 1.2.2. The Russian studies\textsuperscript{15,16} have continued, and a large part of the knowledge of stress effects comes from this Russian work. A summary of this data is given in table I.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Sn</th>
<th>In</th>
<th>Tl</th>
<th>Pb</th>
<th>Hg</th>
<th>Ta</th>
<th>NiBi\textsubscript{3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{dT_C}{dP}$ $\text{OK/degree atm.}$</td>
<td>$-5.8 \cdot 10^{-5}$</td>
<td>-4.7</td>
<td>1.2</td>
<td>&lt; -3</td>
<td>&lt; 0</td>
<td>&lt; 0</td>
<td>0.6</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Metal</th>
<th>RhBi\textsubscript{4}</th>
<th>Bi\textsubscript{2}K</th>
<th>BiLi</th>
<th>Bi\textsubscript{2}Pd</th>
<th>Au\textsubscript{2}Bi</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{dT_C}{dP}$ $\text{OK/degree atm.}$</td>
<td>0.3</td>
<td>5.1</td>
<td>-6</td>
<td>&lt; 0</td>
<td>-3</td>
</tr>
</tbody>
</table>

The next measurements were published in 1953 by Grenier, Spondlin, and Squire\textsuperscript{17} who studied $T_C$ as a function of tension in a single crystal tin rod and found $\left( \frac{dT_C}{dP} \right) = -1.8 \cdot 10^{-5}$ degrees/ atm.
where \( p \) refers to the magnitude of the tension. Further studies by Grenier indicate that anisotropic effects must be considered in evaluating this data.

Also in 1953 Chester and Jones\textsuperscript{18} produced an approximately hydrostatic pressure on a thin wafer of metal by clamping the wafer between two inverted "Bridgeman cones." Although the pressure determination was not precise, the pressures obtained (40,000 atm.) are extraordinary and of particular value in showing that for tin, the displacement of \( T_c \) with pressure is linear with volume change to \( \pm10\% \) from 2,000 to 20,000 atm. Also Chester and Jones caused bismuth, which is normal conducting at least to 0.05\textdegree K, to become superconducting at 7 \textdegree K by exerting a pressure in excess of 25,000 atm. This result is probably associated with a known polymorphic phase transition in bismuth.

In the past year, Fiske\textsuperscript{19} has obtained the first very accurate data on \( \left( \frac{dT}{dp} \right) \) by using pressures obtainable with helium gas. Fiske found that \( \left( \frac{dT}{dp} \right) \) was \(-4.8 \times 10^{-5}\) degrees/atm. for tin and \(+1.3 \times 10^{-5}\) for thallium. The publication of this data was followed by data of Garbor and Mapother\textsuperscript{20} who used the same technique on tin only and found \( \left( \frac{dT}{dp} \right) = -4.4 \times 10^{-5} \) degrees/atm.

Finally we would mention some recent work of Grenier\textsuperscript{21} on anisotropic effects of stress in tin single crystals. We shall discuss Grenier's work and our interpretation of it in section 2.4.
0.2 RESUME OF THEORIES ON THE MECHANISM OF SUPERCONDUCTIVITY

Since this research bears strongly on the interaction mechanism leading to the superconducting state, it seems appropriate to review the status of the theory of the mechanism of superconductivity. The earliest significant attempts toward a theory were made by Slater in 1937. Slater suggested that at very low temperature some sort of cooperation between electrons could occur which would lead to a lower than normal energy state for the electron system. This cooperative phenomenon would be destroyed at higher temperatures, corresponding to the observed disappearance of superconductivity as the temperature is raised above $T_C$. Slater later presented a tentative qualitative model based on a demonstration that if from each atom in a metallic lattice we remove one electron to a distance of the order of 137 atomic diameters from its parent atom, the characteristic perfect diamagnetism ($B=0$) could be obtained. We accomplish this by considering the system of the removed electron and parent ion as one huge atom and applying the usual Langevin theory of the diamagnetism of bound electrons. One then obtains the existence of the critical magnetic field $H_C$, because for $H \sim 100$ gauss the energy associated with the Larmor precession of the huge orbit is comparable with the atomic binding energy, and the Langevin bound electron theory is no longer applicable, then the theory of diamagnetism of free electrons must be used, and this yields a very small diamagnetism. These qualitative suggestions have not led to a satisfactory theory.
In 1947 Heisenberg\textsuperscript{5} proposed a mechanism based on lattices of electrons formed in coordinate space. Heisenberg believed such lattices should arise from the coulomb interaction between electrons. The formation of the lattices corresponds to entrance into the superconducting phase. Each lattice corresponds to a local non-uniform distribution in momentum space, but these non-uniformities are in random orientations giving zero net current. When a field is applied, these local non-uniformities become aligned and thus produce a net current. Heisenberg pursued this theory in some detail, but the predictions did not correspond to experiment. Recently\textsuperscript{5} Heisenberg has acknowledged that it is not the coulomb interaction which is important, but he maintains that the superconducting state must correspond to electron coordinate lattices such as those he originally proposed.

Born and Chang\textsuperscript{6} in 1948 presented a theory which initially showed promise. To discuss this we need the concept of the Fermi sphere: we know from quantum mechanics that electrons in a metal are described by discrete quantum states, and the Pauli Exclusion Principle allows only one electron per state. For free electrons in a finite block of metal, each state corresponds to a unique momentum for the electron occupying that state, and at low temperatures only the states with lowest momentum are filled. This gives a spherical distribution in momentum space. At 0\textdegree K a surface of the sphere is defined, since all states up to a certain magnitude of momentum are filled, and all of greater momentum empty. This is the Fermi sphere,
and to a first approximation the radius of the Fermi sphere depends
only on the density of free (conduction) electrons. We also need to
recall that the lattice of a metal acts as a band pass filter on electron
waves: certain electron wave lengths are attenuated, giving rise to
non-allowed values of electron momentum, which, in momentum space,
are bounded by polyhedrons which are called Brillouin zones. The
Brillouin zone structure is determined by lattice geometry. Born ob-
served that the ratio of the radius of the Fermi sphere to the distance
to a set of corners of a Brillouin zone was nearly unity for supercon-
ductors and less than unity for non-superconductors. This observation
is accurate for a majority of the superconducting elements. Born
proposed an explanation for his rule as follows: the interaction between
electrons (the same coulomb interaction as in Heisenberg's theory) is
such as to cause electrons in the corners of a Brillouin zone to migrate
into the trough of the next zone, providing that the Fermi level is not
too far away from the corner of the zone. The $\Delta E$ for removing from
the $w_0$ zone corners $n_1$, $n_2$, ..., $n_{w_0}$ electrons may be written as a sum
of terms giving (1) $\Delta E$ due to coulomb force (2) $\Delta E$ due to filling of Fermi
surface (3) $\Delta E$ due to change in effective electron mass. We minimize
the total $E$ with respect to the occupation numbers $n_1$, $n_2$, ..., $n_{w_0}$
and find that the energy of the system is a minimum if, $2 \cdot 10^{18}$
electrons are removed from each of $(w - w_0)$ corners while the remain-
ing corners are left intact. This can lead to an asymmetric occupation,
corresponding to a persistent current, and it is this asymmetric
occupation which is the superconducting state. As in the case of the Heisenberg theory, the coulomb interaction between electrons is probably not the important interaction, and although some features introduced by Born and Chang may be present in an eventual successful theory, the Born-Chang theory itself is not successful.

In 1950 Fröhlich and Bardeen independently presented theories based on electron-lattice vibration interactions. Although developed in a slightly different manner, the theories are basically similar. Each theory is somewhat controversial, but it is the method of treating the electron-lattice vibration interactions which is criticised, and probably it is correct that these interactions are responsible for superconductivity.

To understand the Fröhlich-Bardeen theories, we first recall that at any temperature it is the departure of a metal lattice from a perfect lattice that gives rise to electrical resistance. For pure metals, this departure from a perfect lattice is due largely to the thermal lattice vibrations. One observes that an electron near the Fermi level (only such electrons are involved in the scattering process) moves of the order of 10 interatomic distances during a period of the highest lattice vibration mode. Thus, to a good approximation, we may regard the lattice vibration as fixed and obtain electron wave functions $\psi_{\kappa}(\mathbf{r})$ in which the lattice displacements enter only as parameters. However, this approximation neglects the effect that the moving electron has on the lattice vibrations. To treat this, one
usually makes the so-called adiabatic approximation by assuming that a suitable wave function for the system (electron and lattice) can be given as a simple product of the electron wave functions $\psi_e(x_e)$ in which the lattice coordinates enter as parameters and the lattice wave functions $\phi(x_l)$ which do not contain electron coordinates. This sort of treatment should be sufficiently accurate for consideration of the normal state.

According to Fröhlich and Bardeen, an interaction responsible for superconductivity is obtained by extending this adiabatic approximation. This is a difficult task and so far the treatments have been made only for $T = 0^\circ$K. Fröhlich uses a second order perturbation treatment and Bardeen uses an equivalent approximation method which apparently circumvents Fröhlich's essential difficulty: Fröhlich's condition for superconductivity is the same condition that his perturbation method no longer be valid.

The direct result of these theories are (1) a criterion for which metals should be superconductors (2) an expression for the energy difference between normal and superconducting states at $T = 0^\circ$K (3) a demonstration that the lower energy state found is actually the superconducting state. The criterion (1) of Bardeen is $\rho n > 10^6$ for superconductors, where $\rho$ is the room temperature resistivity in e.s.u. and $n$ is the number of conduction electrons per cm$^3$. This criterion proves to be about 90% accurate. The energy difference (2) has been shown to be equal to $\frac{\mu^2 H_0^2}{2}$ where $H_0$ is the critical magnetic field at
0°K. One finds $H_0$ should vary as $(\text{isotopic mass})^{-1/2}$, and indeed this prediction fits experiment very closely. Bardeen indicates that the lower energy state obtained is actually the superconducting state (3) since the Landau-Peirels diamagnetism becomes sufficiently large when his very small effective electron mass is used. This assumes that it is sufficient to demonstrate that perfect diamagnetism is associated with the lower energy state.

With this introduction in the form of a survey of previous studies of stress effects and status of the fundamental theory, we now proceed to present our experimental methods and results.
PART I

1.1 APPARATUS

1.1.1 General Description. Figure 1A is a photograph of the experimental arrangement. Figures 1B, 1C, and 1D show stages of disassembly. Figure 2 gives an overall sketch of the apparatus and illustrates the inner dewar containing the liquid helium temperature bath surrounded by the outer dewar containing liquid nitrogen. A pressure cell containing the sample metal is immersed in the liquid helium. The vapor pressure, and hence temperature, of the helium bath is controlled by pumping off the vapors with mechanical and oil diffusion pumps. The vapor pressure above the liquid is sampled by a long tube extending from just above the liquid to a mercury manometer or McLeod gauge. A vertical magnetic field is produced around the sample metal by a large solenoid (figure 1B) designed to produce uniform fields over the dimensions of the sample. The normal-superconducting transition is detected by coils (figure 1C) located in the liquid nitrogen. Pressure is produced in the pressure cell (figure 1D) either by applying helium gas pressure through a capillary tube or by an ice expansion technique. Auxiliary equipment consists of vacuum pumps, vapor pressure regulator, manometer, McLeod gauge, magnetic field power supply, galvanometers, potentiometers, and bridge circuits.

To present the experimental details, we divide the experimental problem into the following operations:
1. control and measurement of low temperatures
2. control and measurement of magnetic fields
3. detection of normal-superconducting transition
4. production of hydrostatic pressure at low temperatures
5. preparation of metal specimens.

These details are presented in the following sections.

