A Study of Superconducting Molybdenum.

Ahmad Waleh

Louisiana State University and Agricultural & Mechanical College

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A STUDY OF SUPERCONDUCTING MOLYBDENUM.

The Louisiana State University and
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A STUDY OF SUPERCONDUCTING MOLYBDENUM

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in

The Department of Physics and Astronomy

by

Ahmad Waleh
B.E., (Electrical) American University of Beirut, Beirut, Lebanon, 1966
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ABSTRACT

The thermodynamic critical field and associated supercooling field are measured and analyzed in superconducting molybdenum. The zero-field transition temperature and the zero-temperature critical field are found to be $T_c = 0.903 \pm 0.003^\circ K$ and $H_c(0) = 96 \pm 2 G$, respectively. The coexistence of a superconducting surface sheath with a supercooled normal bulk is confirmed. Assuming a temperature dependence of the Ginzburg-Landau parameter $\kappa$ of molybdenum, similar to that of type II superconductors, it is found that only when $\kappa < \kappa_c = 0.375$, is the supercooling field identical with the surface nucleation field. When $\kappa > \kappa_c$, a superconducting surface sheath coexists with a supercooled bulk and the supercooling field is no longer the same as the surface nucleation field.

The thermal conductivity measurements on molybdenum, in both the superconducting and normal states, are analyzed. A quantitative comparison with the theory of BRT yields energy gap values of $2\varepsilon(0) = 3.4 \pm 0.1$, close to $T_c$, and $2\varepsilon(0) = 3.2 \pm 0.1$ at lower temperatures. The discrepancy of the results are discussed in terms of the anisotropy of the energy gap in molybdenum and also in terms of possible sd-interband scattering. Equivalently, the results have been discussed in terms of both an isotropic one-band model and an overlapping spherical two-band model for superconductivity.
CHAPTER I
INTRODUCTION

The purpose of the present study is to conduct a comprehensive investigation of the superconducting transition and of the transport properties of single crystals of molybdenum, a type I superconductor and a transition metal. The properties investigated are the critical magnetic field and associated supercooling, and also the thermal and electrical conductivity in both the superconducting and the normal states. The interest in molybdenum arises from the position it occupies among the transition metals in the periodic table. The study of Mo yields a basis for the comparison of its superconducting properties to those of its neighboring elements and thus provides more insight into the phenomenon of superconductivity in the transition metals. Therefore, before dwelling upon the details of the investigations carried out in this experiment, it seems most pertinent to present first a sketch of the situation in the transition metals and discuss the properties of molybdenum as a member of this group.

The superconducting properties of the transition metals have been the subject of many experimental and theoretical investigations in recent years. The new purification techniques have made it possible to discover superconductivity in many of the elements of this group and their alloys, and furthermore, have made available a wealth of experimental observations on their related properties.
These observations have revealed marked differences between the superconducting properties of the transition and non-transition metals. Unlike the latter, the transition metals do not seem to obey some of the laws derived from the simple theory of phonon-induced superconductivity of Bardeen, Cooper, and Schrieffer\(^1\) (BCS). However, within their group, these elements seem to behave in a regular and symmetric manner\(^2\) for which even empirical laws can be established. Moreover, the variation of the properties from one element to the next, along a series, is rather smooth as can be observed from the study of alloys of these elements with their nearest neighbors. The major distinction between the transitions and non-transition metals is the presence of a partially filled d-band in the transition metals. It should also be noted that some of the rare earth elements, too (with partially filled f-bands), have anomalous superconducting properties similar to the transition metals. Therefore, one associates the anomalies in the superconducting properties with the role of the unfilled bands. With this in mind, to explain the superconductivity of the transition metals, one can either look for new mechanisms as the cause of superconductivity or apply the electron-phonon-interaction model by taking into account the details of the energy band of the d-electrons. In the following discussion, we briefly review some of the crucial observations on the transition metals as well as the theoretical models and calculations which have been proposed to explain them. We concentrate on the central transition metals since Mo belongs to this group. We restrict the mentioning of the
observations to the case of Mo, and only when necessary, we discuss the experimental results on its neighboring elements. Table I shows the central transition metals with some of their superconducting and normal states properties.

Molybdenum has a bcc crystal structure with the number of conduction electrons per atom, \( Z = 6 \). Superconductivity in molybdenum was first reported by Geballe et al.\(^3\) Its properties can best be understood by comparison to those of its neighboring elements in the periodic table. Theoretical calculations of the band structure of Mo along with that of W and Cr have been made by Loucks;\(^4\) the Fermi surfaces of Mo and W are found to be identical and different from that of Cr. In fact the role of W in the 5d-series is similar to the role of Mo in the 4d-series. Thus we limit the discussion to the comparison of the superconducting properties of Mo with those of its neighboring elements in the 4d-series. It is helpful to study the empirical information relating the band structure and other properties of these metals. The comparison is made as a function of \( Z \). Because of the extensive mutual solubility of the transition metals, one can, by making alloys of neighboring elements, smoothly vary a given property from one element to the next. Therefore, the parameter \( Z \) can be considered as a continuous variable. In the present discussion we consider the region \( 5 \leq Z \leq 7 \). In this region, the study of the specific heat constant \( \gamma \) which is a measure of the Fermi surface density of states, shows a minimum\(^5\) at \( Z \approx 6 \). A similar minimum is observed in the magnetic susceptibility, \( \chi \).\(^6\) The
TABLE II. Some Typical Superconducting and Normal State Properties of the Central Transition Metals. The entries under each element are: * the superconducting transition temperature (°K), the temperature dependence of the electrical resistivity at low temperatures, the specific heat constant (mJ/mole-deg$^2$), and the isotope effect coefficient.

<table>
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<tr>
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<th>Ti</th>
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<td>1.22</td>
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*See ref. 2.
variation of the superconducting transition temperature, $T_c$ with $\gamma$ is also very similar to that of $\gamma$ in this region. The behavior of $T_c$ can be understood in terms of the original BCS expression:

$$k_B T_c = 1.14 \hbar \omega_o \exp(-1/g)$$  \hspace{1cm} \text{(1.1)}$$

where,

$$k_B \theta_D = \hbar \omega_o$$  \hspace{1cm} \text{(1.2)}$$

$$\xi_{BCS} = N(0) V$$

$$N(0) = 3\gamma / 2\pi^2 k_B^2$$

$\omega_o$ is a characteristic phonon cutoff frequency, $\theta_D$ is the Debye temperature, $V$ is the pairing potential arising from the electron-phonon interaction, and $N(0)$ is the bare Fermi surface density of states. The minimum in the density of states at $Z = 6$ for the transition metals has qualitatively been explained in terms of a universal model for the conduction band: a "rigid band structure" into which electrons are "poured" and the properties of a given element depend on its number of conduction electrons. According to the rigid band model, the effective potential seen by an electron of d-symmetry consists of a screened ion interaction, $-ze^2/r$ and a centrifugal barrier $3\hbar^2/mr^2$ and forms a potential well. If an electron is scattered from such a potential well, it is possible that the scattering cross section shows a sharp peak as a function of energy corresponding to a virtual bound state of energy $E_d$ in the potential well, i.e., a scattering resonance.
Anderson, in the discussion of transition metal band structure, argues that, roughly in the middle of a d-series (Cr, Mo, W), the ionic potential is strong enough to produce a deep well and a sharp resonance and therefore narrow bands. In terms of the "rigid band structure", one can qualitatively understand the minimum in the density of states in the central transition metals, if one takes into account the octahedral symmetry of the d-functions (in this region, the metals have body-centered-cubic crystal structure), and allows hybridization between the d- and s-bands. Another possible explanation for the experimental density of states minimum in the center of the transition metals has been given by Engelhardt et al. These authors relate the extent of involvement of the d-electrons in the superconductivity of the transition metals to their d-shell stability. In the case of Mo and W, this stability is maximum because of the lowering of the energy due to a half-filled d-shell, and because of the high lattice stability due to d^5^s^1^ configuration, therefore, the interaction of s- and d-electrons is minimum. Experimentally, W has the minimum transition temperature among the 5d-series, while the minimum T_c among the 4d-series occurs between Nb and Mo, Nb. The extent of the s-d interaction in the transition metals can be deduced from the temperature dependence of the normal state electrical resistivity data. At low temperatures (T < 0/10), the transition metals display three types of temperature dependent resistivities: (1) a T^2^-dependent term due to electron-electron scattering, (2) a T^3^-dependent term due to scattering of s-electrons by phonons into the d-band,
and (3) a $T^5$-dependent term due to scattering of electrons by phonons within the $s$-band. From the resistivity data, Mo$^{15,16}$ and W$^{15,17}$ exhibit a $T^5$-behavior characteristic of monovalent metals, while Nb$^{15,18}$ exhibits a $T^3$-behavior characteristic of $s$-$d$ interaction.

The BCS theory which is based on an isotropic one-band model predicts a superconducting transition temperature according to Eqs. I.1 and I.2. A natural consequence of Eq. I.1 is the isotope effect which is obtained from the ionic mass dependence of $\omega_0$, i.e., $T_c \propto M^{-1/2}$. Among the categories of the experimental observations which disagree with the results of the BCS theory are: (1) dependence of $T_c$ on $N(0)$, the total density of states at the Fermi surface, $^{19}$ (2) the absence or considerable reduction of the isotope effect, $^{20}$ (3) the pressure dependence of the transition temperature, $^{21}$ and finally (4) the magnetic impurity effect. $^{22}$ Of the last two effects very little theoretical and experimental information is available to draw any conclusion.

