THE ELECTRICAL RESISTANCE OF NIOBIUM AND VANADIUM
SINGLE CRYSTALS AT LOW TEMPERATURES

by

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We accept this thesis as conforming to the
standard required from candidates for the
degree of MASTER OF APPLIED SCIENCE

Members of the Department of
METALLURGY

THE UNIVERSITY OF BRITISH COLUMBIA

January  1963
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Date October 1, 1963
ABSTRACT

An investigation into the variation of electrical resistance with temperature for high purity niobium and vanadium single crystals has been carried out.

Niobium was studied over the temperature range -30°C to -146°C. It was found that in its highest purity there was little or no anomaly. At lower purities an anomaly in the region of -120°C was discovered which was attributed to oxygen or nitrogen or both changing their position on the lattice to one of higher strain energy because of changes in energy associated with the bonding between interstitials and the lattice.

Hydrogen doping of niobium produced an overall increase in resistivity. A drop in the resistance curve was noted at -100°C which was thought to be due to hydrogen, being mobile and non-bonded, moving off the high strain energy sites under the influence of thermal contraction. Hydrogen embrittlement was attributed to hydrogen occupation of high strain energy sites.

Vanadium was found to have a slope change at -170°C when tested between -130°C and -196°C. No definite explanation of this is suggested.

Ultrasonic testing of vanadium showed attenuation minima at -100°C and -170°C.
ACKNOWLEDGEMENT

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THE ELECTRICAL RESISTANCE OF NIOBIUM AND
VANADIUM SINGLE CRYSTALS AT LOW TEMPERATURES

I. INTRODUCTION

In view of the recent general interest in the body-centred cubic transition metals a considerable amount of work on the physical properties of Nb, V and Ta has been undertaken in this department.\(^1\)\(^-\)\(^4\) These studies have been mainly in the field of yield stress dependence upon temperature and the mode of deformation of single and polycrystalline specimens of the above metals. It was found that there was an anomalous dependence of yield stress upon temperature below room temperature for single crystals of Nb and V. Examination of the results of other workers for polycrystalline specimens also showed a similar effect.

Yield stress vs. temperature plots gave two intersecting curves whereas a plot of log yield stress vs. \(T\) gave two intersecting straight lines. The mechanism responsible has not been definitely substantiated. Snowball\(^2\) proposed that different dislocation locking effects for each species of interstitial atom were responsible for the effect. Harding\(^4\) considered two mechanisms to explain his work on Nb:

1. Interstitial ordering involving the movement of interstitials away from dislocations, which Harding subsequently rejects.

2. Dislocation - solute interaction where the magnitude of the interaction of screw and edge dislocation with solute atoms varies differently with temperature.
At high temperature the screw dislocations are more easily released. As the temperature decreases and deformation requires higher stresses both screw and edge dislocations acquire jogs. Movement of a jogged screw dislocation requires a diffusion process, thus edge dislocations become more easily moved eventually i.e. below the anomaly temperature.

If 1. were the mechanism it would be expected to affect electrical resistivity. Previous workers have reported resistance anomalies in the form of slope changes in resistance vs. temperature curves in V. 2, 5-9

This investigation was undertaken with the intention of verifying the previously reported work of Snowball, determining the temperature dependence of electrical resistance of Nb and the manner in which the addition of interstitial elements affects this relationship. Very low temperature measurements have been made on the transition metals, in the temperature range 0 to 200K, but little has been reported in the way of detailed work from 200K to room temperature.

In the case of Nb the temperature range studied was \(-30^\circ\text{C}\) to \(-146^\circ\text{C}\), and in the case of V it was \(-130^\circ\text{C}\) to \(-196^\circ\text{C}\).
II. REVIEW OF PREVIOUS WORK

A. The Electrical Resistance of Metals

Resistance to the flow of an electric current is usually regarded as being expressible in the form of two terms:

\[ R = R_t + R_i \]

where \( R \) = total resistance

\( R_t \) = resistance due to thermal vibrations

\( R_i \) = resistance due to impurities

The latter term may also be said to be the sum of two terms;

"impurity" in practice is any deviation from a perfect lattice.

Thus

\[ R_i = R_{\text{phys}} + R_{\text{chem}} \]

where \( R_{\text{phys}} \) = resistance due to physical defects

\( R_{\text{chem}} \) = resistance due to chemical impurities

Therefore

\[ R = R_t + R_{\text{phys}} + R_{\text{chem}} \]

This leads to the concept that chemical and electrical purity are not synonymous as a metal containing very few foreign atoms but having undergone heavy deformation so as to contain a high concentration of vacancies, interstitials and dislocations could have a higher resistivity than the same metal in the annealed condition containing more foreign atoms.

