INFORMATION TO USERS

This material was produced from a microfilm copy of the original document. 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 original submitted.

The following explanation of techniques is provided to help you understand markings or patterns 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 thru an image and duplicating adjacent pages to insure you complete continuity.

2. When an image on the film is obliterated with a large round black mark, it is an indication that the photographer suspected that the copy may have moved during exposure and thus cause a blurred image. You will find a good image of the page in the adjacent frame.

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

4. The majority of users indicate that the textual content is of greatest value, however, a somewhat higher quality reproduction could be made from “photographs” if essential to the understanding of the dissertation. Silver prints of “photographs” may be ordered at additional charge by writing the Order Department, giving the catalog number, title, author and specific pages you wish reproduced.

5. PLEASE NOTE: Some pages may have indistinct print. Filmed as received.

Xerox University Microfilms
300 North Zeeb Road
Ann Arbor, Michigan 48106
73-21,556

HAYES, Donald James, 1943-
HALL EFFECT, RESISTIVITY, AND ELASTIC CONSTANTS
OF Nb AND Nb-RICH Zr ALLOYS.

Rice University, Ph.D., 1973
Physics, solid state

University Microfilms, A XEROX Company, Ann Arbor, Michigan
RICE UNIVERSITY

HALL EFFECT, RESISTIVITY, AND ELASTIC CONSTANTS
OF Nb AND Nb-RICH Zr ALLOYS

by

Donald James Hayes

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

DOCTOR OF PHILOSOPHY

Thesis Director's signature:

Houston, Texas
January 1973
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>HALL EFFECT AND RESISTIVITY OF Nb AND Nb-Zr CRYSTALS FROM 295K TO 4.2K</td>
<td>1</td>
</tr>
<tr>
<td>I. Introduction</td>
<td>2</td>
</tr>
<tr>
<td>II. Theory</td>
<td>5</td>
</tr>
<tr>
<td>A. Boltzmann Transport Equation</td>
<td>5</td>
</tr>
<tr>
<td>B. The Relaxation-Time Approximation</td>
<td>9</td>
</tr>
<tr>
<td>C. Resistivity of Transition Metals</td>
<td>12</td>
</tr>
<tr>
<td>D. The Hall Effect</td>
<td>16</td>
</tr>
<tr>
<td>III. Literature Review</td>
<td>23</td>
</tr>
<tr>
<td>A. Nb</td>
<td>23</td>
</tr>
<tr>
<td>B. Nb-Zr Alloys</td>
<td>25</td>
</tr>
<tr>
<td>IV. Experimental Methods</td>
<td>27</td>
</tr>
<tr>
<td>A. Single-Crystal Growth</td>
<td>27</td>
</tr>
<tr>
<td>B. Sample Preparation</td>
<td>29</td>
</tr>
<tr>
<td>C. Voltage Measurements</td>
<td>30</td>
</tr>
<tr>
<td>V. Experimental Results</td>
<td>32</td>
</tr>
<tr>
<td>VI. Discussion and Conclusion</td>
<td>35</td>
</tr>
<tr>
<td>A. Variation of $R$ with Composition</td>
<td>35</td>
</tr>
<tr>
<td>B. Variation of $R$ with Temperature</td>
<td>36</td>
</tr>
<tr>
<td>1. Alloys</td>
<td>36</td>
</tr>
<tr>
<td>2. Pure Nb</td>
<td>38</td>
</tr>
<tr>
<td>C. Variation of $\rho$ with Composition and Temperature</td>
<td>39</td>
</tr>
<tr>
<td>VII. References</td>
<td>42</td>
</tr>
</tbody>
</table>
ELASTIC CONSTANTS OF Nb-RICH Zr ALLOYS IN THE TEMPERATURE RANGE 4.2K TO 298K

I. Introduction .............................................. 46
II. Experimental Procedure ..................................... 47
III. Results .................................................. 51
IV. Discussion .................................................. 52
   A. Compositional Dependence of the Elastic Constants .... 52
   B. Temperature Dependence of the Elastic Constants ...... 55
   C. Debye Temperature ...................................... 58
   D. Grüneisen Constant ..................................... 61
V. References ................................................. 64

ACKNOWLEDGEMENTS ........................................... 66
PART I

HALL EFFECT AND RESISTIVITY OF Nb AND Nb-Zr CRYSTALS FROM 295K TO 4.2K
I. INTRODUCTION

Transition metals are known for their relatively poor conductivity, large cohesive energy, high electronic specific heat and the tendency to form magnetic structures. Mott\(^1\), as early as 1935, tried to explain these unusual properties in terms of band models. These properties arise from the fact that near the Fermi level there is a narrow band of d-like states and an overlapping s-like conduction band similar to that found in simple metals. The density of this d-like band is an order of magnitude greater than that of the s-like conduction band so that the d-states dominate the observed properties.\(^2\) Within the last decade the band structures of many of the transition metals have been studied theoretically, and in many respects they agree quite well with experimental data. When one deals with alloys, a rigid band model is usually assumed. The rigid band model assumes that the shape of the bands and therefore the density-of-states curve does not change very much with alloying neighboring elements; only the number of electrons put into these bands changes. In this way one can estimate the density of states at the Fermi level and the shape of the Fermi surface of an alloy, if that of the solvent is known.
In the past few years considerable attention has been directed to the study of the temperature dependence of the Hall effect in efforts to obtain information about the scattering mechanisms in metals and alloys. Most of the experimental work has been devoted to the noble and alkali metals where anomalies, such as extrema in the Hall coefficient, $R$, at very low temperatures, have been observed.\textsuperscript{3-8} A similar effect has been reported for a single crystal of Mo,\textsuperscript{9} but measurements of $R$ as a continuous function of temperature down to 4.2K are generally lacking for other single-crystal transition metals and alloys. Likewise, detailed interpretation of the widely varying temperature effects appearing in the available Hall data has often proved difficult, partly because of the lack of a model of sufficient generality to include electron-relaxation-time anisotropy but tractable enough to apply at least qualitatively to experimental results. Such a model was recently developed by Kimura and Honda\textsuperscript{10}, who demonstrated that most of the observed temperature variations of the Hall coefficients of metals and alloys could arise from specific differences in the anisotropies of the scattering of charge carriers by different mechanisms.

In order to extend the investigation of electron-relaxation-time anisotropy to the transition metals, the Hall coefficients and resistivities of two oriented single-
crystals of Nb and of a series of three Nb-rich Zr alloy-
samples were measured as a function of temperature from
295K to 4.2K. Attempts were also made to correlate the
compositional dependence of the Hall and resistivity data
with the band-structure calculations of Mattheiss31 for
Nb using the rigid band model.

This work is divided into three principal sections.
The first establishes the necessary background in basic
transport theory which encompasses Chapter II and reviews
the previous related work on Nb and Nb-Zr alloys in Chapter
III. The second section presents the experimental tech-
niques and the measured results. This is contained in
Chapters IV and V. The final section (Chapter VI) con-
tains a discussion of the results and the conclusions which
can be drawn from them.
II. THEORY

A. Boltzmann Transport Equation

Before one can begin to correlate the experimentally determined transport properties with their theoretical counterparts, a brief review of transport theory is necessary. Most of the background material discussed in sections A and B will come from the works of Ziman\textsuperscript{11} and Blatt\textsuperscript{12}. The nomenclature will follow that used by Blatt in his book "Physics of Electronic Conduction in Solids."\textsuperscript{12}

The transport equation, which will be the basis of all that will follow, has its origin in classical rather than quantum mechanics. The Boltzmann transport equation was originally derived for a classical gas of hard spheres. In this case, each particle has a definite momentum and position at any instant except for the split second during which it undergoes a collision when these quantities change by a fixed amount. The state of the whole system can then be specified by the distribution of particles in these individual states, and the numbers entering and leaving such states through collisions can easily be obtained.\textsuperscript{11}

When applying this classical theory to the problem of electron conduction in solids we hope to use the quantum theory of solids to specify the states of the electrons in the system. We will then use a distribution function
$\dot{f}(\vec{k}, \vec{r}, t)$ to describe the assembly of conducting electrons. This distribution function is defined such that $\frac{1}{4} \pi^3 \frac{\partial f(\vec{k}, \vec{r}, t)}{\partial t}$ is the number of electrons in the volume element $\frac{\partial f(\vec{k}, \vec{r}, t)}{\partial t}$ at time $t$. At equilibrium, $f(\vec{k}, \vec{r}, t)$ depends only on the energy $\varepsilon$ and reduces to the Fermi distribution $f_o(\varepsilon)$.\textsuperscript{12}

