INFORMATION TO USERS

This was produced from a copy of a document sent to us for microfilming. While the most advanced technological means to photograph and reproduce this document have been used, the quality is heavily dependent upon the quality of the material submitted.

The following explanation of techniques is provided to help you understand markings or notations which may appear on this reproduction.

1. The sign or “target” for pages apparently lacking from the document photographed is “Missing Page(s)”’. If it was possible to obtain the missing page(s) or section, they are spliced into the film along with adjacent pages. This may have necessitated cutting through an image and duplicating adjacent pages to assure you of complete continuity.

2. When an image on the film is obliterated with a round black mark it is an indication that the film inspector noticed either blurred copy because of movement during exposure, or duplicate copy. Unless we meant to delete copyrighted materials that should not have been filmed, you will find a good image of the page in the adjacent frame.

3. When a map, drawing or chart, etc., is part of the material being photographed the photographer has followed a definite method in “sectioning” the material. It is customary to begin filming at the upper left hand corner of a large sheet and to continue from left to right in equal sections with small overlaps. If necessary, sectioning is continued again—beginning below the first row and continuing on until complete.

4. For any illustrations that cannot be reproduced satisfactorily by xerography, photographic prints can be purchased at additional cost and tipped into your xerographic copy. Requests can be made to our Dissertations Customer Services Department.

5. Some pages in any document may have indistinct print. In all cases we have filmed the best available copy.

University Microfilms International
300 N. ZEEB ROAD, ANN ARBOR, MI 48106
18 BEDFORD ROW, LONDON WC1R 4EJ, ENGLAND
LIN, AN-CHUNG
THERMOELECTRIC POWER OF MOLYBDENUM-RICH RHENIUM, MOLYBDENUM-NIOBIUM, NIOBIUM-RICH ZIRCONIUM AND TUNGSTEN-TANTALUM ALLOYS.
RICE UNIVERSITY, PH.D., 1978

COPR. 1978 LIN, AN-CHUNG
University Microfilms
International 300 N. ZEEB ROAD, ANN ARBOR, MI 48106

© 1978
AN-CHUNG LIN

ALL RIGHTS RESERVED
PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy. Problems encountered with this document have been identified here with a check mark √.

1. Glossy photographs ______
2. Colored illustrations ______
3. Photographs with dark background √
4. Illustrations are poor copy ______
5. Print shows through as there is text on both sides of page ______
6. Indistinct, broken or small print on several pages ______ throughout ______
7. Tightly bound copy with print lost in spine ______
8. Computer printout pages with indistinct print ______
9. Page(s) ______ lacking when material received, and not available from school or author ______
10. Page(s) ______ seem to be missing in numbering only as text follows ______
11. Poor carbon copy ______
12. Not original copy, several pages with blurred type ______
13. Appendix pages are poor copy ______
14. Original copy with light type ______
15. Curling and wrinkled pages ______
16. Other __________________________
RICE UNIVERSITY

THERMOELECTRIC POWER OF Mo-RICH-Re, Mo-Nb, Nb-RICH-Zr AND W-Ta ALLOYS

by

An-Chung Lin

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

Thesis Director's signature:

Houston, Texas

July, 1978
THERMOELECTRIC POWER OF Mo-RICH-Re, Mo-Nb, Nb-RICH-Zr AND W-Ta ALLOYS

by

An-Chung Lin

ABSTRACT

The absolute thermoelectric power $S$ of Mo-Nb, Mo-rich-Re, Nb-rich-Zr and W-Ta alloy crystals was measured between 4.2K and 300K. The composition of the alloys covered the entire composition range in which the b.c.c. structure was observed. The diffusion component of the thermopower vs. composition curves is generally proportional to the slope of the density of states as function of composition at the Fermi level. A generalization of this rule was discussed. For the W-Ta alloys, this rule does not hold as well as for Zr-Nb-Mo-Re alloys. However, it applies to the transition-metal alloys consisting of the elements of nearest neighbors in the periodic table. The Zr-Nb-Mo-Re alloys exhibit two large peaks at about 5.35 and 6.09 valence electrons per atom of the $S$ vs. composition curve. The W-Ta alloys exhibit a large peak at about 5.5 valence electrons per atom. The abnormal effect appears at 5.1 and 5.9 electrons per atom of the $S$ vs. composition curve for the Zr-Nb-Mo-Re alloys and at 5.1 and 5.67 electrons per atom for the W-Ta alloys. This anomalous effect appears only in alloys of the transition metal of group VI and group V in the periodic table, probably because of the similarity of the Fermi surface of these alloys.

The phonon-drag components of the thermopower $S_g$ of all these alloys are positive. The hole-like character of the Fermi surface was used to explain this results. For the Zr-Nb-Mo-Re alloys, $S_g$ is greatly
attenuated in the concentrated alloys but is still detectable. $S_g$ is not attenuated in the Ta-rich alloys. The performance of dilute Mo alloys and dilute W alloys is similar. $S_g$ of the pure Mo is very sensitive to impurities. The phonon-drag thermopower is smaller for the Mo-rich-Re alloys than for the Mo-Nb and Nb-rich-Zr alloys.

The correlation of the thermopower with other physical properties of these alloys was discussed in detail using the density of states at the Fermi level, the Fermi surface and the band structure. Physical properties vs. composition curves show the extrema at the same position as the thermopower curve, indicating that the sharp change of the density of states at the Fermi level is responsible for these phenomena.

The effect of alloying on the Fermi surface of these alloys was discussed. The Fermi surfaces of alloys were determined by shifting the Fermi level on the band structure for the Mo-Nb and W-Ta alloys. This method was roughly supported by some measurements. The distortion of the Fermi surface by alloying should be considered in more detail.
ACKNOWLEDGEMENTS

I wish to thank Dr. Franz R. Brotzen for suggesting this project and, about all, for his continued support and guidance through difficult times. I also wish to thank Al Ehlert for his technical assistance throughout the duration of this work and Dr. Richard B. Loftin for his enthusiastic assistance at the beginning of this research.

Finally, I would like to thank the National Science Foundation for its financial support.
TABLE OF CONTENTS

I. INTRODUCTION 1

II. LITERATURE REVIEW AND THEORY 4
   (1) Diffusion Thermopower, $S_d$ 4
   (2) Phonon-Drag Thermopower, $S_g$ 8
   (3) Density of States, Band Structure and Fermi Surface 13
   (4) Alloying Effect on the Fermi Surface 21
   (5) Correlation between Phonon Drag Thermopower and Fermi Surface 22
   (6) Comparing the Thermopower with the Other Transport Properties 24

III. EXPERIMENTAL METHODS 27
   (1) Sample Preparation 27
   (2) Apparatus and Experimental Technique 31

IV. RESULT AND DISCUSSION 39
   (1) Diffusion Thermopower 39
      (a) Zr-Nb-Mo-Re Binary Alloys 40
      (b) W-Ta Alloys 51
      (c) Generalization of the Rule of the Diffusion Thermopower and Temperature Dependence of Electric Resistivity 58
   (2) Phonon-Drag Thermopower 62
      (a) Zr-Nb-Mo-Re Alloys 63
      (b) W-Ta Alloys 66
      (c) Fermi Surface of These Alloys 68
(d) Other Effects on Phonon-Drag Thermopower

V. CONCLUSIONS

VI. REFERENCES
I. INTRODUCTION

The transition metals are characterized by incomplete d shells. The energy level of the s shell is close to the d shells such that the overlapping or hybridization of d and s bands must always be considered. The density of states of the d band is much greater than that of the free-electron-like s band. The d bands consist of five subbands, and the variations in these subband structures, as revealed in the density of states, are important features. Most physical properties of metals are closely related to the density of states and to the Fermi surface.

The rigid-band model is a reasonable approximation for the description of alloys of transition metals with their neighbor on the periodic tables. In this model, changes in the Fermi surface with alloy composition arise from changes in the Fermi level relative to these rigid bands.

The thermopower $S$ is a transport property which is a particularly sensitive test compared to the other transport properties, such as electric conductivity. Generally speaking, $S$ of the transition elements is roughly an order of magnitude greater than that of simple metals at any temperature.¹

The alloys of the early 4d transition elements, Mo-Nb, Mo-Re, and Nb-Zr possess a body-centered cubic structure in the range from about 4.83 to 6.35 valence electrons per
atom,\textsuperscript{2} or possibly even from 4.4 to 6.35 valence electrons per atom.\textsuperscript{3} W-Ta alloys belong to the early 5d transition-metal alloys. They have a body-centered cubic structure over the whole composition range, just like Mo-Nb alloys. The single-phase region of the alloys was chosen to simplify the interpretation of sensitive measurements. Most alloys were measured here in the form of single crystals, which have the advantage of producing specimens of high purity and low defect concentrations. It was supposed that the orientation of the cubic structure will not affect the thermopower measurements.

Some alloys of 4d and 5d transition metals\textsuperscript{4} have been studied for their thermopower, as have certain alloys of 3d transition metals of the early period,\textsuperscript{5,6,7} notably the Cr-V alloys,\textsuperscript{5} which lie at the equivalent position in the periodic table with Mo-Nb and W-Ta alloys. It was interesting to find out whether these alloys show some similarity in their thermopower, so that in the present work, measurements were extended to the 4d and 5d transition-metal alloys of the early period. This constitutes a promising approach to a better understanding of transport properties of the transition-metal alloys.

Very few data of the thermopower have been investigated for the concentrated transition alloys at temperatures at which phonon drag is important (near $\Theta_{d}/5$, where $\Theta_{d}$ is Debye temperature). This work would make it possible to determine whether or not phonon-drag thermo-
power can be disregarded in concentrated alloys of some transition metals in this temperature region.

The band structure and Fermi surface of the Mo-Nb and W-Ta alloys will be investigated in detail, and many physical properties of these alloys are thought to be related to the band structure and topology of Fermi surfaces.
II. LITERATURE REVIEW AND THEORY

It is customary to divide thermopower into two terms: $S = S_d + S_g$; the thermal diffusion of charge carriers leads to the diffusion thermopower $S_d$, and $S_g$ is the phonon-drag component.

(1) Diffusion Thermopower, $S_d$.

Using the Boltzmann transport equation, Mott's equation of the thermopower can be derived for a first order approximation:

$$S_d = + \frac{n^2 k T}{3|e|} \left[ \frac{d \ln \rho(E)}{dE} \right]_{E_f}$$  \hspace{1cm} (1)

where $\rho(E)$ is the electrical resistivity for a metal whose energy is at $E$, and $E_f$ is the Fermi energy. $k$ is Boltzmann's constant, $e$ the carrier charge, and $T$ is the absolute temperature.