The first term is due solely to thermal vibrations
interfering with electron flow by interaction with the lattice. Electron - phonon interaction is dependent upon temperature, being approximately proportional to $T^5$ at very low temperature and to $T$ at higher temperatures. Thus at absolute zero there will be no electron-phonon interaction and

$$R = R_{phys} + R_{chem}$$

Depending upon the material and the amount of cold work, $R_{phys}$ would in general be expected to remain constant as the temperature decreased below room temperature, the physical defects being frozen into the lattice. The $R_{chem}$ term arises due to the presence of foreign atoms which also destroy the periodicity of the lattice. In the case of unworked single crystals $R_{chem}$ and $R_{phys}$ will be roughly of the same magnitude, though this would not be so in a worked metal of high chemical purity where $R_{phys}$ would be larger.

Size and electronic structure play an important part in the determining of the magnitude of the effect that the foreign atom will have upon the resistivity of the parent metal. Obviously a substitutional atom which is very much larger or smaller than the parent lattice atom will have a greater disturbing effect upon the periodicity of the lattice than one that is of approximately the same size. As would be expected a difference of electronic structure between the
lattice and substitutional atoms also results in a pronounced effect.

(1) Matthiessen's Rule.

This states that the contributions to resistivity resulting from the addition of impurities are temperature independent i.e. the $R$ vs. $T$ curve retains its original slope and shape on the addition of impurity atoms but the position will be elevated.

The lower curve is for a large specimen of a physically perfect, chemically pure, ideal metal. Such a specimen would have $R_i = 0$ so that at $0^\circ K$, $R = 0$. Upon the addition of impurities the curve is elevated and at $0^\circ K$ where $R_t = 0$, $R = R_i$. $R$ at $0^\circ K$ is known as the residual resistivity and is due solely to impurities. Larger amounts of impurity continue to increase the residual resistivity so

Figure 1 Hypothetical Variation of Resistance $R$ with Temperature at Various Impurity Contents.
long as the impurity atoms remain in solid solution. Precipitation of a second phase results in a decrease in residual resistivity. It is found on closer inspection that $R_i$ is not completely temperature independent but may vary with temperature in certain metals under certain conditions which will be discussed below.

In order that Matthiessen's Rule be obeyed two conditions must be fulfilled:

(i) The addition of foreign atoms must not result in a change in the effective number of free electrons in the metal.

(ii) Scattering resulting from thermal vibrations of the lattice must be identical for solvent and foreign atoms.

These requirements are not met exactly but the rule provides a practical working basis for estimating the change in residual resistivity due to the addition of foreign atoms in most cases. Exceptions are Cr and Co.

(2) Resistance at High Temperatures

Curves of $R$ vs. $T$ at temperatures above the Debye characteristic temperature usually give an almost linear plot. In the case of Cu, Ag, Au and W the slope increases with increasing temperature. In the case of Pd, Pt, and Ta the slope decreases with increasing temperature. These, in common with all the transition metals, have a relatively high resistivity which is not due to a lack of s(conduction) electrons but
rather to the fact that there are vacant energy levels in the d band. The major part of the resistivity of transition metals is due to scattering of electrons from the s to the d band taking place. It can be shown that the probability of such scatter taking place is proportional to the density of energy states in the d band in the energy range kT at the surface of the Fermi distribution. Pd and Pt have almost completely filled d bands thus the number of available energy levels into which electrons may be scattered decreases rapidly with increasing temperature. W, however, is not explainable on this basis as it does not possess a nearly full d band.

(3) Resistance at Low Temperatures

At temperatures well below the Debye temperature only lattice waves of long wavelength can be excited by the current carrying electrons which results in the electrons being scattered through only small angles i.e. energy transfer is limited. Theoretical consideration of this state of affairs leads to $R$ being proportional to the fifth power of the temperature at very low temperature. In the case of divalent metals where electrons and holes are present, collisions between electrons can change the current, but the effect is small compared to that due to scattering by lattice waves at ordinary temperatures as both must be in states lying in the energy range kT at the surface of the Fermi direction both before and after the collision. Detailed analysis shows that $R$ due to this cause is proportional to $T^2$ and is only of importance at very low temperatures.

It has been postulated $R \propto T^m$ at low temperatures.
In the cases of Co, W and Rh, \( m = 3.9, 4.2 \) and 5.1 respectively, indicating a complex situation.

In the cases of Rh and Ir there appears to be insufficient overlap in \( k \) space of the Fermi surfaces of the \( s \) and \( d \) electrons for \( s-d \) transitions to occur at low temperature, though there is no discontinuous resistivity change, which indicates a gradual shrinkage of the surfaces.

In discussing the electrical conductivity of the transition metals Mott\(^{11}\) says that under the influence of lattice vibrations the probability that a conduction electron will make a transition is much greater for its passage into the \( d \) band than for it to remain in the \( s \) band. Unoccupied \( d \) states are responsible for ferromagnetism or high paramagnetism and there is a direct connection between magnetic and electrical properties.

In a magnetic field at sufficiently low temperature the resistance will decrease due to the fact that all unoccupied states ("positive holes") in the \( d \) shell will have a spin direction anti-parallel to the direction of magnetization which will result in only half the conduction electrons being capable of making the \( s-d \) transition i.e. those with the anti-parallel spin direction. Above the Curie temperature all conduction electrons can go into the \( d \) band and a corresponding increase in \( R \) will occur.