The total rate of change of this distribution function can arise through the following processes:\textsuperscript{11,12}

a) Electrons may leave the element $\frac{\partial f}{\partial t}$ centered about $\vec{r}$, while others may enter, as a result of their spatial velocities. This change in $f(\vec{k}, \vec{r}, t)$ due to this mechanism will be given by

$$\dot{f}_{\text{diff}} = - \vec{v} \cdot \nabla f(\vec{k}, \vec{r}, t)$$

b) The existence of force fields will change the $\vec{k}$ vector and electrons may leave the element $\frac{\partial f}{\partial k}$ centered about $\vec{k}$. This change can be expressed by

$$\dot{f}_{\text{fields}} = - \frac{e}{\hbar} \left( \vec{E} + \frac{1}{c} \vec{v} \times \vec{H} \right) \cdot \nabla_k f(\vec{k}, \vec{r}, t)$$

c) Finally, the electrons may be scattered out of the element $\frac{\partial f}{\partial k}$ by collision processes. This term will be discussed in more detail shortly; as for now we will refer to it as $\dot{f}_{\text{c}}$
Now we can write the total rate of change of the distribution function df/dt as the sum of a, b and c.

\[
\frac{df}{dt} = f_{\text{diff}} + f_{\text{fields}} + f_c
\]

If we only consider the steady state condition (df/dt = 0), the Boltzmann transport equation may be written

\[
\bar{v} \cdot \nabla f(k,r) + \frac{e}{\hbar} \left( E + \frac{1}{c} \bar{v} \times \bar{H} \right) \cdot \nabla_k f(k,r) = f_c \quad (1)
\]

Formally, then, the central problem is one of finding the correct distribution function under certain specified boundary conditions. Once this distribution function is known, the electronic properties of a conductor are specified. For example, we can calculate the electron-current density by summing the individual current contributions of all the electrons. The current density \( \bar{J}(r) \) is then given by

\[
\bar{J}(r) = \frac{e}{4\pi^3} \int \nabla_k f(k,r) \, dk \quad (2)
\]

The procedure then appears to be straightforward: first, solve the apparently simple integro-differential equation (1), then use \( f(k,r,t) \) to obtain the transport coefficients. Problems come about because equation (1) is
not at all simple. This can easily be seen when we attempt to write out the collision term. The term \( \dot{f} \) represents the difference between the rate at which the state \( \overline{k} \) is entered and the rate at which carriers are lost from it due to collisions in the lattice.

Let \( \sigma(\overline{k}, \overline{k}') \) be the probability per unit time that an electron in the state of \( \overline{k} \) will be scattered into the state \( \overline{k}' \). Then in terms of \( \sigma(\overline{k}, \overline{k}') \) the collision term can be written\(^{12}\)

\[
\dot{f} \bigg|_c = \int \left\{ \sigma(\overline{k}', \overline{k}) f(\overline{k}') \left[ 1 - f(\overline{k}) \right] - \sigma(\overline{k}, \overline{k}') f(\overline{k}) \left[ 1 - f(\overline{k}') \right] \right\} \, d\overline{k}'
\]

(3)

Let \( -\dot{\sigma}(\overline{k}, \overline{r}) \partial f / \partial \varepsilon \) express the 'out-of-balance' part of the electron distribution from the thermal equilibrium distribution \( f_0(\varepsilon) \) such that

\[
f(\overline{k}, \overline{r}) = f_0(\varepsilon) - \dot{\sigma}(\overline{k}, \overline{r}) \frac{\partial f_0}{\partial \varepsilon}
\]

(4)

Then the collision term can be written

\[
\frac{1}{kT} \int \sigma(\overline{k}, \overline{k}') f_0(\varepsilon) \left[ 1 - f_0(\varepsilon') \right] \left[ \dot{\sigma}(\overline{k}') - \dot{\sigma}(\overline{k}) \right] \, d\overline{k}'
\]

(5)

One should refer to the work of Blatt\(^{12}\) to see the details in going from (3) to (5). The basic assumptions used were that \( \sigma(\overline{k}, \overline{k}') \) is not a function of fields and that the deviation of the steady-state distribution from the
equilibrium distribution is rather small. The transport equation now becomes

\[
\begin{multline}
\exp \left[ \frac{E}{k_B T} + \frac{1}{\hbar} \mathbf{v}_k \cdot \mathbf{e} \times \mathbf{H} \right] \cdot \frac{1}{h} \mathbf{v}_k f(k, r) + \frac{1}{\hbar} \mathbf{v}_k \varepsilon \cdot \mathbf{v}_r f(k, r) \\
= \frac{1}{kT} \int \sigma(k, k') f_0(\varepsilon) [1 - f_0(\varepsilon')] [\xi(k') - \xi(k)] \, dk'
\end{multline}
\]

(6)

where we have used \( \mathbf{v}_k = \frac{1}{\hbar} \mathbf{v}_k \varepsilon \). In general, a solution to equation (6) cannot be obtained in closed form. The variational principle is the backbone of the most powerful method of solving this equation. Solutions using the variational method, which requires explicit expressions for the transition probabilities \( \sigma(k, k') \), will be given in section C. The only simple method that exists for the exact solution of the linearized Boltzmann equation is the relaxation-time approximation.

B. The Relaxation Time Approximation

We will start with the assumption that a relaxation time \( \tau(k) \) exists and is defined such that in the absence of any applied fields the distribution function \( f(k, r) \) relaxes to its thermal equilibrium value \( f_0(\varepsilon) \) according to \( 11, 12 \)
\[
\frac{\delta f}{\delta t} = - \frac{f(k, r) - f_0(\varepsilon)}{\tau(k)} = \frac{\delta f_0}{\delta \varepsilon} \frac{\delta f}{\delta \varepsilon}
\]

(7)

where \(\tau(k)\) is independent of the initial form of \(\varphi(k)\).

This means we are assuming \(\tau(k)\) is the same function independent of what perturbs the system and the magnitude of the perturbation.

For the simplest case, namely d.c. electrical conduction where the boundary conditions are \(E\) = constant, \(H = 0\), and \(T = constant\), equations (6) and (7) reduce to

\[
eE \cdot \frac{1}{h} \nu_k \bar{f}(k, r) = \frac{\delta \varphi(k)}{\delta \varepsilon} \frac{\delta f_0}{\delta \varepsilon}
\]

(8)

Equation (8) simplifies to

\[
eE \cdot \nu_k \frac{\delta f_0}{\delta \varepsilon} = \frac{\delta \varphi(k)}{\delta \varepsilon} \frac{\delta f_0}{\delta \varepsilon}
\]

(9)

where we have dropped all terms of order \(E^2\) or higher, which would correspond to deviations from Ohm's Law.\(^{12}\)

Rearranging equation (9) gives the following form to the distribution function,

\[
f(k, r) = f_0(\varepsilon) - e^{\left(\frac{\delta f_0}{\delta \varepsilon}\right)} \tau(k) \nu_k \cdot E
\]

(10)
Finally, the conductivity can be expressed as an integral over the Fermi surface:

$$\sigma = \frac{e^2}{4\pi^3 n} \int \tau(\mathbf{k}) \frac{\mathbf{v}_k \mathbf{v}_k}{\mathbf{v}_k} \, dS_F.$$  \hfill (11)

Here we used the fact that in a metal the function $\left(\frac{\delta f^0}{\delta \varepsilon}\right)$ behaves like a delta function at the Fermi level.$^{12}$

The most general possible solution to the integral equation

$$e\mathbf{E} \cdot \mathbf{v}_k \frac{\delta f^0}{\delta \varepsilon} = \frac{\delta f}{\delta \varepsilon} \bigg|_c$$

is

$$f(\mathbf{k}, \mathbf{r}) - f^0(\varepsilon) = \left(- \frac{\delta f^0}{\delta \varepsilon}\right) e\mathbf{E} \cdot \overline{\Lambda}(\mathbf{k}),$$  \hfill (12)

where $\overline{\Lambda}(\mathbf{k})$ would be a vector defined at each point $\mathbf{k}$ of the Fermi surface. In the general case $\overline{\Lambda}(\mathbf{k})$ is not necessarily parallel to $\mathbf{v}_k$ over the Fermi surface. The electrical conductivity of a cubic metal can be expressed,

$$\sigma = \frac{e^2}{4\pi^3} \int \mathbf{v}_k \cdot \overline{\Lambda}(\mathbf{k}) \left(\frac{\delta f^0}{\delta \varepsilon}\right) \, d\mathbf{k}.$$  \hfill (13)

It is always possible to express the scalar product $\mathbf{v}_k \cdot \overline{\Lambda}(\mathbf{k})$ as $\tau(\mathbf{k}) \mathbf{v}_k^2$ where $\tau(\mathbf{k})$ is now an anisotropic relaxation time$^{14}$ which permits the correct conductivity to be calculated using
\[ \bar{\Lambda} = \tau(\vec{k}) \bar{v}_k. \] (14)

No longer is \( \tau(\vec{k}) \) a relaxation time in the sense of (7) but rather a parameter in the theory, with the dimensions of time. In other words, \( \tau(\vec{k}) \) here is a parameter which is defined to give the correct value of the electrical conductivity. It may not give the correct value for other transport coefficients.