1.1.2 Temperature Control and Measurement. Temperature is controlled by adjusting the vapor pressure of the helium bath according to the Agreed Temperature Scale of 1949*\(^23\), several points of which are given below:

<table>
<thead>
<tr>
<th>Temperature (°K)</th>
<th>Vapor Pressure (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.2</td>
<td>751.7</td>
</tr>
<tr>
<td>3.0</td>
<td>181.2</td>
</tr>
<tr>
<td>2.0</td>
<td>23.45</td>
</tr>
<tr>
<td>1.0</td>
<td>1.21</td>
</tr>
<tr>
<td>0.1</td>
<td>3.4 \times 10^{-32}</td>
</tr>
</tbody>
</table>

Very low temperatures are difficult to obtain, not only because of the vanishing vapor pressure, but also because of the superfluid character of liquid helium at temperatures below 2.19°K. The superfluid helium flows in a thin film up the walls of the dewar toward warmer regions where it subsequently evaporates, thus causing a large effective heat

*Recent measurements have shown this scale to be slightly in error.\(^24\) Whenever a corrected scale is adopted, the data presented can be suitably altered without affecting the conclusions.
Figure 1A  Overall view of apparatus

Figure 1B  Solenoid with helium dewar in place
Figure 1C

Helium dewar removed from solenoid, showing drop coil (1) and compensating coil (2)

High pressure cell not visible but located inside dewar at (3)

Figure 1D

High pressure cell removed from helium dewar
leak. With our present equipment, temperatures from 4.5°K to 1.0°K are easily obtained, but much lower temperatures are impossible. The high pumping speed required to reach low temperatures is provided by a Consolidated Vacuum Corporation oil diffusion pump, model M.B.200 rated at 200 liters/sec at 500 microns and operated at 200% rated power input. The fore pump is a Kinney 8-8-11 model with a free air capacity of 46 cu. ft./min.

The accuracy of control required is seen from the fact that some phases of this work require temperature control of 0.0002°K at 3.6°K, corresponding to pressure control of 0.05 mm. Hg at 400.0 mm. Hg. This accuracy can be achieved only by electronic regulation. The regulator used was designed by Dr. H. E. Rorschach, Jr. and consists of a mercury U-tube with provision for sealing the desired pressure in one side and admitting the actual pressure into the other side. Two platinum contacts placed at the mercury surface sense a rise or fall in actual pressure. The sensing signal is sent to the electronic section which operates an open-shut solenoid valve to correct the actual pressure. The open-shut valve is located in the pump line in parallel with a large adjustable orifice which passes most of the gas, making the open-shut signal only a small correction. To eliminate small pressure fluctuations in the helium dewar resulting from the open-shut type control, an eight cubic foot ballast tank is located between the regulator and the dewar. The result is a pressure regulation of, for example, ±.05 mm. at a pressure of 400.0 mm. Hg. From table II
it is apparent that for a fixed uncertainty in pressure, the uncertainty in
T increases rapidly as T decreases. Thus the regulator just described
provides relatively poor temperature regulation below about 1.8°K.
However, below 1.8°K a stable temperature can be obtained by fixing
the pumping orifice and allowing the system to come to equilibrium with
the pumps. Below 1.2°K the diffusion pump is used, and the system
allowed to come to equilibrium with the pump for fixed power input to
the diffusion pump.

The measurement of temperature involves special difficulties,
since the measured vapor pressure yields only the temperature of the
surface liquid, whereas the sample is immersed at some depth in the
liquid. Under some circumstances, the sample temperature can be
0.1°K less or 0.015°K greater than the surface temperature. Since a
precision of .0002°K is sometimes required, this situation must be
studied. A full discussion of temperature gradients in liquid helium is
given in Appendix 1, where it is shown that for T greater than 2.19°K,
the measured vapor pressure usually must be increased by the hydro-
static pressure head above the specimen in order to obtain the specimen
temperature.

In addition to this large hydrostatic head correction, certain
other minor precautions were observed. Corrections were made when
necessary for the temperature of the manometer. Care was taken to
insure that the vacuum side of the manometer was highly evacuated by
continual check with a thermocouple gauge. We insured that the pressure
reaching the manometer or McLeod gauge was actually that of the liquid surface by extending the sensing tube almost to the liquid level and by eliminating most of the rubber tubing from the connecting tube. The mercury manometer was clean and of large bore (1 cm.). The only level read was the top of the meniscus. However, the manometer tubes were tapped vigorously prior to each reading, so that from consideration of the bore and cleanliness of the tubes, the correction for differences in surface tension depression could be neglected. All levels were read with a traveling telescope equipped with a vernier scale allowing readings to ± 0.025 mm.

To complete the subject of temperature measurement, the matter of carbon resistors must be mentioned. Standard carbon-composition radio resistors (Allen-Bradley, 1 watt and 1/2 watt, 10Ω to 1000Ω) were used for several purposes. The liquid level, which was required to obtain the hydrostatic correction and which was not visible due to the presence of the solenoid, was determined by spacing resistors 5 cm. apart vertically in the helium bath. As the liquid fell below a resistor, the resistance decreased suddenly by about 15%. The level at other times was obtained by interpolation. For level measurement, 1/2 watt 160Ω resistors were found to be ideal.

A second use of carbon resistors was in the determination of small variations in local temperature. To obtain the precision required for this purpose it was found necessary to bond the resistor in a large mass of metal. Otherwise, large fluctuations in resistance are observed
at temperatures above 2.190K. When used in conjunction with a type K potentiometer, the bonded resistors provide a precision greater than 0.00010K. Unfortunately, this precision seems not to be reflected in long term accuracy, and over periods of 12 hours after calibration the accuracy is probably only 0.0010K. A 560Ω 1 watt resistor bonded with Aralydite cement into a bolt screwed into the pressure cell was used in some early measurements and in studying the hydrostatic head correction.

1.1.3 Magnetic Field. The required magnetic fields were produced by a large solenoid designed to provide a uniform axial field over the dimensions of the sample. The solenoid provides 0 to 400 gauss uniform on the axis for a length of 12 cm. to ± 0.04% with a calibration of 17.55 ± 0.02 gauss/ampere. The uniformity was determined by moving a test coil of 4000 turns along the axis on a rigid guide. The calibration was determined with the same test coil used in conjunction with a very long, small diameter solenoid wound in machined grooves so that the calibration could be calculated accurately.

To produce fields of 25 gauss and less, Edison cells and rheostats were used. For larger fields, batteries and rheostats cannot give sufficient precision, and instead an 8 kw. direct current generator was used in conjunction with an electronic regulation system. This generator, which was originally self-excited, was modified by disconnecting the field windings from the output terminals and providing separate excitation from a rectifier. This excitation current is varied electronically
in response to small changes in output current, so that the output
current remains essentially constant. For example, at 10 amperes
the current is constant over half hour periods to 2 parts in $10^4$. This
figure neglects the ripple voltage, which is 2%. This ripple was not
filtered out, since it has a negligible effect on the superconductivity
measurements. The electronic regulator circuits are given in
Appendix 4.

In addition to the large field just described, a small field was
produced to cancel the earth's field to within 4%. The large solenoid
was used to cancel the vertical component, and a set of horizontal
Helmholtz coils properly orientated were used to cancel the horizontal
component.

Current was measured using a potentiometer, standard cell,
and standard resistors. One standard cell was recently calibrated at
the Bureau of Standards, and the other cells used were periodically
checked against this. No discrepancies larger than .01% were ob-
served in cell voltage. Current could be measured at least as accu-
rately as it could be controlled.

1.1.4 Apparatus for Detection of Transition. Since the normal-
superconducting transition is characterized by both a change in resistiv-
ity $\rho$ from a finite value to zero and by a change in permeability $\mu$
from one to zero, the transition may be detected by measuring either
\( \rho \) or \( \mu \). The criterion \( R = 0 \) is sometimes used. However, resistance cannot be related to an average \( \rho \), since only a thin superconducting filament is necessary to give \( R = 0 \). Accordingly, in this work \( \mu = 0 \) and not \( R = 0 \) has been taken as the criterion that the specimen be superconducting.

There are several ways in which to measure permeability, and the task is simplified by the fact that only a large change in permeability, and not the absolute value of the permeability, need be measured. This change in \( \mu \) can be detected through observation of the change in mutual inductance of two coils wound around the specimen. This method, using a 30 cps. bridge null method, was the first used in the present work. It was desirable to improve temperature control by placing the detection coils in the nitrogen instead of the helium dewar. When so located, the change of inductance was 0.5% for fairly pure specimens, and the transition could be determined with accuracy. However, for the extremely pure crystals used in the bulk of this work the change was only 0.08% and, while the transition was easily observed, the accuracy required was difficult to obtain. This small change was the result of a small skin depth for 30 c. p. s. in the normal state, and showed that for tin, the conductivity of pure specimens is approximately 17 times greater than the values given by the International Critical Tables. Although some data was taken using this 30 c. p. s. inductance bridge method, it was found that a direct current method provided more accurate results and, therefore, all data presented was obtained by the direct current
method.

The direct current method is as follows: consider a coil of wire placed in a magnetic field and connected to a galvanometer. If a specimen of normal conducting metal (excluding ferromagnetics) is inserted in the coil, we may consider that \( \mu = 1 \) and thus no deflection is observed. However, if a superconductor is inserted, the flux excluded from the cross section of the superconductor produces a galvanometer deflection. By using a coil of \( 10^4 \) turns, this deflection is easily observed in fields of a few gauss. One needs only a convenient means for moving the sample in and out of the coil. This was accomplished by holding the sample fixed and lifting and dropping the coil. This "drop coil" operates in the annular space between the 4 inch outside diameter helium dewar and the 5 inch inside diameter nitrogen dewar. For the drop coil to withstand repeated thermal shock and dropping, it was found necessary to make the coil form of brass. The coil is raised manually by two strings, lowered by gravity, and guided in its motion by two 1/8 inch diameter brass rods. The coil has 9,000 turns of #36 formvar copper wire giving a resistance when in the liquid nitrogen bath equal to \( 4/3 \) of the critical damping resistance of the galvanometer used.

In order to separate the electromotive force that resulted from dropping the coil over the superconducting specimen from the electromotive force due to small variations in the magnitude of the magnetic field, a second coil similar to the drop coil is fixed in place above the
uppermost position of the drop coil and connected in series, but in
opposite sense, with the galvanometer. By this device the deflection
resulting from a change in magnet current has been reduced by 99%.
This second compensating coil is a necessity when batteries are used
to supply magnet current, and is useful even when the electronic
current regulator is used.

1.1.5 Apparatus for Producing Hydrostatic Pressures at Low
Temperatures. We distinguish between "low pressure" measurements
made with truly hydrostatic pressures of small magnitude (100 atm.),
and "high pressure" measurements made with approximately hydro-
static pressures of large magnitude (1.9 \times 10^3 \text{ atm.}) The equipment
for low pressures consists of a pressure cell containing the specimen
and immersed in liquid helium. A capillary connects this cell with an
external valve and gauge arrangement which is in turn connected to a
standard 225 cu. ft. 2250 p.s.i. cylinder of helium gas. When the
measurements are begun, the helium gas which is supplied to the cell
condenses until the cell becomes filled with liquid helium. Thereafter
the pressure may be adjusted as desired providing that the solidification
pressure 25 is not exceeded. Since the solidification pressure is
26 atm. at 1^\circ K and 100 atm. at 3.5^\circ K, this limitation is very restrictive.
The pressure was measured by a 10 inch Heise 0-1500 p.s.i. gauge
which could be read with a precision of 1 p.s.i. and an estimated
accuracy of 2 p.s.i.
MATERIAL: ASTM SPEC. B-196
CU-38 ALLOY

NON-MAGNETIC PRESSURE CELL FOR 30,000 P.S.I.

FIGURE 3
High pressures were obtained by freezing water in a constant volume cell in a technique described later. Although the design of a non-magnetic cell and seal for 100 atm. at low temperatures is not difficult, the design of a similar cell and seal for 1900 atm. is rather exacting. The design is complicated by the requirement that the cell must swell a measurable amount under the maximum pressure. The cell used is shown in figures 1D and 3, and is described in Appendix 2. This cell and seal as first designed were used successfully throughout this work for both high and low pressure measurements.

1.1.6 Preparation of Metal Specimens. TIN was obtained in ingot form from the Vulcan Detinning Company in stated purity of 99.998%. The ingots were melted and cast under vacuum in a pyrex tube. Cooling was controlled by lifting the cylindrical oven at a rate of 6 cm. per hour so that cooling progressed from the bottom. The glass was then removed and the ends of the cylinder carefully shaped in a lathe so as to produce an approximate ellipsoid with major and minor axes of 12.5 cm. and 1 cm., respectively. The demagnetizing coefficient for this shape is 1.6%\(^2\).