In the simple theory,

$$\rho = \frac{12 \pi^3 \hbar}{e^2 \Lambda}$$  \hspace{1cm} (2)

where $\Lambda$ is the mean free path of the electrons at a Fermi surface of area $A$. Thus,

$$S_d = - \frac{n^2 k T}{3|e|} \left[ \frac{1}{\Lambda} \frac{d \Lambda}{dE} + \frac{1}{A} \frac{dA}{dE} \right]_{E_f}$$  \hspace{1cm} (3)

From linear-response theory, equation (2) can be written as
\[ \rho = \frac{3}{e^2 v_f^2 \tau N(E_f)} \]  \hspace{1cm} (4)

where \( v_f \) is the velocity of electron at the Fermi surface, \( \tau \) is the relaxation time, and \( N \) is the density of states, so that

\[ S_d = -\frac{n^2 k^2 T}{3|e|} \left[ \frac{1}{N(E)} \frac{dN(E)}{dE} + \frac{1}{v^2} \frac{d(v^2)}{dE} + \frac{1}{\tau} \frac{d\tau}{dE} \right] E_f \]  \hspace{1cm} (5)

For correct interpretation, care should be taken in the choice of equation (3) or (5) so that the energy variation of the various factors can be properly assessed.

Considering equation (3) first, the quantity \( d\Lambda/dE \) is generally positive, since the more energetic an electron the less likely it is to be scattered and the greater should be its mean free path. For a spherical Fermi surface, the area always increases with increasing energy, so that \( d\Lambda/dE \) is positive. In transition metals, however, the Fermi surface deviates from spherical shape and hole sheets may exist, so that \( d\Lambda/dE \) can be negative or positive.

It is well known that s-d scattering is a predominant cause of resistivity. The probability of this scattering is proportional to the density of state \( N_d \), such that

\[ \Lambda \propto 1/N_d. \]  \hspace{1cm} (9)

If then the first term in the equation (3) is changed to \( -\frac{1}{N_d} \frac{dN_d}{dE} \bigg|_{E_f} \), this term, too, can be positive or negative. We will show later that this term is the main contribution to \( S_d \). Some authors considered that the conduction band does not change very much as a result of
alloying; hence \( \frac{\text{dlnA}}{\text{dE}} \) should be small and only the first term in equation 3 is important. But the factors in equation 3 may not be properly assessed by omitting the second term.

It is more practical to use equation 5 here. In the transition metals, if the conduction is associated only with s electrons, equation 4 yields \( \rho = \frac{3}{c^2 v_s \tau_s N_s(E)} \) because \( \frac{1}{\tau_s} = \frac{1}{\tau_{s-d}} \sim N_d(E_F) \). Then, from equation (5),

\[
S = -\frac{\pi k^2 T^2}{3|e|} \left[ \frac{1}{N_s(E)} \frac{\text{d}N_s(E)}{\text{d}E} + \frac{1}{v_s} \frac{\text{d}v_s}{\text{d}E} - \frac{1}{N_d(E)} \frac{\text{d}N_d(E)}{\text{d}E} \right] E_F.
\]

(6)

If the s electrons are considered to be free,

\[
S = -\frac{\pi k^2 T}{3|e|} \left[ \frac{3}{2E_F} - \frac{1}{N_d(E)} \frac{\text{d}N_d(E)}{\text{d}E} \right] E_F.
\]

(7)

Similar to the Mott model of s-d scattering, a four-band model was derived from the Boltzmann equation by Aisaka and Shimizu.\textsuperscript{10} For Mo and W, the four bands are contributed by the two types of hole sheets around the N and H position of the Fermi surface, and two types of the electron sheets around \( \Gamma H \) and \( \Gamma \) position. The Fermi surface of Mo and W will be discussed later. Considering electron-phonon scattering only and using the classical theory of conduction, we obtain

\[
S = -\frac{1}{e} \left( \frac{1}{T} \frac{G_2}{G_1} \right)
\]

(8)
where \[ G_n = -\int \frac{\delta f^0(E)}{\delta E} (E-E_f)^{n-1} g(E)\,dE \] (9)

and \[ g(E) = \frac{1}{N(E)} \sum_\lambda \frac{\hbar^2}{m_\lambda} v_\lambda^{3/2} \] (10)

\( f^0(E) \) is the Fermi-Dirac distribution function, \( m_\lambda \) is the effective mass ratio of electrons in the \( \lambda \)th band and

\[ \varepsilon = \begin{cases} E-E_e & \text{for an electron band} \\ E_h-E & \text{for a hole band} \end{cases} \] (11)

in which \( E_e \) or \( E_h \) is the energy at the bottom or top of the respective band. \( E_e, E_h, \) and \( m_\lambda \) can be determined from the calculated electronic bands and observed results of the de Haas-van Alphen effect. For Mo and W, the calculated result is qualitatively similar to the experimental results, although the absolute magnitude of the theoretical curves is too great by about a factor of 2.

Khanna and Jain\textsuperscript{11} showed that thermopower of many complex metals like W and Mo can be explained quite simply by considering the variation of backward scattering cross section with Fermi energy. They assumed that a phase shift, \( \eta_d \), is dominant, so that the thermopower is

\[ S = -\frac{n^2 k_B^2 T}{3E_f} \left[ 2 \frac{1}{S(q)} \frac{\partial S(q)}{\partial q} \right]_{q=2k_f} \left[ 2 k_f - 2E_f \cot \eta_d \frac{\partial \eta_d}{\partial E} \right] \] (12)

where \( S(q) \) is the structure factor describing the dynamics of the ions; it is based on a dynamical matrix constructed from experimental force constants or force constants calculated from elastic constants. The calculated and experimental values of W and Mo are in excellent agreement at room
temperature. Because the elastic constants of the Zr-Nb-Mo-Re binary alloys have been measured, the force
constants can be computed. Equation 12 and the other model
described by Khanna and Jain provide one way to cor-
relate the diffusion thermopower with the elastic constants
of these alloys.

(2) Phonon-Drag Thermopower, \( S_g \).

\( S_g \) was calculated by Bailyn to be

\[
S_g = \frac{K}{e|q|} \left( \frac{2}{3} e^2 \sum q \frac{\partial N_0(q)}{\partial kT} \right) \sum (q) \prod (q) \prod \alpha(\mathbf{q}, \mathbf{k}_l, \mathbf{k}'l') \left[ \mathbf{v}(\mathbf{k}_l) \cdot \mathbf{v}(\mathbf{k}'l') \right] \cdot \mathbf{v}(\mathbf{j}_l),
\]

where

\[
v(\mathbf{k}_l) \text{ is the velocity of an electron with wave vector } \mathbf{k}_l \text{ on the } l^{\text{th}} \text{ sheet of the Fermi surface, and } j \text{ indicates the}
\]
polarization of the phonon of wave vector \( \mathbf{q} \). \( N_0(q) \) is
the equilibrium distribution of phonons in state \( q \),
velocity \( v(q) \). \( \alpha(q, \mathbf{k}_l, \mathbf{k}'l') \) is the relative probability
that a \( q \) phonon will interact so as to change the electron
state from \( k_l \) to \( k'_l \), related to all other interactions in
which this phonon may enter. The factor 2 in equation 13
and equation 14 comes from the sum over the spins, and the
factor 1/3 from replacing \( v_x(q) \) by \( 1/3 \) \( v(q) \), valid for
cubic materials.
The Bailyn expression is complicated but makes it possible from a theoretical point to deal with $S_g$. Equation 13 was modified to include scattering of electrons by impurities by adding a term containing the relaxation time $\tau$. At low temperatures $S_g$ may be quite sensitive to the impurity content through $\tau(\vec{k}k)$. The scattering of the phonon by impurities has been included in the quantity $a$. From equation 13, the sign of $S_g$ depends on the sum of contributions from all transitions, each of these decided by the sign of

$$[\vec{v}(\vec{k}k)\tau(\vec{k}k)-\vec{v}(\vec{k}'k')\tau(\vec{k}'k')] \cdot \vec{v}(\vec{q}q)$$

(15)

The selection rule $\vec{k}'-\vec{k} = \vec{q} + \vec{K}$ must be satisfied, where $\vec{K}$ is a reciprocal-lattice vector. For the case of free-electron spherical-energy surfaces and $\tau$ constant: (a) For normal processes ($\vec{K} = 0$), term (15) is negative, so that $S_g$ is negative. (b) For Umklapp processes, term (15) yields a positive sign in general. Of course, a hole surface would provide the opposite behavior.

Because the different regions of the Fermi surface act differently, it is helpful to analyze the complex situations by dividing the Fermi surface into different sections labeled $i$,\textsuperscript{17}

$$S_g = \sum_i (\sigma_{i}/\sigma)S_{g_i}$$

(16)
Here, $\sigma_i$ has the significance of the conductivity of region i and $S_{gi}$ that of the phonon-drag thermopower of region i. The factor $\sigma_i/\sigma$ is mainly affected by the ratio of relaxation times $\tau_i/\tau$. Equation 16 has been used to interpret the experimental result of the alloys of noble metals. The Fermi surface is separated into a few parts for this model.

Many features of $S_g$ have been analyzed by the method of relaxation times. One advantage of this method is that one can still use it without knowing the details of the scattering mechanism. It is usual to assume that the total probability is the sum of the individual probabilities, so that the total relaxation time $\tau_{p,x}$ for phonon scattering by other phonons ($\tau_{p,p}$), impurities ($\tau_{p,I}$), and boundaries ($\tau_{p,b}$) can be expressed as

$$\frac{1}{\tau_{p,x}} = \frac{1}{\tau_{p,p}} + \frac{1}{\tau_{p,I}} + \frac{1}{\tau_{p,b}}.$$ (17)

As a simplifying approximation

$$S_g \propto \frac{\tau_{p,x}}{\tau_{p,x} + \tau_{p,e}}.$$ (18)

where $\tau_{p,e}$ is phonon-electron relaxation time (which results in phonon creation or annihilation). If $\tau_{p,x} < \tau_{p,e}$, a phonon is more likely to impart its momentum into the lattice than into the electron system. If $\tau_{px} > \tau_{pe}$, the reverse is true. The relaxation time is appropriate for the probability.
It has generally been assumed that the effect of impurities on $S_g$ stems from a reduction of $\tau_{p,x}$ through anisotropic phonon scattering. From the equations 17 and 18, we obtain an idea how impurity scattering affects $S_g$. This important effect of alloying is to increase the preponderance of elastic impurity scattering so that the Fermi surface topology becomes less and less important in determining the scattering.