C. Resistivity of Transition Metals

In 1936 Mott\(^1\) proposed a simple picture of the electronic band structure to explain the resistivity of transition metals. The valence electrons in a transition metal are divided up into two groups. The first forms an s-band with a spherical Fermi surface and high mobility, and the second, a d-band with a complex Fermi surface with a much lower mobility. Since the s-electrons are considered to be the predominant charge carriers the resistivity arises from both s-s and s-d scattering. The lattice resistivity can be divided into two parts \( \rho_{ss} \) and \( \rho_{sd} \).

Using the variational principle (mentioned in A) to solve the Boltzmann transport equation the electrical resistivity has been obtained\(^1\)\(^,\)\(^1\)\(^5\). The results of such a calculation are shown in equations\(^1\)\(^5\) (15) and (16):
\( \rho_L \propto \text{const} \times \left[ A \left( \frac{T}{\theta_D} \right)^2 + \frac{G_{sd}}{G_{ss}} \frac{N_d(0)}{N_s(0)} \right] \left( \frac{T}{\theta_D} \right)^3 \) \hspace{1cm} (15)

\( T >> \theta_D \quad \rho_L \propto \text{const} \times \left[ 1 + c \frac{N_d(0)}{N_s(0)} \right] T \nu_{ph} \) \hspace{1cm} (16)

where \( A = \) parameter which varies between 10 and 20 as \( T \) decreases in the region \( \theta_c \leq T \leq \theta_D \); \( \theta_c = \) cutoff temperature corresponding to the temperature below which there exist no phonons of sufficient size to cause interband transitions; \( \theta_D = \) Debye Temperature; \( G_{ss} \) and \( G_{sd} = \) the average matrix elements for intra- and interband electron-phonon scattering; \( N_s(0) \) and \( N_d(0) = \) the band-structure density of states at the Fermi level for the s and d bands, respectively; \( c = \) constant, approximately equal to \( 2^{1/3} \).
From the experimental data it is clear that $\frac{c_{sd}^2}{G_{ss}^2}$ must be of the order of unity. Equations (15) and (16) have been obtained considering only Normal processes ($\vec{k} - \vec{k}' = \vec{q}$). Calculation of the contribution to $\rho_L$ from Umklapp processes is much more difficult, as the relation between $\vec{q}$ and $\vec{k} - \vec{k}'$ is complicated by the addition of an arbitrary reciprocal lattice vector.

Another topic which should be touched upon in this section is the resistivity of dilute alloys and Matthiessen's rule. This rule states that the partial resistivities, which arise from the scattering of conduction electrons by different types of imperfections, are simply additive. It is usually written

$$\rho(T) = \rho_0(x) + \rho_L(T) \quad (17)$$

where $\rho_L(T)$ is the temperature-dependent resistivity characteristic of the pure metal due to phonon scattering and $\rho_0(x)$ is the residual resistivity due to $x$ amount of solute concentration.

Three main sources of deviation from Matthiessen's rule for non-magnetic impurities are$^{14,17,18}$

a) Alteration of the band structure and therefore changing the Fermi surface with alloying.

Equation (15) shows how the resistivity $\rho_L(T)$
depends on the density of states at the Fermi level and also the scattering matrices, both of which are band-structure sensitive.

b) Changes in the phonon spectrum due to different elastic constants and different masses of the impurities. This is reflected in equation (15) by the scattering matrices and the Debye temperature.

c) Phonon and impurity scattering may have different anisotropic relaxation times.

If we restrict our attention to alloys of solute concentration less than a few atomic percent, contributions from a and b can be considered negligible compared to those from c. \(^{14,17}\)

Departures from Matthiessen's rule are usually expressed in terms of \(\Delta(T)\) as defined by

\[
\Delta(T) = \rho(T) - \rho_0(x) - \rho_L(T)
\] (18)

where \(\rho(t)\) is the measured resistivity. Considering a two-band model, Dugdale and Basinski\(^{17}\) showed that \(\Delta(T)\) could be expressed as

\[
\Delta(T) = \frac{\rho_0(x) \rho_L(T)(\beta - \alpha)^2}{\alpha \rho_0(x)(1 + \beta)^2 + \beta \rho_L(T)(1 + \alpha)^2}
\] (19)
where the subscripts 1 and 2 distinguish the two bands, the subscripts 0 and L stand for impurity and phonon scattering, respectively, and \( \alpha \) and \( \beta \) are given by

\[
\alpha = \frac{\alpha_{1L}}{\alpha_{2L}}, \quad \beta = \frac{\alpha_{10}}{\alpha_{02}}.
\]

Looking at equation (19) we see that Matthiessen's rule will hold if \( \alpha = \beta \). Thus, the ratio of phonon scattering to impurity scattering in the first zone must differ from the same ratio in the second zone for \( \Delta(T) \) to be different from zero.

D. The Hall Effect

When a magnetic field as well as an electric field is present, the solution to Boltzmann's equation takes on a much more complex nature. Assuming a constant temperature and the existence of a relaxation time, equation (6) can be written

\[
eE \cdot \nabla_k \left( -\frac{\partial f_0}{\partial \epsilon} \right) = \frac{\Phi}{\tau} \frac{\partial f_0}{\partial \epsilon} + \frac{e}{\hbar c} (\nabla_k \times \vec{H}) \cdot \nabla_k \left( \frac{\partial f_0}{\partial \epsilon} \right)
\]

If the energy \( \epsilon \) is given by the relation \( \epsilon = n^2 k^2 / 2m^* \), then the solution of this differential equation is of the form \( \Phi = \vec{k} \cdot \vec{q} \) where \( \vec{q} \) is independent of the direction of \( \vec{k} \).
but may be a function of $\varepsilon$ as well as the $\vec{E}$ and $\vec{H}$ fields. On solving equation (2) one obtains

$$
\vec{\psi} = \frac{e}{\hbar} \cdot \frac{\left[ e\vec{e} - \frac{\tau e}{m \ast e} \vec{H} \times e\vec{E} + \left( \frac{e \tau}{m \ast e} \right)^2 \vec{H} (\vec{H} \cdot e\vec{E}) \right]}{1 + \left( \frac{e \tau}{m \ast e} \vec{H} \right)^2} \cdot (21)
$$

From equation (2) we can calculate the current density:

$$
\vec{J} = \frac{e}{4\pi^3} \int \vec{\psi} \frac{\partial \mathcal{O}}{\partial \varepsilon} \vec{v} \, dK \quad . \quad (22)
$$

If we substitute equation (21) into equation (22), along with the restriction that the magnetic field is perpendicular to the electric field, we obtain

$$
\vec{J} = \sigma_E \vec{E} + \sigma_H \vec{H} \times \vec{E} \quad (23)
$$

where $\sigma_E$ and $\sigma_H$ are the appropriate volume integrals in $k$-space. For the geometry shown in figure 4 the Hall coefficient $R$ is defined by

$$
E_y = R J_x H_z \quad , \quad (24)
$$

where $J_y = J_z = 0 = H_x = H_y$. Equation (23) can now be rewritten

$$
J_x = \sigma_E E_x - \sigma_H E_y \quad \quad \quad (25)

0 = \sigma_E E_y + \sigma_H E_x \quad .
$$
By eliminating $E_x$ from these simultaneous equations we can solve for the Hall coefficient. The result is given by

$$ R = \frac{-\sigma_H}{\sigma_E^2 + H^2\sigma_H^2} \quad (26) $$

For the free electron model this reduces to

$$ R = \frac{1}{n_{0ec}} \quad (27) $$

The sign of $R$ in equation (26) is determined by the sign of $\sigma_H$, which is determined by the product $em^*$. For electron conduction $R$ is negative, whereas it is positive for hole conduction.

In polyvalent metals one usually deals with a complex Fermi surface where some parts are hole-like and some parts are electron-like. As one moves on the surface, the nature of the carriers may gradually change from electron-like to hole-like. In this situation, multiband models are usually invoked. At best they are very crude attempts to shed a little light on a complex problem, but when one is groping around in darkness, a little light is better than no light at all.

Detailed calculations for a two-band model may be found in Wilson's book.\textsuperscript{19} He assumes two overlapping bands,
each of which has spherical symmetry. For the weak field approximation \( (w_c \tau \ll 1) \) the Hall coefficient is given by

\[
R = \frac{e}{c} \frac{\tau_a \sigma_a/m_a^* + \tau_b \sigma_b/m_b^*}{(\sigma_a + \sigma_b)^2},
\]  

(28)

where the subscripts a and b signify the two bands.

As early as 1955 Coles\textsuperscript{20} recognized the importance of the scattering mechanisms in determining the Hall coefficients. Since then many investigators\textsuperscript{21,10} have attempted to explain the Hall effect in the noble metals and noble-metal alloys using the concept of anisotropic relaxation times. Ziman\textsuperscript{21} in 1961 proposed a theory to explain the temperature dependence of R in noble metals. In this analysis, he tried to show how the temperature dependence of the relaxation times for phonon scattering varied on different parts of the Fermi surface. By considering both 'belly' and 'neck' electrons, he was able to show that the 'freezing out' of U-processes for 'belly' electrons caused the ratio \( \tau_N/\tau_B \) to decrease as the temperature was lowered. He also discussed how the magnitude of R for alloys would depend on \( \tau_N/\tau_B \) due to impurity scattering.