It suffices here to mention that iron impurities seem to be magnetic $^{3,23}$ in some transition metal hosts and non-magnetic $^{24}$ in others. Resistivity work of Coles$^{25}$ indicates that a resistance minimum occurs in Mo-Fe, but not in Nb-Fe, which is consistent with the Kondo theory $^{26}$ and the existence of a moment on the Fe in Mo but not in Nb. Effect (1) can be observed by studying the alloys of an element with its nearest neighbors. The behavior of $T_c$ in Nb-Mo alloys has been studied by Reins et al. $^{27}$ Although their result is in qualitative agreement with Eqs. I.1 and I.2,
it appears that the original BCS theory predicted too strong a
dependence on $\gamma$ or else $V$ was not even roughly constant.

McMillan\textsuperscript{28} has calculated the transition temperature in a number
of metals and alloys as a function of the electron-phonon and
electron-electron coupling constants within the framework of the
strong-coupling theory. He has found an accurate expression for
$g$ in Eq. I.1 by first solving the integral equations for the gap
parameter using phonon density of states of Nb. Then Eqs. I.1 and
I.2 are to be replaced by

$$T_c = \frac{\theta_D}{1.45} \exp(-1/g) \quad \text{I.3}$$

where

$$g = \frac{N(0) \, V_{ph} \left[1+0.62 \, N(0) \, V_{ph} \right] N(0) \, U_c}{1.04 \left[1+N(0) \, V_{ph} \right]}$$

$$\gamma = \left[2\pi k_B^2 \frac{N(0)}{3}\left[1+N(0) \, V_{ph} \right]\right]$$

$$U_c = \frac{V_c}{\left[1+N \, V_c \, \ln\left(E_F/\omega_o\right)\right]} \quad \text{I.4}$$

$V_{ph}$ and $V_c$ are the matrix elements for the phonon and Coulomb
interaction respectively, $U_c$ is a Coulomb pseudo-potential, and $\overline{N}$
is the density of states averaged over an energy band of the order
$E_F$ wide centered about the Fermi surface. McMillan has found
that (in V, Nb, Ta, Mo, and W) there is a definite dependence of
$V_{ph}$ on the Fermi surface density of states, $N(0)$.
Therefore, the behavior of $T_c$, at least in the central transition elements, is in agreement with a strong-coupling model of superconductivity induced by phonons.

The ionic mass dependence of $T_c$ comes from the mass dependence of $\Theta_D$ in Eq. I.3. If $U_c$ were small, one would obtain $T_c \propto M^{-1/2}$ which is the original BCS result. When $U_c$ becomes appreciable, the exponent deviates from $-1/2$. If we write $T_c \propto M^{-\alpha}$, a simple expression for $\alpha$ can be derived from Eq. I.4, i.e.,

$$\alpha = \frac{1}{2} \left[ 1 - \left( \frac{\delta U_c}{V_{ph} \delta U_c} \right)^2 \frac{1.04[1+N(0) V_{ph}] N}{N(0) N^2} \right]$$

where

$$\delta = 1 + 0.62 N(0) V_{ph}$$

The value of $\alpha$ depends on the details of the band structure not only at the Fermi surface but far above and far below it, as well as on the nature of the interactions among the electrons. A similar result has been obtained by Morel and Anderson. From Eq. I.5 it is observed that a large $U_c$ leads to a small $\alpha$.

Below also we discuss how the problem can be treated using specific models of band structure.

Another attempt to explain the superconductivity in the transition metals is to consider a two band model. Here, one has to be cautious that the two-band effect becomes important only in the "clean" transition metals as has been suggested by Anderson and reemphasized by Garland. Physically, the impurity scattering
mixes up the character of the electron states, and one can treat
the "dirty" transition metals as single-band superconductors.

The first treatment of the two-band model was the work of
Suhl et al. \textsuperscript{32} These authors, by analogy with the one-band BCS
theory, treated the case of two overlapping itinerant electron
bands, and allowed pairs to be scattered, between the two bands,
by the emission or absorption of a phonon. In the spirit of the
two-band model, Garland \textsuperscript{33} has proposed that, in "clean" transition
metals, the heavy d-electrons can overscreen s-electrons, just as
the ions do, and thus one can obtain an attractive ss-interaction.
Garland has carried out the calculations of the isotope effect
to dirty\textsuperscript{30} materials. The basic idea of Garland's calculations
is that, in the transition metals, because of a "peaky" nature of
the band structure, the Coulomb pseudo-potential is larger than
in the non-transition metals. Garland's calculations show only a
qualitative agreement with experiment and are shown\textsuperscript{34} to be valid
only in the limit of sufficient dirtiness.

To summarize: The experimental normal state properties of
transition metals can be explained by the "rigid band model", but
they can also be understood in terms of the explanation of
Engelhardt \textit{et al.}; the superconducting state properties, likewise
are consistent with the phonon-induced strong-coupling model,
but they also lead to consideration of other possible mechanisms
for superconductivity. The two-band model calculations are not
well supported by the experimental results on the transition
metals, but then the character of the electron states are very
sensitive to impurities and the investigated metals may not have been pure enough to exhibit two distinct bands. Though it may be that the electron-phonon interaction is responsible for superconductivity of the transition metals and no new mechanisms are involved, it is really the incomplete knowledge of the band structure and other normal state properties of these elements that has hindered the understanding of their superconductivity.

The experimental data on the superconducting transition metals, and in particular molybdenum, have not yet been able to offer a clear evidence in support of any specific theory. Detailed measurements of the isotope effect, the specific heat, the critical magnetic field, the ultrasonic attenuation, and the magnetization have been made on Mo. The specific heat measurements exhibit observable deviations from the predictions of the BCS theory and they are attributed to the anisotropy of the energy gap. The energy gap anisotropy of Mo has been observed in the ultrasonic attenuation measurements. The effect of the departure, if any, from the weak-coupling limit of the BCS theory can most strikingly be seen in the deviation function $D(t) = \left[ \frac{H_c(t)}{H_c(0)} \right] - (1-t^2)$, where $H_c$ is the critical magnetic field and $t$ is the reduced temperature, $T/T_c$. The calculations of this function obtained from the specific heat and magnetization measurements agree with the results of the BCS theory, as first tabulated by Muhlschlegel within the experimental uncertainty.

Within the framework of the one-band isotropic model of BCS,
Bardeen, Rickayzen and Tewordt\(^{43}\) (BRT) have calculated the electronic contribution to the thermal conductivity when elastic impurity scattering predominates. An attempt has been made by Vasudevan and Sung\(^{44}\) to improve this calculation for application to transition metals. They adopt the spherical two band model of Suhl et al.\(^{32}\) and carry out a calculation, using the method of BRT, in the region \(T/T_{c} > 0.5\), where quasi-particles, scattered by impurities, are the primary heat current carriers. They find a ratio for superconducting to normal electronic conductivity which is lower than the result of BRT. This is consistent with a shortening of the quasi-particle mean free path due to the added possibility of sd-interband scattering. Care must be taken in the comparison of the experimental results of the thermal conductivity with the two-band calculations for the following two reasons. First, two-band superconducting elements are overly sensitive to the addition of small amount of impurities and second, the conductivity ratio is rather sensitive to the method of sample preparation.\(^{45}\)

In Chapter II, we present the results and discussion of the critical magnetic field measurements on a molybdenum single crystal. The experimental data are compared with the results of the BCS theory and the calculations from the specific heat measurements.\(^{36}\) The latter part of the chapter is devoted to the discussion of the supercooling phenomenon. A discussion of the theory of supercooling is presented and the experimental results of molybdenum are interpreted in terms of the bulk and surface
nucleation fields.

The results of the thermal and electrical conductivity measurements are presented in chapter III. The results are interpreted in terms of the single-band-model calculations of BRT. The possibilities of sd-interaction and the validity of a two-band-model have been discussed.
CHAPTER II

THE CRITICAL MAGNETIC FIELDS AND SUPERCOOLING OF MOLYBDENUM

For reversible superconductors, the critical magnetic field is a readily measurable thermodynamic quantity, and is directly related to the superconducting energy gap. The thermodynamic critical field is defined by the relation

\[ H_c^2(T) = \frac{F_n(T) - F_s(T)}{8\pi} \]

where \( F(T) \) is molar free energy of the appropriate state and \( v \) is the molar volume. \( H_c(T) \) is related to another measurable thermodynamic quantity, the specific heat, and can be calculated from the results of the latter through the relations of the BCS theory, such as

\[ \frac{v}{\gamma} \left( \frac{dH}{dT} \right)_{T=T_c} = 19.4 \]

The deviations of the measured critical field from the BCS predictions can generally be attributed to the violations of the simplifying assumptions of that theory. The comparison between the BCS theory and experiment can most strikingly be made in terms of their deviations from the two-fluid-model results, \( H_c(T) = H_c(0)[1-(T/T_c)^2] \).
In type I superconductors, $H_c(T)$ has the significance of being the field which destroys superconductivity. This is in contrast with the type II superconductors where, according to the phenomenological Ginzburg-Landau equations, the superconductivity is completely destroyed at a field $H_{c2}$ which is larger than $H_c$. $H_{c2}$ is related to $H_c$ through the relation, $H_{c2} = \kappa H_c$, where $\kappa$ is the Ginzburg-Landau parameter. In type I superconductors, $H_{c2} < H_c$ meaning that, $\kappa < 0.707$ and the field $H_{c2}$ is considered to be the lowest field to which the normal phase can persist, i.e., the lower limit to which an ideal superconductor can be supercooled. There are many experimental observations that when a specimen is placed in a greater than critical magnetic field which is then reduced, the normal phase persists in fields less than $H_c$. H. London pointed out that the existence of a positive surface energy at the interphase boundary must under suitable conditions give rise to phenomena analogous to superheating and supercooling in the more familiar phase transitions. In fact a stable nucleus for the phase transition cannot exist at all if the surface energy is everywhere positive. Much information on the nucleation of the superconducting phase and on its relation to the surface energy has been obtained by Faber in a series of measurements on supercooling in tin and aluminum.