For phonon scattering by certain imperfections, at low temperatures where only long-wavelength phonons are excited, the scattering will be weaker than that of high temperature. $S_g$, however, is predominant only at low temperatures, so that electron scattering by impurities also need to be considered, that is, temperature-independent scattering.

The phonon scattering by impurities also depends on the characteristics of the lattice perturbations, which are influenced by the size of the impurity and its atomic mass difference from the host. The former is comparable to the strain field effect. The latter is proportional to the $(\Delta M/M)^2$, where $\Delta M$ is the mass difference between the solvent and solute atoms, $M$ is the atomic mass of the alloy.

Most experimental studies of $S_g$ of alloys have been done with dilute alloys only. In general, the $S_g$ peak is attenuated even in the dilute concentration of the solute.
For the concentrated alloys, $S_g$ is even more attenuated but still can exist as the small maximum in some cases, such as in Ag-Au alloys$^{20}$ and Pd-Pt alloys.$^{21}$

$S_g$ is not only closely related to the electric conductivity, but also to the thermal conductivity. The relation of $S_g$ with the lattice thermal resistivity was used for Pd and Pt alloys.$^4$ By writing $S_g = S_g^0 \alpha$, where $S_g^0$ is the phonon drag that would be observed if all the phonons would collide with electrons or holes.

$\alpha = W_{ge}/W_g$ meas, where $W_{ge}$ is the lattice thermal resistivity arising from the phonons by electrons and $W_g$ meas is the measured or total resistivity.

Fletcher and Greig$^4$ explained the sign of $S_g$ of the Pt alloys and Pd alloys as follows: from experiment, the lattice thermal resistivity is high (note that $W_{ge}$ is responsible for $S_g$) and is the result of phonon-induced hole-hole (d-d) scattering or electron-hole (s-d) scattering. It is already known that phonon scattering on a hole surface (hole-hole scattering) gives rise to a positive $S_g$. The s-d interband transition will also lead to a positive phonon-drag contribution. This is because of the strong similarity between phonon-induced s-d transitions and electron-phonon U-processes on a closed electron surface. In both cases the effect is to reduce the electron velocity in the direction of the phonon wave vector. Thus, the results of d-d and s-d scattering both make $S_g$ positive for these alloys. At sufficiently low temperatures, the
hole-hole scattering will produce a phonon drag which increases as $T^3$, there being no lower limit on the phonon wave vector. Yet, $S_g$ can exist only for phonon wave vectors in the order of magnitude of the closed hole surface of the Fermi surface. The electron-hole scattering will only be possible with phonon wave vectors greater than some critical value, so that any phonon drag from this source should decay exponentially at low enough temperatures. After Blood and Greig measured the data of Pd-Pt alloys, they concluded that $S_g$ of Pd and Pt alloys originate from hole sheets of the Fermi surface, that is, d-d phonon-induced scattering. The electron sheets and hole sheets for Pd and Pt are very close to each other, so that the critical value of phonon wave vectors could be low enough for electron-hole scattering to contribute to $S_g$. For group V and VI transition metals, however, the hole and electron sheets are not so close to each other, so that interband scattering will not be a dominant factor at the lower temperatures.

(3) Density of States, Band Structure and Fermi Surface

Looking at the general features, the density of states obtained from specific heat and paramagnetic susceptibility data show great similarity in the transition metals and alloys of the I, II, and III series of the periodic table. Passing from transition metals of the I-series to that of the II and then to that of III-series, the density of states
gradually diminishes. This means that the total width of the d-band must increase continuously in the same direction.\textsuperscript{24} When paramagnetic susceptibility is plotted as a function of n/a, the curve differs only slightly from that of the specific heat, because the influence of the molecular field and the orbital paramagnetism tend to contribute to the susceptibility.

The de Haas-van Alphen effect is a powerful technique to predict the Fermi surface of pure metals and very dilute alloys. But it cannot be applied to concentrated alloys. Moreover, the dHvA effect cannot be used to describe all the details of the Fermi surface. Thus, mathematical models are used to compute the Fermi surface and the dHvA effect and other techniques are employed to corroborate them. For the group V,\textsuperscript{25} group VI\textsuperscript{26,27} and Re\textsuperscript{28} metals, the Augmented-Plane-Wave method (APW) has been used successfully. First, the energy bands along symmetry directions in the Brillouin zone can be calculated. From these, the density of states curve is calculated, and the Fermi level is located, then the Fermi surface also can be drawn from the energy band results. Generally speaking, the energy band of the V and VI group metals is similar. The Fermi surfaces are similar for each group, because they depend on the position of the Fermi level at the energy band. Based on the rigid-band model, the Fermi level depends on the n/a ratio, and the density of states vs. energy curve is similar for these metals and more similar
for the nearest neighbor in the periodic table, such as Nb with Mo, and Ta with W.\textsuperscript{25,26}

The experimental density of states curve of Nb-Mo and Ta-W alloys was determined from specific heat data.\textsuperscript{29,30} After correction by the enhancement factor due to electron-phonon interactions in the heat-capacity density of states, the experimental data agree with the calculated data of the density of states, as shown for Mo-Nb alloys in Fig. 1. This situation is similar to that as shown previously for the W-Ta system.\textsuperscript{30,31} This type of agreement indicates that for the density of states of these alloys depends only on the n/a ratio. The Fermi level of alloys can then be located from the density of states histogram, coupled with the known band structure. This is shown in Fig. 1 for Mo-Nb alloys; this same procedure can be utilized for the W-Ta system. In the W-Ta system, however, the Fermi surface can only be determined from the band structure of W.\textsuperscript{26} The band structure of Ta\textsuperscript{25} yields a Fermi surface which is inconsistent with the known Fermi surface of W. From a theoretical point of view, the Fermi surface of Mo-Nb and W-Ta alloys can be determined just as in the pure metals, with changes in the Fermi surface by alloying depending only on the n/a ratio.

The optical properties of the Mo-Nb\textsuperscript{32} and W-Ta alloys\textsuperscript{33,34} have been measured in recent years. The peak position of the dielectric function $\varepsilon_2$ is discussed in terms of the interband transition and, again, the rigid-
Fig. 1. Band structure and density-of-states curves for Nb according to Mattheiss,\textsuperscript{25} together with the empirical density of states data (circles) for the Zr-Nb-Mo-Re b.c.c. alloys,\textsuperscript{30} and Fermi level of Mo (\textendash\textendash\textendash\textendash\textendash), Mo-Mb 25\% (\textendash\textendash\textendash\textendash\textendash\textendash), Mo-Nb 50\% (\textendash\textendash\textendash\textendash\textendash\textendash\textendash) and Nb (\textendash\textendash\textendash\textendash) at the band structure.
band model is assumed. The proposed shift of the Fermi level in the energy band by alloying can be roughly explained by some of these transitions. The examination of these alloys shows that there probably are distortions of the bands due to strain and potential differences, but the disorder of the alloys does not destroy the band structure.

For the W-Ta alloys, the change of the peak position of high W-content alloys cannot be explained in the way as that of high Ta-content alloys. The curve for the alloy W-Ta 50% bears no resemblance to the absorption of the alloys with high Ta or W content. So at the intermediate composition of the solid solution system, the band structure apparently has no similarity to that of either of the constituent parts.

Generally speaking, the optical properties and phonon dispersion curves of these alloys (which will be discussed later), assume the above band structure of alloys. Based on this band structure the Fermi surface of alloys is determined. A four-band model derived by Aisaka and Shimizu can be used to derive the calculated data of electric resistivity, thermal conductivity, and thermo-power of these alloys.

The Fermi surface of the chromium-group transition metals proposed by Lomer and the Fermi surface of W modified by the DLW effect is shown in Fig. 2. It consists of two principal closed surfaces that have been
Fig. 2. (a) Proposed Fermi surface for the chromium-group transition metals by Lomer.  
(b) Perspective sketch of the model Fermi surface for tungsten from Girvan et al., showing the extremal orbits which are expected to give rise to a dHvA effect.
described as an electron "jack" centered at the origin of the Brillouin zone \( \Gamma \) and hole "octahedra" at the symmetry points \( H \). The electron "jack" consists of an octahedral body connected to six bell-like protrusions along the (100) or \( \mathbf{1}H \) directions. Within the "necks" which join the electron octahedral body to the bells are the electron "lenses." Hole pockets ("ellipsoids") centered at the points \( N \) in the Brillouin zone. The separation between the octahedron and the jack is due to spin-orbit coupling. The Fermi surface of W and Mo is qualitatively similar, except\(^{26}\)

(1) that W does not have lenses, (2) that the hole pockets are much larger in Mo than in W, and (3) that the electron jack of Mo is quite a bit larger in body, bell, and neck dimensions than in the W. It should be noted that for each of these compensated metals the volumes of the electron Fermi surface pieces must equal the volumes of the hole Fermi surface pieces.

The Fermi surface of Nb proposed by Mattheiss\(^{26}\) is shown in Fig. 3. The first Brillouin zone is filled and the closed second-zone hole surface is centered at \( \Gamma \). The open surface of holes in the third zone referred to as the "jungle-gym" surface. It also has the hole pockets centered at \( N \) in the third zone. The Fermi surface of Ta is similar to that of Nb and both show the hole-like nature. The hole sheet around \( \Gamma \) is smaller for Nb than Ta, and \( N \) hole pockets are bigger for Nb than Ta. Also, the d band-widths are wider for Ta than for Nb.
Fig. 3. Proposed Fermi surface for the vanadium-group transition metals by Mattheiss.\textsuperscript{26} (a) second zone, (b) third zone.
(4) Alloying Effect on the Fermi Surface

Concerning materials which ideally possess perfectly regular crystal structures, as a result of Bloch's theorem each eigenstate of an electron in such a crystal can still be characterized by a unique value of \( \mathbf{k'} \), where the allowed values of \( \mathbf{k'} \) are determined by the periodicity of the crystal structure and are completely independent of the detailed forces acting on the electron. From a purely formal point of view, even if only a very small number of impurity atoms are introduced into a crystalline specimen of a pure host metal, the perfectly regular periodic structure of the ideal pure crystal of the host metal will be destroyed. Consequently the wave vector \( \mathbf{k} \) is no longer a good quantum number of the system and all the concepts of Brillouin zones and Fermi surfaces that are used so extensively for a pure metal are no longer strictly relevant. Any given one-electron state is characterized not just by a single wave vector \( \mathbf{k} \) but by a spread of wave vectors \( \mathbf{k} \). The effect of addition of impurities could be observed in any property of a metal that depends on the behavior of the conduction electrons.