In 1971 Kimura and Honda\textsuperscript{10} proposed a simple procedure to discuss the general behavior of R without any particular assumptions about \( \tau(k) \). They performed a variational
calculation to obtain the Hall coefficient of a cubic metal under the conditions of weak magnetic fields. They showed that it can be expressed in the general form:

$$R = R_0 [\varepsilon(\mathbf{k})] A[\varepsilon(\mathbf{k}), \tau(\mathbf{k})]$$

(29)

where $R_0$ is a characteristic constant determined by the band structure $\varepsilon(\mathbf{k})$, while $A$ is a temperature-dependent factor whose magnitude is determined by the anisotropy of the electron relaxation time $\tau(\mathbf{k})$ over the Fermi surface. If there exists two different mechanisms, $a$ and $b$, for the scattering of charge carriers which result in differing amounts of relaxation-time anisotropy, then the magnitude of the anisotropy factor $A$ should vary with temperature in response to changes in the relative contribution, $\rho_a$ or $\rho_b$, from each mechanism to the total resistivity, $\rho$. For most metals $A$ is expected to vary smoothly within the limits $A_a$ and $A_b$ as the fractional resistivity

$$x = \rho_a / (\rho_a + \rho_b)$$

varies with temperature. In a pure metal, where the charge-carrier scattering is mainly by phonons via normal (N) and umklapp (U) processes, any difference in the scattering-anisotropy factors, $A_N$ and $A_U$, for the two mechanisms arising from Fermi-surface topology could lead to a temperature-dependent Hall coefficient. By assuming the usual power law $(T/\Theta_D)^5$ for $\rho_N$ and
exponential form $\exp(-\frac{\theta^*}{T})$ for $\rho_U$, Kimura and Honda demonstrated that $x = \rho_U/(\rho_U + \rho_N)$ can pass through a maximum at low temperatures. This results in an extremum in $A$ and hence in the magnitude of the Hall coefficient $|R|$. The temperature at which an extremum in $R$ is observed for a particular metal should be related to the Debye temperature $\theta_D$ and to some sort of average characteristic temperature $\theta^*$ for $U$-processes, which depends on the geometry of the Fermi surface.\(^{10}\)

In alloys, a temperature dependence of the Hall coefficient can arise from a difference in the anisotropies of scattering by phonons ($N$ and $U$ processes combined) and by impurities. As the temperature is reduced from 295K, the fraction of the scattering due to impurities increases. This fraction is $x = \rho_o/(\rho_o + \rho_L)$, where $\rho_o$ and $\rho_L$ are the residual and ideal resistivities, respectively. This can lead to an increase or decrease in $A$, and hence in $|R|$, depending on whether the impurity-scattering anisotropy factor $A_o$ is greater or less, respectively, than the anisotropy factor $A_L$ for phonon scattering at 295K.\(^{10}\) An increase in impurity concentration results in a similar increase in $x$ and hence should affect $A$ in the same way as a reduction in temperature. A corresponding variation in the magnitude of the Hall coefficient would then be expected, so long as
the value of $R_0$ is not significantly altered by the shifting of the Fermi level with the change in composition.
III. LITERATURE REVIEW

A. Nb

The Group-VB transition metal Nb crystallizes in the BCC structure. It has five electrons outside the filled bands. These valence electrons are associated with the 4d⁴ and 5s¹ levels in the isolated atom.

The Hall coefficient has been measured at liquid-helium, liquid-nitrogen and room temperatures by Berlincourt²² in polycrystalline Nb. He obtained a room temperature value for R = 8.72 x 10⁻⁵ cm³/coul. The residual resistivity ratio for his sample was less than 15. High-field Hall data have been obtained on high-purity Nb at liquid-helium temperature by a number of investigators.²³-²⁶ The high-field investigations are usually undertaken to study the dimensions of the Fermi surface. The results of these studies agree quite well with the proposed theoretical Fermi surface for Nb.²³,²⁴

There are clear indications for the presence of a positive phonon-drag contribution in Nb.²⁷-²⁹ The low temperature peak occurs in the vicinity of θₚ/5, where θₚ is the Debye temperature. Phonon-induced transition across a hole region of the Fermi surface is the simplest picture which will explain the positive contribution to the thermo-power.²⁷ This picture is consistent with the proposed Fermi
surface of this metal, which will be discussed shortly. In the vicinity of $\theta_d/5$ the phonon-drag thermopower usually begins to decrease because of phonon-phonon scattering.\textsuperscript{27}

White and Woods\textsuperscript{30} have measured the resistivity for many transition elements. As can be seen from their results, Nb exhibits a low temperature $T^3$ behavior which is similar to other high-density-of-states (at the Fermi level) transition elements. The high-temperature data showed the expected linear $T$ dependence.

Within the past five years, several researches have calculated the band structure of Nb. Mattheiss\textsuperscript{31} used the augmented-plane-wave method, while Deegan and Twose\textsuperscript{32} used a modified version of the orthogonalized-plane-wave method. The overall agreement of these two independent methods is excellent.\textsuperscript{31} The Fermi surface proposed by Mattheiss\textsuperscript{31} can be seen in Figure 1. For Nb the first Brillouin zone is filled. The Fermi surface sheets, which enclose the unoccupied portion of the second and third zones, are shown to the left and right, respectively, in this figure. The closed surfaces in the second and third zone along with the multiply connected sheet in the third zone are all of a hole-like nature.
THE FERMI SURFACE OF Nb

SECOND ZONE       THIRD ZONE

Figure 1. Proposed Fermi surface of Nb by Mattheiss.
B. Nb-Zr

The phase diagram\textsuperscript{33} for these alloys is shown in Figure 2. Complete solid solubility exists from below the solidus line to about 1000°C. As the temperature is lowered farther the solid solubility breaks up except at the Nb-rich side. Interest in this work lies solely in the BCC solid solubility region on the Nb-rich side. To retain the high-temperature BCC structure for Zr content, greater than 20\%, the alloys must be cooled rapidly through the two-phase region. An \(\omega\) phase forms in a diffusionless manner in Nb-Zr alloys for Nb compositions between 6 and 30\%.\textsuperscript{34} This cannot be eliminated by rapid quenching; therefore, to study low-temperature properties on BCC-solid solution of these alloys, one is limited to the niobium-rich end or to quenched samples with less than 70\% Zr.

In 1962, Schindler and Gillispie\textsuperscript{35} measured the normal-state Hall coefficient of a Nb-25\% Zr polycrystalline sample. The Hall coefficient was found to be \(1.14 \times 10^{-10}\), \(1.05 \times 10^{-10}\), and \(0.84 \times 10^{-10}\) m\(^3\)/A-sec at 4.2, 77 and 317 K, respectively.

Room temperature resistivity of the Nb-Zr alloys was measured by Rogers and Atkins\textsuperscript{33} in the determination of the phase diagram. Their results will be referred to later in Chapter VI.
Figure 2. Nb-Zr phase diagram by Rogers and Atkins. 
The final topic to be mentioned in this review chapter is the work of Weinberg and Schultz. In 1965 they measured the thermoelectric power in Nb-Zr alloys. Their results indicate that the height of the phonon drag peak for the dilute Nb-rich Zr alloys decreases with increasing Zr content. They feel that this decrease cannot be explained by phonon scattering by the Zr atoms since the mass difference between Zr and Nb is small. Therefore, they concluded that "It appears likely then that lattice distortion and alterations in the relative importance of U- and N-processes, as a result of alloying, are predominant mechanisms leading to phonon drag attenuation, at 75°K, in these alloys."
IV. EXPERIMENTAL METHODS

A. Single Crystal Growth

The single crystals were prepared by a floating-zone, electron-beam melting method. The starting materials were high-purity metal powders. These powders were mixed, compressed into rod shapes, and sintered under vacuum (pressures less than $10^{-6}$ Torr). They were melted into solid rods during one pass in the zone refiner and then seeded to insure proper orientation. The number of passes made on each sample after seeding varied with the Zr concentration. Samples with higher Zr concentration needed more passes before giving large enough single crystals. Each pass leads to changes in the alloy composition because of the higher vapor pressure of Zr at the alloy melting point. It was noticed that in general the Nb-Zr single crystals required more passes and at slower rates (as slow as 1/2" per hour) than Nb-Mo crystals grown with the same equipment and techniques. The reason for this is believed to be twofold: first, zirconium oxide has a lower vapor pressure and higher melting point (Figure 3) than pure Zr, and a small amount of ZrO$_2$, which would be difficult to eliminate, would serve as nucleation sites for grain growth, and secondly, as the Zr concentration increases past 15% there is a two-phase region;
Figure 3. Transition Metal and Transition Metal Oxides Melting Points.
therefore, homogeneity is very important so that local concentrations do not exceed this amount. It was found firstly that the oxygen concentration could be reduced considerably by using low-mesh-size, high-purity powders and, secondly, that homogeneity could be improved by making more passes at slower rates. The second step had the disadvantage of lowering the Zr concentration by vaporization, as mentioned earlier. This can be seen from the fact that the starting composition of the Nb-3.6% Zr single crystal was approximately 9% Zr.