Saint-James and de Gennes have shown that, close to $T_c$, in an external magnetic field parallel to the surface the boundary condition applicable to the Ginzburg-Landau equations leads to the persistence of an outer superconducting surface
sheath up to a field

\[ H_{c3} = 1.695 \ H_{c2} = 2.392 \ \kappa \ H_c \]

The surface sheath exists in type I superconductors also but can be detected only if \( H_{c3} > H_c \), i.e., \( \kappa > 0.418 \). For smaller values of \( \kappa \), and the above boundary conditions, \( H_{c3} \) rather than \( H_{c2} \), should be the supercooling field. It has been shown by Feder that, in bulk materials for which \( 0.406 < \kappa < 0.418 \), a metastable superconducting surface sheath exists on a supercooled normal bulk of a type I superconductor.

In this chapter, following a brief review of the experimental procedure, the results and discussion of the critical magnetic field measurements on a single crystal of molybdenum are presented and compared with the calculations from the specific heat measurements and with the predictions of the BCS theory. The latter part of the section 2 is devoted to the comparison of the theory of supercooling to the experimental results on the supercooling field of Mo.

1. Experimental Procedure

The sample used for these measurements was a triple electron-beam-zone-refined single crystal in the form of a rod 1 in. long and 1/8 in. diam. purchased from Materials Research Corporation. The resistance ratio of the sample was measured and found to be \( R_{300}/R_{1.2} = 10^4 \) with the residual resistivity \( \rho_o = 5.7 \times 10^{-10} \Omega \text{-cm} \). From the measurement of \( \rho_o \), the mean free path was estimated by
using the relation $\lambda = V_F \tau = \frac{3\sigma}{2e^2} N(0)V_F$, where $\sigma$ is the residual electrical conductivity, $V_F$ is the Fermi velocity, and the density of states is $N(0) = \frac{3\gamma}{2\pi^2} \hbar^2$. Deducing the electronic specific heat constant $\gamma$, the Fermi velocity $V_F$, and coherence length $\xi_0$ from our critical field measurements, yields $\lambda = 2.8 \times 10^{-2}$ cm and its ratio to the coherence length $\xi_0$, $\lambda/\xi_0 \approx 780$.

The transition at a given temperature was detected by observing the emf induced in a pickup coil wound around the sample, as an axial external field was swept linearly at a rate of about 0.25 G/sec (see Appendix C) through the value of the critical field. The emf was used to drive the y-axis of a x-y recorder, the x-axis of which was driven by a voltage proportional to the current in the solenoid. Two methods were used to observe the emf. In the first method, hereafter referred to as modulated-field technique, the external dc field was modulated by a 270 cycle/sec field and the emf induced in the coil was fed to a lock-in amplifier, the output of which was connected to the y-axis of the recorder. Though the detection of the transition was accurate, as shown in Fig. 1(a), the method failed to reveal the details of the transition. An alternate method in which there was no modulation superimposed on the external field, hereafter referred to as dc field technique, was to observe the emf directly after amplification by a dc amplifier. This method proved satisfactory in producing the details of the transition in a manner similar to that observed in other measurements.$^{36,41}$ In Fig. 1(b), a typical
(a) Modulated Field

(b) dc Field

Fig. 1
transition signal is shown. The sample was first cooled down to the lowest temperature in zero field. The field was then linearly increased and the external field at the transition to the normal state was identified with the thermodynamic critical field $H_c$. The direction of the field sweep was then reversed until the completion of the normal to superconducting transition, and the value of the external field at which the transition started was identified with the supercooling field $H_s$. The sample was brought to the normal state again by increasing the field, and the value of $H_c$ was observed to be reproducible. The bath temperature was then raised to a higher value, and the values of $H_s$ and $H_c$ at the new temperature were respectively determined by a downward sweep followed by an upward sweep of the external field such that the final state of the sample was normal. The bath temperature was then raised further and the procedure was repeated until the transition temperature $T_c$ was reached.

2. Experimental Results and Discussions

A. The Thermodynamic Critical Field

The temperature dependence of the thermodynamic critical field $H_c$ and the supercooling field $H_s$ are plotted in Fig. 2 for the two techniques. The solid lines are least-square fits of the form

$$ H = H_0 + \sum a_n T^{2n} $$

to the data from the modulated field technique. The values $H_c(0) = 96 \pm 2$ and $T_c = 0.903 \pm 0.003$ are calculated from the expression corresponding to the upper curve at the two limits $T = 0$ and $H = 0$, respectively. The data from the modulated field technique were used for the least-square fit.
Critical Field (Gauss)

$H_0 = 96 \pm 2$

$T_c = 0.903 \pm 0.003 \degree K$

Modulated Field

- $H_C$
- $H_S$

DC Field

- $H_C$
- $H_S$

Temperature (°K)
because they extend to lower temperatures than the dc field data. The latter, however, proved more useful in producing the details of the transition signal. It was observed that the normal to superconducting transition is very sharp while the superconducting to normal transition has distinct individual peaks\textsuperscript{36,41} that show complete reproducibility at all temperatures, although they smear out into one smooth peak close to \( T_c \). Fig. 1(b) shows a typical transition signal from the dc field technique, and the individual peaks are clearly distinguished. The onset \( P_0 \) of the transition was attributed to the end effects, and the first peak \( P_1 \) was taken to represent the penetration of the external field into the bulk of the sample, i.e., \( H_c \). For the completeness of the comparison of the two techniques, however, the values of the external field at \( P_4 \) are plotted in Fig. 2 and those at \( P_1 \) in Fig. 3. With the exception of Fig. 2, \( H_c \) is to correspond to the peak \( P_1 \) throughout the present work. Fig. 3 is the plot of \( H_c \) vs. \( (T/T_c)^2 \). We have also plotted the values of critical field computed by Rorer \textit{et al.}\textsuperscript{36} from their specific heat data. Their Mo - 4 sample was chosen for comparison because it seemed closer in characteristics to ours (same commercial source). With the exception of the value for the transition temperature \( T_c \), the overall agreement of the results is excellent. The values of the electronic specific heat constant and the energy gap parameter at \( T = 0 \) were obtained from the expressions of BCS, \( \gamma = 1/19.4 \) \( (dH_c/dT)^2 \text{ at } T = T_c \) and \( 2\epsilon(0)/\kappa T = 4\pi/\sqrt{3} \left[ H_c^2(0)/8\pi\gamma T_c^2 \right]^{1/2} \), using the experimental values of \( T_c \) and \( (dH_c/dT) \text{ at } T = T_c \) and \( H_c(0) \). As shown
Fig. 3

- Rorer et al.
- Modulated Field
- dc Field
in Table II, they are in good agreement with those of the specific heat measurements. In Table II, some of the results of this work are presented and compared with other experiments and available calculations. To complete the comparison, the deviation of the critical field of molybdenum from a simple parabolic law, together with the results of BCS, in the limit of weak coupling, are shown in Fig. 4. The deviation is found to be similar to that predicted by the BCS theory.

B. Supercooling and Other Critical Fields of Molybdenum

The temperature dependence of the supercooling field \( H_s \) in molybdenum was shown in Fig. 2, and it is observed that \( H_s \), at which the transition to the Meissner state takes place, is always smaller than \( H_c \) at all temperatures. The significance of \( H_s \) is in its relation with the surface nucleation field \( H_{c3} \) and its distinction from the bulk nucleation field \( H_{c2} \) in a type I superconductor. Here both \( H_{c3} \) and \( H_{c2} \) have to be given special meanings. Saint-James and de Gennes, using the Ginzburg-Landau equation, have shown that in a magnetic field parallel to the sample surface, a localized superconducting region can be present near the surface (surface sheath) up to a field \( H_{c3} \), significantly higher than \( H_{c2} \), with \( H_{c3}/H_{c2} = 1.695 \) at \( T = T_c \). Recent calculations \(^{53-55} \) of \( H_{c3}/H_{c2} \) show that this ratio increases as the temperature is lowered below \( T_c \). In type I superconductors, \( H_{c2} \) is smaller than \( H_c \) and, depending on the Ginzburg-Landau parameter, so may be \( H_{c3} \). Nevertheless, both critical fields still have significance: \(^{53} \) \( H_{c2} \) as the smallest field for which
| Technique                     | \( T_c,^\circ\text{K} \) | \( -\frac{dH_c}{dT}|_{T_c},^G/\circ\text{K} \) | H(0), G    | \( \frac{2\varepsilon(0)}{kT_c} \) | \( \gamma, \text{mJ/mole-deg}^2 \) |
|------------------------------|----------------|-----------------|---------|----------------|----------------|
| Critical magnetic field\( ^a \) | 0.930          | 98.2            |         |                | 1.61           |
| Critical magnetic field\( ^b \) | 0.916          | \( \sim188 \)   | 86 \pm 1.5 |                |                |
| Specific heat\( ^c \)          | 0.917          | 178 \pm 2      | 96 \pm 3 | 3.40 \pm 0.10  | 1.87 \pm 0.02  |
| Magnetization\( ^d \)          | 0.903          | 98              |         |                |                |
| Ultrasonic attenuation\( ^e \) | 0.92 \pm 0.01  | 114             | 3.5 \pm 0.2 (q\|[100]) |
| Ultrasonic attenuation\( ^f \) | 0.92 \pm 0.01  |                 | 3.3 \pm 0.2 (q\|[100]) |
| Present work:                 |                |                 |         |                |                |
| Critical magnetic field       | 0.903 \pm 0.003| 187 \pm 3   | 96 \pm 2 | 3.4 \pm 0.1    | 1.80 \pm 0.06  |
| Thermal conductivity          | 0.903 \pm 0.003|                 |         | 3.2 \pm 0.1    |                |