Filling of these positive holes occurs when Au is added to Pd but the resistance increases. Similar Pd - Ag alloys show a decrease in \( R \) if Pd \( \geq 40\% \) and hydrogen is added,
thus indicating that electrons from hydrogen are filling the holes and that the residual resistance effect of adding protons is outweighed by the hole plugging, at least initially. $R$ will start to increase as more hydrogen is added.

(4) Effect of Change in Magnetic Properties

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\caption{Variation of Resistance of Ni with Temperature.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{image.png}
\caption{Variation of Resistance of Ni with Temperature.}
\end{figure}

$I$ shows the observed change of resistance with temperature for Ni. An extrapolation of the higher temperature portion of $I$ gives $II$. Below 300°C, Ni is no longer paramagnetic. From theory $IV$ would be the expected curve for paramagnetic Ni, which meets the observed curve at 0 K. Theory predicts $III$ as being the curve for ferromagnetic Ni which coincides with $I$ below about -100°C. Thus it is to be expected that changes in magnetic characteristics with temperature in a metal will affect the $R$ vs. $T$ curve at or in the region of the same temperature.

Spin-disorder effects in metals and alloys were
discussed by Coles\cite{12} in which he maintained that if atoms
in the metal possessed localised but randomly oriented spins
this would lead to the scatter of conduction electrons
resulting in a resistance effect. Thus it would be
expected that temperatures at which magnetic ordering took
place would be also associated with anomalies in the \( R \) vs.
\( T \) curve in those metals with localised spins. This leads
him to propose that Matthiessen's Rule is composed of three
terms, \( R_t \), \( R_i \) and \( R \) due to spin disorder. The contribution
from spin disorder should be temperature independent above
the Curie temperature.

Klemens discusses the scattering due to extended
imperfections\cite{13} using the Hunter and Nabarro method of
treating electron scattering by a static strain field, namely
that surrounding a dislocation.

Low temperature lattice thermal conductivity is limited
by the scattering of phonons by electrons which can be used
to derive a measure of electron-phonon coupling from
experimental thermal conduction measurements. Derived from
this is an expression for the scattering of electrons by
dislocations and stacking faults. Klemens derives expressions
for the scattering of phonons by dislocations, grain boundaries
and stacking faults. Hunter and Nabarro maintain that
electrons are scattered only in an inhomogeneous strain
field and it is strain rather than displacement which is
the governing factor controlling resistivity. The expression
obtained is valid only for slowly varying strain fields.
Unfortunately electrons of Fermi energy have wavelengths of the order of the interatomic distance so that much of the scattering emanates from the dislocation core whose physical characteristics are inadequately described. It is suggested that, as an unsatisfactory state of affairs exists with regard to explaining the fact that the major contribution to the increase in resistivity upon deformation is due to point imperfections in some instances and to dislocations in others, when the dislocations are the larger contributor it is because stacking faults are formed. As there is no dilatation associated with a stacking fault, perfectly free electrons cannot be influenced by it; results confirm that in noble metals at least, conduction electrons are far from free.

B. Previous Work on Electrical Resistance

Anomalies

A general survey of all reported resistance anomalies occurring in metals, with the exception of semi-conductor effects, was undertaken because the mechanisms postulated as being responsible are not necessarily unique to one class of metals.

(1) Alkali Metals

It was noted that the resistivity of Na decreased if the specimen were kept over a period of months, the conclusion being that annealing occurred. Lithium presented no anomalies.

A slight anomalous bump of greater than 1/3% of total
resistance at 10-14K was found in a K specimen. Testing of a purer specimen yielded a 1% bump at 13.4 K, which was repeated in third and fourth specimens. It was suspected its presence was due to Na so preparation of a specimen in K glass apparatus was undertaken which yielded no bump on testing from which it was deduced that the anomaly was caused by very small numbers of impurity atoms.

Ce showed anomalies at 4° and 6°K in one specimen and at 4° and 11°K in another. If a specimen were cooled relatively slowly to liquid O2 temperature it was found that on warming a discontinuity occurred at -20°C in the form of a large drop in R. Extremely slow cooling gave a R vs. T curve with a small bump at -20°C and no anomaly at all on heating, although the curve was displaced upwards slightly. However, the discontinuity could be a "one-shot" effect, though it is explained as an anomalous thermal contraction. The low temperature anomalies are attributed to Na. These small anomalies due to Na, which should merely give a temperature independent effect according to Matthiessen's Rule, are not explained.

MacDonald noted an anomaly in the R vs. T curve of Rb at 180°K. Hedgcock did further work on this metal after it had been shown a crystallographic change was not responsible for the effect. MacDonald had suggested some change in distribution of 5s and 4d electrons resulting in an increased probability of scatter of conduction electrons into the d band at temperatures above 180 K. Any such change should be confirmable by magnetic susceptibility measurements as this
quantity is proportional to the density of states at the Fermi level and a transition should result in an increase in paramagnetism above 180°K. No such increase is found.