INDIUM was obtained in the form of shot from the Indium Corporation of America in stated purity of 99.97%. The shot was melted in clean diffusion pump oil and well stirred to bring the slag to the surface. A small amount of slag was present as a result of the large surface area of shot exposed to oxidation. A crystal was slowly
drawn from the molten indium which was maintained at its melting temperature. A 25 cm crystal was obtained, the crystal being nearly circular in cross section but of varying diameter as a result of imperfect temperature control. The best 12 cm section was chosen and shaped somewhat using a sharp blade. The result was nearly ellipsoidal with major and minor axes 0.8 cm. and 12 cm. respectively.

**THALLIUM** was obtained in rod form from the Johnson-Mathey Company in stated purity 99.98%. The ellipsoid used was of the same dimensions and produced by the same technique as the tin specimen. The heavy oxide which forms on thallium was minimized by a layer of grease applied after machining. The oxide is easily removed before measurements are performed, since it is readily soluble in water.

**ALUMINUM** was supplied through the courtesy of the Aluminum Corporation of America in the form of rod of purity 99.99%. The rod had been hardened by cold work to allow machining. An ellipsoid similar to the tin ellipsoid was cut from this rod and then annealed by heating to 650°F for twenty-four hours.

1.2 TECHNIQUE

1.2.1 Determination of Superconducting Transition

The detection methods are those commonly used in studying superconductivity. Only the d.c. magnetic method will be discussed. The mechanism of the d.c. drop coil is given in figure 1D and in
section 1. 1. 4. Here we describe the measurement procedure. The bath temperature is fixed by maintaining the vapor pressure constant. A vertical magnetic field is applied in small increments. Actually, the solenoid current I is the measured quantity, and from this H is obtained through knowledge of the solenoid calibration in gauss/ampere. Between each incremental increase in field current I, the drop coil is lowered and the resulting galvanometer deflection recorded. These deflections are proportional to I until I reaches about 0.99 I_C, where I_C is the current corresponding to the critical field H_C at the given temperature. For I > I_C, the deflections ideally should be zero, but actually a small deflection proportional to I arises from inhomogeneities of the solenoid field. Figure 6 presents a typical transition curve at constant temperature in which galvanometer deflection is plotted as a function of magnet current for a small range of currents above and below I_C. In general, the width of a superconducting transition is due to the demagnetizing effect of the specimen shape, to impurities, and to mechanical strains. The demagnetizing factor for specimens used is 0.016, and the impurities of all samples are negligibly small. The width of transition due to strain is negligible in the case of zero pressure and low pressure measurements, but not in the case of the ice bomb. The ice bomb transition curves in large fields are identical in width and shape to the zero pressure transition curves, while in small fields the ice bomb transitions are similar in shape, but of greater width than the corresponding zero pressure transitions. This
TYPICAL TRANSITION CURVE
—THIS FOR INDIUM AT 1.9x10^3 ATM
NUMBER 8 TAKEN ON 3-8-55

$I_c = 8.362 \pm 0.003$ AMPERES

$I_c = 8.411 \pm 0.003$

$F = 2.229 \, ^\circ K$

FIGURE 6
is the expected result of inhomogeneous strains, since the strain effect is a constant $AH$ independent of $H_C$, and is masked in sufficiently large fields by the percentage-wise demagnetizing effect. Analysis of the width of transition in small fields yields a measure of the inhomogeneity of the pressure produced by the ice bomb. This homogeneity did not vary much from run to run, and was 4%.

Since the transition is of finite width, a common method of determining $H_C$ is to take the half-height value of $H$, as shown in figure 4. $H_C$ was determined in this manner for all measurements in which the difference $(H_C (0) - H_C (p))$ was of prime interest, since this value of $H$ may be determined with the greatest precision. However, a second and more correct determination of $H_C$ has been used when the transition field itself, and not differences in $H_C$, is of importance. In this case $H_C$ is taken as the smallest value of $H$ such that none of the specimen is superconducting. From figure 4 it can be seen that the second determination of $H_C$ yields a value 0.5% greater than the first determination. Accordingly, a systematic error of -0.5% exists in the $(3H_C/\delta \phi)$ data, but this is much less than the spread in $(2H_C/\delta \phi)$ data, and therefore is neglected.

The transition from normal to superconducting state requires a finite time, sometimes as much as several minutes when the thermal contact of sample with bath is poor. This transition time is due to the large eddy currents that must decay and to the latent heat of transition which must be absorbed.\textsuperscript{27,28} If the transition is made slowly, the
form of the transition curve is nearly reversible. The departures from reversibility are probably associated with frozen-in flux. All of the transition data presented were obtained in passing from the superconducting to the normal state, rather than vice-versa.

1.2.2 Production of High Pressure As stated earlier, the chief difficulty in work with hydrostatic pressure at low temperature is the fact that no fluids exist at temperatures below 4ºK and pressures above 130 atm. The technique used to circumvent this difficulty will now be described. The high pressure cell is shown in figures 2d and 3. To obtain a high pressure, the specimen is placed in this cell and the cell is filled with water and sealed, leaving no air space. As the cell is cooled preparatory to low temperature measurements, the water in the cell begins to freeze. As is well known, water expands on freezing so that, after a fraction of the water has frozen, the pressure in the bomb rises, and complete freezing cannot occur until the temperature is lowered considerably below 0ºC. Lazarev and Kan have made careful studies\(^{14}\) of this process, and find that the pressure in the cell is very closely that to be expected from Bridgman's phase diagram\(^{44}\) of ice given in figure 5. Since we know elastic constants for the ice, container, and specimen, and the percentage change in volume of water in freezing, we can estimate the final pressure produced as 3,000 atm. It is essential, however, that the first polymorphic phase transition occurs in ice at about 2,200 atm., which is less than the estimated
3,000 atm. Thus, as the pressure generated tends to rise above 2,200 atm., a fraction of the ice undergoes a polymorphic phase transition from ice I to ice III. Since ice III is more dense than ice I, this phase transition operates to maintain a pressure everywhere as great as 2,200 atm., but nowhere greater. As the temperature is lowered into the region of I - II transition, the II - III and I - III transitions proceed very slowly. If the bomb is cooled in a period of a few hours, as we have done, the I - III transition pressure is frozen-in. The heavy dashed line of figure 5 gives the observed pressure as a function of temperature, for "rapid" cooling. The final pressure at 4°K is that of the I - III transition reduced about 15% by the differential thermal contraction of the cell, ice, and specimen. The pressures mentioned were studied by the Russian scientists by means of a mechanical optic-lever type strain gauge mounted directly on the cell. We have not repeated these measurements of pressure. The chief shortcoming of the ice method of generating pressure is that only two pressures can be obtained. The method does produce a reproducible pressure uniform to about 4%. For very low temperatures, it is particularly convenient, since the cell needs no external connections and may be suspended by a fiber having negligible heat leakage.

1.3 LOW PRESSURE RESULTS

1.3.1 Tin Figure 7 is representative of the low pressure data taken for tin. The pressure was cycled a number of times, with
$T = 3.674^\circ K$

CRITICAL FIELD AS A FUNCTION OF PRESSURE—TYPICAL DATA FOR TIN

$T = 3.311^\circ K$

CRITICAL FIELD AS A FUNCTION OF PRESSURE—TYPICAL DATA FOR INDIUM
several transitions measured during each cycle. No permanent displacement of zero pressure $H_c$ could be detected. The data shown has been corrected (see Appendix 1) for the change in the liquid helium bath level during the run. This correction is essential, since it accounts for an apparent shift in $H_c$ of the same order as that produced by the stress. The data shown, together with similar data obtained from three separate runs, yields:

$$\left( \frac{\partial H_c}{\partial P} \right)_{T = T_c} = -6.9 \pm 0.4 \cdot 10^{-3} \text{ gauss/atm.}$$

$$\left( \frac{\partial \theta}{\partial P} \right)_{T} = -4.7 \pm 0.3 \cdot 10^{-5} \text{ degrees/atm.}$$

The spread in data points of figure 7 is due chiefly to temperature uncertainty. The pressure is measured to 2 p.s.i., the $H_c$ for each pressure is measured to 0.1 mm. Hg corresponding to $\pm 0.002^\circ\text{K}$ or $\pm 0.03$ gauss for tin at $3.6^\circ\text{K}$. The uncertainty in temperature arises from the thermal gradients in the helium bath, as discussed earlier. The bath temperature at the sample is $0.005^\circ\text{K}$ warmer than the vapor pressure indicates. This $0.005^\circ\text{K}$ corresponds to 0.75 gauss, so that if the corrections for thermal gradients are made to 8%, the corresponding uncertainty is $0.0004^\circ\text{K}$ or 0.06 gauss. These uncertainties are sufficient to explain the observed spread in data, and indicate that a precision greater than that of the present data is not likely to be obtained from experimental apparatus of this type.
1.3.2 **Indium**  The remarks concerning low pressure tin measurements apply equally well to indium. However, since the transition temperature of indium is lower than that for tin, the hydrostatic head corrections are larger and the maximum pressure obtainable with liquid helium is less. Consequently, the indium data is slightly less accurate than the tin data. Representative data for indium is shown in figure 8 and yields:

\[
\left( \frac{\partial \mu}{\partial \rho} \right)_{T,T_0} = -6.1 \pm 0.4 \cdot 10^{-3} \text{ gauss/ atm.}
\]

\[
\left( \frac{\partial T_c}{\partial \rho} \right)_{H} = -4.0 \pm 0.3 \cdot 10^{-5} \text{ degrees atm.}
\]

1.3.3 **Other Metals**  Only indium and tin were studied at low pressures. The reason for limiting study to these metals is seen from consideration of the other superconducting elements with \( T_c \) in the available temperature range, \( 1^0 \leq T_c \leq 4.5^0 \text{K} \): Ga(1.1^0), Al(1.1^0), Th(1.4^0), Tl(2.3^0), Hg(4.15^0), Ta(4.4^0). Low pressure measurements on the first four metals using present methods are not possible due to inherent limitations of temperature control. Measurements were not attempted on Ta since Ta is available only in sintered form. Hg was not studied because of handling difficulties which hazard the bronze pressure cell and prevent the production of a strain free crystal. When these various difficulties can be surmounted, this study should be extended.
1.4 RESULTS AT HIGH PRESSURE

1.4.1 Tin Figure 9 gives the critical field data for tin at zero pressure and at $1.9 \cdot 10^3$ atm. and from $T_c$ to $1.3^0K$. This data was obtained from six separate runs extending over a period of several months. Runs were made alternately at zero pressure and at $1.9 \cdot 10^3$ atm. with the apparatus being disassembled between runs. The solid curve for tin in figure 9 is a cubic polynomial fitted to the zero pressure points:

$$H_c = 307.3 - 26.80T^2 + 1.255T^3 \text{ gauss}$$

$$T_c = 3.728 \pm 0.002^0K$$

where the r.m.s. deviation for the 38 points fitted is 0.8 gauss. The same data may be expressed in more general form by:

$$H_c = H_o \left[ 1 - 1.2117\left(\frac{T}{T_c}\right)^2 + 0.2117\left(\frac{T}{T_c}\right)^3 \right] \text{ gauss} .$$

Further we obtain

$$\left(\frac{\partial H_c}{\partial T}\right)_{T_c} = -147.4 \pm 1 \text{ gauss} / ^0K.$$  

Since 1950, attempts, such as the present, to measure very small changes in $T_c$ due either to stress or to isotope effects have produced as a by-product data on $T_c$ for $H_o$ for tin that is generally of much greater precision than data obtained prior to 1950. For comparison, we present in table III these recent determinations. The first two listings refer to the same specimens. $T_c = 3.752^0K$ was obtained before annealing, and $T_c = 3.727^0K$ was obtained after annealing.