The problem of oxygen impurity could be eliminated by starting with high-purity metal rods and forming the alloys by inert gas arc melting. As long as powders are used the ZrO₂ layer on the powder surface will cause a problem. The arc-melting method was not tried here due to the lack of the proper equipment.

A measure of the possible purity levels that can be obtained using an electron beam zone refiner can be seen by the residual resistivity ratio ($\rho_{295K}/\rho_{4.2K}$). Values of RRR for Nb and Mo single crystals grown in this equipment were 150 and 5000 respectively.
B. Sample Preparation

The Hall samples were cut from the rods in the shape of a plate approximately 20 x 5 x 0.4 mm in size by the spark erosion and finished by spark planing. They were then electropolished to remove any contaminants that might have been picked up in the spark-erosion or spark-planing process. The plates were oriented to within 1.5° (prior to cutting and planing) by Laue back-reflection techniques. The final conditions and orientations of the samples can be seen in Table I.

TABLE I

Sample Compositions, Geometries and Residual Resistivity Ratio

<table>
<thead>
<tr>
<th>Composition at 1%</th>
<th>Current Direction</th>
<th>Field Direction</th>
<th>$\frac{\rho(295K)}{\rho(4.2K)}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>100</td>
<td>001</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td></td>
<td>011</td>
<td>150</td>
</tr>
<tr>
<td>Nb 1.4% Zr</td>
<td>110</td>
<td>101</td>
<td>20</td>
</tr>
<tr>
<td>Nb 3.6% Zr</td>
<td>100</td>
<td>001</td>
<td>6.3</td>
</tr>
<tr>
<td>Nb 15% Zr</td>
<td></td>
<td>polycrystalline</td>
<td>2.8</td>
</tr>
<tr>
<td>Nb 60% Zr</td>
<td></td>
<td>polycrystalline</td>
<td>1.1</td>
</tr>
</tbody>
</table>
C. Voltage Measurements

The crystals were mounted with silicone grease onto a 'hot' plate consisting of manganin heater wire wound uniformly around a copper bar and sealed by a thin layer of high-termal epoxy. On the opposite side of the plate a copper-constantan thermocouple was similarly mounted, with which the temperature could be measured down to about 10K with an absolute accuracy of better than 2K. Use of the heater in conjunction with a variable-temperature dewar made possible continuous temperature control to within less than 0.1K between room and liquid helium temperatures. A dc current of 2 amp was maintained through the samples via spring-loaded, copper-bar contacts. Copper-needle contacts at the ends and edges of the flat faces of the samples were used to detect voltages parallel and transverse, respectively, to the current direction. These voltages were then measured in magnetic fields up to 9 kOe directed perpendicular to the flat faces of the samples, using a 6-dial potentiometer and a nanovoltmeter (see Figure 4).

The elimination of any extraneous voltages due to temperature gradients and probe misalignment was accomplished in the usual way by current and field reversals. A 5-nanovolt resolution capacity for the voltage-measuring system permitted accurate relative data to be obtained for
Figure 4. Electronic circuitry for measuring $R$ and $\rho_L$. 
each sample. However, the difficulty of measuring precisely both the distances between voltage probes and the cross sections of the individually cut samples resulted in uncertainties in the absolute values of $R$ and $\rho$ as high as 5%. Errors due to thermal expansion over the range 295K - 4.2K should be an order of magnitude less$^{37}$, so the data were not corrected for such effects.
V. EXPERIMENTAL RESULTS

The Hall coefficients of the alloys are independent of magnetic-field strength (up to 9 kOe) and crystal orientation even at 4.2K, due to their large residual resistivities. A field dependence for the Nb crystals begins to show up at temperatures below about 15K as expected for a relatively pure, non-compensated metal.

The Hall coefficient for Nb and Nb-rich Zr alloys is positive as can be seen in Figure 5. Here R is plotted as a function of the outer-electron/atom ratio at three different temperatures. The data from the work of Schindler and Gillispie for Nb 25% Zr, and Nb 35% Mo and Nb 8% Mo from the work of Cox, et al., are also shown in this figure. The Hall coefficient of the Nb 60% Zr sample (e/a = 4.4) was determined only between LN₂ and room temperatures. There is some question of the metallurgical condition of the Nb 60% Zr sample. It was cooled rapidly and the resistivity agrees with that determined by Rogers and Atkins for a sample of the same composition cooled rapidly from high temperature. The high value of \( \rho_\infty \), the apparent deviation from Nordheim's rule, and metallographic studies which show slight traces of what appears to be a second phase cast doubt on the accuracy of the values for this sample plotted in Figure 5.
Figure 5. Hall coefficients as a function of crystal composition at 290K, 80K, and 4.2K. Data for Nb 25%Zr is from the work of Schindler and Gillispie; and Nb 35%Mo and Nb 8%Mo from the work of Cox, et al.
Data in Figure 6 indicate that $R$ in pure Nb is relatively independent of temperature in the range 100 to 300K, and it decreases slightly as $T$ is lowered below 100K reaching a minimum at about 35K and then increasing as the temperature is further lowered.

The temperature dependences of the Hall coefficients for the alloys are also shown in Figure 6. A general increase of $R$ with decreasing temperature is found for all of the Nb-rich Zr samples. The magnitude of the total change in the Hall coefficient from 295K to 4.2K is greater for the more dilute alloys.

The resistivities of Nb and the alloys are plotted as a function of temperature in Figure 7. Log $\rho$ vs. log $T$ plots have been used to determine both the high and low temperature dependence of $\rho_L$. The phonon resistivities were found to vary as $T^N$ at both high and low temperatures, and the values of $N$ determined from these plots are given in Table II.

Figure 8 shows how $\rho_O$ was determined for pure Nb. At 4.2K in the superconducting state $\rho$ was measured as the magnetic field was increased from 0 to 9 kOe. The superconducting to normal transition can be seen to occur between 3 and 5 kOe. The value of $\rho_O$ was obtained by extrapolating the normal portion of the curve to zero field.
Figure 6. Hall coefficients of pure Nb and of Nb-Zr alloys as a function of temperature.
Figure 7. Resistivity as a function of temperature for (a) Nb, (b) Nb 1.4%Zr, (c) Nb 3.6%Zr, and (d) Nb 15%Zr.
TABLE II

Temperature Dependence of the Phonon Resistivity

\( \rho_L \propto T^N \)

<table>
<thead>
<tr>
<th>Composition (at %)</th>
<th>N (high T)</th>
<th>N (low T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>1.02</td>
<td>2.7</td>
</tr>
<tr>
<td>Nb 1.4% Zr</td>
<td>1.00</td>
<td>2.6</td>
</tr>
<tr>
<td>Nb 3.6% Zr</td>
<td>0.94</td>
<td>2.8</td>
</tr>
<tr>
<td>Nb 15% Zr</td>
<td>0.93</td>
<td>2.9</td>
</tr>
</tbody>
</table>
Figure 8. Resistivity of Nb as a function of magnetic field at 4.2K.
VI. DISCUSSION AND CONCLUSIONS

A. Variation of R with Composition

The Hall coefficients for Nb 35% Mo and Nb 8% Mo from the work of Cox et al.,\textsuperscript{38} and Nb 25% Zr from the work of Schindler and Gillispie\textsuperscript{35} are shown in Figure 5 -- along with the present data. The gross feature of this graph shows an increase in $R$ as the outer electron/atom ratio varies from 4.40 to 5.35. In pure Nb there is about one hole-like carrier/atom,\textsuperscript{31} so that a positive Hall coefficient is expected in spite of rather strong scattering of the charge carriers due to the relatively high density of states $N_{bs}(0)$. As Mo is added progressively to Nb, the rapid reduction in $N_{bs}(0)$ and the correspondingly sharp increase in hole mobilities result in a steady increase in $R$. As Zr is added to Nb, the reverse situation is expected to occur. The density of states increases sharply and correspondingly the hole mobilities go down, which should result in a decrease in the Hall coefficient. As more and more Zr is added, the electron-like Fermi-surface pieces begin to emerge and further decrease in $R$ would be expected.

The band structure calculations\textsuperscript{31,32} and the density of states obtained from calorimetric data\textsuperscript{38} seems to be sufficient to explain the overall compositional dependence
of the Hall coefficient, but not the finer details such as the small peak in $R$ at about 15% Zr. This small peak most probably has its origin in the scattering anisotropy and not in changes in the electronic band structure. Evidence to support this lies in the fact that, as the temperature is increased and the scattering becomes more isotropic, the peak begins to disappear as can be seen by comparing the curve at 295°K with the one at 10°K (see Figure 5).