As mentioned earlier, the change in the n/a ratio occurs with alloying, and with it the movement of the Fermi level and the resulting changes in the shape of the Fermi surface. For the indirect or macroscopic properties the situation is more complicated. The behavior of such
properties depends not only on which states, \( \vec{k} \), are actually at the Fermi surface, but also on the relaxation times \( \tau(\vec{k}) \) of these states for the process in question. The theoretical determination of values of \( \tau(\vec{k}) \) would involve the calculation of the appropriate matrix elements for transitions from the states \( \vec{k} \) under the influence by some operator. Even within the rigid-band model there is no reason to suppose that such matrix elements should remain constant while \( \vec{k} \) is allowed to vary corresponding to the changes in the shape of the Fermi surface. Therefore, a complete explanation of the indirect or macroscopic properties of an alloy is far from simple.

These statements can explain why many physical properties of these alloys cannot be described completely clearly by the band structure or topology of the Fermi surface of the alloys derived from pure metals.

(5) Correlation between Phonon-Drag Thermopower and Fermi Surface

Carter et al.\(^{37}\) have measured the low-temperature thermopower of the transition metal Nb, Ta, Mo, W, and Re. They showed that the features of \( S_g \) were roughly related to the topology of Fermi surface, e.g., the sign of \( S_g \) is determined by the smallest or almost smallest hole or electron sheets of the Fermi surface. In general the dominant phonon transition across an electron sheet leads to negative \( S_g \), and across a hole sheet, to positive \( S_g \).
In group V metals (V, Nb and Ta), $S_g$ is therefore positive, because the Fermi surface of these metals is made of hole sheets. In Re, the three smallest sheets of the Fermi surface are also hole sheets, so that $S_g$ is also positive. For W the smallest pieces of Fermi surface are hole sheets (at N) with dimensions significantly smaller than the next largest surface, which is an electron sheet. This may account for the initial positive thermopower and the large negative dip thereafter.\textsuperscript{37} In Mo, analogous pieces of the Fermi surface are much closer to being equal. Furthermore, Mo has an additional small electron sheet (lenses). It would appear, therefore, that contributions from these sheets tend to cancel and produce a comparatively small negative contribution only in Mo.

It is still too early to calculate $S_g$ through formulas, such as Bailyn's equation (Eq. 13), even for a simple metal. For the pure transition metals and alloys discussed here, the Fermi surface is more complicated even when compared to the noble metals, Eq. 16, $S_g = \sum_i (\sigma_i / \gamma) S_{g_i}$, has been used and discussed for the alloys of noble metals.\textsuperscript{18} It is therefore a possible approach to take. It is reasonable to separate the Fermi surface of the Mo-rich or W-rich alloys into five parts: (1) hole surface at N; (2) hole surface at H; (3) electron neck along $\Gamma\mathbf{H}$; (4) electron surface at $\Delta$ ($\Gamma\mathbf{H}$ direction, bell-like protrusions); (5) electron surface at $\Gamma$. For the Nb-rich or Ta-rich
alloys, one may separate the Fermi surface into the parts: (1) hole surface at \( \Gamma \), (2) hole surface at \( N \), and (3) jungle-gym hole surface. The latter may be subseparated into hole surfaces at \( H \), at neck (\( HH \) direction) and at \( \Gamma \), where parts (2) and (3) are in the third zone. The relaxation time seems to be very different between each part of the Fermi surface. The larger impurity scattering in part (i) leads to the smaller relaxation time \( \tau_i \).

(6) Comparing the Thermopower with the other Transport Properties

Besides thermopower, the other two transport properties, electric conductivity and thermal conductivity, can be derived through a similar approach to that which led to Mott's equation. Many theoretical calculations deal with these three properties at the same time. From a theoretical point of view, any calculation of electric conductivity through Mott's equation allows the result of the thermopower also to be found.

Because the transport properties are closely related to each other, the total view of the transport properties of these alloys is valuable. Also, the temperature dependence of resistivity and the Hall effect of Zr-Nb-Mo-Re binary alloys have been measured.\(^{38}\) The information of the electron scattering of impurity can be obtained from the residue resistivity of these alloys.\(^{38}\)
The experimental procedure for these transport properties differ. The thermopower and thermal conductivity are measured as a temperature difference exist, and a dynamic equilibrium of the phonon flux is set up. Thus, the scattering of phonons is important. The electric resistivity and the Hall effect are measured under a driving force of an electric or magnetic field. The dynamic equilibrium of the electron flux was set up and scattering of the electrons is more important. In the transition metals, electron-electron scattering is crucial to an understanding of the electric resistivity, while its influence in determining thermopower can almost be completely neglected. It may only exist in the thermopower at very low or high temperature, because thermopower is dominated by the phonon-electron scattering. The phonon-drag effect is mainly contributed by the phonon-phonon scattering that drives the electron into positive or negative directions along the specimen, dominating at low temperatures. Some mechanism of scattering may be controlled by the same electron properties in the metal, such as the electron-electron scattering and phonon-electron scattering, that are related through Mott's equation.

In general, the different transport properties reveal different kinds of dominance of the mechanism of scattering. The direct comparison of these transport properties is difficult; yet, all these transport properties are to some degree related to the density of states at the Fermi level or the topology of the Fermi surface.
As an example, the Hall coefficient of a cubic metal may be expressed in the general form by

\[ R = R_o \epsilon(\vec{k}) A[\epsilon(\vec{k}), \tau(\vec{k})], \]

where \( R_o \) is a characteristic constant determined by the band structure \( \epsilon(\vec{k}) \), while \( A \) is a temperature-dependent factor whose magnitude is determined by the anisotropy of the electron-electron relaxation time \( \tau(\vec{k}) \) over the Fermi surface. Thus the Hall effect is closely related to the band structure and Fermi surface.
II. EXPERIMENTAL METHODS

(1) Sample Preparation

The samples were made from the powder of the constituent elements. The tungsten powder (-100 mesh) and Tantalum (-60 mesh) were 99.98% pure and were obtained from Alfa division, Ventron Corporation, Danvers, MA. The characteristics of Mo, Nb, Re and Zr were replaced earlier.\textsuperscript{12,14,15} The powders were mixed in the desired compositions and then pressed to form the rod. In the case of W-Ta alloys, the rod was too weak to allow the growing of a single crystal. The rod was therefore wrapped in Ta foil and then presintered in a vacuum of less than $10^{-5}$ mm Hg for one hour at 1100°C.

Single crystals were produced by the floating-zone electron-beam melting method. The sample was floated vertically and rotated simultaneously. An electron beam of high current and voltage was emitted from a hot circular thoriated tungsten wire around the sample in $10^{-5}$ mm Hg vacuum. The filament traveled along the sample rod at about 0.5" per hour, insuring homogenizing of the sample. The W-Ta alloys have a very high melting point. This technique was improved so as to concentrate more radiant energy on the sample by adjusting the position of tungsten plates near the filament for shielding and by using higher voltage and current. The beam current was stabilized by using feedback control circuits. Water-cooling plates shielded
other parts of the melting device. A water seal consisted of a nickel gasket that can be reused after annealing.

For Re-Mo-Nb-Zr binary alloys, the crystals were grown along certain crystallographic directions, as shown in Table I. The samples were about 1/8" in diameter and 1 to 2 inches long. Samples that were not available in proper shapes had to be cut by the spark cutting. The samples were electropolished in a solution of 90 parts by volume sulphuric acid and 10 parts by volume of 48 per cent hydrofluoric acid. This method gave a shining sample surface. The purpose of electropolishing was to remove the rough layer that was produced by spark cutting.

The Mo-Nb 1% and Mo-Nb 5% alloys were produced as polycrystals. The pressed rods were melted several times in an argon arc-furnace, then wrapped in Mo foil and sealed in a quartz tube with some small pieces of tantalum metal. The tantalum metal was used as an oxygen getter. The tubes were heated in about 1/3 atmosphere of helium for 2 hours at 1470°C, then quenched in water, spark cut and electropolished as above.

The orientation of single crystals was determined by the Laue back-reflection method. The zone-melted sample of Nb-Zr 60% was not a perfect single crystal but rather a bicrystal. The W-Ta alloy samples were produced as single crystals of arbitrary orientation and in the regular form (1/8" diameter and 1.5--2 inches long). The com-
<table>
<thead>
<tr>
<th>Composition</th>
<th>Crystal direction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo-Nb 1%</td>
<td>polycrystal</td>
</tr>
<tr>
<td>Mo-Nb 5%</td>
<td>polycrystal</td>
</tr>
<tr>
<td>Mo-Nb 9%</td>
<td>(110)</td>
</tr>
<tr>
<td>Mo-Nb 25%</td>
<td>(100)</td>
</tr>
<tr>
<td>Mo-Nb 42%</td>
<td>(100)</td>
</tr>
<tr>
<td>Mo-Nb 65%</td>
<td>(110)</td>
</tr>
<tr>
<td>Mo-Nb 75%</td>
<td>(110)</td>
</tr>
<tr>
<td>Mo-Nb 83%</td>
<td>(100)</td>
</tr>
<tr>
<td>Mo-Re 8%</td>
<td>(110)</td>
</tr>
<tr>
<td>Mo-Re 15%</td>
<td>(110)</td>
</tr>
<tr>
<td>Mo-Re 25%</td>
<td>(112)</td>
</tr>
<tr>
<td>Nb-Zr 9%</td>
<td>(110)</td>
</tr>
<tr>
<td>Nb-Zr 13%</td>
<td>(100)</td>
</tr>
<tr>
<td>Nb-Zr 60%</td>
<td>bicrystal</td>
</tr>
<tr>
<td>W-Ta 2%, 15%, 33%, 50%, 75%, 90%, 95%</td>
<td>arbitrary direction</td>
</tr>
</tbody>
</table>
position of these alloys was determined by density measure-
ments with the assumption that the density was a linear
function of composition. The density was determined by
the Archimedean method, using a Mettler microbalance and
benzene as a medium. The measured compositions changed
only within few atomic per cent from the nominal compositive.