\( ^a \text{See Ref. 37} \\
\( ^b \text{See Ref. 38} \\
\( ^c \text{See Ref. 36} \\
\( ^d \text{See Ref. 41} \\
\( ^e \text{See Ref. 40} \\
\( ^f \text{See Ref. 39} \)
the sample can be kept metastably normal in a "supercooling" situation, when surface effects are not important; and $H_{c3}$ as the smallest field for which the sample can be kept metastably normal in a "supercooling" situation when the field is parallel to the surface. SJdG were first to suggest that in type I superconductors, when the field is parallel to the surface, the supercooling field is $H_{c3}$ (wherever $H_{c3} < H_c$) rather than $H_{c2}$. However, from the one dimensional Ginzburg-Landau equations, Feder has predicted the existence of a metastable superconducting surface sheath on a supercooled material, even when $H_{c3} < H_c$, if the Ginzburg-Landau parameter $\kappa$ is larger than a critical value $\kappa_c$. This introduces the crucial notion that the supercooling field $H_g$ has to be distinguished from $H_{c3}$ for values of $\kappa$ in a certain range. Thus it is only when $\kappa < \kappa_c$ that $H_{c3}$ can be identified with the supercooling field. The limiting field, below which there are no surface solutions (the field at which transition to the Meissner state takes place), has been calculated by Park who has shown that there are metastable surface solutions below $H_c$ even when $H_{c3} > H_c$. The magnetization experiments of McEvoy et al. on lead and tantalum have shown a qualitative agreement with the above theoretical predictions. The reported values of $\kappa_c$ from the theories and from experiment range from 0.406 to 0.409.

Since it is apparent, following, Feder's and Park's ideas, that $H_{c3}$ cannot be identified with $H_g$ over the whole range of temperature, and a direct measurement of $H_{c3}$ was not possible
in the present experiment, it is our purpose to compare the experimental values of $H_g$ with the theoretical calculations\textsuperscript{53,54} of $H_{c3}$. This comparison is more meaningful if made as a function of the Ginzburg-Landau parameter $\kappa$ rather than as a function of temperature. The temperature dependence of $\kappa$ can be determined from the ratio $H_{c2}(t)/H_c(t)$, but $H_{c2}(t)$ cannot be observed without difficulty in type I superconductors. Fortunately, the theoretical computations of $\kappa$ and $H_{c2}$ can be made with relative confidence.

Using a gauge-invariant solution of the linearized Gor'kov\textsuperscript{58} equations, Helfand and Werthamer\textsuperscript{59} have calculated the bulk nucleation critical field $H_{c2}$ and the Ginzburg-Landau parameter $\kappa$ for all impurity concentrations and all temperatures below $T_c$. Their impurity concentration parameter $\lambda = 0.882 \frac{V_0}{\ell}$ is estimated to be of the order of $10^{-3}$ for our sample, thus putting the molybdenum well within the pure limit of their theory. From their calculations, $\kappa(\lambda,t) = \kappa(\lambda,T_c) \times f(\lambda,t)$ where $t = T/T_c$ and $f(t,\lambda)$ is a normalized known function of the reduced temperature and the parameter $\lambda$. Therefore, one can determine $\kappa(t)$ if the value of $\kappa$ at the transition temperature is known. From the preliminary analysis of the data, it was predicted that $\kappa(T_c) < \kappa_c$ and, we are therefore, assuming that in the region close to $T_c$, $H_{c3} = H_g$. Then, assuming the validity of SJdg's relation,\textsuperscript{50} $\kappa(T_c)$ can be obtained from the extrapolation of the experimental values of the ratio $H_{c3}/1.695/2H_c$ to $T = T_c$, which yields $\kappa(T_c) = 0.365 \pm 0.005$. From $\kappa(t)$ and the relation $H_{c2}(t) = \kappa(t) H_c(t)$, one can
determine $H_{c2}(t)$ using the experimental temperature dependence of $H_c(t)$. The calculated values of $H_{c2}(t)$ are shown in Fig. 5 together with experimental data of $H_s$ and $H_c$. The slope of $H_{c2}(t)$ at the transition temperature is $(dH_{c2}(t)/dt)_{t=1} = 84.4$.

In Fig. 6 the experimental ratio $H_s/H_c$ vs. $\kappa(t)$ is plotted together with the results of Park from his table of calculated values. The straight line is the ratio $H_{c3}/H_c = 2.392 \kappa(t)$ assuming the validity of SJdg's relation to extend to all temperatures. This line coincides, as it should, with the extrapolation of the results of Park to lower values of $\kappa$. As typical calculations of the ratio $H_{c3}/H_c$, we have plotted that of Hu and Korenman\textsuperscript{53} for the case of specular reflection of the electrons from the surface and that of Luders\textsuperscript{54} for the two cases of $P = 0.5$ and $P = 1$ where $P$ is a parameter proportional to the diffuseness of the surface. The crossing of the experimental points from the curve of Park to the curve of $H_{c3}/H_c$ is not contrary to his theoretical predictions and can be attributed to his wrong choice of $H_{c3}$, thus confirming the recent theoretical calculations\textsuperscript{53,54} of $H_{c3}$. The value of $\kappa$ at which the experimental points deviate from the curve of $H_{c3}/H_c$ is taken, in agreement with Feder's definition, to be $\kappa_c = 0.375$ and only if $\kappa < \kappa_c$ can $H_{c3}$ be identified with the supercooling field. The fact that the range of $\kappa$ characteristic of our sample was such as to display this region is fortuitous; however, the range of comparison of the possible experimental points with the theoretical calculations of $H_{c3}/H_c$ is too small to allow a
$T_c = 0.903 \pm 0.003\, ^o K$
quantitative comparison between the different theories. From Fig. 6 one can obtain \( \kappa_b = 0.389 \) at which \( H_{c3} \) changes from smaller to larger than \( H_c \). At higher values of \( \kappa \), i.e., \( \kappa > \kappa_b \), the experimental points fall systematically below the calculated values of Park and show but a faint tendency to approach the value \( H_s/H_c = 1 \) in the limit of large \( \kappa \).

Thus, one can clearly distinguish three regions: firstly, \( \kappa < \kappa_c \) where \( H_s = H_{c3} < H_c \), secondly, \( \kappa_c < \kappa < \kappa_b \) where \( H_s < H_{c3} < H_c \), and, finally, \( \kappa > \kappa_b \) where \( H_s < H_c < H_{c3} \). These regions are shown in Fig. 5 where \( H_{c3} \) is plotted along with other critical fields of molybdenum vs. temperature. In the region where the supercooling field is smaller than \( H_{c3} \), a metastable surface sheath co-exists with a supercooled normal bulk. It would be of interest to extend the results of the present work to lower values of \( \kappa \) and compare the supercooling field with the calculations of \( H_{c3} \). The early work of Pinatti and Rorschach on supercooling of molybdenum shows a decrease in \( \kappa \) by annealing. Unfortunately, the complete temperature dependence of their data was not available to determine whether it falls on the extension of the present data to lower values of \( \kappa \).
CHAPTER III

THERMAL CONDUCTIVITY OF MOLYBDENUM SINGLE CRYSTAL IN

THE SUPERCONDUCTING AND NORMAL STATES

The thermal conductivity $K$ of a metal is the sum of two
parts: one is the contribution $K_e$ of the electrons, and the
other is the contribution $K_g$ of the phonons:

$$K = K_e + K_g$$ \hspace{1cm} \text{III.1}

In the normal state the electronic conductivity, at
$T < \frac{1}{10} \theta_D$, is given by\textsuperscript{60,61}

$$\frac{1}{K_{en}} = AT^2 + \frac{B}{T}$$ \hspace{1cm} \text{III.2}

The first term on the right is the resistivity due to the electron
scattering by phonons, and predominates at higher temperature; the
second term is the resistivity due to scattering by static
imperfections. The ratio, $a = AT^3/B$ is then the ratio of the
phonon scattering to the static imperfection scattering in the
thermal resistivity of the normal state. Also in the normal
state the phonon conductivity $K_{gn}$, at very low temperature, is
given by\textsuperscript{60}

$$\frac{1}{K_{gn}} = \frac{A}{T^2} + \frac{B}{T^3}$$ \hspace{1cm} \text{III.3}
The first and second terms arise from the scattering of phonons by electrons and by crystal boundaries respectively.