B. Variation of $R$ with Temperature

1. Alloys

The strongest evidence that impurity scattering is the primary source of the temperature dependences of the Hall coefficients of the Nb-Zr alloys lies in the correlation between Hall and resistivity data. As seen in Figure 6, the Hall coefficient of Nb containing 1.4% Zr remains relatively constant until the temperature drops below about 80K, at which point a rapid increase in $R$ begins. As the solute concentration is raised, the increase in the Hall coefficient appears to begin at higher temperatures, but the magnitude of its total change is reduced. This behavior is to be expected for dilute alloys if $|R|$ were
roughly proportional to the fractional contribution by impurities to the total scattering, i.e., to \( x = \frac{\rho_0}{\rho_0 + \rho_L} \). Indeed, when this quantity \( x \) is calculated from the corresponding resistivities of the alloys (Figure 7) and plotted as a function of temperature, the results (Figure 9) resemble quite closely the temperature dependences of the Hall data (Figure 6). It was pointed out in section II.D that the increase of \( x \) with decreasing temperature for a given alloy could lead to either an increase or a decrease in \( R \), depending on whether the impurity-scattering anisotropy is greater or smaller than the anisotropy of phonon scattering at high temperatures. The magnitude of the change in \( R \) over the range 295K to 4.2K should vary with the magnitude of the difference in anisotropies for the two mechanisms, but, as indicated in Figure 9, it should also be greater for the more dilute alloys where the room-temperature values of \( x \) are smaller. For the present alloy data this implies that impurity scattering is more anisotropic than phonon scattering in the Nb-rich Zr alloys. Likewise, for Nb it can be seen in Figure 9 that the fractional contribution of trace impurities to the total scattering rises sharply at very low temperatures, so that corresponding changes in \(|R|\) may be expected if the anisotropy of the trace-impurity scattering differs from that of phonon scattering.
Figure 9. Fractional resistivity due to impurity scattering, $\rho_0 / (\rho_0 + \rho_L)$, as a function of temperature for Nb and Nb-rich Zr alloys.
2. Pure Nb

The fact that the Hall coefficient of pure Nb is independent of temperature above about 100K indicates that in this metal any anisotropies in phonon scattering by N- or U-type processes are insensitive to temperature changes so long as there are phonons available of sufficient momenta to span the Brillouin zone. At lower temperatures the possibility of a change in anisotropy for one or both of these scattering mechanisms arises, and, indeed, extrema in $|R|$ are possible if the anisotropy associated with U processes differs significantly from that due to scattering by N processes (Section II.D). The low temperature minimum seen here (Figure 6) in the magnitude of the Hall coefficient of Nb occurs in the same temperature range as the maxima in $R$ which were previously reported for some noble and alkali metals and their dilute alloys.\textsuperscript{3-8} Tentative explanations for the causes of the extrema found in the earlier data have included phonon-drag effects, scattering of charge carriers by trace impurities, and transitions between 'low field' and 'high field' conditions.\textsuperscript{3,8}

An anisotropy of U-type phonon scattering at low temperatures may exist for Nb due to its multiconnected Fermi surface (Figure 1); however, it is difficult to establish a direct connection between the suspected anisotropies and the details of the Fermi-surface topologies.
The complexity of the situation is especially understandable if scattering by trace impurities is involved, since even for a simple metal like K the effects of such scattering appear to be extremely sensitive to the exact nature of the impurity. 8

C. Variation of $\rho$ with Composition and Temperature

The residual and phonon components of the resistivity of Nb and Nb-rich Zr alloys are shown as functions of composition in Figure 10 along with the data for Nb-Mo and Mo-rich Re alloys from Cox et al. 38 At high temperatures the phonon resistivities are seen to vary with composition in rough proportion to the density of states at the Fermi level (shown as a dotted curve in Figure 10). The data for Nb-Mo and Mo-Re are shown so that the connection between $\rho_L$ and $N_{bs}(0)$ can be seen clearly. This agrees well with the theory of Section II.C, especially equations (15) and (16). Since the density of states at the Fermi level is high for Nb and Nb-rich Zr alloys a phonon resistivity roughly proportional to $T^3$ would be expected at low temperatures. Table II indicates that this is what was observed. At high temperatures phonon resistivities reveal an approximately linear variation with $T$ for all samples.
Figure 10. Phonon (O) and residual (∆) components of the resistivities as a function of composition. (●) Phonon resistivities from Cox et al.\textsuperscript{36}. The right scale is for the band-structure density of states from Ref. 14.
From the resistivity data (Figure 7), the deviation from Matthiessen's rule, $\Delta(T)$, given by equation (18) was plotted (Figure 11) for the Nb 1.4% Zr crystal as a function of temperature. The important feature of this curve is the peak at about 35K. The gradual rise in $\Delta(T)$ above 100K could be due to a number of conditions, one of which is inaccuracy in the resistivity measurements since the shape of the sample and type of contacts were not the optimum design for resistivity measurements. (The error bars in this figure correspond to a 2% absolute error in the resistivity which, as expected, is much greater for higher temperatures.) Dimensional errors, which cause the most uncertainty, are systematic and could not lead to the observed peak, although such errors could shift the position of the peak slightly. Relative accuracy is much better than 0.5%.

For dilute noble metal alloys Dugdale and Basinski\textsuperscript{17} have noted that $\Delta/\rho_0$ vs. $T$ plots show a maximum at about $\theta_D/5$. (For Nb 1.4% Zr, $\theta_D/5$ is approximately 55K.) Dugdale and Basinski\textsuperscript{17} were able to show that equation (19) could be used to explain a peak in $\Delta$ vs. $T$ for their system. The only temperature-dependent terms in equation (19) are $\rho_L(T)$ and $\alpha$, where $\alpha$ is the ratio of the phonon resistivities for the two bands. One would expect that $\alpha$ would be
Figure 11. Deviation of Mattheissen's rule $\Delta$ for Nb 1.4%Zr as a function of temperature.
fairly constant at high temperatures where the phonon scattering can be considered isotropic. At lower temperatures \( \alpha \) would depend on the relative importance of U- and N-type scattering on each band and vary from the high temperature value. If \( \beta \) was approximately equal to the high temperature value of \( \alpha \), then a peak in \( \Delta(T) \) vs. \( T \) would be possible. As the temperature increases from 4.2K the increase in the resistivity \( \rho_L(T) \) causes \( \Delta(T) \) to rise; at approximately 40K the increase in \( \Delta(T) \) due to further increases of \( \rho_L(T) \) is countered by a decrease in \( (\alpha - \beta)^2 \). At higher temperatures \( \alpha \) approaches \( \beta \) and \( \Delta(T) \) decreases. If \( \alpha \) approaches a limiting value not equal to \( \beta \) then \( \Delta(T) \) would be expected to rise again at high temperatures. This may explain the increase in \( \Delta(T) \) above 100K, but, as mentioned before, this could easily be due to the inaccuracies in the resistivity measurements.
VII. REFERENCES


2. J. C. Philips, from lectures on: Band Theory of Transition Metals.


36. Zr powder was supplied by Teledyne Wah Chang Albany Corp., Albany, Oregon; and Nb powder by Shieldalloy Corp., Newfield, N. J.


38. R. W. Cox, D. J. Hayes, and F. R. Brotzen, accepted for publication by Phys. Rev.

PART II

ELASTIC CONSTANTS OF Nb-RICH Zr ALLOYS IN THE
TEMPERATURE RANGE 4.2K TO 298K
I. INTRODUCTION

Nb-rich Zr alloys form a continuous series of BCC solid solutions, which extend to approximately 12% Zr at 600°C. As Zr (4d$^3$5s$^1$) is added to Nb (4d$^4$5s$^1$), the outer-electron/atom ratio of the alloy is decreased. In Part I of this thesis a possible correlation was shown between the electronic properties and the density-of-states curve (both as a function of e/a). The theory, which relates the lattice resistivity with the density of states at the Fermi level, agreed quite well with the experiment results given in Part I. Also, it was found that the compositional dependence of the Hall coefficient could be discussed in terms of the relationship between electron scattering and the density of states over the Fermi surface. In Part II the elastic constants of Nb-rich Zr alloys will be presented in the temperature range 4.2K to 298K. As was done in Part I, an attempt will be made to discuss the experimental results in terms of the electronic configuration of the alloys. From the elastic-constant data, the Debye temperatures of the alloys and pure Nb will be calculated, and the Grüneisen constant will be obtained for pure Nb at both high and low temperatures.
II. EXPERIMENTAL PROCEDURE

The adiabatic elastic constants of Nb and Nb-rich Zr alloys have been obtained from room-temperature down to liquid-helium temperature by measuring the transit times of elastic waves in single crystals using the pulse-superposition method first introduced by McSkimin.\textsuperscript{1}

The preparation of the Nb and Nb-rich Zr single crystal samples has been discussed in Part I. The single crystals were cut into cylinders of length between 0.5 and 1.0 cm and the end faces were made parallel to within .001 cm by the spark-erosion process. The parallel faces were aligned perpendicular to either the [100] or [110] axes to within 1.5° by the Laue back-reflection method prior to the spark planing.