There is considerable evidence to indicate that small amounts of $O_2$ can produce a marked change in the properties of Rb and it is suggested that $O_2$ is also responsible for the resistance anomaly.

(2) Rare Earth Metals

Gadolinium, Dysprosium and Erbium all conform to the spin-disorder model in that a resistance anomaly is found at the Curie temperature. As temperature decreases and Dy and Er become ferromagnetic small anomalies occur. Immediately below the Neel temperature in Dy and Er the resistance falls less rapidly with temperature. Short range ordering is postulated as being responsible for this, though in what manner is not clear.

Later work on Er single crystals was done with the resistance being measured parallel to the c axis and parallel to the a axis, $R_{II}$ and $R_\perp$. A complex magnetic lattice exists above 530°K in this high purity material. The two curves behave as shown.

Figure 3
$R_\perp$ suffers a small slope change at the Neel point, while $R_{||}$ shows a sharp increase, decreasing again at 53.5°K. Ordering or disordering of spins, or spin modification to another type of antiferromagnetism is possibly responsible for bringing this about.

Annealed La\textsuperscript{18} shows an increase in $R$ after being allowed to stand for 90 days due to a crystallographic transformation from f.c.c. to h.c.p.; this transition was inhibited by extrusion of the specimen.

Ce\textsuperscript{18} has a similar transformation to f.c.c. which is thought to be a result of an electron shifting from a 4f to a 5d orbit. At approximately 12°K an anomaly occurs which is attributed to splitting of the lowest energy level of the ion by the field of its neighbours which results in the redistribution of electrons amongst the states. This becomes more pronounced with successive cycles. It is possible that level splitting may trigger 4f electrons to go to the 5d shell, as this transition makes the transition to the condensed f.c.c. structure more likely. The onset of ferromagnetism is not ruled out as an explanation.

Praseodymium\textsuperscript{18} shows an increase in $R$ on successive runs due to the h.c.p. modification being formed. However\textsuperscript{19} other work shows lower $R$ on later runs. An anomaly in the $R$ curve is also found in the form of an increase in the rate of fall of $R$ with $T$ between 61° and 95°K which has no corresponding magnetic susceptibility anomaly, although there is a broad peak in the specific heat vs. $T$ curve between 60° and 100°K.

Neodymium\textsuperscript{18,19} shows anomalies in the $R$ vs. $T$
corresponding to magnetic transitions.

It is concluded that the rare earths are very sensitive to presence of impurities. Rare earths react strongly with negative impurities such as O, C, N and H and small amounts of these elements are believed to have pronounced effects upon the resistivity of the solvent lattice.

(3) Transition Metals

The $R$ vs. $T$ curve for a recrystallised specimen Cr shows a pronounced cusped minimum at $35 \pm 2^\circ C$ which was thought due to an antiferromagnetic transformation. Powder determination of the Neel temperature gave a value of $175^\circ C$. As many other metals showed a similar effect at the Neel temperature it was thought and subsequently demonstrated that the internal strains present in the powder grains give the high Neel temperature.

![Graph of $R$ vs. $T$ for Cr](image.png)

Figure 4  $R$ vs. $T$ for Cr

It would be expected that below $T_n$ the loss of spin disorder would reduce the resistance but this is not the case. It has been shown that below $T_n 180^\circ$ spin reversals occur every 14 unit cells which constitutes an antiphase arrangement.
of magnetic spin domains which could cause the observed resistance increase. Small chemically ordered domains are known to increase electron scatter.

From 65 to 35°C the curve departs from linearity, this being considered due to short range magnetic ordering.

A plastically deformed specimen follows the broken line curve because, it is suggested, plastic deformation smears out the Neel temperature. It is known that Tn varies with hydrostatic stress. When a specimen is plastically deformed the density of dislocations resulting is thought to produce the same result, positive and negative pressures being found in the strain field of a dislocation gives both increase and decrease in the Tn value.

Mn shows the initial increase in R below Tn, then the curve falls steeply probably due to ordering in the spin system.

![Graph](image)

**Figure 5**  R vs. T curve for Mn
The impurity component of resistance for Cu shows a marked increase upon the addition of 2% Zn, but this shows no significant increase on plastic deformation although a large change in dislocation density has taken place. It is therefore suggested that vacancies may be responsible for the increase in resistance.


N. Thompson found that the electrical resistance of single crystals of Bi were very sensitive to small amounts of impurity. R was always measured twice at each temperature, the second time with the current reversed and different R values were usually observed due to thermal gradients, which procedure, was found to provide a very sensitive method of detecting the presence of such a gradient.

Observations showed that in some cases Bi had a negative temperature coefficient of resistance which was not caused by a change in crystalline state or the precipitation of another phase.