In the superconducting state, the thermal conductivity of a metal can be qualitatively predicted in terms of the two-fluid model. The condensed "superconducting" electrons cannot carry thermal energy nor can they scatter phonons. With decreasing temperature their number increases and that of the normal electrons correspondingly decreases, which will result in a rapid decrease of the electronic heat conduction. At the same time the conduction by phonons will be enhanced, as these are no longer scattered as much by electrons. In pure specimens, the total conductivity in the superconducting phase will then be much smaller than in the normal phase.

The most definitive information about thermal conductivity can be obtained when only one of the contributions to the conductivity, electronic or phonon, is dominant and even then, when only one type of scattering mechanism for the dominant carrier is important. In the case of our molybdenum sample, because it has a very high Debye temperature relative to its superconducting transition temperature and because it has a large electronic mean free path due to its high purity, one may expect firstly a negligible lattice conductivity compared to the electronic conductivity and secondly a negligible scattering of electrons by thermally excited lattice vibrations compared with their scattering by static imperfections such as impurities, lattice defects, or at even lower temperatures by the boundaries.
Then one can compare the experimental results with a theory appropriate to the contributions of the dominant carrier and the mechanism by which it is scattered. One such calculation is the work of BRT who, within the framework of the one-band isotropic model of BCS, have calculated the electronic thermal conductivity when elastic impurity scattering or lattice scattering predominate. They have also calculated the lattice contribution $K_g$ when electronic scattering is predominant. The calculations of BRT yield the ratio of the superconducting to normal conductivity, and only for the case of the electronic contribution and when the boundaries or impurities are the major electron scattering mechanism, does their theory fairly agree with experiment. Vasudevan and Sung have carried out a calculation of $K_{es}/K_{en}$ in the region $T/T_c > 0.5$, for impurity scattering using the method of BRT and adopting the spherical two-band model of Suhl et al. which is applicable to the transition metals. They find a conductivity ratio which is lower than that obtained by BRT. One would expect the comparison of the two calculations with the experiment to determine the extent of the validity of either of the two models adopted by their authors. In practice, however, such determination is made difficult because of problems involved in separating the lattice and electronic contribution to the conductivity and also because of the problems introduced by a possible anisotropy of the energy gap. One expects that in the presence of anisotropy, the smallest gap becomes more important at lower values of $T/T_c$.

In this chapter, following a brief description of the
experimental techniques, the results and discussion of the thermal conductivity measurements on both the superconducting and normal states of a molybdenum single crystal have been presented. A comparison of the results with the theory of BRT is made and the possibility of sd-interband scattering is discussed.

1. Experimental Procedure

The sample used for the thermal measurements was 3 in. long and had original characteristics similar to the first sample. This sample was first reduced to a rectangular cross section of approximately 1 mm x 1 mm by grinding with Carborundum powder and polishing with emery paper #600. It was then annealed at about 1200°C and 10⁻⁵ Torr for 16 h. The surface oxidation and the local strains close to the surface were removed in a strong acid solution (H₂SO₄, HNO₃, HF and H₂O₂) and finally the sample was etched several times in a strong etchant (HCl and H₂O₂). The final average cross section of the sample was approximately 1/3 mm x 2/3 mm. The electrical resistance stayed constant between 4.2°K and 1°K with a resistance ratio of $\Gamma = \frac{R_{300}}{R_{1.2}} = 3500$ and a residual resistivity $\rho_0$ of $15.8 \times 10^{-10}$ Ω cm. The resistance ratio was smaller than that of the first sample suggesting a higher concentration of structural defects and probably incomplete annealing. Using $V_F$, $\gamma$ and $\xi_0$ of the first sample, the electronic mean free path was estimated to be $\ell = 1.0 \times 10^{-2}$ cm with the ratio $\ell/\xi_0 = 285$, indicating the high purity of the sample. The sample, inside a vacuum calorimeter, was soldered to the He³ copper cup. A heater of Constantan wire No. 40 was wound at the
end of the sample and covered with General Electric No. 7031 glue. The temperature gradient along the sample was measured by two carbon resistance thermometers whose copper windings were soldered to copper spots on the sample. The temperature measuring circuit and the method of measuring thermal gradient in the He\textsuperscript{4} range of temperature have been described by Wasim et al.\textsuperscript{62} A similar method was followed in the He\textsuperscript{3} range of temperature. The two thermometers, at the two ends of the sample, were electrically connected as two arms of a bridge which was initially balanced at a bath temperature $T_0$ in the absence of any heat flow through the sample. The temperature of the bath was then lowered to $T_0 - \Delta T$, where $\Delta T$ was of the order of 30 to 50 mK. Then the heat current was adjusted so that the thermometer closest to the heat source had the same resistance as at $T_0$. The resistance of the calibrated thermometer, placed at the cold end of the sample, would then correspond to $T_0 - \delta T$ where $\delta T$ is the temperature drop along the sample and, therefore, the temperature gradient was obtained directly from the characteristics of only one thermometer.

2. Experimental Results and Discussion

The temperature dependence of the thermal conductivity of molybdenum in the superconducting state $K_s$ and in the normal state $K_n$ is plotted in Fig. 7. $K_s$ and $K_n$, below 10K, are also plotted in Fig. 8. The critical temperature $T_c$ is estimated to be the same as that determined from the critical field measurements. The solid line passing through the normal points is a least-square fit of the form $K_n = (\Delta T^2 + B/T)^{-1}$ to the data, where
$K_n = \frac{L_0 T}{\rho_0}$

$T_c = 0.903 \pm 0.003$

$K = \frac{W \text{ cm}^{-1} \text{ deg}^{-1}}{\rho_0}$
Fig. 8

\[ K \text{ (W cm}^{-1} \text{ deg}^{-1}) \]

\[ \frac{T}{T_c} \]

\[ T_c = 0.903 \pm 0.003 \]
A = 5.13 \times 10^{-5} \text{ (W}^{-1} \text{ cm deg}^{-1}) \text{ and } B = 6.40 \times 10^{-2} \text{ (W}^{-1} \text{ cm deg}^{2}).

The straight dashed line which very nearly fits the data below 1^\circ K is obtained from the residual resistivity \(\rho_0\) by assuming the validity of the Wiedemann-Franz relation

\[ K_n = \frac{L}{\rho_0} \text{ cm deg}^{-1}. \]

\[ \rho_0 = 1.58 \times 10^{-9} \Omega \text{ cm}, \quad K_n = 15.5 \times 10^6 \text{ W cm}^{-1} \text{ deg}^{-1}. \]

The tendency of the experimental data to fall below this line above the transition temperature is attributed to a small resistive component due to scattering of electrons by phonons. The analysis of the normal-state conductivity in terms of different scattering mechanisms has been made for a free-electron model. \(^{61}\) The electronic thermal conductivity \(K_{en}\) at \(T < \theta_o/10\) (\(\theta_o\) is the Debye temperature) is given by

\[ \frac{1}{K_{en}} = AT^2 + \frac{B}{T}, \]

III.4

where \(A = 95.3N_a^{2/3}/K_\infty^2\) and \(B = \rho_0/L_o\); \(N_a\) is defined as the effective number of conduction electrons per atom, \(K_\infty\) is the limiting value of the electronic thermal conductivity at high temperatures, \(\rho_0\) is the residual electrical resistivity, and \(L_o\) is the Lorentz number. The first term on the right hand side of Eq. III.4 represents the electronic thermal resistivity due to phonon scattering, and the second term represents the electronic thermal resistivity due to impurity scattering. Figure 9 shows the plot of \(T/K_n\) vs \(T^3\). The straight line represents a least square fit to the data. The slope of the straight line gives the value of the constant \(A = 5.13 \times 10^{-5} \text{ W}^{-1} \text{ cm deg}^{-1}\). The
intercept gives \( B = 6.40 \times 10^{-2} \text{ W cm}^{-2} \text{ deg}^{-1} \), which differs by about 1% from the result obtained from the residual resistivity measurements. From the experimental value of \( A \) and using \(^{36} \theta = 456^\circ K\) and \(^{63} K_\infty = 0.8 \text{ W cm}^{-1} \text{ deg}^{-1} \), we derive an effective number of conduction electrons per atom, \( N_a = 0.89 \). The BRT theory assumes elastic impurity scattering of the electrons in the calculations of the ratio \( K_{es}/K_{en} \) where \( K_{es} \) and \( K_{en} \) are the electronic contributions to the thermal conductivity in the superconducting and normal states. Kadanoff and Martin\(^ {64} \) have calculated the ratio \( K_s/K_n \) taking into account electron-phonon interaction and impurity scattering. Their calculation involves a parameter \( \alpha = \frac{A T^3}{B} \) which is the ratio of the phonon scattering to the impurity scattering in the thermal resistivity. In the limit of predominance of impurity scattering, i.e., \( \alpha \approx 0 \), their result is identical with that of BRT. Using the experimental values of \( A \) and \( B \), one finds \( \alpha \approx 10^{-3} T^3 \) and, therefore, the phonon contribution to the scattering below \( 1^\circ K \) is estimated to be at most 0.1% of the total thermal resistivity. This corresponds to the case of \( \alpha = 0 \) in the theory of Martin and Kadanoff. Thus the preponderance of the impurity scattering below \( 1^\circ K \) allows us to make a direct comparison of the temperature dependence of \( K_s/K_n \) to the theory of BRT. The predominance of the electronic contribution to the thermal conductivity of the sample is confirmed from its electrical and thermal conductivity measurements in high magnetic fields.\(^ {65} \) It was observed that the normal lattice conductivity \( K_n \) was not more than 0.1% of the total conductivity...
It is also shown later in the text that the superconducting lattice conductivity $K_s$ does not exceed more than 3% of $K_n$ for $T/T_c > 0.4$. Therefore, $K_s/K_n \approx K_{es}/K_{en}$ in the case of our sample. The BRT relation for the case of elastic impurity scattering of electrons is:

$$\frac{K_{es}}{K_{en}} = \left[ 2F_1(-y) + 2y \ln (1+e^{-y}) + y^2 (1+e^{-y})^{-1} \right] / 2F_1(0) \tag{III.5}$$

where $y = \frac{\epsilon(t)}{kT} \approx \left[ \frac{\epsilon(t)}{\epsilon(0)} \right] \left[ \frac{\epsilon(0)}{kT_c} \right] (1/t)$, $\epsilon(t)$ being the half width of the energy gap at temperature $T$ in the BCS theory.