In order to reduce thermal contact resistance at the
differential thermocouple-sample interface, two holes were
spark cut near the ends of the sample by using 18 gauge
copper wire as the tool. The thermocouples were firmly
cemented inside these holes with GE 7031 varnish after
having been insulated with lens paper. This varnish per-
mits rapid thermal response and electrical insulation of
the junctions from the sample.\textsuperscript{39}

Thermal emf measurements on compact samples are
usually difficult to execute, because the thermal resistance
of these samples is much lower than that of wire samples.
The thermal contact resistance and response time between
sample and holder, heater, thermocouple and temperature
bath had therefore to be minimized.

Solder provides excellent thermal and electrical con-
tact, but ordinary solders would not wet directly these
alloys. So the 0.00125 mm thick pure nickel foil was cut
about 1 mm wide, then spark welded at a place near the two
holes in the sample, i.e., forming a nickel band around the
hole. Copper leads were soldered to these nickel bands with
Wood's metal, using Stay-Clean flux. This procedure resulted in a strong low-resistance connection to the sample which could be cycled repeatedly by cooling or heating without deterioration. Copper and nylon clamps had been tested prior to the experiment. Because the thermal expansion will change the contact resistance and the oxide film on the surface will increase the contact resistance, these procedures were not as successful as that of soldering of the nickel band.

(2) Apparatus and Experimental Technique

The sample holder used is shown in Figure 4. For the upper heater, the heating coil was made of one foot of 50 ohm per foot Constantan wire (No. 40 B&S). The coil was wound around the upper end of the sample on a layer of lens paper and cemented down with GE 7031 varnish. The lower heater was made of 17.5 ohm per foot Nichrome wire (No. 34 B&S) and had about 45 ohm resistance. The coil was wound on the O.F.H.C. copper holder, which was used because of its good thermal conductivity.

The binding post was made part of O.F.H.C. copper. The sample can above the copper holder was made of a thin-wall brass tube. The copper leads were wound a few times around the binding post on a layer of lens paper and cemented with GE 7031 varnish. This procedure insured the rigidity of the solder joints even after moving the copper holder from the brass tube. It also kept the copper wires
Fig. 4. Diagram of the sample holder and chamber.
at about the same temperature of the sample. This helped to eliminate large temperature gradients which might develop across solder joints on the sample, leading to measurement errors.

One hole was drilled on the copper holder to fit the 1/8 inch diameter sample. The bottom of the sample was spark welded with nickel foil then soldered with pure indium into the hole of copper holder. This provided a high thermal conductance to the holder. Soldering was accomplished by heating the entire copper holder on a heating plate to above the melting point of indium (156.4°C) and then pressing the fluxed sample into the hole. One circular groove was made on the copper holder to fit the 0.0040 B&S indium wire. The sample can was vacuum sealed by squashing the indium wire with 8 No. 72 screws.

The Au-0.07 at.% Fe - Chromel thermocouple was used as a differential thermocouple to measure the temperature at the middle of the sample. This thermocouple has a Seebeck coefficient of 8.7 μV/K at 1.0K; thus, it is ideal for determining small temperature differences and satisfactory for measuring temperatures below 10K. The thermocouple and reference temperature junctions were spark welded. The spark welding devices were set up for these thin wires in a way similar to that described by Rosenbaum. The Au-0.07 at.% Fe - Chromel thermocouples were obtained from Sigmund Cohn Co. The wires came insulated with fiber glass. The calibrated table for this
thermocouple was that by Sparks and Powell. It should be noted that the leads of the differential thermocouple were fitted to the two holes of the sample. The lead of the absolute-temperature thermocouple was bound by a cotton wire on the middle of the sample then cemented with GE 7031 varnish. Liquid nitrogen was used as a reference point.

From the definition, \( S = \frac{\Delta E}{\Delta T} \), where \( \Delta E = E_1 - E_2 \) is the potential difference. If \( \Delta E \) is positive for positive \( \Delta T = T_1 - T_2 \), then \( S \) is positive. Note that two copper wires were soldered to the nickel bands on the sample to measure the potential difference. The formula \( S_{\text{absolute}} = S_{\text{Cu}} - S_{\text{measured}} \) holds whenever \( S_{\text{measured}} \) is the ratio of the potential difference to the temperature difference between two points in the sample. Gauge No. 32 copper wires (Belden 8082, HNC NYLCLAD) were used. At low temperatures (below about 100°C) the \( S_{\text{Cu}} \) is greatly affected by the impurity of the transition metals. Measurement of the thermopower of even very pure copper samples showed surprising variations between samples. As a result, it was necessary to determine the thermopower of the particular leads used in the measurements in order to obtain accurate values of the absolute thermopower of the alloy samples. Pure lead and niobium were employed as a standard in an initial experiment in order to calibrate the copper wires as a substandard. 1/8" diameter 99.999% pure lead supplied by
Materials Research Corporation was treated as the alloy samples (it had spark-cut holes and nickel bands). Pure lead was used because it is a well known reference material at low temperatures.\(^43\) Polycrystalline niobium was also used, because it has similar characteristics, such as contact and spark welding behavior to the alloys to be measured. Also, \(S\) of Nb had been measured at low temperatures by two investigators.\(^37,44\)

The upper heater was operated by a manually-controlled Kepco DC regulated power supply to provide the temperature gradient along the sample. The lower heater was controlled by a PAR model 152 Cryogenic Temperature Controller. GaAs diodes were used as a sensor. The controller utilizes the thermal relaxation method for controlling. The position of the heater, sample, and sensor were so close (shown in Figure 4) that thermal response times were short and best balance and stability of temperature at the end of the sample were obtained. In the temperature range between room temperature and liquid nitrogen, a 1/4 W, 82K ohm carbon resistor can also be used as sensor for the PAR 152 controller. The resistor was stripped of its insulating coating and cemented to the hole with GE 7031 varnish.

The temperature controller can quickly match the thermal dynamic equilibrium or maintain the sample at some desired temperature. For very slow cooling or heating, one can just turn on the upper heater for a few minutes and then take data.
A schematic block diagram of the system is shown in Figure 5. The entire sample can was evacuated to a pressure of about $10^{-5}$ mm Hg. The vacuum provides the thermal insulation and eliminates the gas convection. The temperature difference and the potential difference were measured by a Honeywell model 2773 six-digit potentiometer with the use of a Keithley model 148 nanovoltmeter. This potentiometer has a resolution of 0.01 μV. The temperature of the sample was measured by a Leeds & Northrup K-3 potentiometer.

The cryostat used in these measurements was an Andonian gas-flow helium dewar system. The helium flow into the sample chamber was controlled by a needle valve. The slow cooling or heating also helped to eliminate the extra thermo emf. All the leads were brought out of the cryostat through vacuum seal stainless steel tubing. This also provides thermal and electrical shielding to minimize pickup and stray thermoelectrical potentials.

Shown in Figure 5, one 10-pin feedthrough was used to bring out the four leads of thermocouple and two copper leads. Pyseal cement, a compound melting at soldering pencil temperature, was used as a vacuum-seal at the pins. The copper wire of heater and sensor were soldered to an easily disconnected plug. At the bottom of the sample chamber of the cryostat a heater controlled by a manual Kepco DC power supply was installed to heat up the specimen from low temperatures. Braided copper was used to shield
Fig. 5. Schematic diagram of the experimental apparatus.
the leads of potential and temperature difference from the feedthrough to the 6-digital potentiometer.

Ordinarily, a temperature difference of some 0.8--1°K was established between two ends of the sample for the measurements. The experimental error of the measurement is estimated to be ±0.1μV/°K.
IV. RESULT AND DISCUSSION

(1) Diffusion Thermopower

Defining \( N(E) = \frac{d(n/a)}{dE} \), where \( n/a \) is the number of valence electrons per atom, and using Eq. 7 with the approximation \( N(E_f) \approx N_d(E_f) \), one obtains

\[
S_d = \frac{n^2k^2T}{3} \left[ -\frac{3}{2E_f} + \frac{dN_d(E_f)}{d(n/a)} \right]
\]

or

\[
\frac{dS_d}{dT} = \frac{n^2k^2}{3e} \left[ -\frac{3}{2E_f} + \frac{dN_d(E_f)}{d(n/a)} \right]
\]

The calculated Fermi energies of these metals is as follows: Zr(0.59Ry), Nb(0.696Ry), Mo(0.736Ry), Re(0.825Ry), Ta(0.76Ry), and W(1.15Ry).\(^{46}\) As an example, the Fermi energy of Mo-Nb alloys lies between those of the two pure metals and increases with higher Mo content. Then the first term in Eqs. 19 and 20 varies from 0.15(ev)\(^{-1}\) --- 0.16(ev)\(^{-1}\). The second term \( dN(E_f)/d(n/a) \) varies from -1.06(ev)\(^{-1}\) --- +1.0(ev)\(^{-1}\), as shown in Fig. 10. The variation and magnitude of the first term are much smaller than those of the second term, so that the first can be neglected as was already done in Mott's equation. Thus, for a qualitative approximation
\[ S_d \sim \frac{n^2 k T}{3|e|} \frac{dN(E_F)}{dn/a} \]  

\[ \frac{dS_d}{dT} \sim \frac{n^2 k}{3|e|} \frac{dN(E_F)}{dn/a} \]  

(a) Zr-Nb-Mo-Re Binary Alloys

The temperature dependence of the thermopower for the Zr-Nb-Mo-Re alloys is shown in Figs. 6, 7, and 8. Generally speaking, the magnitude of the thermopower of Mo-rich-Re alloys is greater than that of Mo-Nb and Nb-rich-Zr alloys. S vs. temperature curves for the Mo-Nb and Mo-rich-Re alloys spread out at higher temperature. For the Nb-rich-Zr alloys, however, the curves lie closely together near room temperature. The features of the S vs. T curve are similar to those of Ta and Nb, the phonon drag \( S_g \) being determined by the hole sheets.\(^6\) On this basis, one may explain the behavior of Mo-rich-Re and Mo-Nb alloys, which display similar features which are not found in the Nb-rich-Zr alloys. The results of Mo-Nb dilute alloys are shown in Fig. 9. Here, data for the Mo-Nb 1% polycrystalline alloy are similar to those of the Mo-Nb 5% alloy. For Mo-Nb 9% alloy crystal, however, the curve is about 1 to 2 \( \mu V/\circ K \) higher in amplitude. S of the Mo-Nb 9% and Mo-Nb 25% alloys are almost the same at temperatures below \( 110^\circ K \).