Although so far we have presented only the zero pressure tin data, our principal interest lies in the temperature dependence of the
SUPERCONDUCTING STATE

CRITICAL FIELD DATA
TIN AND INDIUM
- ZERO PRESSURE
- \(-1.9 \times 10^8\) KGS/CM²

FIGURE 2
Table III

TRANSITION DATA FOR Sn$^{118.7}$

<table>
<thead>
<tr>
<th>$T_c$(°K)</th>
<th>$H_0$ (gauss)</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.727</td>
<td>305</td>
<td>Brü, Mendelssohn, and Olsen$^{29}$</td>
</tr>
<tr>
<td>3.752</td>
<td>304</td>
<td>Lock, Pippard and Shoenberg$^{30}$</td>
</tr>
<tr>
<td>3.752</td>
<td>304</td>
<td>Serin, Reynolds, and Lohman$^{31}$</td>
</tr>
<tr>
<td>3.740</td>
<td>306.8</td>
<td>E. Maxwell$^{22}$</td>
</tr>
<tr>
<td>3.728 ± .0015</td>
<td>---</td>
<td>Garbar and Mapother$^{20}$</td>
</tr>
<tr>
<td>3.728 ± .002</td>
<td>307.3</td>
<td>present</td>
</tr>
</tbody>
</table>

pressure shift in critical field. This pressure shift $H_c$ is determined by subtracting the pressure data points from the zero pressure data. For this purpose, the smooth zero pressure curve of figure 9 was not used, since there are systematic deviations from this curve. Instead, large scale (.02°K/inch) piecewise plots of figure 9 were prepared. Then zero pressure points in the neighborhood of each pressure point were fitted by a line of proper slope but usually slightly displaced from the smooth curve. The $H_c(T)$ of each pressure point was then subtracted from this adjusted zero curve to obtain $\Delta H_c(T)$. The pressure $\Delta p$ was not measured directly, since a knowledge of $\Delta p$ is not necessary to determine the desired temperature dependence of the pressure shift, provided only that $\Delta p$ does not change with temperature. In the temperature range of interest, the change in $\Delta p$ can be due only to differential thermal expansion, which is entirely negligible. However,
since from low pressure measurements we know \( \left( \frac{\partial H_e}{\partial p} \right)_{T_e} \) for 100 atm., and since Chester and Jones\(^{18}\) have shown \( \left( \frac{\partial H_e}{\partial p} \right)_{T_e} \) is independent of pressure, we are able to measure \( \Delta p \) by measuring \( \Delta H_C \) at \( T_C \). The \( \Delta p \) thus obtained is \( 1.9 \cdot 10^3 \) atm., in good agreement with both the pressure expected from the I - III ice transition and the results of the Russian work\(^{15}\).

In order to avoid the necessity for direct measurement of \( \Delta p \), we express the temperature dependence of \( \left( \frac{\partial H_e}{\partial p} \right)_T \) by giving:

\[
R = \frac{\Delta H_C(T)}{\Delta H_C(T_e)} = \frac{\left( \frac{\partial H_C}{\partial p} \right)_T}{\left( \frac{\partial H_C}{\partial p} \right)_{T_e}}.
\]

Figure 10 gives the experimental values for \( R \) as a function of temperature. Also given is the only data available for comparison. This is the Russian data\(^{15}\) for \( R \) at 2.50K, 3.00K. The limited Russian data is roughly in agreement with, but slightly lower than the present data. It should be noted that the present data indicates that \( \left( \frac{\partial^2 H_C}{\partial T^2} \right)_{T=0^0K} \) is not zero, providing that the Third Law of Thermodynamics is taken into account in extrapolating the data to 00K. We will later show that this law requires that \( \left( \frac{\partial^2 H_C}{\partial T^2} \right) = 0 \) at \( T = 0 \). Assuming a \( T^2 \) dependence of \( R \) so that this condition is satisfied, we obtain from a least squares fit:

\[
R = 0.61 + 0.029 T^2.
\]

The solid curve of figure 10 is that derived in section 2.2 based principally on the "similarity" assumption that \( H_0/T_C \) is constant. It is apparent that within experimental limits, the data agrees with this curve.
\( \frac{(\frac{\partial H}{\partial T})_{T=1.648^\circ K}}{(\frac{\partial H}{\partial T})_{T=}} \)
1.4.2 Indium  Figure 9 gives the critical field data for indium at zero pressure and at $1.9 \cdot 10^3$ atm. This data was obtained from five separate runs, with the first, second, and fifth at zero pressure, and the third and fourth at $1.9 \cdot 10^3$ atm. The apparatus was disassembled between successive runs. It will be noted that the indium data is of somewhat greater precision than the tin data, this being the result of refined temperature and field control. The critical field at zero pressure is given by:

$$H_c = 284.5 - 27.68T^2 + 0.9489T^3 \text{ gauss}$$

or

$$H_c = 284.5 \left[ 1 - 1.1325 \left( \frac{T}{T_c} \right)^4 + 0.1325 \left( \frac{T}{T_c} \right)^3 \right] \text{ gauss}$$

with an r.m.s. deviation for 45 points of 0.25 gauss.

$$T_c = 3.412 \pm 0.002 \degree K$$

$$\left( \frac{\partial H_c}{\partial T} \right)_{T_c} = 155.8 \pm 1 \text{ gauss/}\degree K$$

The transition data given above is of special interest, since it is probably the most accurate available. For comparison, we give the existing data:

<table>
<thead>
<tr>
<th>$T_c (\degree K)$</th>
<th>$H_c$ (gauss)</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.414\degree K</td>
<td>275</td>
<td>Daunt, Horseman, and Mendelsohn</td>
</tr>
<tr>
<td>3.367</td>
<td>---</td>
<td>Meisner</td>
</tr>
<tr>
<td>3.374</td>
<td>284.3</td>
<td>Stout and Gutman</td>
</tr>
<tr>
<td>3.396</td>
<td>278.4</td>
<td>Clement and Quinelli</td>
</tr>
<tr>
<td>3.412</td>
<td>284.5</td>
<td>present</td>
</tr>
</tbody>
</table>
Of the data presented, the purity of all specimens is comparable. The $T_C$'s given are corrected to the 1949 temperature scale. The more recent data\textsuperscript{34, 35} would appear to be better than the two earliest measurements.\textsuperscript{32, 33} However, Clement and Quinnell determined $H_C$ from measurements on a sphere, which is particularly unsuited for this purpose due to its large demagnetizing factor. Also, the hydrostatic head correction apparently was not applied to the data of Stout and Guteman; this may account in part for the low value of $T_C$ obtained.

As an indication of relative accuracy of the critical field data, we note that probably the best previous data is that of Stout and Guteman who have 10 data points with an r.m.s. deviation of 1.1 gauss, as compared to the present 45 points with an r.m.s. deviation of 0.25 gauss.

As in the case for tin, our principal interest in the indium data lies in the temperature dependence of the pressure shift $\Delta H_C$ in critical field. Figure 11 gives the experimental values of $R$

$$R = \frac{\Delta H_C(T)}{\Delta H_C(T_C)}$$

for the temperature range from $T_C$ to 10K. Also given are the four high temperature values of $R$ obtained by the Russians\textsuperscript{15}. It should be noted that the indium data is similar to the tin data, but the value of

$$R = 0.77 + 0.02T^2$$

for indium does not change with temperature as rapidly as does $R$ for tin. This difference is important, since for indium the value of $R$ deduced from the similarity principle (given by the solid line in figure 11) does not represent the data points, and hence it appears that the
\[
\frac{\left(\frac{\partial H}{\partial P}\right)_T}{\left(\frac{\partial H}{\partial P}\right)_{T=0}} = 3.381 \, ^\circ K
\]

**Figure 11**

- Indium
- Symbols: ○ 3-8-55, △ 3-14-55, † KAN, LAZAREV, & SUDOVSTOV
- Line: Simplicity Principle
- Line: \((H_0/T_0)_{1.9 \times 10^9 \text{ atm}} = 0.004 (H_0/T_0)_{P=0}\)
similarity principle is perhaps of limited applicability. This will be discussed in section 2.2.

1.4.3 Thallium Thallium is of special interest because, of the superconducting elements studied so far, it is the only element for which \( \left( \frac{\partial H_c}{\partial P} \right)_T > 0 \). Actually some doubt has existed regarding the sign of \( \left( \frac{\partial H_c}{\partial P} \right)_T \) since of the three existing measurements, two\(^{15,19}\) have obtained the positive sign and one\(^{18}\) the negative sign, with no clear agreement as to magnitude. In regard to the sign of \( \left( \frac{\partial H_c}{\partial P} \right)_T \) it should be remarked that the negative sign was obtained from studies on a thin disc clamped between two inverted cones at a pressure of 20,000 atm., whereas the positive sign was obtained by the methods used in the present work. It may be that the negative sign was associated with the plastic deformation involved, or with an unknown polymorphic phase transition in thallium. A third possibility is that for thallium \( \left( \frac{\partial H_c}{\partial P} \right)_T \) is a function of pressure, becoming negative only at high pressures.

The present thallium data extends from \( T_c \) to 2.04\(^{0}\)K and yields:

\[
\begin{align*}
\left( \frac{\partial H_c}{\partial P} \right)_T &= 0.8 \pm 0.2 \cdot 10^{-3} \text{ gauss/atm.} \\
\left( \frac{\partial H_c}{\partial T} \right)_P &= -135.5 \pm 2 \text{ gauss/}^{0}\text{K} \\
\left( \frac{\partial T_c}{\partial P} \right)_n &= 0.6 \pm 0.2 \cdot 10^{-5} \text{ }^{0}\text{K/atm.} \\
T_c &= 2.385 \pm 0.004 \text{ }^{0}\text{K}.
\end{align*}
\]

The \( \Delta H_c \) produced by pressure was measured in the same manner as for tin and indium. However, the corresponding \( \Delta p \) was not measured
directly but, instead, we observe that the $\Delta p$ produced by the cell when filled with water is determined essentially by the polymorphic phase transition in ice. Only negligible pressure differences should exist for specimens with different thermal expansion coefficients. In the case of tin and indium, these conclusions appear valid since the pressure is found to be completely reproducible and of magnitude $1.9 \times 10^3$ atm. Consequently, we can believe that replacing indium or tin with thallium will not substantially change the pressure produced by the ice. However, the quoted uncertainty in $\left( \frac{\partial H_c}{\partial T} \right)_{T_c}$ is given as 25% largely in order to allow for unforeseen deviations in ice bomb pressure. Moreover, there can be no doubt that the sign of $\left( \frac{\partial H_c}{\partial T} \right)_{T_c}$ is positive at these pressures, and thus thallium is unique among superconducting elements thus far studied.

1.4.4 Aluminum The quantity $\left( \frac{\partial H_c}{\partial T} \right)_{T_c}$ has not previously been measured for aluminum. The present measurements were obtained with great difficulty due to the low critical temperature of aluminum, and to certain associated factors which are not well understood. Measurements by Mapother\(^{36}\) have shown that pure specimens of aluminum may be supercooled by as much as $0.1^\circ$K below the critical field curve of aluminum without entering the superconducting state. Although this seems true for all superconductors to some extent, the effect is generally negligible among metals studied, except in the case of aluminum. This effect, and probably associated superheating, results in
inaccurate critical field data, as indicated in the following results:

\[ \left( \frac{\partial T_c}{\partial P} \right)_n = -2.6 \pm 0.8 \cdot 10^{-5} \text{K/atm.} \]

\[ \left( \frac{\partial H_c}{\partial P} \right)_T = -4.4 \pm 4.2 \cdot 10^{-5} \text{gauss/atm.} \]

\[ \left( \frac{\partial H_c}{\partial T} \right)_P \mid _E = -157 \pm 5 \text{gauss/degree} \]

\[ T_c = 1.176 \pm 0.006 \text{K.} \]

Thus far we have presented our experimental results for tin, indium, thallium, and aluminum without discussion except for comparison of zero pressure data for tin and for indium. We now proceed to discuss and analyze our stress data.
PART 2

2.1 SUMMARY OF PRESENT STRESS DATA AND COMPARISON WITH EXISTING DATA

We begin our discussion of stress results by giving in table IV a summary of data relating to stress effects in tin, indium, thallium, and aluminum. This covers all elements for which stress measurements of any precision have been obtained, since for the remaining elements Pb, Ta, and Hg that have been studied, only the sign of \( \left( \frac{\partial \sigma}{\partial \tau} \right)_\tau \) has been obtained. Table IV does not include data obtained from simple tension on tin single crystals; this data is reserved for section 2.3 since \( \left( \frac{\partial \sigma}{\partial \tau} \right)_\tau \) cannot be deduced from such studies without a knowledge of crystal orientation. In table IV values for both \( \left( \frac{\partial^2 \sigma}{\partial \tau^2} \right)_\tau \) and \( \left( \frac{\partial^2 \tau}{\partial \sigma^2} \right)_\tau \) are given. In the instances in which the original work gave only one derivative, we have utilized a knowledge of \( \left. \left( \frac{\partial \sigma}{\partial \tau} \right) \right|_\tau \) to obtain the other derivative. In table V is given our best estimate of the pressure derivatives based on a consideration of all data. We should remark that here, and throughout this thesis, the tolerance on the data has been set somewhat larger than the self-consistency of the data and probable systematic errors indicate. It is expected that in each case the results of more precise determinations that may later be made will fall within this tolerance. We note that our data on temperature dependence of \( \left( \frac{\partial \sigma}{\partial \tau} \right)_\tau \) for tin and indium as given in section 1.4 is not included in table IV, since the only data available for comparison consists of the four Russian points shown in figures 10 and 11, and is
insufficient to give a temperature dependence of \( \left( \frac{\partial H_c}{\partial T} \right)_T \) such as we have determined. Since this temperature dependence is essentially new information of some significance, we devote the following sections to its discussion.