Jones explains this by noting that Bi possesses a Brillouin Zone of five electrons per atom so that the conductivity is due to a few vacancies in the Zone and to electrons overlapping into the next Zone. Thus it would be expected that the addition or removal of a few free electrons would have a pronounced effect upon electrical conductivity. On this basis impurities should have a marked effect upon
electrical properties. Pb would increase the number of holes, Te and Se would increase the electrons, mixing the two would tend to produce a null effect except upon $R_{\text{chem}}$. It is suggested that the addition of Pb or Sn will result in the number of overlapping electrons being very small but that these will increase rapidly with temperature thus produced a negative coefficient in a certain temperature range when the increase in $N_{\text{eff}}$ offsets the increased lattice vibration.

G. Vanadium and Niobium

1. Vanadium

There has been reported a considerable amount of work on electrical resistivity anomalies in $V^{23-26}$. Loomis and Carlson$^{28}$ found an anomaly in electrical conductivity with anomalies in lattice constant, Young's Modulus, internal friction, thermal expansion and intensity of X-ray reflections at similar temperatures. Hren and Wayman$^{24}$ agreed with the exception of the Young's Modulus anomaly.
Rostoker, McPherson and Hansen measured the variation of electrical resistance of V wire of unspecified purity with temperature and obtained the curve below (Figure 6)

![Electrical Resistance versus Temperature for Vanadium](image)

**Figure 6** Electrical Resistance versus Temperature for Vanadium.

An anomaly of the step type occurs in the region of -30°C.

Magnetic susceptibility experiments gave the curve below for 99.9% Van Arkel Vanadium of the following composition

<table>
<thead>
<tr>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>.005</td>
<td>.001</td>
<td>.008</td>
<td>.020</td>
</tr>
</tbody>
</table>
Room temperature resistivity was 23 ±or - 1 microohm cm. An absolute accuracy of ±5% was claimed with a very much higher relative accuracy.

Rostoker and Yamamata\textsuperscript{26} suggest that a lattice transition from b.c.c. to body centred tetragonal is
responsible for the anomaly, but all efforts to find such a phase have failed.

Shull and Wilkinson used a neutron diffraction method in an effort to obtain a \{100\} reflection which would indicate magnetic ordering. No such reflection was found, leading to their conclusion that if magnetic ordering were present the moment was of small magnitude.

Cr and Co were added to V separately and 2\% of the former or 5\% of the latter resulted in a drop in the anomaly temperature of 15°C which evidences a magnetic origin for the anomaly, due to the onset of antiferromagnetism, but this has not thus far been confirmed.

With regard to the neutron diffraction evidence, a thermal neutron passes from one electron to another in about 10^{-13} sec, a Fermi electron requires 10^{-16} sec; if, therefore, the antiferromagnetic element is subjected to a process fluctuating more rapidly than 10^{-13} second neutron diffraction will not reveal a (100) peak.

Alloying was used by Taylor and Llewellyn Smith in an effort to explain the anomaly. Carefully prepared specimens from three sources were used for a series of experiments wherein the resistivity was measured to 1\%, the error residing mainly in variations in cross section area as the resistance was measured to .005 \mu ohms and the temperature to 1/10°C.

It was found that the source of material did not greatly affect results, but that the temperature at which
The anomaly occurred was dependent on all previous thermal and mechanical treatment.

![Graph showing variation of anomaly temperature with Cr content.](image)

**Figure 8** Variation of anomaly temperature with Cr content.

Irregular variation of resistivity with composition suggests that Nd(E) or $N_{\text{eff}}$ is responsible. Variation of Nd(E) is known from magnetic susceptibility measurements and does not appear to be responsible. It is deduced therefore either that $N_{\text{eff}}$ must follow a different fine variation with composition, or that alloys cannot be described in terms of a common conduction band, or that Matthiessen's rule is grossly incorrect in these alloys.

Plots of the resistance due to impurity above and below the anomaly temperature have the same form so that the mechanism for the variation of resistivity with composition does not appear to be simply related to the anomaly mechanism.

If the lack of neutron diffraction peaks is taken as final with regard to a density of states explanation, there remains the possibility that hydrogen atoms order at the anomaly temperature ($-46^\circ\text{C}$). There is no hysteresis effect between heating and cooling and at $-46^\circ\text{C}$ only
hydrogen could move with sufficient dispatch to accomplish this. It is thought the detailed variation of anomaly temperature with Cr content is not simply related to Nd(E) or N\textsubscript{eff} but is probably partially dependent upon interaction between neighbouring atoms.

No magnetic ordering effects have been found in the earlier members of the first transition group, in which category V is found.

Variation of the Hall effect with temperature is similar to the specific heat curves which suggests that changes in scattering mechanisms rather than N\textsubscript{eff} are responsible for the observed temperature dependence of electrical properties.

2. Niobium

No reported anomalies of R vs. T curves have been found for Nb. Nb has no discovered magnetic ordering effects and is similar to V in its Hall effect behaviour.