The variation of the thermopower with composition at three different temperatures is shown in Fig. 10. These curves can only show the trends of S roughly, because
Fig. 6. Thermoelectric power vs. temperature of Mo-Nb alloy crystals.
Fig. 7. Thermoelectric power vs. temperature of Mo-rich-Re alloy crystals.
Fig. 8. Thermoelectric power vs. temperature of Nb-rich-Zr alloy crystals.
Fig. 9. Thermoelectric power vs. temperature of dilute Mo-Nb polycrystalline alloys.
Fig. 10. The thermoelectric power vs. composition of Zr-Nb-Mo-Re b.c.c. binary alloys at three different temperatures.

The derivative of density of states vs. composition (line - - - -) is calculated from McMilian.\textsuperscript{30} For Mo-rich alloys, values are also shown (line - - - - -) as calculated from Morin and Maita.\textsuperscript{29}
additional data are needed to cover all compositions. From this figure we can see how the phonon drag affects the curve near the composition range of the pure metal. One of the curves was chosen at 60K, because at that temperature $S_g$ is close to a maximum. Even at this temperature, $S_d$ is still dominant for the alloys, and $S_g$ is strong only near the composition range of the pure metals. Comparing the $S$ vs. composition curve, with the $dN(E_f)/d(n/a)$ curve, both show a minimum near $n/a = 5.35$ and a maximum near $n/a = 6.1$, the anomalous effect in the thermopower as a function of $n/a$ occurring near $n/a = 5.1$ and 5.9. The small peak exhibited in that region will be discussed in more detail in the next section. For the higher temperature range, $\frac{dS}{dT}$ as a function of $n/a$ is shown in Fig. 11, where $\frac{dS}{dT} = \frac{S(280^\circ K) - S(180^\circ K)}{100^\circ K}$. Most curves have a nearly linear slope in this temperature range, and therefore yield a reasonable average of temperature derivatives. The $\frac{dS}{dT}$ curve has similar features as the $dN(E_f)/d(n/a)$ curve and is predicted by Eq. 22. The anomalous effect does not appear in the range near pure Mo, but it is noticeable at compositions near pure Nb. It is conceivable that another scattering mechanism produces the anomalous effect, which may in some way be related to $S_g$ at higher temperatures. The anomalous effect may change the magnitude and slope of the $S$ vs. temperature curve. It is believed that a greater $S_g$ exists in the Nb curve than in that of Mo at higher temperature, but $S_g$ in Nb is not as sensitive to the
Fig. 11. The temperature coefficient of the thermoelectric power of Zr-Nb-Mo-Re alloys as a function of composition; here $dS/dT = \frac{S(280K) - S(180K)}{100K}$. The derivative of density of states as in Fig. 10.
impurity content as $S_g$ in Mo. This will be discussed later. This experiment reveals that Eq. 21 and Eq. 22 govern the behavior of transition metals alloyed with their nearest neighbors in the periodic table.

The correlation of the thermopower of these alloys with other physical properties is through the density of states at the Fermi level. The density of states curve can also be roughly determined by measurements of magnetic susceptibility. The Hall coefficient $R$ varies with composition roughly as the reciprocal of the density of states at the Fermi level, because the hole mobility is reciprocal to the density of states at the Fermi level. The Hall coefficient is always positive when the Fermi surface has hole character, so that for Nb the Hall coefficient is positive in spite of strong scattering of these charge carriers due to the relatively high density of states. Hence, two factors influence the Hall coefficient vs. n/a curve, the major factor being the density of states at the Fermi level and the minor factor the number of charge carriers available.

At room temperature, the ideal resistivity $\rho_L \approx \rho(E_F)$. From Eq. 1,

$$S_d \approx \frac{n^2 k^2_T}{3|e|} \frac{d\rho_L}{d(n/a)}$$

(23)

It is seen from the data of $\rho_L$ that it varies with composition roughly proportionally to the $N(E_F)$. This will be discussed further in detail. It is interesting that the
extrema found in the S vs. n/a curve (e.g., the maximum at n/a = 5.35 in Mo-Nb alloys) appear also in such parameters as the residual resistivity,\textsuperscript{38} which is related to the impurity scattering of electrons. Also, the heat of solution of hydrogen in these alloys decreases markedly in the range of 5.02 < n/a < 5.4\textsuperscript{47} and the critical temperature of superconductivity, T\textsubscript{c}, reaches a minimum at n/a = 5.43.\textsuperscript{47} According to the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity,\textsuperscript{48}

\[
T_c = 1.14\langle \omega \rangle \exp[-1/N(E_F)\lambda],
\]

where \langle \omega \rangle is the typical phonon energy and \lambda is the pairing potential arising from the electron-phonon interaction.

From this equation, it is known that T\textsubscript{c} is directly related to the density of states at the Fermi surface. When small amounts of iron are dissolved in the alloys, the iron atoms exhibit no effective magnetic moment until the ratio n/a reaches about 5.45. Furthermore, temperature dependence of the elastic constant c\textsubscript{44} attains a maximum near n/a = 5.35.\textsuperscript{14} In Nb-Mo alloys the temperature dependence of the elastic constants is affected by the first and second derivatives of electronic density of states with energy, evaluated at the Fermi level.\textsuperscript{49} All of these observations showing a maximum near n/a = 5.35 seem to be connected to the sharp change detected in the N(E\textsubscript{F}) vs. n/a curve.
The density-of-states curve was determined from specific-heat data by Morin and Maita.29 This density of states is altered by electron-phonon interactions.30 The density of states at the Fermi surface is calculated from dividing density of states as determined from the heat capacity by an enhancement factor 1+λ, where λ is the electron-phonon coupling constant. Deviations from the true density of states at the Fermi level may still appear either by error of the experiment or calculation. Such deviations will be amplified in the curve of dN(E_F)/d(n/a). It is therefore difficult to compare this curve with S or dS/dT vs. n/a curves quantitatively. This may be the reason for shifting the dN(E_F)/d(n/a) peak from n/a = 5.10 to 5.15 after renormalization by the enhancement factor in Mo-rich-Re alloys, shown in Fig. 10. It may also be the reason for the dN(E_F)/d(n/a) vs. n/a curve of W-Ta alloys, shown in Fig. 13, being only roughly comparable to the dS/dT vs. n/a curve, especially in the Ta-rich range.

The C/T vs. T² plot shows a change of slope at low temperatures for the Nb and Nb-rich-Mo alloys,29 where C is the heat capacity. This change decreases when n/a increases and disappears at n/a = 5.39. Note that this composition point lies also near the extreme point of S vs. T curve. The change of slope in the C/T plot might be related to electron-phonon interactions, because the heat-capacity density of states is enhanced by this interaction for n/a < 4.35. The deviation of the density of states
curve calculated from the data of McMillan\textsuperscript{30} agrees better with our $dS/dT$ curve than that calculated from the heat-capacity density of states, especially in the region of $n/a < 4.5$. The maxima in the $S$ and $dS/dT$ vs. $n/a$ curves at $n/a = 5.1$, agree with the derivative of the heat-capacity density of states, the $dN(E_F)/d(n/a)$ curve calculated from McMillan being shifted to $n/a = 5.15$; the possible reason for this was discussed earlier. The calculated $dS/dT$ values from the $dN(E_F)/d(n/a)$ curve were obtained from experimental data and are about $1 \sim 2 \times 10^{-3} \text{V/°K}^2$, or roughly speaking, the uncertainty is less than a factor of 2 for the data of Zr-Nb-Mo-Re alloys.

The thermopower of the Nb-Zr 60\% alloy is almost zero to temperatures as low as 55°K. The thermopower of Mo-Re 27\% alloy is also almost constant ($-2 \text{μV/°K}$) to temperatures down to 165°K. Note that both alloys are more near the critical composition of changing b.c.c. structure to h.c.p. structure\textsuperscript{3} than any other alloys that were studied.

(b) W-Ta Alloys

The temperature dependences of the thermopower for the W-Ta alloys are shown in Fig. 12. As expected, the general features of the curves for these alloys are more similar to the Mo-Nb alloys than to any other alloys. While the data for the Mo-Nb 1\% alloy almost match that of pure Mo near the room temperature, Fig. 9, in the W-Ta 2\% alloy, $S$ departs from the pure W about $1.5 \text{μV/°K}$ near
Fig. 12. Thermoelectric power vs. temperature of W-Ta alloy crystals.
room temperature. For the W-Ta 95% alloy, S differs from the pure Ta by about 1μV/°K. It appears that S₉ prevails and impurity scattering plays a role in S of dilute W-Ta alloys even at high temperatures.

The variation of the dS/dT with composition in the higher temperature range is shown in Fig. 13. The dN(Eₓ)/d(n/a) curve vs. n/a curve was shown in the same figure. These curves do not resemble each other as much as those for the Mo-Nb alloys. The curves show a minimum at n/a = 5.5. The curves reveal that Eq. 21 is still dominant for the W-Ta alloys, but to a lesser degree than those for the Zr-Nb-Mo-Re b.c.c. alloys, so that they may be more affected by other factors. Note that the S vs. n/a curve at 295°K, shown in Fig. 14, also has a minimum at n/a = 5.5. The thermopower of Cr-V alloys was measured by Giannuzzi et al. The S vs. composition curve shown in Fig. 15 is roughly plotted from these data, does not include many data points for alloys. It seems that the minimum of S vs. n/a curves appears at n/a = 5.5 at 500K. The dN(Eₓ)/d(n/a) vs. n/a curve calculated from Cheng et al. differ from that of the S vs. n/a curve, showing the minimum close to n/a = 5.7. The difference between the two curves may have two reasons: (1) the magnetic effects due to Cr. (2) the degree of validity for calculating the dN(Eₓ)/d(n/a) curve from available specific-heat data; this factor has been mentioned before.
Fig. 13. The temperature coefficient of the thermoelectric power as a function of composition of W-Ta alloys; here $\frac{dS}{dT} = \frac{S(280K) - S(180K)}{100K}$. The derivative of density of states vs. composition (dashed line) is calculated from McMilian. 