### Table IV

<table>
<thead>
<tr>
<th>Metal</th>
<th>( \left( \frac{\partial H_c}{\partial T} \right)_{T=T_c} ) ( \text{gauss/atm.} )</th>
<th>( \left( \frac{\partial H_c}{\partial T} \right)_{M} ) ( \text{GK/atm.} )</th>
<th>Pressure ( \text{atm.} )</th>
<th>Author</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin</td>
<td>(-4 \cdot 10^{-3})  (-3 \cdot 10^{-5})</td>
<td>(&lt; 95)</td>
<td>1730</td>
<td>Kan, Lazarev, and Sudovstov(^{15})</td>
</tr>
<tr>
<td></td>
<td>(-8.5)</td>
<td>(-5.8)</td>
<td></td>
<td>Chester and Jones(^{18})</td>
</tr>
<tr>
<td></td>
<td>(-6.3)</td>
<td>(-4.3)</td>
<td>11,500</td>
<td>Garbor and Mapother(^{20})</td>
</tr>
<tr>
<td></td>
<td>(-6.6)</td>
<td>(-4.5)</td>
<td>17,500</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-7.2)</td>
<td>(-4.5)</td>
<td>(&lt; 115)</td>
<td>Fiske(^{19})</td>
</tr>
<tr>
<td></td>
<td>(-6.5)</td>
<td>(-4.4)</td>
<td>(&lt; 100)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-6.9 \pm 0.4)</td>
<td>(-4.7 \pm 0.3)</td>
<td>(&lt; 100)</td>
<td>present</td>
</tr>
<tr>
<td>Indium</td>
<td>(-6)</td>
<td>(-4)</td>
<td>(&lt; 95)</td>
<td>Sizoo and Onnes(^{13})</td>
</tr>
<tr>
<td></td>
<td>(-7.5)</td>
<td>(-4.8)</td>
<td>1750</td>
<td>Kan, Lazarev, and Sudovstov(^{15})</td>
</tr>
<tr>
<td></td>
<td>(-6.2 \pm 0.4)</td>
<td>(-4.0 \pm 0.3)</td>
<td>(&lt; 1000)</td>
<td>present</td>
</tr>
<tr>
<td>Thallium</td>
<td>(+0.8)</td>
<td>0.6</td>
<td>1370</td>
<td>Kan, Lazarev, and Sudovstov(^{15})</td>
</tr>
<tr>
<td></td>
<td>(+1.9)</td>
<td>1.4</td>
<td>1730</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(-0.5)</td>
<td>(-0.4)</td>
<td>13,400</td>
<td>Chester and Jones(^{18})</td>
</tr>
<tr>
<td></td>
<td>(+1.8)</td>
<td>1.3 \pm 0.2</td>
<td>48</td>
<td>Fiske(^{19})</td>
</tr>
<tr>
<td></td>
<td>(+0.8 \pm 0.3)</td>
<td>0.6 \pm 0.3</td>
<td>1900</td>
<td>present</td>
</tr>
<tr>
<td>Aluminum</td>
<td>(-4.1 \pm 1.2)</td>
<td>(-2.6 \pm 0.8)</td>
<td>1900</td>
<td>present</td>
</tr>
</tbody>
</table>
Table V

ESTIMATED "BEST" VALUES FOR PRESSURE COEFFICIENT

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\left(\frac{\Delta H}{\Delta P}\right)_{T=T_c}$ gauss/atm.</th>
<th>$\left(\frac{\Delta T_c}{\Delta P}\right)_{H=0}$ °K/atm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tin</td>
<td>$-6.7 \pm 0.3 \cdot 10^{-3}$</td>
<td>$-4.6 \pm 0.2 \cdot 10^{-5}$</td>
</tr>
<tr>
<td>Indium</td>
<td>$-6.2 \pm 0.4$</td>
<td>$-4.0 \pm 0.3$</td>
</tr>
<tr>
<td>Thallium</td>
<td>$1.4 \pm 0.4$</td>
<td>$1.0 \pm 0.3$</td>
</tr>
<tr>
<td>Aluminum</td>
<td>$-4.1 \pm 1.2$</td>
<td>$-2.6 \pm 0.8$</td>
</tr>
</tbody>
</table>

2.2 TEMPERATURE DEPENDENCE OF $\left(\frac{\Delta H}{\Delta P}\right)_T$

The critical field curve for a superconductor is usually given in the form of a power series in $\frac{T}{T_c}$:

$$H_c = H_0 \left[ 1 + \alpha \left(\frac{T}{T_c}\right)^2 + \beta \left(\frac{T}{T_c}\right)^3 \right]$$  \hspace{1cm} (1)

where the linear term must be absent for thermodynamic reasons, and where $\beta$ is much smaller than $\alpha$, and higher order terms in $T$ are usually negligible. We will assume that $\alpha$ and $\beta$ are constants characteristic of the particular metal (electronic structure) and in particular are independent of stress and isotopic mass. We will further assume that the ratio $H_0/T_c$ is a constant for each metal. The latter assumption constitutes what will be called the "similarity" relation, since it requires that transition curves for different isotopic masses and for different stress states can be brought into coincidence by a uniform change in the scale of $H$ and $T$ simultaneously. The justification for the similarity relation will be discussed later. Here we investigate certain consequences that follow from these assumptions.
We first differentiate (1) with respect to pressure, and remembering
that $\alpha$ and $\beta$ are constant, we have:

$$\frac{\partial^2 \mu}{\partial T \partial p} = \frac{\partial \mu}{\partial T} + \left[\alpha \left(\frac{\partial^2 \mu}{\partial T^2}\right) - \frac{2\alpha \mu}{T} \left(\frac{\partial \mu}{\partial T}\right)^2\right]\left(\frac{T}{T_c}\right)^2$$

$$+ \left[\beta \left(\frac{\partial \mu}{\partial T}\right) - 3\lambda \frac{\mu}{T} \left(\frac{\partial \mu}{\partial T}\right)^3\right]\left(\frac{T}{T_c}\right)^3.$$

Now since $H_0/T_c$ is constant, we obtain

$$\frac{\partial^2 \mu}{\partial T \partial p} = \frac{H_0}{T_c} \frac{\partial \mu}{\partial p}.$$ Inserting this into the last expression we have

$$\frac{\partial^2 \mu}{\partial T \partial p} = \frac{\partial \mu}{\partial T} \left[1 - \alpha \left(\frac{T}{T_c}\right)^2 - 2\beta \left(\frac{T}{T_c}\right)^3\right].$$

We remark that since the difference of Gibbs potential of normal and superconducting states is $G_n - G_s = \mathcal{V}_m \mu H_c^2$, we have

$$S_n - S_s = -\mathcal{V}_m \mu H_c \frac{\partial \mu}{\partial p} + \mu H_c^2 \frac{\partial \mathcal{V}_m}{\partial T}.$$ where the last term is negligible.

Thus

$$\frac{\partial}{\partial p} (S_n - S_s) = -\mathcal{V}_m \mu H_c \frac{\partial^2 \mu}{\partial p^2} - \mathcal{V}_m \mu \frac{\partial \mu}{\partial T} \frac{\partial H_c}{\partial T}.$$

The Third Law of Thermodynamics requires that $\Delta S = S_n - S_s = 0$ as $T \to 0$, so that we have $\frac{\partial^2 \mu}{\partial T \partial p} \to 0$ as $T \to 0$ and the critical field curve cannot contain a linear term. Also it follows that $\frac{\partial^2}{\partial p} (\Delta S) \to 0$ as $T \to 0$, from which we see that

$$\frac{\partial^2 \mu}{\partial T \partial p} = 0 \text{ at } T = 0.$$ We note that the expression just obtained for $\frac{\partial^2 \mu}{\partial T \partial p}$ does satisfy this Third Law requirement.

To study the temperature dependence of $\frac{\partial^2 \mu}{\partial T \partial p}$, it is convenient to consider the ratio

$$R = \frac{\frac{\partial^2 \mu}{\partial T \partial p}}{\frac{\partial \mu}{\partial T}} = \frac{1 - \alpha \left(\frac{T}{T_c}\right)^2 - 2\beta \left(\frac{T}{T_c}\right)^3}{1 - \alpha - 2\beta \left(\frac{T}{T_c}\right)^3}.$$
The solid curves in figure 10 and 11 represent $R$ for tin and indium, respectively, using the values of $\alpha$ and $\beta$ obtained from the zero pressure critical field curves. We see that for tin the agreement is within experimental error, whereas for indium all experimental points lie above the curve given by the similarity principle. That is, for indium $H_0$ is decreased a greater amount than expected from the observed decrease in $T_c$. It would seem that the internal consistency of the data and the precautions observed in performing the measurements preclude the possibility of error in data as large as the deviation of the indium data from the predicted value of $R$. Thus we conclude that the similarity principle does not hold rigorously for indium, and therefore it seems appropriate to examine the basis for the similarity principle. First of all we wish to establish to what extent the similarity principle is in error for indium. This is accomplished by repeating the previous analysis without assuming similarity, and fitting the result to the data at any one chosen temperature, say 10K. We have written:

$$
\left( \frac{\partial H_c}{\partial \rho} \right)_T = \left( \frac{\partial H_c}{\partial \rho} \right)_T + \left[ \alpha \left( \frac{\partial H_c}{\partial \rho} \right)_T - 2\alpha \frac{H_0}{T_c} \left( \frac{T}{T_c} \right) \right] \left( \frac{T}{T_c} \right)^2 \\
+ \left[ \beta \left( \frac{\partial H_c}{\partial \rho} \right)_T - 3\beta \frac{H_0}{T_c} \left( \frac{T}{T_c} \right) \right] \left( \frac{T}{T_c} \right)^3.
$$
Whereas previously we inserted \( \left( \frac{\partial H}{\partial p} \right)_T = \left( \frac{\partial T_c}{\partial p} \right)_T \) obtained from the similarity principle, we now avoid this assumption and simply insert experimental values for \( \left( \frac{\partial H}{\partial p} \right)_T \) and \( \left( \frac{\partial T_c}{\partial p} \right)_T \), and

\( \frac{H_0}{T_c^2} \), where the pressure variations in the last ratio can be neglected in comparison to the ratio itself. Inserting these experimental values we have:

\[
R = \left( \frac{\partial H/\partial p}{\partial H/\partial p} \right)_T = 0.77 + 0.28T^2 - 0.00275T^3
\]

which is the dashed curve of figure 11. From this we find

\[
\left( \frac{H_0}{T_c} \right)_{1.9 \cdot 10^3 \text{ atm.}} = 0.993 \left( \frac{H_0}{T_c} \right)_{\phi=0}
\]

so that for a pressure of \( 1.9 \cdot 10^3 \text{ atm.} \), corresponding to a volume change of 0.7%, the similarity principle is in error by 0.7%.