D. Internal Friction Measurements on Vanadium and Niobium

The variation of internal friction with temperature of V containing various amounts of interstitially dissolved oxygen and nitrogen has been reported\textsuperscript{27}. At frequencies of the order of 1 c.p.s. plots of logarithmic decrements of damping vs. temperature exhibit two sharp maxima between 150\degree and 300\degree which were ascribed to the reversible diffusion of
interstitial species. Changing the oxygen concentration changed the height of the lower temperature peak, whilst the higher temperature peak was similarly affected by changes in the nitrogen concentration. Vacuum annealing at $1550^\circ$C for four hours substantially reduced the height of the lower temperature peak indicating that oxygen was removed, but no such effect was observed on the higher temperature peak.

Stanley and Werts$^{29}$ reported that the damping peaks for nitrogen decreased with time, indicating that precipitation was occurring.

Marx$^{29}$ et al have carried out ultrasonic testing at 37 and 111 kilocycles on Nb between $-160^\circ$C and $1000^\circ$C. Doping with O and N was done and peaks corresponding to these two interstitials noted in the region of $400^\circ$C.

Their results led them to the conclusion that the activation energy for the diffusion of O and N in Nb and other metals is not constant with temperature. This could be due to the effective charge of an interstitial impurity i.e. its degree of ionization, varying with temperature in a transition metal. A change in degree of ionization would produce a corresponding change in ionic radius of the solute atom which would alter the activation energy of diffusion. Such a change should be detectable by electrical resistance measurements.
III. EXPERIMENTAL

A. Materials

1. High Purity Niobium Rod

Centreless ground Nb rod 0.200" in diameter was obtained for this investigation from the Wah Chang Corporation. It was supplied in two production lots of comparable impurity content.

<table>
<thead>
<tr>
<th>Element</th>
<th>Parts per million</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>60</td>
</tr>
<tr>
<td>O</td>
<td>55</td>
</tr>
<tr>
<td>N</td>
<td>45</td>
</tr>
<tr>
<td>H</td>
<td>2</td>
</tr>
<tr>
<td>Total</td>
<td>162</td>
</tr>
</tbody>
</table>

The average B.H.N. of the as-received material was 63.
No second phase was found upon metallographic examination.

2. High-Purity Vanadium Rod

The Vanadium used in this investigation was supplied by Union Carbide Company in the form of .25" diameter rod the analysis of which is given below.
TABLE II

<table>
<thead>
<tr>
<th>Element</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>314 p.p.m.</td>
</tr>
<tr>
<td>N</td>
<td>259 p.p.m.</td>
</tr>
<tr>
<td>O</td>
<td>0.068%</td>
</tr>
<tr>
<td>H</td>
<td>8.9 p.p.m.</td>
</tr>
</tbody>
</table>

Snowball observed a second phase in the as-received material which he accepted as being $V_2 C$.

3. Hydrogen Gas

Hydrogen was used to dope specimens of Nb. It was of commercial purity but was subject to the action of a "Deoxo" catalytic unit to remove oxygen and then passed through silica gel to ensure the absence of moisture before entering the doping furnace.

B. Purification

Niobium and Vanadium were both purified in a vertical floating-zone electron bombardment Zone-refiner, the technique of which has been completely described elsewhere$^{3, 4}$. Two passes were made on all single crystals grown; the drive was set to give a travel rate of 10 cm/hr. and the vacuum maintained was of the order of $10^{-5}$ mm. of Hg.

Table III gives the estimated interstitial content of the Nb based on the as-received values and Harding's work$^{4}$,
material from the same batch being used in both investigations.

TABLE III

Interstitial Content of Zone-Refined Nb.

<table>
<thead>
<tr>
<th>Element</th>
<th>Parts per Million</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>50</td>
</tr>
<tr>
<td>N</td>
<td>30</td>
</tr>
<tr>
<td>O</td>
<td>40</td>
</tr>
<tr>
<td>H</td>
<td>2</td>
</tr>
<tr>
<td>Total</td>
<td>122</td>
</tr>
</tbody>
</table>

V specimens were analysed by Ledoux and Company after two passes in the zone refiner and the results are given below.

TABLE IV

Interstitial Content of Zone-Refined V.

<table>
<thead>
<tr>
<th>Element</th>
<th>Parts per Million</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>136</td>
</tr>
<tr>
<td>N</td>
<td>318</td>
</tr>
<tr>
<td>O</td>
<td>160</td>
</tr>
<tr>
<td>H</td>
<td>7.2</td>
</tr>
<tr>
<td>Total</td>
<td>621</td>
</tr>
</tbody>
</table>

C. Single Crystal Orientation

Nb single crystals were grown from a common seed and all had an axial direction of [110].
Several Laue back reflection x-ray photographs were taken at intervals down a zone-refined rod in order to verify that, in fact, a single crystal had been produced. Such was found to be the case, though some crystals exhibited sub-structure effects in their x-ray photographs.

Applying the same process to V it was found that single crystals were produced of axial orientation approximately 20° from [001].

Several of the V single crystals were radiographed and it was found that they were highly subject to porosity, gas bursts as large in diameter as 3/16" being found. Great care had thus to be exercised in the selection of lengths from which specimens were to be prepared, though in this type of work the presence of porosity in small amounts is not of great importance.