The temperature dependence of $\frac{\epsilon(t)}{\epsilon(0)}$ has been calculated by Muhlschlegel based on the BCS theory and the term $F(-y)$ is given by the expression

$$F_n(-y) = \int_0^\infty \frac{z^n dz}{(1+e^{z+y})}$$

The experimental values of $K_s/K_n$ vs reduced temperature are plotted in Fig. 10 together with the theoretical curves of BRT computed for several values of the energy gap. It is observed that the value of energy gap $2\epsilon(0)/kT_c = 3.4 \pm 0.1$ agrees reasonably well with the experimental results for temperatures $T > 0.5 T_c$.

This value coincides with the one we obtain from the critical field measurements. At lower temperature, however, there is a definite tendency of the experimental points to deviate from the BRT relation, and this deviation is more than the probable experimental error.
Fig. 10

- $K_n, K_s$ both measured
- $K_s$ measured, $K_n$ interpolated

(BRT)

- $2\epsilon(0) = 3.2\; kT_c$
- $2\epsilon(0) = 3.3\; kT_c$
- $2\epsilon(0) = 3.4\; kT_c$
- $2\epsilon(0) = 3.5\; kT_c$
In view of the overall agreement of the experimental ratio $K_s/K_n$ with the result of BRT for $K_{es}/K_{en}$, and the close agreement of the critical field measurements with the theory of BCS, one may choose to give an immediate and self-contained explanation: that superconductivity in molybdenum is the same as that in the non-transition metals, and the deviation of the experimental data from the BRT curve, at lower temperatures, is due to the increase of the lattice contribution to the thermal conductivity in the superconducting state. From BRT's theory $K_{gs}$ increases with decreasing temperature and is proportional to $T^{-3}$. In fact, Engelhardt et al. have argued that the s-d interaction in molybdenum, owing to the intrinsic stability of a half-filled d-shell and high lattice stability for a d$^{5}$s$^{1}$ configuration, such as the molybdenum configuration, is small; and the s-electrons, much in the manner of non-transition elements, are the major contributors to the superconductivity. This argument is supported by the $T^{5}$ dependence of the resistivity of molybdenum in the normal state which is attributed to the scattering of the s-electrons by phonons into s-states. However, the discussion below will show that the assumption of non-transition-like superconductivity in molybdenum and the complete absence of s-d interaction, which is inherent in that assumption, leads to several shortcomings.

The s-d Interaction: The energy gap parameter obtained by fitting the experimental data to the theory of BRT is larger than the value determined by ultrasonic attenuation in the study of the
anisotropy of the energy gap in molybdenum as shown in Table II. Moreover, a consequence of fitting the experimental data to a BRT curve is to attribute the deviations from the curve, at low temperatures, to the lattice contribution to the thermal conductivity. This deviation, as seen in Fig. 10, amounts to a 15% increase over the electronic conductivity in the superconducting state at temperature $T = 0.4 T_c$. This would indicate that the lattice contribution is about $K_g \approx 0.225 \text{ W cm}^{-1} \text{ deg}^{-1}$. It can be shown, using magnetoresistance measurements, that such high lattice conductivity in the superconducting state leads to an unreasonably high ratio $K_{gs}/K_{gn} \approx 400$ since $K_{gn}$, at this temperature, is estimated to be only $0.0006 \text{ W cm}^{-1} \text{ deg}^{-1}$. Comparison of this result with the calculations of BRT, for the case of lattice conductivity limited by electron scattering, shows that it is approximately 5 times larger than their prediction. Thus a generous estimate of the lattice contribution $K_{gs}$ to the thermal conductivity $K_g$ does not, at $T = 0.4 T_c$, exceed more than three percent of the total conductivity. Therefore, the source of the deviation of the experimental data of $K_{gs}/K_{en}$ from the BRT curve must lie elsewhere.

It is well known that the transport properties of transition metals, both in the normal and superconducting states, should be influenced by the presence of a narrow energy band with high density of states: the d-band. The role of the d-band in conduction seems mostly that of providing a number of alternative
states in which s-electrons can be scattered. Following the initial work of Suhl et al.\textsuperscript{32} who proposed that in transition elements the superconducting state may be characterized by a two-band structure with contributions arising from interband s-d scattering, Vasudevan and Sung\textsuperscript{44} extended the BRT calculation on thermal conductivity due to impurity scattering to the two-band model.

The basic feature of these results is that the added resistance due to interband scattering is prominent only close to $T_c$. Qualitatively, for the transition metals, this means that when one fits experimental results to the BRT curve, one should expect the points close to $T_c$ to fall below the theoretical curve and only points at lower temperatures should be expected to agree with BRT and to yield a reliable value of the energy gap.

From this point of view, we reinterpret figure 10 as follows: Fitting the lowest group of points to BRT yields an energy gap $2\xi(0)/kT_c = 3.2 \pm 0.1$ while the shift of the points at higher temperatures gives an indication of the effect of allowing interband transitions due to impurity scattering.\textsuperscript{69} An extension of the data to lower temperatures would be needed to make this argument more than qualitative. The disagreement between the above value of the energy gap and the results of the specific heat measurements\textsuperscript{36} and our critical field measurements is believed to be due to the anisotropy of the energy gap.\textsuperscript{68}

There exists corroborating evidence in the experimental
results obtained in niobium by Wasim and Zebouni. The straight fit to BRT curves presented in their work yield an energy gap of 3.96. This result is higher than most previous experimental determinations, especially those made by tunneling.

We now think that the niobium data, taking into account the influence of impurity scattering in the two-band model, should be fitted to a BRT curve of approximately \(2\xi(0)/kT_c = 3.8\). The situation in the niobium case is evidently complicated by the sharp rise of lattice conductivity at lower temperatures.

In conclusion, we are suggesting that results of thermal conductivity in the superconducting state of transition metals, when they are fitted to a BRT curve, yield only an upper limit of the value of the energy gap. The situation is quite delicate since not only is there added scattering close to \(T_c\), but there also is added conductivity due to the increase in the lattice contribution at the lower end of the temperature range.
CHAPTER IV

CONCLUSION

The present study indicates that the critical magnetic field of molybdenum is in fair agreement with the predictions of the BCS theory in the limit of weak coupling. The value of the energy gap calculated from the thermodynamic critical field data is in agreement with the value obtained from the specific heat measurements.\(^36\)

The persistence of a supercooling field smaller than the thermodynamic critical field, at all temperatures, has been established. Assuming a temperature dependence of the Ginzburg-Landau parameter, \(\kappa\) of molybdenum, similar to the one suggested by Helfand and Werthamer,\(^59\) it is observed that only close to \(T_c\) where \(\kappa < \kappa_c = 0.375\), is the supercooling field, \(H_s\) the same as the surface nucleation field, \(H_{c3}\). Furthermore, \(H_{c3}\) has to be obtained from the recent calculations of Hu and Korenman\(^53\) or Luders\(^54\) (our experiment cannot distinguish between the two calculations) rather than the calculations of Saint-James and de Gennes.\(^50\) For values of \(\kappa\) larger than \(\kappa_c\), the experimental supercooling field deviates from the theoretical values of the surface nucleation field while the latter is still smaller than the thermodynamic critical field. This is attributed, following the calculations of Feder,\(^51\) and Park,\(^56\) to the existence of a metastable superconducting surface sheath on a supercooled normal
bulk. Even when \( \kappa > \kappa_b = 0.389 \), i.e. even when \( H_{c3} > H_c \), the observed \( H \) is smaller than \( H_c \). This is in agreement with the predictions of Park that a metastable superconducting surface sheath exists even when \( H_{c3} > H_c \). In short, the supercooling field data can be explained in terms of a unified picture of the different thermodynamic critical fields calculated from the Ginzburg-Landau equations, with the main assumption that such calculations apply to type I superconductors just the same as to type II.

The study of the thermal conductivity of molybdenum in both the superconducting and normal states provides a basis of comparison with the theory of BRT. The value of the energy gap obtained from such a comparison at temperatures close to \( T_c \) is in agreement with the result of the critical field measurements and also with the value calculated from the specific heat measurements. However, a comparison of the experimental results at lower temperatures with the theory, yields an appreciably lower value of energy gap. The apparent discrepancy can be explained either in terms of the anisotropy of the energy gap of molybdenum or in terms of the \( \text{sd-interband scattering} \), since either effect may be appreciable because of the high purity of the sample.

From the point of view of energy gap anisotropy, one can argue that in a volume effect measurement, the mean value of the energy gap is dominant close to \( T_c \), while the smaller value of the gap predominates at lower temperatures. If this is the case, the agreement between the energy gap obtained from the thermal
conductivity results, close to $T_c$ and that obtained from the critical field measurements is not surprising since the latter depends on the value of the slope of the critical field at $T_c$. The lower value of the energy gap, indicated by the thermal conductivity results at the lower temperatures, is also consistent with the reported values of the anisotropy of the energy gap from ultrasonic attenuation measurements.