The electronic portion of the experimental setup has been described in detail by Hubbell\textsuperscript{2} and will not be repeated in this work. The gas-flow helium dewar system discussed in Part I was employed in conjunction with a PAR Model 152 cryogenic temperature controller to provide precise continuous temperature control in the range of 4.2K to 300K. The temperature sensor for this system was a calibrated gallium arsenide diode with a sensitivity of approximately 3.0 millivolts per degree Kelvin.
To obtain the elastic constants from the time-of-flight data, accurate density and length data are required. The density was determined by the Archimedean method using a Mettler microbalance and benzene as a medium. These density measurements were also used to determine the composition of the various alloys. The length measurements were corrected using the thermal expansion data of Hubbell et al.\textsuperscript{3} and White\textsuperscript{4}, both for pure Nb.

Measurements were made with 20 MHz X-cut and Y-cut quartz-crystal transducers. Nonaq stopcock lubricant was used as the bond material between the transducer and the specimen over the entire temperature range.

The list of single crystal specimens are shown in Table I along with their density measurements.

The relationships between the crystal orientation, measured velocities and the elastic constants are shown in Table II.
TABLE I

Densities and Sample Geometry of Nb-Zr Alloys

<table>
<thead>
<tr>
<th>Composition (at %)</th>
<th>Crystal Orientation</th>
<th>Density (gm/cm$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>[100] &amp; [110]</td>
<td>8.566</td>
</tr>
<tr>
<td>Nb-1.4 Zr</td>
<td>[110]</td>
<td>8.533</td>
</tr>
<tr>
<td>Nb-3.6 Zr</td>
<td>[100]</td>
<td>8.512</td>
</tr>
<tr>
<td>Nb-5.8 Zr</td>
<td>[110]</td>
<td>8.446</td>
</tr>
<tr>
<td>Nb-6.0 Zr</td>
<td>[100]</td>
<td>8.440</td>
</tr>
</tbody>
</table>
TABLE II

Relations Between the Acoustic Wave Velocities and Elastic Constants

<table>
<thead>
<tr>
<th>Crystal Axis</th>
<th>Displacement Direction</th>
<th>Wave Type</th>
<th>Relation</th>
</tr>
</thead>
<tbody>
<tr>
<td>[100]</td>
<td>[100]</td>
<td>longit.</td>
<td>((v_1)^2 = (c_{11})/\rho)</td>
</tr>
<tr>
<td>[100]</td>
<td></td>
<td>transv.</td>
<td>((v_2)^2 = (c_{44})/\rho)</td>
</tr>
<tr>
<td>[110]</td>
<td>[110]</td>
<td>longit.</td>
<td>((v_3)^2 = \left[\frac{1}{2} (c_{11} + c_{12}) + c_{44}\right]/\rho)</td>
</tr>
<tr>
<td>[110]</td>
<td>[100]</td>
<td>transv.</td>
<td>((v_4)^2 = c_{44}/\rho)</td>
</tr>
<tr>
<td>[110]</td>
<td>[110]</td>
<td>transv.</td>
<td>((v_5)^2 = \frac{1}{2} (c_{11} - c_{12})/\rho)</td>
</tr>
</tbody>
</table>

\(v_i = \) wave velocity, \(c_{ij} = \) elastic constant, and \(\rho = \) density.
III. RESULTS

The temperature dependences of the elastic constants $C_{11}$, $C'$, and $C_{44}$ are shown in Figures 1, 2 and 3. It should be pointed out that both $C_{11}$ and $C'$ exhibit the normal temperature dependence of zero slope at 0K and a negative slope at higher temperature. However, $C_{44}$ exhibits a zero slope at approximately room temperature. It was shown in 1966 by Armstrong et al.\textsuperscript{5} that in pure Nb the plot of $C_{44}$ as a function of temperature exhibits a positive slope between 150°C and 650°C.

The room-temperature elastic constants are plotted as a function of composition in Figure 4. All three elastic constants decrease with an increase in the Zr concentration. The smallest change appears in the $C_{44}$ elastic constant.
Figure 1. The temperature dependence of the $C_{11}$ elastic constant for the Nb-rich Zr alloys.
Figure 2. The temperature dependence of the $C'$ elastic constant for the Nb-rich Zr alloys.
Figure 3. The temperature dependence of the $C_{44}$ elastic constant for the Nb-rich Zr alloys.
Figure 4. The $C_{11}$, $C'$, and $C_{44}$ elastic constants for the Nb-rich Zr system at 298K.
IV. DISCUSSION

A. Compositional Dependence of the Elastic Constants

As Zr is added to Nb the outer-electron/atom ratio is reduced. The electrons outside of the closed shells are the ones which give stability to the BCC structure since the interaction between closed ionic shells, in metals or alloys with the BCC structure, leads to a negative contribution to shear elastic constant $C'$.\[^6\] Zener\[^7\] has proposed that the structural stability of the transition-metal BCC structures, and therefore a large value of $C'$, are due to overlapping d-electron repulsive exchange forces between second-nearest neighbor ions in an antiferromagnetic spin array. The BCC structure is a good candidate for an antiferromagnetic spin system and it has been observed in Cr and V by neutron diffraction, but unfortunately not in any other group VA or VIA transition metals. Whether or not there is any basis for this antiferromagnetic array argument for Nb is questionable, but it is certain that the outer-electrons in some way provide a positive contribution to $C'$. If accurate band structure calculations were possible, it may be found that the stability of the BCC structure for transition metals is due to changes in the Fermi energy as a result of distortion of the Brillouin zone with shearing.
Figure 4 shows that as Zr is added to Nb all three elastic constants decrease. DeLauney\(^8\), in 1953, presented relationships between the elastic constants and the interatomic force constants based on the Born-von Kármán lattice theory. He considered first the central forces between nearest and second-nearest neighbors and then later in the same review article\(^8\) he took into account the binding due to the electron gas. Based upon his results it is found that the force constants between first- and second-nearest neighbors, \(\alpha_1\) and \(\alpha_2\), decreased with an increase in Zr concentration. Table III shows that the percent change in \(\alpha_2\) was much larger than that of \(\alpha_1\) in going from 0 to 6 percent Zr. This rapid decrease of \(\alpha_2\) could be an indication of the phase transformation that occurs at higher Zr concentration.

The part these results play in the total picture of the elastic constants of the BCC transition metals can be seen in Figure 5 where the elastic shear constants \(C'\) and \(C_{44}\) are plotted as a function of the outer-electron/atom ratio for e/a between 4.20 to 6.26. The Mo-Re data were taken from the work of Davidson and Brotzen\(^9\); the Nb-Mo data are from Hubbell and Brotzen\(^3\); and the Zr-rich Nb values were given by Goasdoue, Ho and Sass.\(^10\) Two observations can be made from these curves: first, the BCC
Figure 5. The $C'$ and $C_{44}$ elastic constants as a function of the outer electron per atom ratio for $e/a$ of 4.2 to 6.3. Zr-rich Nb data from Goasdour et al.\textsuperscript{10}; Nb-Mo data from Hubbell and Brotzen\textsuperscript{3}; Mo-rich Re data from Davidson and Brotzen.\textsuperscript{9}
structure is stable at room temperature approximately over the range where \( C' > C_{44} \); and secondly, a broad dip appears in \( C_{44} \) centered at an e/a value of about 5.2. A slight indication of this also appears in the \( C' \) curve. In the next section it will be seen that in this same region an anomaly in the temperature dependence of the shear elastic constants occurs.

### TABLE III

Force Constants Between First- and Second-Nearest Neighbors

<table>
<thead>
<tr>
<th></th>
<th>( \alpha_1 )</th>
<th>( \alpha_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>1.399</td>
<td>1.887</td>
</tr>
<tr>
<td>Nb 6% Zr</td>
<td>1.342</td>
<td>1.736</td>
</tr>
<tr>
<td>Percent Change</td>
<td>4.07%</td>
<td>8.00%</td>
</tr>
</tbody>
</table>
B. Temperature Dependence of the Elastic Constants

Huntington\textsuperscript{11}, in a review article on the elastic constants, stated that "The thermal variation of elastic constants are characterized by two general features: (1) an approach with zero slope to the $T = 0$ axis, and (2) a negative slope at higher temperatures." Based upon this description, the shear elastic constants $C_{44}$ for Nb-rich Zr and Nb-rich Mo alloys and $C'$ for some Nb-rich Mo alloys can be considered anomalous in their temperature dependences. Several investigators\textsuperscript{5,12,13} have observed a broad minimum in the value of $C_{44}$ in Nb near room temperature, and their results are in very good agreement with the measurements of this investigation below room temperature.

This anomalous temperature dependence of $C_{44}$ seems to cover the range from Nb 6\% Zr to Nb 35\% Mo with the largest effect occurring in the Nb 34\% Mo sample. The $C'$ constant also increases with temperature over a smaller range, from Nb 23\% Mo to Nb 34\% Mo. Figure 6 shows the behavior of $C_{44}$ at low temperatures for the most pronounced case, Nb 34\% Mo. To understand how a positive $dC/dT$ can arise it is necessary to investigate the temperature dependence of the internal energy.