We will now show that, under certain assumptions, the similarity principle may be obtained from the two-electron fluid theory of superconductivity. Alternately, F. London in a discussion of specific heats has obtained what is essentially the similarity principle, but his treatment is based on experimental data that the specific heat of the superconducting state is purely cubic in temperature, and this is not the case for most superconductors. The usual two-fluid treatments also contain such an assumption, but the more general two-fluid treatment can avoid this. As mentioned in the introduction, the Gibbs free energy in the normal and superconducting states can be written:

\[
G_n = U_n - V \frac{\gamma}{2} \frac{T^2}{T_n} + G(\tau)_{\text{lattice}}
\]

\[
G_s = U_s - (1 - \phi)^x \frac{V}{2} \frac{\gamma}{T^2} + V \phi + G(\tau)_{\text{lattice}},
\]
where $\beta$ is the ratio number of super electrons at $T$ to the number at $0^\circ K$, $V_m$ is gram molecular volume, $\gamma$ is the assumed energy separation per unit volume, and $\gamma$ is the Sommerfeld's specific heat constant in cal. degree$^{-2}$/mole. If $x$ is chosen $1/2$, then the superconducting state specific heat is cubic and the critical field curve is parabolic. We note, for example, that Maxwell's tin data requires that $x = 0.4$ and also that, as the present work shows, neither the tin nor indium transition is purely parabolic. Accordingly, we will retain $x$ as a parameter characteristic of the superconducting state in each metal.

Then for equilibrium in the superconducting state we minimize $G_S$ with respect to $f$: 

\[
\frac{\partial G_S}{\partial f} = 0 = -\beta V - x(1-f)^{x-1} \frac{xT^2}{2V_m} V
\]

\[
f = 1 - \left( \frac{\beta V_m}{x\gamma T^2} \right)^{1/(x-1)}.
\]

At $T = T_c$, $f = 0$ and we have shown in the introduction that $\beta = \frac{\mu H_0}{2}$. Thus

\[
\beta = x \frac{xT_c}{V_m}
\]

\[
\frac{H_0}{T_c} = \left( \frac{x}{\mu V_m} \right)^{1/2}
\]

This is seen to be the similarity principle, providing both $x$ and $\frac{\gamma}{V_m}$ are constant. The parameter $x$ is essentially the shape factor of the critical field curve, and neither our measurements on stress nor Maxwell's measurements on isotope effects have detected a change in shape of the critical field curve. The parameter $\gamma$ is given in the free electron approximation by $\gamma = 3.26 \times 10^{-5} \frac{q^1/2}{V_m} \text{cal.deg}^2/\text{mole}$, where $q$ is the number of valence electrons per atom. Then the
expected change in $H_0/T_c$ due to pressure is given by

\[ \frac{\partial}{\partial P} \left( \frac{H_0}{T_c} \right) = \frac{2}{3} \left( \frac{\sqrt{\frac{\gamma}{\nu_m}}} \right)^{\frac{1}{2}} \]

\[ = \left( \frac{x_0 \gamma}{\mu \sqrt{\nu_m}} \right)^{\frac{1}{2}} \frac{2}{3} \left( \frac{\nu_m^{\frac{3}{2}}}{\nu_m} \right)^{\frac{1}{2}} \]

\[ = \left( \frac{H_0}{\nu_m} \right) \left( \frac{\nu_m^{\frac{3}{2}}}{\nu_m} \right) \left( \frac{2 \nu_m}{3} \right) \frac{\partial \ln \left( \frac{H_0}{\nu_m} \right)}{\partial P} = -\frac{1}{2} \frac{\partial \ln \nu_m}{\partial P} \]

\[ = \frac{1}{2} B \]

\[ d \left[ \ln \left( \frac{H_0}{\nu_m} \right) \right] = 0.13 \%, \quad \text{for} \quad P = 1.9 \times 10^3 \text{ atm}. \]

Thus, although the similarity principle is volume dependent, the predicted deviation is one-fifth as large and of opposite sign from the observed deviation in indium. Thus the deviation cannot be explained by explicit dependence of $\frac{\gamma}{\nu_m}$ on pressure, where $\gamma$ is the free electron $\nu_m$. Probably the fault lies in the approximations of the free electron model for specific heats. Although the free electron gives fair agreement (30%) with specific heat data for superconductors, the electrons are not free (otherwise, for example, there would be no superconductivity). In the absence of specific knowledge, it is perhaps believable that for some electronic structures a 0.7% volume change can result in a change of similar magnitude in the actual $\gamma$, and thus explain the deviations from similarity for indium.
2.4 COMPARISON OF STRESS AND ISOTOPE EFFECTS

The present data together with data on the isotope effect can yield information on the interaction mechanism leading to superconductivity. The Fröhlich - Bardeen theory would seem to predict that, for a given metal, $H_c(T)$ should be a function only of the mean square amplitude of zero point lattice vibrations. If this is strictly correct, then the change in $H_c(T)$ resulting from a given change in zero point amplitude should be independent of the manner in which the amplitude change was produced, i.e., whether by stress or isotope change.

This conclusion can be investigated by a quantitative comparison of the stress and isotope effects. This comparison has been carried out here, and it will be shown that for the metals considered the change in $H_c(T)$ cannot be dependent on zero point amplitude alone. Instead, it appears that the change in volume produced by stress or isotope change must also be considered. These statements will be clarified and made precise by the following analysis.

We assume that in so far as low temperature electron-lattice interactions are concerned, the lattice of a metal can be altered in two fundamental ways: by a change in volume, and by a change in amplitude of zero point vibrations. Accordingly we write $H_c = H_c(T, V, q_i^2)$ where $V$ is gram-molecular volume and $q_i^2$ is the mean square amplitude of zero point vibration of the $i$th longitudinal lattice mode, averaged over all $i$. We do not consider transverse modes since these can be expected to have little effect on electron-lattice interaction.
Now we can write:

\[
\left( \frac{\partial H}{\partial P} \right)_T = \left( \frac{\partial H}{\partial q^2} \right)_T \frac{\partial q^2}{\partial P}_T + \left( \frac{\partial H}{\partial q} \right)_T \left( \frac{\partial q}{\partial P} \right)_T
\]

(1)

\[
\left( \frac{\partial \mu}{\partial P} \right)_T = \left( \frac{\partial \mu}{\partial q^2} \right)_T \frac{\partial q^2}{\partial P}_T + \left( \frac{\partial \mu}{\partial q} \right)_T \left( \frac{\partial q}{\partial P} \right)_T
\]

(2)

where we consider isotopic mass \(M\) as a variable and have chosen logarithmic derivatives to eliminate a number of constants from the final results. In (1) and (2), the left members are known from experimental data on stress and isotope effects, and the coefficients of

\[
\left( \frac{\partial H}{\partial q^2} \right)_T \quad \text{and} \quad \left( \frac{\partial \mu}{\partial q^2} \right)_T
\]

and

\[
\left( \frac{\partial \mu}{\partial q} \right)_T \quad \text{can be computed. Therefore} \quad \left( \frac{\partial H}{\partial q} \right)_T \quad \text{and} \quad \left( \frac{\partial \mu}{\partial q} \right)_T
\]

\[
\left( \frac{\partial H}{\partial \ln q^2} \right)_T \quad \text{can be determined.}
\]

Before giving detailed results, it seems appropriate to outline the steps used to obtain

\[
\left( \frac{\partial H}{\partial q^2} \right)_T, \quad \left( \frac{\partial \mu}{\partial q^2} \right)_T, \quad \left( \frac{\partial \mu}{\partial q} \right)_T \quad \text{and} \quad \left( \frac{\partial \mu}{\partial q} \right)_T
\]

since the results are dependent upon the numerical values of these coefficients. The following notation will be used:

- \(\alpha\) volume coefficient of thermal expansion
- \(B\) compressibility
- \(\gamma\) Grüneisen's constant
- \(\Theta\) Debye temperature at 0\(^\circ\)K
- \(h\) Plank's constant
- \(k\) Boltzman's constant
- \(K\) average interatomic force constant
- \(N\) Avagadros number
- \(V\) gram molecular volume.

We have immediately:

\[
\left( \frac{\partial \mu}{\partial q^2} \right)_T = -B
\]

(3)

To determine the coefficients involving \(q^2\), we must express \(q^2\) in terms of known parameters. Thus:

\[
N(1/2Kq^2) = \frac{1}{3}(1/2 \text{ total zero point energy/mole})
\]
where the factor 1/3 is required since \( q^2 \) represents longitudinal modes only. Thus

\[
\overline{q^2} = \frac{3}{8} \frac{k \Theta_o}{R}.
\]

We express \( K \) in terms of known parameters by writing

\[
k \Theta_o = \hbar \nu_{\text{max}} = \hbar \sqrt{\frac{E}{M}} = M \left( \frac{k \Theta_o}{h} \right)^2
\]

\[
R = M \left( \frac{k \Theta_o}{h} \right)^2
\]

\[
\Rightarrow \overline{q^2} = \frac{3}{8} \frac{\hbar^2}{MK \Theta_o}
\]

\[
\left( \overline{\frac{2 \nu}{\rho}} \right)_T = \frac{3}{8} \frac{\hbar^2}{MK} \left[ \frac{3}{2} \left( \frac{1}{\Theta_o} \right)_T \right]
\]

\[
= - \frac{3 \hbar^2}{EMK \Theta_o} \left( \frac{2 \ln \Theta_o}{\Theta_o} \right)_T \left( \frac{2 \ln \nu}{\nu} \right)_T.
\]

Recalling that Grüneisen's constant is given by:

\[
\gamma = - \left( \frac{\partial \ln \Theta_o}{\partial \ln \nu} \right)_T,
\]

we have

\[
\left( \frac{\partial \ln \overline{q^2}}{\partial \rho} \right)_T = - \gamma B.
\]

(4)

To evaluate \( \left( \frac{\partial \ln \overline{q^2}}{\partial M} \right)_T \), we recall that

\[
k \Theta_o = h \left( \frac{1}{\nu_1^2} + \frac{1}{\nu_2^2} \right)^{-\frac{1}{2}} \left( \frac{q_N}{M} \right)^{\frac{1}{2}}
\]

\[
\nu = \text{constant} \cdot \sqrt{\frac{R}{M \nu}}.
\]
Thus
\[ \bar{\alpha}^2 = \frac{3}{2} \frac{h}{k} \left( \frac{\partial N}{\partial V} \right)_T \left( \frac{V}{N} \right)^2 \]

\[ \left( \frac{\partial \ln V}{\partial m} \right)_T = -\frac{1}{2} \alpha + \frac{\epsilon}{\Gamma} \left( \frac{\partial N}{\partial m} \right)_T \]  

(5)

where we will show that the second term can be neglected. To find
\[ \left( \frac{\partial \ln V}{\partial m} \right)_T \]
we note that the molar volume of a metal is determined to a first approximation by electronic structure, and this is unchanged by a change in isotopic mass. At temperatures of a few degrees Kelvin, the only change of volume with isotopic mass is due to a change in zero point vibration amplitude, the thermal energy having negligible effect on vibration amplitude. The change in volume resulting from a change in vibration amplitude is dependent upon the anharmonic terms in the lattice potential, just as in the case of thermal vibrations. For thermal vibrations
\[ \frac{\Delta V}{V} = \int_{T_1}^{T_2} \alpha \delta V \, dT = \int_{T_1}^{T_2} \frac{\delta B}{V} C_v \, dT = \frac{\delta B}{V} \Delta U. \]

Therefore we assume that the fraction of volume \( \frac{\Delta V}{V} \) at 0°K which may be attributed to zero point energy \( U_0 \) can be written \( \frac{\Delta V}{V} = \frac{\delta B}{V} \Delta U_0 \).