From the point of view of sd-interband scattering, one can assign to the energy gap the value obtained by fitting the experimental data, at lower temperatures, to the theory of BRT, and thus interpret the apparent fall in the thermal conductivity, close to $T_c$ (see Fig. 10), in terms of sd-scattering: the interband sd-scattering, effectively provides new states for the s-electrons to scatter into and therefore decreases the mean free path of the electrons, i.e. reduces the thermal conductivity. It should be noted that the sd-scattering picture is still consistent with the observed anisotropy of the energy gap if one assumes that the thermal conductivity is anisotropic. In such a case, the energy gap component in the direction of the heat current dominates at all temperatures and an upper limit to its magnitude is obtained from the thermal conductivity data at lower temperatures where the sd-scattering effect is small. As a matter of fact the present measurements were carried out in a crystallographic direction very close to [111] and the result agrees with that of the ultrasonic attenuation measurements in the same direction.
Finally, it should be pointed out that, if sd-scattering is responsible for the behavior of the thermal conductivity close to $T_c$, the disagreements between the values of the energy gap obtained above and that obtained from the critical field measurements is simply due to the fact that the latter can still be considered as a volume effect and therefore dependent on the mean value of the energy gap.
APPENDIX A

APPARATUS

a. He\textsuperscript{3} Refrigerator

The He\textsuperscript{3} refrigerator used in these experiments was the one constructed by Blewer\textsuperscript{70} who has given a complete description of the basic construction and operation of the system. The system was similar to the one described by Reich and Garwin.\textsuperscript{71} Several modifications were made on this system and the procedure of its operation. Also, a new electronic temperature regulator was designed and built for the purpose of maintaining constant temperature in the system. In this appendix, we discuss the modifications introduced in the He\textsuperscript{3} refrigerator and the changes in the procedure of its operation. The description of the temperature regulator is presented in Appendix B. Figure 11 shows a schematic of the He\textsuperscript{3} refrigerator. The only changes in the original construction of Blewer were addition of valve G and the replacement of valve F by a high quality throttling value. The function of valve G was to provide access to the He\textsuperscript{3} system in the case that it was necessary to keep the section between the storage pump and valve F under vacuum. The function of valve F, similar to that of valve C,\textsuperscript{70} was the manual regulation of temperature during the continuous operation of the system. It provided a control over the flow of He\textsuperscript{3} gas into the low temperature section of the system. The partial closure of valve F
was effectively the same as increasing the pumping speed on the liquid $\text{He}^3$, therefore, the temperature of the system could be maintained constant, at any desired value between $0.65^\circ\text{K}$ and the lowest attainable temperature, through the use of this valve. The fine control over the temperature regulation, in both the continuous and batch operation, was provided by an electronic heater-feed-back system. (see Appendix B).

The modified operation of the $\text{He}^3$ system differed from that described by Blewer only in the precooling period. In the modified operation, at no time was $\text{He}^4$ introduced inside the $\text{He}^3$ system, and therefore, there would be no danger of contamination of $\text{He}^3$ gas by $\text{He}^4$ impurity. Below, the operation of $\text{He}^3$ refrigerator is described starting from the room temperature. The complete procedure is given by Blewer in an appendix to his doctoral thesis. 70

The $\text{He}^3$ refrigerator was prepared for operation (valves A, B, E, G and H closed; valves C, D and F open) by evacuating it, at room temperature, to a pressure of approximately $7 \times 10^{-6}$ mm Hg through valve D (see Fig. 11), which was then closed. The "insulation vacuum" space, surrounding the sample holder was then flushed several times with helium-free nitrogen gas. The schematic of the flushing system is shown in Fig. 12 which also shows the details of the sample holder. A virgin gum rubber tube, one end of which was immersed in liquid nitrogen, was connected to the free end of valve 2. With valve 1 open, the valves 2 and 3 could be manipulated in turn to first evacuate the system, fill
Fig. 12

- **FORE PUMP**
- **LIQUID NITROGEN**
- **CONDENSER**
- **He^3**
- **He^4**
- T.I.
- SHIELD

Components labeled as A, B, D, E, H, IV, S.
it with nitrogen gas (evaporated liquid nitrogen), then re-evacuate it. This process was repeated three or four times. After the last flushing the "insulation vacuum" space was pumped to a pressure of approximately 100 microns and sealed off by closing valve 1. Then liquid nitrogen was added to the outer flask of the experimental apparatus followed after a few hours by the addition of the He\textsuperscript{4} exchange gas to the He\textsuperscript{4} dewar. The weak atmosphere of nitrogen gas remaining in the "insulation vacuum" space and the exchange gas in the He\textsuperscript{4} dewar acted as a thermal linkage to the exterior environment for the purpose of heat extraction from the sample holder which is, otherwise, thermally isolated through the stainless steel tube shown in Fig. 12.

When liquid He\textsuperscript{4} was transferred, the nitrogen remaining in the "insulation vacuum" space froze out on the inner walls of the can (see Fig. 12) leaving a very high vacuum. To bring the temperature of the sample holder the remaining way, from liquid nitrogen temperatures to liquid helium temperatures, He\textsuperscript{3} gas, stored in the pump, was circulated in the closed He\textsuperscript{3} system. The circulation was started by first turning the He\textsuperscript{3} pump on and then closing valve C and opening valves B and A in that order. Meanwhile, the temperature of the outer bath was lowered by pumping on the He\textsuperscript{4} dewar. The temperature of the sample holder could be monitored by an Allen-Bradley-resistor thermometer. As the circulation of the He\textsuperscript{3} gas continued, the incoming He\textsuperscript{3} gas would cool down to the outer bath temperature before coming in contact with the sample holder copper cup where it would warm up by
extracting heat from the cup, and the warmed gas would then be pumped back in the storage pump. A time of five to seven hours was required before the sample holder would reach the temperature of the outer bath. Since the effectiveness of the outer bath was diminished when the level of He$^4$ liquid reached below the condenser (see Fig. 12), a second transfer of He$^4$ liquid was required before the precooling was complete. The second transfer was kept at 4.2°K as the precooling continued.

When the sample holder reached the temperature of the outer bath, valve A was closed and the He$^3$ gas was continuously pumped out of the system through valve B. For a successful liquification of the He$^3$, it was important that the He$^3$ gas be completely evacuated prior to the refrigeration cycle. Complete evacuation was insured if the outer bath temperature was kept at 4.2°K. As the evacuation continued preparations were made for a third transfer since, by this time, the level of the He$^4$ liquid would be too low to allow sufficient length of time for experimentation. The vapor pressure sensing tube gauge (T.I. gauge) was set to a reading of zero with respect to a reference vacuum and then was connected to the He$^3$ system by opening valve G.

After the third transfer was completed, if the reading of the T.I. gauge was sufficiently close to zero, the system was ready for refrigeration. The outer bath temperature was then lowered to 1.2°K. The complete evacuation of the He$^3$ system had to precede the last step to avoid any condensation of the He$^3$ gas inside the tube leading to the condenser. The refrigeration cycle
was started by opening valve A to allow re-circulation of He\(^3\) gas. Under normal conditions, cooling of the sample holder to about 0.7°K required less than three minutes.

Once in the continuous operation, the temperature of the sample holder could be manually regulated, above and below 0.7°K, by careful manipulation of valves C and F respectively. The fine control over the temperature regulation was obtained by employing an electrical heater feed-back system (see Appendix B). The system could also be operated in batch by simply closing valve A and thus continuously pumping on the liquid He\(^3\). The lowest attainable temperature in the batch operation was 0.33°K. The temperature regulation in the batch operation could only be done by the heater feed-back system.

b. Sample Holder

Figure 12 shows a schematic of the sample holder (S), "insulation vacuum" space (IV), and part of the low temperature section of the He\(^3\) system. The sample holder and the He\(^3\) evaporator (E) were built as an integral unit to reduce the occurrence of thermal boundary resistance between the sample and the He\(^3\) bath. The unit was thermally insulated from the 1.2°K outer bath by the stainless steel tube (D). The sample holder section of the unit was so designed to reduce the possibilities of radiation particularly in the thermal effect measurements. The main sources of radiation are the temperature regulator heater and the "insulation vacuum" can. The basic features of the sample holder were two flanges (see Fig. 12). The upper flange (A) and the
evaporator (E) were used to house and shield the temperature regulator heater (H). The lower flange (B) could be used to support a copper shielding can that would house the sample and the thermometers and would shield them against the radiation from the "insulation vacuum" can. This flange was provided with several cutouts on its periphery. The wires connected to the sample could be distributed evenly among the cutouts and the shielding can would then be slipped in place, over the wires, and soldered to the flange B. In the present experiment, no use was made of the shielding can and the flange B served only as an extra shielding against the temperature regulator heater.
APPENDIX B
TEMPERATURE REGULATOR

The temperature control for the He$^3$ refrigerator was provided by an electrical heater feedback system. The basic principles of the operation of the control system are described in full by Blewer. The present design differs from that of Blewer in the feedback system in that there is no optical coupling between the different parts of the system and the D'Arsonval galvanometer is replaced by a high gain dc amplifier to serve as the null detector of the Bridge. The original system built by Blewer had the disadvantage of being sensitive to external vibrations and thus having inherent noise problems. This would place a limit over the ac amplification of the feedback signal to the heating element. The amplification was further limited because of the restrictions on the input signal to the ac amplifier. The input signal was provided by a photocell placed to receive an increasing portion of the beam of the galvanometer. However, only a small portion of the beam could be used effectively since once the full beam was received by the photocell, the sensitivity of the system would diminish to the extent that there would be no control over the direction of the deflection of the galvanometer. The system as a whole was unstable under a strong transient signal.