D. Addition of Hydrogen to Nb

This process, referred to hereinafter as "doping" was solely applied to Nb and was accomplished by allowing the single crystal specimen to sit at elevated temperature in the presence of the gas, where absorption and diffusion occurred. Details of the process are described elsewhere.

Hydrogen, having been purified, is admitted to a vacuum annealing furnace of the horizontal type with a wheel mounted electrical furnace as the heat source.

Flushing of the furnace is accomplished by pumping down to 10⁻⁶ mm. of Hg, allowing hydrogen to enter the furnace until atmospheric pressure is attained whereupon the hydrogen valve is closed and the fore pump connected to remove the hydrogen.
This is done three times, ensuring complete flushing. As the hydrogen enters the furnace a pressure slightly above that of the atmosphere is maintained between the gas cylinder and the furnace to avoid contamination of the hydrogen.

The specimen, having been previously placed in the furnace tube supported clear of the glass on Mo wire, is then subject to a temperature of 1000°C. Varying periods of time were used on different specimens to attain varying hydrogen concentrations in the specimens.

The gas reservoir held its pressure indefinitely, indicating that hydrogen leakage was of an insignificant quantity.

Hydrogen's extremely rapid diffusion removed the necessity for any homogenisation period after doping. The furnace was merely switched off after the prescribed time period had elapsed and slowly rolled back from the specimen, giving a fairly rapid cool.

E. **Annealing of Niobium**

Annealing was carried out in the same furnace, the furnace being evacuated to $10^{-6}$ mm. of Hg.

Unfortunately, the type of glass used in the construction of the furnace has a maximum operating temperature of 1050°C., which is marginal for the annealing of Nb.

Specimens to be annealed were held at this temperature for 24 hours.

F. **Specimen Preparation**

1. **Machining.**

In order that a practical value of electrical resistance be obtained from the specimen it was necessary that it be much
longer than the standard .125" tensile specimen machined from these single crystals, or of approximately the same length but of smaller diameter.

Machining problems were posed by both possibilities but in view of material savings it was deemed advisable to adopt the latter alternative.

Small diameter specimens were able to sustain only very small stresses at right angles to the specimen axis. In order that these stresses be minimised a hook shaped tool was used. The point of the hook was in the machining direction and thus the loading was largely compressive and down the axis of the specimen. A high angle of relief was ground on the tool bit - approximately 60°. To further ease the right angle load surface speeds as high as compatible with lathe performance were used (2400 r.p.m. - 70 s.ft/min) together with slow tool travel. Trichloroethylene was used as a lubricant.

Lengths 2" to 2\(\frac{1}{2}\)" long were cut from the single crystal using a fine bladed jeweler's saw, they were then centre drilled and mounted in a lathe. Initial cuts of .006" were made, being reduced as the diameter of the specimen decreased so that at .120" .003" cuts were taken, .001" down to .100" and .0005" cuts below .100". Some specimens were machined to a diameter less than .090".

Careful polishing followed with 0 through 0000 emery paper utilising high speed rotation of the specimen in the lathe coupled with light pressure.

Both Nb and V specimens were prepared as above except V was found somewhat easier to machine. Because of the geometry of the apparatus the V specimens were shorter in length than
2. Surface Preparation.

(i) Niobium

Following removal from the lathe the specimens were usually electro-polished in a solution of 85% concentrate sulphuric acid and 15% hydrofluoric acid (35% strength). Rotation of the specimen round its axis during electropolishing by means of an electric stirrer and rheostat was practiced in an effort to give uniform removal of the metal. Where only .003", the amount necessary to remove machining deformation, was taken from the diameter, no anisotropy was observed. Electro-polishing was used to reduce cross-section area as much as possible - removal of up to .020" from the diameter being accomplished - but this resulted in the formation of two ridges diametrically opposite one another, giving the cross-section roughly the form of an ellipse.

A current density of 1.15 amps per square inch was used.

(ii) Vanadium

This was electropolished in a solution of 40 cc. of concentrated sulphuric acid, 160 cc. of methyl alcohol and approximately 20 drops of water. Using a current density of about 3.5 amps per square inch .003" was removed from the specimen diameter.
G. Resistance Measurements

1. Specimen Mounting

(1) Niobium

Each end of the specimen was centre drilled and drilled and tapped to receive a 2-56 mild steel screw, the head of which was cleaned and a short length of copper wire 1/32" in diameter soldered on.

![Figure 9]

The specimen could then be placed in split grips as shown in Figure 9.

This assembly fitted into the test jig shown in Figure 10 which was bolted onto a Tinius Olsen tensile testing machine, the ends of the copper wires being soldered to the jig as shown. Insulated potential leads soldered to the loops thus formed led off to the vernier potentiometer.

The current in the circuit was led down to the specimen via the drill steel rod and the specimen grips, out at the bottom of the specimen and back up the stainless steel columns which comprised the compressive load bearing members of the jig and thence through the structure of the Olsen testing machine to the vernier potentiometer.