To find the change of \( V \) with \( M \), we need consider only the change of this \( \Delta V \) with \( M \), so that
\[ \left( \frac{\partial V}{\partial m} \right)_T = \left( \frac{\partial (\alpha V)}{\partial m} \right)_T = \frac{\delta B}{V} \left( \frac{\partial N}{\partial m} \right)_T, \]
where the dependence of $\chi$ and $B$ on $M$ is negligible. Therefore:

\[
\left(\frac{\partial V}{\partial M}\right)_T = \frac{8B}{3} \frac{g}{6Nk} \left(\frac{\partial \theta}{\partial M}\right)_T \\
= \frac{8B}{3} Nk \theta_0 \left(\frac{1}{2M}\right) + \text{small terms.}
\]

\[
\left(\frac{\partial V}{\partial \Lambda}\right)_T = \frac{8B}{3} \frac{g}{6Nk} Nk \theta_0 \left(\frac{1}{2M}\right). \tag{6}
\]

Thus we have from (1) thru (6):

\[
\left(\frac{\partial H_c}{\partial V}\right)_T = \left(\frac{\partial H_c}{\partial \mu_0 q^2}\right)_V (-8B) + \left(\frac{\partial H_c}{\partial \mu_0 V}\right)_q (-B) \tag{1A}
\]

\[
\left(\frac{\partial H_c}{\partial \Sigma}\right)_T = \left(\frac{\partial H_c}{\partial \mu_0 q^2}\right)_V \left(\frac{1}{2M}\right) + \left(\frac{\partial H_c}{\partial \mu_0 V}\right)_q \left(\frac{1}{2M}\right) \frac{8Nk \theta_0}{V} 8B. \tag{2A}
\]

For tin, we have the following constants:

- $M = 118.$ a.m.u.
- $B = 18.8 \cdot 10^{-13} \text{cm}^2/\text{dyne}$
- $\nu = 15.5 \text{ cm}^3/\text{gm. mole.}$
- $\gamma = 2.14$
- $\Theta_0 = 260^\circ \text{K.}$

From superconductivity measurements we have

\[
\left(\frac{\partial H_c}{\partial \mu_0 q^2}\right)_T = -2.0 \quad \text{gauss/ a.m.u.} \tag{22}
\]

\[
\left(\frac{\partial H_c}{\partial \mu_0 V}\right)_T = -6.7 \cdot 10^{-9} \quad \text{gauss-cm}^2/\text{dyne.}
\]

Inserting these values into (1) and (2) and solving simultaneously, we have for tin:

\[
\left(\frac{\partial H_c}{\partial \mu_0 q^2}\right)_V = 5.5 \left(\frac{\partial H_c}{\partial \mu_0 q^2}\right)_V. \tag{7}
\]

Performing the same substitutions for thallium, where
\begin{align*}
M & = 204.4 \text{ a.m. u.} \\
B & = 34.8 \times 10^{-13} \text{ cm}^2/\text{dyne} \\
V & = 17.3 \text{ cm}^3/\text{gm. atom} \\
\gamma & = 2.73 \\
\Theta_0 & = 100^\circ \text{K}
\end{align*}

and where from superconductivity measurements

\begin{align*}
\left( \frac{d\mu}{d\eta} \right)_T & = -1.5 \text{ gauss/a.m.u.} \\
\left( \frac{dH_c}{d\eta} \right)_T & = 1.4 \times 10^{-9} \text{ gauss-cm}^2/\text{dyne}
\end{align*}

we find

\begin{equation}
\left( \frac{d^2H_c}{d\eta d\mu} \right)_T = -3.3 \left( \frac{dH_c}{d\ln q^2} \right)_V \ldots \tag{8}
\end{equation}

We observe that this analysis does not lend insight into the problem of the plus sign of \( \left( \frac{dH_c}{d\eta} \right)_T \) in thallium. However, it is clear that the effects of volume change are at least as important as the effects of zero point amplitude change. The volume effect, holding \( q^2 \) constant, probably enters through changes in the Fermi level and Brillouin zone dimensions. We recall the Born-Chang theory in which the ratio \( R \) of Fermi radius to distance to a corner of a Brillouin zone is found to be approximately unity for superconductors, and less than unity for non-superconductors. Hence a change in volume may be important if \( R \) is volume dependent. To a first approximation, both the Fermi level and the size of a Brillouin zone vary as \( \sqrt{V} \). Therefore, the volume dependence of \( R \) is a second order effect that involves more detailed knowledge than is now available on the electronic energy structure in metals.
2.4 **ANISOTROPIC EFFECTS OF STRESS**

Thus far we have confined our consideration of stress effects to hydrostatic stresses, except for a statement of results by Sizoo and Onnes\(^{13}\) and by Grenier, Spöndlin, and Squire\(^{17}\) on displacement of \(T_C\) in tin crystals due to simple tension. Recently Grenier\(^{21}\) has obtained some interesting results from studies of simple tension in tin crystals. Grenier prepared a number of long cylindrical crystals with different crystal orientations with respect to the cylinder axis. From measurements on each of these samples, Grenier obtained the data of figure 12 giving \(\left( \frac{\Delta T_C}{\Delta \varphi} \right)\) as a function of the angle \(\varphi\) between tetragonal crystal axis and cylinder axis. It is seen that \(\left( \frac{\Delta T_C}{\Delta \varphi} \right)\) is a maximum for \(\varphi = 0\), and nearly zero for \(\varphi = \frac{\pi}{2}\). Moreover, the maximum value for \(\left( \frac{\Delta T_C}{\Delta \varphi} \right)\) is approximately equal to \(\left( \frac{\Delta T_C}{\Delta \varphi} \right)\) from pressure (algebraic sign must be ascribed to \(p\); tension increases \(T_C\), pressure decreases \(T_C\)). Binary axis orientation was found to be unimportant.

By considering both the angular dependence and the magnitude of \(\left( \frac{\Delta T_C}{\Delta \varphi} \right)\) from Grenier's tension studies in conjunction with \(\left( \frac{\Delta T_C}{\Delta \varphi} \right)\) from the present hydrostatic study, we are able to establish a relation giving \(\Delta T_C\) as a function of lattice strains. We begin quite generally by writing:

\[
\Delta T_C = A_1 \varepsilon_{11} + A_2 \varepsilon_{22} + A_3 \varepsilon_{33} + A_4 \varepsilon_{23} + A_5 \varepsilon_{31} + A_6 \varepsilon_{12}
\]

where \(A_i\) are coefficients to be determined and \(\varepsilon_{ij}\) are the lattice strains.

Unpublished studies by M. D. Fiske show that pure shear exerted by twisting a hollow tin cylinder does not change \(T_C\). Therefore we can immediately set \(A_4 = A_5 = A_6 = 0\). Also since \(\varepsilon_{11}\) and \(\varepsilon_{12}\) refer
to the indistinguishable binary axes, we have

\[ \Delta T_e = A_1 (\epsilon_{ii} + \epsilon_{zz}) + A_3 \epsilon_{zz}. \]

To determine \( A_1 \) and \( A_3 \) we first need to find \( \epsilon_{ii} \) as a function of tension denoted by \( \tau \) and the angle \( \Theta \). We fix \( x, y, z \) coordinates with \( z \) being the cylinder axis, and \( 1, 2, 3 \) crystal coordinates with \( 3 \) being the tetragonal axis and \( 1 \) and \( 2 \) being binary axes. The stress tensor for tension along \( z \) when \( 1, 2, 3 \) coincide with \( x, y, z \) is simply

\[ \tau_{ij} = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & \tau \end{pmatrix}. \]

We now rotate \( 1, 2, 3 \) about \( X \) through \( \Theta \), which thus is the \( \Theta \) of figure 12. Then we rotate about \( z \) through \( \phi \). The resulting stress tensor is

\[ \tau_{ij} = \begin{pmatrix} n^2 \tau & -n \tau s & \tau m \\ -n \tau s & n^2 s^2 & -n \tau m s \\ \tau m & -n \tau m s & \tau m \end{pmatrix} \]

where \( m = \cos \Theta, n = \sin \Theta, r = \cos \phi, s = \sin \phi \). To obtain the desired \( \epsilon_{ij} \) from \( \tau_{ij} \) we will need the compliance constants for tin relating stress to strain. They have been measured only at room temperature, but velocity of sound measurements at low temperatures indicate these constants are good at low temperatures to within a few percent. The compliance constants for tin are:

\[ S_{ij} = \begin{pmatrix} 18.5 & -9.9 & -2.5 & 0 & 0 & 0 \\ -9.9 & 18.5 & -2.5 & 0 & 0 & 0 \\ -2.5 & -2.5 & 11.8 & 0 & 0 & 0 \\ 0 & 0 & 0 & 57.0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 57.0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 135 \end{pmatrix} \]
where the dimensions are, for example, $18.5 \cdot 10^{-13}$ cm$^2$/dyne. We now obtain directly the strains $\epsilon_{ii}$ as follows:

$$
\epsilon_{11} = \tau \left( S_{11} T^2 + S_{12} T^2 + S_{13} T^2 \right)
$$

$$
\epsilon_{22} = \tau \left( S_{21} T^2 + S_{22} T^2 + S_{23} T^2 \right)
$$

$$
\epsilon_{33} = \tau \left( S_{31} T^2 + S_{32} T^2 + S_{33} T^2 \right).
$$

Substituting in the original equation and collecting terms we have

$$
\Delta T_c = \tau \sin^2 \Theta \left[ A_1 (S_{11} + S_{12}) + A_2 S_{31} \right]
$$

$$
+ \tau \cos^2 \Theta \left[ 2 A_1 S_{31} + A_3 S_{33} \right].
$$

We note that in accordance with Grenier's observations, the above expression does not involve $\phi$ and thus is independent of binary axis orientation. Similarly for the case of hydrostatic pressure we have:

$$
\epsilon_{11} = p \left( S_{11} + S_{12} + S_{13} \right)
$$

$$
\epsilon_{22} = p \left( S_{21} + S_{22} + S_{23} \right)
$$

$$
\epsilon_{33} = p \left( S_{31} + S_{32} + S_{33} \right)
$$

and

$$
\Delta T_c = p \left[ 2 A_1 (S_{11} + S_{12} + S_{13}) + A_2 (S_{31} + S_{32} + S_{33}) \right].
$$

Now using the fact that for $\Theta = 0$, $\Delta T_c \frac{\tau}{p}$ is approximately equal to $\Delta T_c$ for hydrostatic pressure, we obtain after inserting the values for $S_{ij}$ the coefficients $A_1$ and $A_2$. With $A_1$ and $A_2$ thus determined, the stress analysis then predicts the $\Theta$ dependence of $\Delta T_c \frac{\tau}{p}$ to be

$$
\Delta T_c \frac{\tau}{p} = \left( \Delta T_c \right) \Theta^2 \left[ \cos^2 \Theta + 0.06 \sin^2 \Theta \right].
$$

This function is represented by the heavy solid line of figure 12, and does agree with the data points within experimental limits. The ratio of the coefficients is given by $A_2 = 3.0 A_1$, so that we find that the
value of $\frac{\alpha_{11}}{C}$ is proportional, with different constants, to the strain along each of the axes of a tin single crystal. The strain along the tetragonal axis is three times as effective in displacing $T_C$ as the strain along the binary axis. This analysis does not lead to a fundamental understanding of the observed anisotropy in stress effects, since presumably such understanding can arise only from a fundamental theory of superconductivity. However the analysis does serve to reduce the various experimental data into a clear formulation in terms of the crystal lattice.
PART 3

CONCLUSION

We have presented determinations of \( \frac{\partial H}{\partial P} \) \( P = P_c \) and \( \frac{\partial T_c}{\partial P} \) \( H \), giving the displacement of the critical field curve near \( T = T_c \) that occurs when a superconductor is subjected to hydrostatic pressure. Since these changes in critical field curve are extremely small, the measurements have required precision techniques. Also the lack of fluids at low temperatures has necessitated special techniques to obtain hydrostatic pressure. The superconductors studied are tin, indium, thallium and aluminum. Although several measurements of this type have existed for tin, there has been only limited data for indium and thallium, and no data for aluminum. The magnitude of \( \frac{\partial T_c}{\partial P} \) in indium, for example, is such that if \( \frac{\partial T_c}{\partial P} \) \( H \) remains constant, 85,000 atm. pressure would reduce \( T_c \) from 3.40K to 00K. In addition to the measurement of the pressure derivatives at \( T = T_c \), the temperature dependence of \( \frac{\partial H_c}{\partial T} \) has been determined. This temperature dependence has not heretofore been established. It is of interest since the value \( \frac{\partial H_o}{\partial T} \) is obtained, where \( H_o = H_c(00K) \). Following the two-electron fluid theory, we have seen that the energy gap \( \Delta \) separating normal and superconducting electron energy levels is given by \( \sqrt{\frac{\mu H_o}{2}} \), and consequently, a change in \( H_o \) due to pressure has the significance of a change in this energy gap \( \Delta \).