A block diagram of the present temperature control system is shown in Fig. 13. The principles behind the operation of the system are described by Blewer. The basic features of this
Fig. 13

DC AMPLIFIER

SHIELD

He^3 REFRIGERATOR

CARBON RESISTOR

HEATER
feed-back system are: (1) a 10 Ω, 1/10 W Allen-Bradley resistor used as a temperature sensing element in one arm of a Wheatstone Bridge circuit, (2) a high gain null-detector dc amplifier of the type with constant output voltage per full-scale deflection of the null-meter, (3) a rectifying circuit composed of three semiconductor diodes in series with potentiometer to control the dc level of the input to the final stage which is, (4) a high gain current amplifier (emitter follower) the output of which is connected to the heater element in the cryostat. The high gain dc amplifier allows for the increase of the sensitivity of the temperature control. Under ideally quiet condition, the sensitivity range selector of the amplifier could be put on three microvolt per full-scale deflection of the null meter, in which case, the control of the temperature would be to within 0.0001°K. In general the sensitivity should be selected according to the noise conditions and the resistance of thermometer at the controlled temperature. The wide range of sensitivity of the amplifier coupled with the constant output per full-scale deflection of the null-meter assured the stability of the control system at all temperature and under any strong transient signal. The function of the rectifying circuit was to cause the increase of current in the heater element only when the deflection of the null meter corresponded to the cooling of the system. The transient deflections to the other direction would automatically be corrected by continuous pumping on the liquid He²³. The potentiometer following the rectifying circuit provided an initial dc level at the input of the current...
amplifier corresponding to an initial current in the heater element to compensate for the continuous heat extraction, as the result of pumping, at any given temperature. An RC circuit at the input of the current amplifier provided the damping mechanism to prevent oscillations in the system. It should be noted at this point that the circuitry at the output of the dc amplifier draws very little current from the amplifier, and this is an essential requirement for the satisfactory operation of the system. Because of the high impedance of the circuitry in the control system, shielding is of absolute importance. In the present design the entire components with the exception of the sensing thermometer, dc amplifier, and the heater element were placed inside a shasssis, with the input Bridge circuit occupying a separate compartment.
APPENDIX C
MAGNETIC FIELD

The external applied field was provided by a 7-in. long superconducting solenoid (1 3/4 in. in diam.) wound with Nb-Ti wire on a stainless steel core tightly fitting around the vacuum chamber surrounding the sample. The solenoid was calibrated by means of a Hall probe against a precision regulated magnet. The Hall probe was zeroed inside a Co-Netic magnetic shield where the magnetic field of the earth was measured to be reduced to within 10% of its normal value. The characteristic calibration at the center of the solenoid was 420.5 G/A. Since the sample used for critical field measurements was only 1-in. long, the field was considered to be homogenous over the volume of the sample within a fraction of a per cent and no end corrections were made.

For the thermal measurements which were carried out on a 3-in. long sample, the above solenoid was replaced by another one of comparable dimensions but with end corrections to keep the field homogenous within 3 in. from the center of the solenoid. The characteristic calibration at the center of the solenoid was 230 G/A.

The current in the solenoid was provided by a current regulated dc supply which also provided an input for a small modulating signal. The circuit diagram of the supply is shown in Fig. 14.
Fig. 14

MODULATION INPUT

Solenoid

2N4036

2N3906

2N3906

1mμF

47K

1.6K

2K

1K

2.5K

33K

100μF

1K

10Ω

2.7V

6V

1mμF

100μF

MODULATION INPUT
In the He\textsuperscript{3} cryostat, secondary thermometers (Allen-Bradley resistors) were calibrated against the vapor pressure of the He\textsuperscript{3} bath. The best conditions for the calibration were obtained by pumping the system to the lowest temperature attainable, then shutting off the He\textsuperscript{3} system completely from the outside; the system then warmed up slowly over a period of 2-3 h, during which the calibration of the thermometers vs. the slowly rising vapor pressure was carried out. The instrument used to measure the vapor pressure of the He\textsuperscript{3} was a Type I quartz Bourdon tube manufactured by Texas Instruments Incorporated. The tube range was 0-200 mm Hg, and its sensitivity was about 1% in the 100-μ region and 0.1% in the 1-mm region. At the lowest temperatures, a correction to the pressure reading was made\textsuperscript{74} to take into account the thermomolecular effect. The thermometer current was limited to less than 0.25 μA to avoid self-heating.

For the temperature dependence of the critical field measurements a 10 Ω, 1/10 W Allen-Bradley resistor, which was previously calibrated by Blewer et al.,\textsuperscript{70} was calibrated again following the procedure stated above and their calibration curve was found to be reproducible. Subsequently, the temperatures were measured against the calibration of this thermometer.

For the thermal conductivity measurements, new thermometers (with no previous calibration) had to be used, and because of the necessary modifications introduced in the He\textsuperscript{3} system, the
calibration of the thermometers was carried out in the following manner: A 10 Ω and a 30 Ω, 1/10 W Allen-Bradley resistor were calibrated against He\(^3\) vapor pressure in the temperature ranges of 0.3 - 0.9°K and 0.8 - 1.1°K, respectively. The calibrations were repeated several times to insure reproducibility of the results. The thermometers were found to obey, quite accurately, a relation between their resistance \(R\) and the vapor pressure \(p\) of the He\(^3\) liquid given by:

\[
\log R = a + \sum b_n (\log p)^n
\]

with \(n\) being equal to 6 and 5, respectively. This relation is linear over the upper temperatures of either range and this linearity was utilized for further correction in the calibration as follows: The 30 Ω thermometer was calibrated against the vapor pressure of He\(^4\), and the result was converted to a relation between \(\log R\) and \(\log P\) where \(P\) is the He\(^3\) vapor pressure corresponding to the given He\(^4\) vapor pressures. The two calibrations were plotted together and the He\(^3\) calibration was shifted along the log \(P\)-axis to match the continuity of the two straight lines. The shift was assumed to be the same at all temperatures of the He\(^3\) calibration and new temperatures were calculated accordingly. The correction to the He\(^3\) calibration was about 5 mdeg at the lowest attainable temperature and about 15 mdeg at 0.9°K. This correction was accounted for by assuming a systematic error due to the non-ideal conditions prevailing in the measurement of the vapor pressure of He\(^3\).

The temperature between 1.1 - 4.2°K were determined from the calculation of two 50 Ω, 1/10 W Allen Bradley resistors calibrated
against the vapor pressure of He⁴.
REFERENCES


22. B. T. Matthias, IBM J. Res. Develop. 6, 250 (1962);


52. \[ H_c(T) = 95.6 - 144.4 T^2 + 51.8 T^4 - 22.6 T^6 \]
\[ H_s(T) = 89.7 - 120.3 T^2 - 0.5 T^4 + 16.7 T^6 \]


65. In the presence of very high magnetic field, the electronic contributions to the thermal conductivity will be suppressed enough to make the observation of the lattice contribution possible. Then one can write the following:

\[ \frac{K_n(H)}{K_n(0)} = \frac{K_{en}(H) + K_{gn}}{K_{en}(0) + K_{gn}} = \frac{K_{en}(H) + K_{gn}}{K_{en}(0)} \]

and from Wiedemann-Franz relation, it follows that

\[ \frac{K_{gn}}{K_n(0)} = \frac{K_n(H)}{K_n(0)} - \frac{\rho_o(0)}{\rho_o(H)} \]

From the thermal and electrical conductivity measurements of the sample between 1.2°K and 4.2°K, in a transverse magnetic field of about \(10^6\) G, \(K_n(0)/K_n(H) \approx 210\) and \(\rho_o(H)/\rho_o(0) \approx 270\), therefore, \(K_{gn}/K_n \approx 10^{-3}\).


68. The thermal conductivity of the sample was measured along a direction very close to [111]. One expects to observe the effect of the anisotropy of energy gap in the thermal conductivity of a pure sample, while the specific heat and thermodynamic critical field measurements, close to \(T_c\), would only yield a mean value of the energy gap.

69. An alternative explanation for the behavior of the thermal
conductivity of molybdenum is to assume a partial contribution from the s-d interaction. Thus one may propose that the superconducting state in the transition metals should be characterized by a two-band structure in which the contributions from the interband scattering depend on a parameter determined from the lattice stability and the electronic configuration. Such model will be consistent with the observation of Engelhardt et al. on niobium and Tungsten. (see Ref. 9).


73. Supercon T48B was purchased from Supercon Division of Norton Company (Formerly National Research Corp.).


75. S. Cunsolo, M. Santini, and M. Vicentini-Missoni, Cryogenics 5, 168 (1965); P. P. Craig, ibid. 6, 112 (1966).
VITA

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EXAMINATION AND THESIS REPORT

Candidate:  Ahmad Waleh
Major Field:  Physics
Title of Thesis:  A Study of Superconducting Molybdenum.

Approved:

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Major Professor and Chairman
Dean of the Graduate School

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Date of Examination:  July 9, 1971