54
Fig. 14. Thermoelectric power vs. composition for W-Ta alloys at 295K.
Fig. 15. Thermoelectric power vs. composition for Cr-V alloys at 500K, plotted from the data of Giannuzzi et al.⁵
It should be noted that for the Mo-Nb alloys, the anomalous effects in the thermopower as a function of n/a occurring near n/a = 5.1 and 5.9 are amplified for the W-Ta alloys, Fig. 14. Two peaks appear at n/a = 5.1 and 5.67. From Fig. 15, it is seen that this also happens in the Cr-V alloys, at least near the pure V composition side. This anomalous effect is not detected in most other alloys, such as Pd-Ag\textsuperscript{51} and V-Fe\textsuperscript{6} (near the pure V region of composition). Even the Nb-Zr and Mo-Re b.c.c. alloys do not show it. This anomalous effect may only be related to the Fermi surface and band structure of the alloys of neighbors of group VI and group V in the periodic table. The performance of S vs. n/a curve of the Cr-V alloys at 500°K, shown in Fig. 15, is similar to that of dS/dT vs. n/a curve of W-Ta alloys at higher temperatures, shown in Fig. 13. As expected, near room temperature the Cr-V alloys are more influenced by the magnetic effect than that at 500°K.

The temperature coefficient of emissivity is positive in the infrared range and negative in the visible range, and it changes its sign at the so-called X-point.\textsuperscript{52} The change of the X-point with composition in the W-Ta alloys was shown to have a maximum at n/a = 5.5.\textsuperscript{52} The energy of the wavelength of the X-point is very close to the energy difference between the Fermi surface and the next lower peak in the density-of-states curve. The electrical-
conductivity obtained from optical measurements was also shown to have a minimum at \( n/a = 5.5 \).\(^{34}\) These observations may also relate to the sharp change detected in the \( N(E_F) \) vs. \( n/a \) curve.

(c) Generalization of the Rule of the Diffusion Thermopower and Temperature Dependence of Electric Resistivity

The valence electrons per atom are linear in the composition, i.e., \( n/a \propto c \). At a fixed temperature, Eq. 21 shows \( S_d \propto \frac{dN(E_F)}{dc} \). For greater simplicity, we call this the \( dN/dc \) rule. This rule holds very well for the Zr-Nb-Mo-Re b.c.c. binary alloys, and is dominant for W-Ta and Cr-V alloys. It also holds very well for Pd-Ag, Pd-Rh, Pt-Au, and Pt-Ir alloys\(^4\) at extremely low temperatures, where \( S_g \) is absent. It prevails in Pd-Ag alloys of all compositions at higher temperature,\(^{51,53}\) using the \( d\gamma/dc \) values calculated from Fig. 16. Note that all these alloys just mentioned are combinations of elements of the nearest neighbors in the same row of the periodic table. Thus, the \( dN/dc \) rule, at least, holds for the nearest neighbors in the periodic table. The most important factor to control this rule is the rigid-band model. The \( dN/dc \) rule also holds approximately in V-Fe alloys.\(^6\) The deviation from this rule in alloys containing ferromagnetic or antiferromagnetic elements may be contributed by the magnetic effect (e.g., magnon drag), since it affects Eq. 2. Yet, the \( dN/dc \) rule still applies to Cr-rich-Fe
Fig. 16. The ideal resistivity $\rho_L (\rho_L = \rho_{293K} - \rho_R)$ vs. composition of Rh-Pd-Ag binary alloys (solid line) from Coles and Taylor. Dashed line represents specific-heat data from Budworth et al.
alloys at high temperature,\textsuperscript{54,55} based on available values of $\gamma$.\textsuperscript{50}

From Matthiessen's rule

$$\rho(T) = \rho_L(T) + \rho_R(c)$$

(25)

where $\rho_L(T)$ is the temperature-dependent resistivity (ideal resistivity) caused by thermal motion of lattice. $\rho_R(c)$ is the residual resistivity caused by impurity scattering of the electrons and depends on the impurity content, $c$.

The correlation between the $S_d$ and $\rho_L$ is shown in Eq. 23. Comparing Eq. 23 with Eq. 21, $\rho_L \propto N(E_f)$ at higher temperature. This result is supported by the data of $\rho_L$ of the Zr-Nb-Mo-Re alloys.\textsuperscript{38}

The theoretical approach is the following:

1. From Eq. 2, $\rho_L = \frac{12\pi^2k_F^2}{e^2\hbar^2}$, provided the conduction band does not change very much during alloying. Assume therefore that the area $A$ does not change very much during alloying, so that $A \propto 1/N_d(E_f) \sim 1/N(E_f)$, and $\rho_L \propto N(E_f)$.

2. From Eq. 4',

$$\rho = \frac{3}{e^2v_s^2\tau_s N_s(E_f)}$$

and $1/\tau_s \approx 1/\tau_{s-d} \propto N_d(E_f)$

then

$$\rho = \frac{3}{e^2v_s^2 N_s(E_f) N_d(E_f)}$$

(26)
By the same assumption, the conduction band does not change much during alloying, so that $v_s^2 N_s(E_f)$ is close to constant, and $\rho_L \propto N(E_f)$.

The interesting point is that this proportional rule, $\rho_L \propto N(E_f)$, is satisfied in the Zr-Nb-Mo-Re alloys. Does it also work for the other alloys? Equation 21 is, indeed, in excellent agreement for Pd-rich-Ag and Pd-rich-Rh alloys. The experimental data of $\rho_L^{56}$ and $\gamma^{57}$ vs. composition of Rh-Pd-Ag alloys are shown in Fig. 16. The density of states as taken from the $\gamma$ values must be corrected by the enhancement factor$^{30}$; this factor should be less than 2. It is observed that the $\rho_L \propto N(E_f)$ rule holds at room temperature. Coles and Taylor$^{57}$ essentially used the factor $(1-A T^2)$ for $\rho_L$, where

$$A = \frac{n^2 k^2}{6} \left[ \frac{1}{N(E)} \left( \frac{dN(E)}{dE} \right)^2 - \frac{1}{N(E)} \frac{d^2N(E)}{dE^2} \right] E_f$$

(27)

and added certain parameters to fit the data for alloys that contain Ag less than 65%, although this approach has little physical meaning.

Some authors$^{58}$ have dealt with $\rho_L$ of the transition metals by introducing the factor $(1+N(E_f)/N_s(E_f))T$ as well as additional parameters. This factor is related to the $\rho_L \propto N(E_f)$ rule, although this rule has its limitations, since knowledge of the electrical resistivity at room temperature, residual resistivity and $\gamma$ of alloys is required. The magnitude of $\rho_R$ always is comparable to that
of \( \rho_L \) for the alloys, even at room temperature. Unfortunately, the residual resistivity of Cr-V alloys is not available in the literature for comparison. It seems that the resistivity of Cr-V alloys after subtraction of \( \rho_R \) may have some relation to the \( \rho_L \propto N(E_f) \) rule, if one assumes that \( \rho_R \) increases as the content of solute is increased and a maximum exists near the center of composition. However the \( \rho_R \propto N(E_f) \) rule holds for alloys that satisfy Eq. 21. For other transition alloys further experiments must be carried out.

(2) Phonon-Drag Thermopower

From Eq. 1, \( S_d \) is proportional to the temperature, so that the \( S_d \) vs. temperature curve should be a straight line and decreasing to zero when the temperature approaches zero. This is the simplest way to separate out \( S_g \) from \( S_d \). Care should be taken, however, that some other scattering mechanisms and factors may affect the curve. Using this approach, the phonon-drag thermopower is big for pure W and Nb, even at room temperature. \( S_g \) is smaller for the Mo and Ta. In general, impurity scattering plays a small part in \( S_d \). The data for the Mo-Nb 1% alloy are shown in Fig. 9. \( S_g \) is virtually absent at room temperature in pure Mo. A comparison of the data for W-Ta 2% with those of W, Fig. 12, show that there still exists \( S_g \) in the pure W at room temperature. It appears therefore that for W-Ta alloys, \( S_g \) may play a role in the anomalous effect
observed in $S$ at the higher temperature. The phonon-induced interband transition may be responsible for this $S_g$ in this temperature range.

(a) Zr-Nb-Mo-Re Alloys

Investigating the curves of thermopower in the phonon-drag range, it is noted that the phonon-drag thermopower is strongly attenuated for the concentrated alloys, but remains detectable. There are indications of a positive phonon-drag contribution in all the alloys investigated. The phonon-drag thermopower of pure Mo is negative, but dilute alloys, such as Mo-Nb 1%, shown in Fig. 9, exhibit positive $S_g$. The phonon-induced hole-hole transitions are used to explain the positive thermopower $S_g$ for the Pd and Pt alloys.\(^4\)\(^{21}\) Considering the Fermi surface of the V and VI group-transition metals, interband transitions are not dominant in these binary alloys. For these metals, the sign of $S_g$ is determined by the smallest sheets of the Fermi surface having hole or electron character. For the alloys, the scattering of phonons by the solute will attenuate $S_g$ and the net effect of hole and electron sheets is such as to produce positive $S_g$. Also, the electron-electron U processes will lead to a positive $S_g$.

The type of phonon-drag thermopower is dependent on the topology of the Fermi surface. Changes in the Fermi surface with alloying will lead to an alteration in the
relative importance of both Umklapp and Normal processes. The detail of the Fermi surface is still not clear, so that it is difficult to predict the behavior of \( g \). The phonon-dispersion curves of Mo-Nb alloys\(^{35} \) can be correlated qualitatively with the band structure and the Fermi surface. At least, it may indicate something about the effect of changing the topology of the Fermi surface by alloying. The dispersion curves are found to be very different for pure Mo and Nb. From the results for alloys, it is seen that the variation of the dispersion curves with composition is rather complicated indicating changes of the Fermi surface by alloying. The change in the shape of the dispersion curve is closely related to the electronic band structure. For Mo-rich alloys, the shape is very sensitive to alloy composition but it remains substantially unchanged for Nb-rich alloys. \( g \) is sensitive to alloy composition in Mo alloys containing small amounts of Nb but less so for Nb-rich alloys.

The magnitude of the phonon-drag extremum depends on the impurity level of the sample. For the b.c.c. alloys, the data of thermopower do not show much difference between the sample of polycrystals and single crystals at the same impurity level. For example, the thermopower of polycrystalline Cr-rich-V alloys\(^{5} \) agree within experimental accuracy with that of single crystals.\(^{59} \) For \( g \), one must consider that the phonons interact with boundaries and dislocations, and the difference could come from these
mechanisms, that is, not only from the impurity level. More dilute Nb-Zr polycrystal alloys have been measured by Weinberg and Schultz. Their results are similar to our data, although they seem to observe more attenuation of phonon-drag peaks by alloying than our data with single crystals indicate.