We have attempted to understand the temperature dependence of \( \frac{\partial H_c}{\partial T} \) on the basis of the two-electron fluid model. It is seen that
the zero pressure and the displaced critical field curves should be geometrically similar, so that \( H_0/T_C \) is constant, where the constant involved depends explicitly on \( V_m^{-1/6} \). The results for tin agree with this prediction to within experimental error, but for indium a marked (0.7%) deviation is observed. This deviation is assumed to result from a dependence of electronic specific heat on volume.

We have next considered our data on pressure shifts of \( H_C \) near \( T_C \), and compared this with existing data on the shift of \( H_C \) with isotopic mass. From this comparison, we see that if we make the reasonable assumption that \( H_C = H_C(T, V_m, q^2) \), where \( q^2 \) is the mean square amplitude of zero point lattice vibrations, then percentage-wise changes in \( V_m \) with \( q^2 \) fixed are of the order of five times as effective in displacing \( H_C \) as percentage-wise changes in \( q^2 \) with \( V_m \) fixed. The comparison has been made for tin and thallium only, since isotope data is lacking for aluminum and indium.

Finally we have considered recent measurements on the anisotropy of stress effects in tin single crystals under simple tension. From an analysis of this data together with data from hydrostatic studies, we see that the shift in \( T_C \) cannot be explained simply as a volume effect. Rather, the displacement of \( T_C \) is proportional to the strain in each crystal axis independent of the strain in the other axes. A strain in the tetragonal axis is three times as effective in changing \( T_C \) as a change in strain in a binary axis. One is tempted to endeavor to understand both these anisotropic effects and also the hydrostatic effects on the
basis of the Born-Chang criterion that the ratio of the Fermi sphere radius to the distance to a Brillouin zone corner is very nearly unity for superconductors. However, to a first approximation, both Fermi radius and zone dimensions vary as $V^{-1}$, and thus one must seek higher approximations requiring more specific knowledge than is available concerning electron energy surfaces.

We terminate our thesis with the suggestion that the stress studies presented constitute a fairly direct method of investigating certain properties of the mechanism of superconductivity. In particular, we have seen that, contrary to the popular belief, the interaction mechanism responsible for superconductivity apparently cannot be attributed entirely, or even chiefly, to zero point lattice vibrations, since the lattice volume is much more effective than vibration amplitude in determining the energy gap associated with the interaction process. Although we certainly have not achieved an understanding of the interaction mechanism, it would seem that we have contributed to the knowledge of this mechanism, and that we have obtained data which can be expected to be of value to future efforts to understand superconductivity.
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APPENDIX 1  Temperature Gradients in Liquid Helium

The thermal gradients that may exist in a column of liquid helium are large and are of importance, since temperature is measured (1° to 100°K) by measuring vapor pressure above the liquid helium and then referring to the vapor pressure tables for helium. This process yields the temperature of the surface liquid, and only under certain circumstances can this surface temperature be related to the specimen temperature, since the specimen is located at the bottom of the bath.

First, we need consider only $T > T_\text{\perp} = 2.19°K$ for when $T < T_\text{\perp}$ the thermal conductivity of helium II assures uniform temperature throughout. Further, we assume that vapor pressure $p$ has been decreased monotonically, since if $p$ is increased convection currents in the liquid cease and large negative ($T < T_{\text{vapor}}$) gradients may exist for hours. Under these considerations we may establish bounds $\overline{T}$ and $\underline{T}$ as follows: assume small heat influx so that the convection currents are able to adjust the thermal gradient such that the density of the liquid is constant. The thermal gradient corresponding to constant density is easily found from the isopycnals given by W. H. Keesom. The result is a nearly constant positive gradient given by: $\overline{T} - T_{\text{vapor}} = 3.3 \cdot 10^{-5} °K/cm$ of helium. Now assume large heat influx so that the convection currents are unable to maintain constant density. Instead, the liquid is boiling from the bottom, and is at every point in equilibrium with its vapor at the pressure in the liquid at that point. This pressure is equal to the
vapor pressure plus the hydrostatic head pressure of the liquid column, and thus \( T \) is found by adding vapor pressure to hydrostatic pressure before referring to the vapor pressure tables. Figure 13 gives this gradient as a function of temperature. For example, at 2,200K with a 10 cm. column of helium, \( \overline{T} - T_{\text{vapor}} = 0.0087^\circ \text{K} \). Thus the sample temperature may be 0.0087^\circ \text{K} greater than the surface temperature. Usually this uncertainty is not acceptable, and must be removed either by supplying enough heat so that \( T = \overline{T} \), or by stirring with sufficient vigor that the bath temperature is uniform. Although the latter method is used by some investigators, one may suspect that the stirring is often not sufficiently vigorous. No evidence is presented here to support this doubt, but since it is found that the convection currents are insufficient to make \( T = \overline{T} \), then the stirring must produce much larger currents than those arising from convection.

In this work, heat was supplied at the bottom of the dewar in order to fix \( T \) by making \( T = \overline{T} \). The necessary heat input can be determined in several ways. It was found that a 500\( \Omega \) wire wound resistor dissipating 0.005 watts at the bottom of the bath was more than sufficient. Evaporation rate is increased by only 10%. Now when this heat is supplied, the bath temperature \( T \) at any point is just \( \overline{T} \), a function of temperature \( T \) and hydrostatic head \( \Delta h \). Since the sample temperature is desired, the point from which to measure \( \Delta h \) must be ascertained. This was accomplished by requiring that the transition curve be continuous across the \( \Lambda \) transition of helium.
A match of transition curves above and below $T_n$ required, as might be anticipated, that $\Delta t$ must be taken from surface to sample midpoint.

APPENDIX 2  Design of Pressure Cell

A non-magnetic pressure cell was required that would swell sufficiently with 2,000 atm. pressure to permit the pressure to be determined by measuring the strain in the walls of the cell. The relation between cell pressure and strain in the walls could be calculated approximately, but was to be determined accurately by experiment.

Figure 3 shows this pressure cell which was made from A.S. T. M. TENTATIVE SPECIFICATION B 196 = 46 aT (1/2 hard) Cu - Be alloy which consists of 2.15% Be, 0.35% total Fe and Co, the balance being Cu. The stresses in the cell were designed not to exceed 75,000 p.s.i. which was estimated to correspond to the proportional limit of the Cu - Be when hardened to the specified tensile of 168,000 p.s.i. The wall thickness is not significant in itself, but only the ratio $K$ of inside diameter to outside diameter. The determination of $K$ for a thick walled container is dependent on the contained pressure, the yield strength, and the mode of failure which depends upon characteristics other than yield strength. The value of $K$ was determined by computing $K$ from each of three standard engineering formulas known as the maximum shear stress, the maximum stress, and the strain energy theories. The choice between the three results was guided by published experimental data on various
types of metals. 41

The seal was not of the Bridgman type but rather it was designed according to a recent A. S. M. E. paper42, the details of which will not be repeated here. The sealing mechanism should be clear from figure 3. The diameter and thickness of the seal ring, chosen to be K-monomel, is such that when the cap and body are touching the ring is pre-stressed to insure a seal at low pressures. At high pressures the force of the pressure on the ring seal enhances the seal.

The Be-Cu alloy was received and machined in the 1/2 hard condition and then precipitation hardened by heating to 600° ± 10°F for 2-1/2 hours plus 1/2 hour warm-up time. Tensile strength measurements were made at various points on the cell by Brinell hardness tests. The tensile strength was found nearly constant and equal to 138,000 p.s.i. as compared with a specified 168,000 p.s.i. The difference in actual and specified tensile strength is attributed to the hardening time being slightly too great, probably due to an over estimation of warm-up time.

The cell was first tested hydraulically to 26,000 p.s.i. which was the highest pressure available. At this pressure the diameter of the cell increased by .0009" as measured by micrometer. The diameter resumed its original value upon release of pressure. The cell and seal as originally designed has functioned without fault throughout this research.
APPENDIX 3  Design of Solenoid

An air core solenoid illustrated in figure 1B was built to produce uniform fields of 300 gauss continuously and 450 gauss for short periods. Since the diameter to length ratio was fixed by practical consideration at about 1/3.5, the question of uniformity became important. A designed uniformity for the axial field on the axis of .03% over a distance of 20 cm. was obtained by placing at each end additional current loops connected in series with the solenoid windings. The end loops were not restricted to being the same diameter as the solenoid, and thus both the number of end coil turns and the end coil ratio of radius to separation could be chosen. To determine these two parameters two conditions must be imposed on the axial field. For example, both first and second space derivatives of the field at the center might be set equal to zero. Alternately, the axial field on the axis can be made equal at five points: the midpoint of the solenoid, and two points on either side of the midpoint. The latter condition was chosen since it yields quite satisfactory results with considerable less labor. This condition was satisfied by numerical calculation of the solenoid field and the end coil field for various ratio of end coil radius to separation. The ratio thus determined required that the end coils have mean radius equal to 1.7 times the solenoid radius.

The solenoid end coils are wound with 117 turns each, and the center section with 886 turns of #10 glass insulated copper having a total resistance of 2.2 Ω. The measured axial field at the center is 17.55 ± .01 gauss/ampere. The measured inhomogeneity of the axial
field on the axis over 10 cm. either side of center is 0.05%.

APPENDIX 4  Current Regulation System for Control of Magnetic Fields

A prerequisite for accurate transition data is the accurate control of the magnetic fields, which is essentially accurate current control. The fields used require currents up to 20 amperes, and the desired precision is 2 parts in $10^4$. Such precision while not obtainable with batteries and manual rheostats, can be achieved through electronic regulation. The regulation system used here follows that given by Nygard\textsuperscript{43}, as modified by the High Voltage Physics Laboratory at Rice. An eight kw. d. c. generator is used to supply 0.5 to 20 amperes to the load. The load current flows through a water cooled 1Ω resistor. The temperature rise of this resistor is negligible, so that constant resistance is dependent only on water supply temperature. The voltage from this 1Ω resistor is mixed with an adjustable voltage and sent to a very stable d. c. amplifier, which in turn places a signal on the grids of six 6AS7 tubes in parallel. These tubes are in series with the generator field windings and with a large selenium rectifier which supplies field excitation current. The output of the d. c. amplifier is such as to decrease the excitation current whenever the voltage across the 1Ω resistor, plus the adjustable voltage, increases. Thus the output current is regulated by controlling the generator excitation current. Exclusive of a. c. ripple voltage, which is of no consequence in this work, the regulation is $2.0 \times 10^{-4}$ over 1/2 hour periods. The a. c. ripple current has been
VARIABLE CONDUCTANCE
COMPRISED OF SIX
GAS7 TUBES IN PARALLEL.

FILAMENTS
POWER SUPPLY

SW-3 B+

BP.4 +150V

BP.5

BP.6 -150V

D.C. AMPLIFIER

C1 120 mfd

C2 20 mfd

VR-150

VR-150

C.5 125 mfd

C.4 125 mfd

Z1E-2

6SL7

6SL7

R16 3 Meg.

R17 200K

R18 1.8K

R19 10K

R20 1K

R1 15K

R2 750K

R3 750K

R4 500Ω

R5 75K

RICE INSTITUTE

AUTOMATIC CURRENT REGULATOR AND EXTERNAL CIRCUIT SCHEMATIC

T.W. LAWHORN 3-16-55
approximately 2% of the d.c.; this can be reduced by filtering if desired. The electronic circuits were constructed by Mr. T. W. Lawhorn, as his Senior Thesis Project for the Physics Department, the Rice Institute. A circuit diagram of the complete system is included for reference.
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