The internal energy at low temperature is given by

$$U = U_0 + ET^2 + LT^4$$

(1)
where the $E T^2$ term arises from the thermal excitations in the electron gas and the $L T^4$ term comes from the lattice vibrations.\textsuperscript{14} Since the elastic constant, $C$, is given by the second derivative of $U$ with respect to the appropriate strain, $\eta$, we obtain

$$C = C_0 + \left( \frac{\partial^2 E}{\partial \eta^2} \right) T^2 + \left( \frac{\partial^2 L}{\partial \eta^2} \right) T^4 + \left( \frac{dC_0}{dV} \right) \Delta V \quad (2)$$

where the last term corrects for thermal expansion. Usually the coefficient of the $T^2$ term is too small to be detected and therefore a $T^4$ dependence is observed at low temperatures. \(\left( \frac{\partial^2 L}{\partial \eta^2} \right)\) is always negative which leads to the usual negative $dC/dT$.

A possible explanation of the anomalous temperature dependence of the elastic constants is suggested by the work of Bernstein.\textsuperscript{15} He considered the electronic contribution to the elastic constants of cubic metals by calculating the electron energy as a function of elastic strain and temperature. When a lattice in real space is sheared, then a distortion of the Brillouin zone in reciprocal space will occur. If the Fermi surface intersects the zone boundary, as it does for Nb (see Figure 1, Part I), then movement of these bounding planes could cause changes in the electron energies and thus give rise to a contribution
to the elastic shear constants. Bernstein calculated this contribution for the shear constants $C_{44}$ and $C'$, which correspond to volume conserving strains, in terms of the Fermi energy, the density of states at the Fermi level, and the first and second derivatives of the density of states evaluated at the Fermi level. Bernstein noted that the magnitude and algebraic sign of the temperature variation of the elastic constants depend sensitively on the shape of the Fermi surface and the electron-density distribution. He went further to say "The temperature dependence of the elastic constants may exhibit positive or negative coefficients dependent upon whether the Fermi level is at a minimum or maximum of the electron density of states, respectively."\textsuperscript{15}

In 1962, Alers and Waldorf\textsuperscript{16} observed that for the transition metal vanadium the electronic contribution which goes as $T^2$ dominates the observed temperature dependence with the $T^4$ lattice term making only a small contribution. They observed a temperature dependence of $C_{44}$ given by

$$C_{44} = C_{44}^0 (1 - 13.5 \times 10^{-7} T^2 - 7.6 \times 10^{-10} T^4).$$

For Nb-rich Mo crystals an anomalous temperature dependence of $C_{44}$ was first noted by Hubbell, Hayes and Brotzen.\textsuperscript{17} When the data reported for Nb 34\% Mo were extended to 4.2K, a temperature dependence of the following form
Figure 6. Low temperature behavior of $C_{44}$ for the Nb-34at.% Mo alloy.

The Curve is given by: $C_{44} = 30.965(1 + 5.6 \times 10^{-6} T^2 - 2.01 \times 10^{-10} T^4)$.
was observed:

\[ C_{44} = C_{44}^0 (1 + 5.6 \times 10^{-6} T^2 - 2.01 \times 10^{-10} T^4). \]

This temperature dependence is plotted along with the data in Figure 6. It can be seen that below 70K the fit is quite good. This appears to be good evidence that the so-called anomaly can be explained by including the electronic contribution in the calculation of the elastic constants.

C. Debye Temperature

Using the method of Marcus as outlined by Alers, the Debye temperatures of Nb, Nb 1.4% Zr, and Nb 6.0% Zr have been calculated from the 4.2K elastic constants. Table IV presents these results and compares them with the results from specific-heat data of Nb by several investigators. Most of these investigators found a change in the slope of \( C_v/T \) vs. \( T^2 \) at low temperatures, which gave them two possible values for the Debye temperature, \( \theta_D \), depending upon which value of the slope is used to represent the lattice contribution. The value of \( \theta_D \) calculated from the elastic constants agrees very well with the higher values listed in Table IV.
The $\Theta_D(0)$ Debye temperature given in Table IV was obtained from the data taken below liquid-helium temperature. $\Theta_D(1)$ was determined at slightly higher temperatures. The calculation of the Debye temperature from the elastic constants assumes the solid to be an elastic continuum in which the velocity of sound is not a function of frequency. Such an assumption is only valid in the limit of long wavelengths or low temperatures.$^{14}$ Only at temperatures below $\Theta_D/50$ to $\Theta_D/100$ can the Debye temperature obtained from calorimetric measurements be expected to equal that determined from the sound velocities.$^{14}$ For Nb the range $\Theta_D/50$ to $\Theta_D/100$ is approximately 5.5K to 2.7K. Therefore, the agreement between $\Theta_D$ determined by the elastic constants and $\Theta_D(0)$ from calorimetric measurements is understandable.
### TABLE IV

Calorimetric Debye Temperature of Nb and the Debye Temperatures Obtained from the Elastic Constants

<table>
<thead>
<tr>
<th>Investigator</th>
<th>Debye Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_D(0)$</td>
</tr>
<tr>
<td>Da Silva et al.$^{18}$</td>
<td>276</td>
</tr>
<tr>
<td>Leupold and Boorse$^{19}$</td>
<td>275</td>
</tr>
<tr>
<td>Van der Hoeven and Keeson</td>
<td>275</td>
</tr>
<tr>
<td>Heiniger et al.$^{21}$</td>
<td>278</td>
</tr>
<tr>
<td>Shen et al.$^{22}$</td>
<td>270</td>
</tr>
<tr>
<td>Morin and Maita$^{23}$</td>
<td>260</td>
</tr>
<tr>
<td>Present Work (Calculated from elastic constants)</td>
<td>Nb 276</td>
</tr>
</tbody>
</table>
D. Grüneisen Constant

In 1926 Grüneisen\textsuperscript{24} considered the vibrational frequencies of a solid to be a function of the volume. He derived an equation of state which was consistent with the Debye theory. The Debye equation of state is usually written\textsuperscript{25}

\[
P = - \left( \frac{\partial U_O}{\partial V} \right) + \gamma \left( \frac{U_D}{V} \right),
\]

(3)

where $U_O$ is the internal energy at 0K, $U_D$ is the internal energy in the Debye approximation and $\gamma$ is the Grüneisen constant which is given by

\[
\gamma = - \left( \frac{\partial V}{\partial \theta_D} \right) \left( \frac{\partial \theta_D}{\partial V} \right)_T.
\]

(4)

By differentiating equation (3) with respect to temperature at constant volume the Grüneisen constant can be related to physically measurable quantities as given below:

\[
\gamma = \frac{3 \alpha B M}{C_V \rho}
\]

(5)

where $\alpha =$ coefficient of linear expansion;

$B =$ bulk modulus;

$M =$ atomic weight;

$\rho =$ density;

$C_V =$ specific heat at constant volume.
For Nb accurate thermal expansion and specific heat data are available at room temperature and in the liquid-helium temperature region. Most of the low temperature work was conducted in order to investigate both the relatively large electronic specific heat and the superconducting properties of this metal. Table V gives the values of γ for pure Nb at 298K and 10K. Data for α and C_v are not available for Nb-Zr alloys.

In 1964, Brugger 27 presented a method for calculating the generalized Grüneisen parameters, which measure the strain dependence of the lattice vibrational frequencies. He expressed these parameters in the Debye approximation in terms of second- and third-order elastic coefficients for arbitrary crystal symmetry. Grahm, Nadler and Chang, 28 in 1968, measured the room temperature third-order elastic constants of Nb and using Brugger's method obtained a value of 1.511 ± 0.026 for the Grüneisen parameter. This agrees to within 4% of the value obtained in this work.
TABLE V

Grüneisen Constants and Data Used to Obtain Them

<table>
<thead>
<tr>
<th>T (K)</th>
<th>$\alpha(10^{-8}/K)$</th>
<th>$B(10^{11}$ dynes/cm$^2$)</th>
<th>$C_v$(J/mole K)</th>
<th>$\rho$(gm/cm$^3$)</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>$700^4$</td>
<td>17.11</td>
<td>$24.76^{26}$</td>
<td>8.566</td>
<td>1.57</td>
</tr>
<tr>
<td>10</td>
<td>$4.4^4$</td>
<td>17.27</td>
<td>$0.215^{19}$</td>
<td>8.607</td>
<td>1.15</td>
</tr>
</tbody>
</table>
V. REFERENCES


ACKNOWLEDGEMENTS

I wish to thank Dr. Franz R. Brotzen for suggesting this project, for his many helpful discussions concerning Solid State Physics, and for the general encouragement given through the duration of this work.

I also wish to thank: Dr. Royal Cox for his advice dealing with the electrical measurements and his aid in proof reading Part I of this manuscript; Al Ehlert for teaching me the 'art' involved in crystal growing; and Dr. W. C. Hubbell for supplying assistance in solving technical problems.

Finally, I would like to thank the National Science Foundation for the financial support of this work.