The thermopower of many transition elements has been measured by Carter et al. and by Potter. The S vs. T curve for Nb in both investigations are in excellent agreement. They also agree with the results of Weinberg and Schultz at temperatures down to 80°K, i.e., at the maximum of phonon drag, but differ at lower temperatures. If the deviation is due to the reference material used, it would also affect their data for dilute Nb-Zr alloys. In Mo, the attenuation of the phonon-drag peak is very sensitive to the impurity content. This may be the reason for the discrepancy between the results by Potter and those by Carter et al. for Mo. The purity of the Carter's sample is 99.99%, hence higher than that of Potter's. We have measured the thermoelectric power of Mo of 99.9% purity, and the results agree with those by Carter et al. except for the phonon-drag extremum being slightly less deep. The minimum of the S vs. T curve for our Mo-Nb 1% alloys lies at 110°K, about the same position for that of pure Mo observed by Potter. This also proves that the impurity level is higher for Potter's data than those of Carter et al. There is no significant difference
between the dispersion curves of the Nb-Zr 4% crystal alloy and pure Nb. Based on our data, the attenuation of \( S_g \) of this alloy compared to pure Nb is very small.

Hall effect measurements of Zr-Nb-Mo-Re binary alloys suggest that impurity scattering is more anisotropic than phonon scattering in Mo-Nb and Nb-rich-Zr but less anisotropic than scattering by phonons in Mo-rich-Re. This was also borne out by the present measurements of \( S_g \), considering Eq. 18, \( S_g \propto \frac{\tau_{px}}{\tau_{px} + \tau_{pe}} \). For Mo-Nb and Nb-rich-Zr alloys, \( \tau_{px} \) is greater than \( \tau_{pe} \), and for Mo-rich-Re alloys \( \tau_{pe} \) is greater than \( \tau_{px} \), so that \( S_g \) is bigger in the Mo-Nb and Nb-rich-Zr than that in Mo-rich-Re.

(b) W-Ta Alloys

The negative phonon-drag peak of pure W is much deeper than that of pure Mo. The positive phonon-drag peaks are similar for Nb and V, but a little lower for Ta. Considering the dilute alloys, \( S \) for the W-Ta 2% alloy is similar to that of the Mo-Nb 1% alloy. \( S_g \) of both W and Mo is considerably attenuated by impurity content. The small minimum in the \( S \) curve of the Mo-Nb 1% alloy at 110°K and flat minimum in the \( S \) curve of the W-Ta 2% alloy near the 100°K are related to the position of attenuated phonon-drag minimum of the pure metals. Looking carefully at the \( S \) curve of the dilute alloys of W and Mo, the positive \( S_g \) bumps are not changed from that of the negative phonon-drag bump of the pure metals, the positive phonon-drag bump of
Mo-Nb 1% lying at 37°K and that of W-Ta 2% at 25°K. This positive phonon-drag extremum of the dilute alloys may be related to the hole pockets of the Fermi surface centered at the points $N$ in the Brillouin zone. There are two factors which support this suggestion: (1) The small positive peak of $S_g$ at 10°K in pure $W$ is related to the $N$ hole pockets of Fermi surface 37; and (2) the hole pockets are located at the boundary of the Brillouin zone, so that they would have a greater effect than other sheets of Fermi surface. Moreover, the $N$-hole pockets are small and have large curvature, so that after distortion by alloying may show a larger effect than other sheets of the Fermi surface.

Based on this explanation, the effect of the electron sheets distorted by impurity scattering would lead to the positive $S_g$ observed in all alloys here. The phonon induced hole-hole transitions were used to explain the observations with Pd and Pt alloys.

$S_g$ of the Ta-rich alloys behave quite differently from Nb-rich alloys. At least, $S_g$ are not strongly attenuated by alloying. For W-Ta 95% alloy the entire $S$ curve shifts in the direction of the position of $S$ curve for Nb. Even in the W-Ta 50% alloy a big phonon-drag effect was noted, a phenomenon not found in most alloys. Enhancement of $S_g$ by alloying was noted in some alloys 3 and might happen from a theoretical point of view. The closeness of the atomic mass of $W$ and Ta is one condition required for
this phenomenon to happen. S curves of the W-Ta 33% and
W-Ta 15% alloys have the same features as those of the
Mo-Nb 9% and Mo-Nb 25% alloys.

(c) Fermi Surface of These Alloys

If Fermi surface changes by alloying are only de-
dependent upon the composition variation, Fig. 1 shows these
changes as the composition is varied from the pure Mo to
the pure Nb. This effect is also true for compositional
changes from pure W to pure Ta. The Fermi level is shifted
along the band structure. The changing features of the Fermi
surface are the following: The N hole pockets are enlarged
from pure W to pure Ta. The Γ electron jacket becomes
smaller, when the Fermi level passes through the Γ'25 in
the band structure (about at Mo-Nb 55%). The electron
jacket is missing and hole sheets appear which then are
enlarged. Analysis of $S_g$ data of W-Ta and Mo-Nb alloys
shows that not only impurity scattering causes attenuation
of $S_g$ (in some cases it may enhance $S_g$). It may change
the relative probability of U and N processes. Direct
analysis of $S_g$ of alloys from the Fermi surface is there-
fore difficult, and the assumption that the controlling
factor for the sign of $S_g$ is the smallest hole or electron
sheets of Fermi surface applies to the pure metal, but does
not work well for alloys. Nevertheless, the Fermi surface
still needs to be considered as the basis for $S_g$ study
of alloys.
In some superconducting metals, the presence of impurities has an interesting effect on the behavior of the superconducting transition temperature, $T_c$, as a function of pressure. This can be used to give information about the topology of the Fermi surface of the metal, if there is a discontinuity in $dT_c/dp$, as a function of impurity concentration. It indicates a change in the number of depressions (or concavities) on the Fermi surface, as the average number of conduction electrons per atom is changed by varying the amounts of impurity present.

The $dT_c/dp$ vs. n/a curve have been measured for the Zr-Nb-Mo-Re binary alloys$^{61}$ and Ta-W alloys.$^{62}$ The data for $T_c$ are only available for some of the Mo-Nb alloys and for the Ta-rich-W alloys, because $T_c$ is too low and is hard to measure for certain compositions. Alloying Mo with Nb results in a progressive strengthening of the negative pressure dependence of $T_c$, the variation of which with composition follows smoothly from that for the Nb-Zr alloys. An abrupt change in the magnitude of $dT_c/dp$ occurs close to Mo-Nb 65%. In contrast to its smooth passage through Nb, $dT_c/dp$ has a very marked oscillatory character about Mo with a sharp peak occurring at about Mo-Re 10%.

The Fermi energy rises about the $\Gamma_{15}$ electron level where the curvature change occurs at Mo-Nb 34% and this was matched by the maximum in the theoretical curve of $dT_c/dp$.\textsuperscript{61} Adding W to Ta also strengthens the negative pressure dependence of $T_c$. In general, the Fermi surface
may change more smoothly for Nb-rich alloys than for Mo-rich alloys. However, the correction between \(dT_c/dp\) with Fermi surface topology is still not clear.

(d) Other Effects on Phonon-Drag Thermopower

It can be assumed that the mass-difference scattering produces only a negligible effect in the phonon-drag thermopower in these alloys. Furthermore, the Mo-rich-Re alloys have a larger \((\Delta M/M)^2\) factor than other alloys and the \(S_g\) of Mo-rich-Re alloys is very small. It may suggest that the mass difference scattering exerts a small effect in Mo-rich-Re alloys. This effect of greater attenuation of \(S_g\) in Mo-rich-Re alloys was already discussed in terms of the anisotropy of relaxation times, and its relation to the analysis of the Hall effect.

The lattice parameters \(L\) are: \(L(\text{Nb}) = 3.31\,\text{Å}, L(\text{Ta}) = 3.30\,\text{Å}, L(\text{Mo}) = 3.15\,\text{Å}, L(\text{W}) = 3.16\,\text{Å}, L(\text{Zr}) = 3.23\,\text{Å},\) and \(L(\text{Re}) = 2.76\,\text{Å}.\) This may cause a strain-field effect in the alloys of Mo containing Nb and W containing Ta. However, the change in the strain field surrounding solute atoms could produce only a small effect. The energy bands for Nb at normal and reduced lattice parameter have been calculated.\(^6\) They show some minor difference between the two kinds of bands, such as some filled states dropping and empty states rising.
The effects of spin fluctuations which are important for the nearly ferromagnetic case, are believed to be unimportant for the alloys considered here.
V. CONCLUSIONS

(1) The rule \( S_d \sim \frac{\pi^2 k^2 T}{3 |e|} \frac{dN(E_f)}{d(n/a)} \) holds for the transition-metal alloys which are formed by elements of nearest neighbors in the same row of the periodic table. This rule is also dominant for most transition-metal alloys for which the rigid-band model can be applied. From Mott's equation of thermopower for alloys that follow the \( dN/dc \) rule, the ideal resistivity should comply with the \( \rho_L \propto N(E_f) \) rule. Greater generalization of this rule requires that further experiments be carried out.

(2) The phonon-drag thermopower of the alloys gives a positive contribution. \( S_g \) of pure W and Mo is negative. This negative \( S_g \) is very sensitive to impurity content. Scattering of the phonons by the solute is such that \( S_g \) is always attenuated. The hole pockets at the position \( N \) of the Fermi surface may mainly contribute to positive \( S_g \) of these alloys.

(3) The anomalous effect that is observed at compositions near those of the pure metals of these alloys, appears only in alloys of transition metals formed among neighbors of group V and group VI in the periodic table. This anomalous effect may be related to the Fermi surface and band structure of this group of alloys.

(4) The relaxation times of impurities that attenuate \( S_g \) of the alloys are difficult to correlate with the Fermi surface of the alloys.
VI. REFERENCES


45. Pyseal Cement, manufactured by Fisher Scientific, U.S.A.
58. G. Gladstone, M. A. Jensen, and J. R. Schrieffer, 
"Superconductivity" V. 2, Edited by R. D. Parks, 

59. A. L. Trego and A. R. Mackintosh, Phys. Rev. 166, 
496 (1968).

27, 474 (1965).

Phys. 5, 911 (1975).


63. J. R. Anderson, D. A. Papaconstantopoulos, J. W. 
McCaffrey, and J. E. Schirber, Phys. Rev. B 7, 5115 
(1973).