Loading was accomplished by means of the testing machine but was measured by a Detecto spring scale of 400 lb. capacity, this being considered a sufficiently accurate and
Figure 10  Experimental Arrangement for Testing Single Crystals of Niobium
a more direct method than using the balance beam of the machine.

In some of the initial tests loads were applied to a given percentage of the yield stress of high purity Nb at the temperature of resistance measurement; in all other cases the load was of the order 8-12 lbs and was applied merely to hold the specimen in position and maintain good electrical contact.

The cooling vehicle was petroleum ether contained in a Dewar flask and agitated by an electrically driven stirrer comprised of two contra-pitch vanes on a common shaft. This arrangement was found to give thermal gradients down the specimen which were so small as to be undetectable by means of the thermocouple employed in this work.

Resistance measurements were made in the temperature range from -30°C. to -145°C.

(11) Vanadium

As lower temperatures were required for this metal in view of previously reported work by Snowball, a different experimental set up was necessary where the specimen was not in a liquid bath. It was found that severe thermal gradients resulted in using the Nb jig and this could be partially alleviated by

(a) Reducing heat conduction losses
(b) Mounting the specimen horizontally

As no load was to be applied to the specimen the tensile testing machine was not required and horizontal mounting presented no problem. A jig was made up consisting of an insulating board base and two right angles of brass secured to the base in each instance by two screws in a slot so that the distance between
Figure 10B. Experimental Arrangement for Testing Single Crystals of Vanadium.
the two uprights was adjustable. Each upright contained a slot and countersunk hole into which the shoulder of the specimen fitted.

Securing the jig to the base of the brass container in which it sat were two screws. This container had brass loops soldered to its base and sides to hold it at a uniform distance from the walls of the can in which it was placed. Cotton batting filled the space between the two vessels. The whole assembly was placed inside a Dewar flask, permitting liquid nitrogen to surround the outer can.

Current entered and left the specimen by means of copper wires soldered to screws, similar to the arrangement used for Nb specimens.

Potential leads were, of absolute necessity arising from unavoidable thermal gradients, kept to a maximum of simplicity and a minimum of dissimilar metal contact by taking the form of two turns of fine copper wire twisted tightly round the specimen. Reduced contact of dissimilar metals was necessitated by the fact that were such contacts permitted indiscriminately, with the thermal gradients involved, sufficient thermoelectric e.m.f. could be generated to give an abnormal high voltage drop when the current flowed in one direction and a negative voltage drop when the current was reversed. Even with the arrangement as described because of this effect two curves were required on each test with the current flowing in opposite directions. All leads were insulated electrically. Thermal insulation at the top of the Dewar flask was by means of a tightly fitting split polystyrene plug through which all leads, including the thermocouple, emerged via a common hole.

This was accomplished by measurement of current and potential drop in the specimen, the current in the circuit being determined by measurement of the fall in potential across a standard resistance of 0.100 ohms.

Procedure and equipment for resistance measurement were the same for Nb and V.

(i) Circuit

![Circuit diagram](image)

**Figure 1OC**

**Figure 1OD**

Figures 1OC and 1OD give a schematic diagram of the experimental arrangement. Reversing switches were incorporated in the battery and standard cell connections so that the time delay when the current was reversed in the specimen circuit was reduced to a minimum.

The galvanometer used was of the mirror type and was of a sensitivity compatible with that of the vernier potentiometer.

Changing connections from the specimen to the standard resistance was done by a switch on the potentiometer.
Adjustment of the variable resistance was made in order to give a suitable value of current in the circuit at the outset, this being of sufficiently low value (approximately 6 m.a.) so that no significant heating occurred.

(ii) Procedure

After switching the batteries on and cooling to the required temperature the circuit was left for 15 minutes to come to thermal and electrical equilibrium, after which it was possible to standardise the battery against the standard cell.

(a) In the case of Nb, where the procedure was accurate and the cooling slow, as the temperature approached the requisite value the current was measured, then the potential drop down the specimen, after which the temperature was taken again. When the temperature was at the requisite value, the potential drop was checked and recorded provided the standardisation showed an error of no more than one division from zero. Four divisions error in the standardisation were required to produce a discernable effect on the reading. From time to time during a run the current would be reversed. The reading thus produced did not, in general, lie on the curve but the discrepancy was small and almost constant.

Current values remained virtually constant during a run.

(b) Vanadium specimens were cooled more rapidly and in addition two readings were required at each temperature, the second being for the curve with the current reversed. Reversing the current required re-standardization. When, as was frequently the case, cooling was rapid this meant that readings were made continuously and as fast as possible in order to have
sufficient points on the curves.

3. Temperature Control and Measurement.

(i) Niobium

Petroleum ether was used as the medium and in conjunction with the contrapitch stirrer this gave very stable thermal conditions.

Cooling the petroleum ether was performed by liquid nitrogen which was pumped from a vacuum flask by means of a rubber bulb onto the surface of the petroleum ether.

When the temperature was being reduced in decrements of the order of 1-2°C, as was usual, three minutes or less was sufficient for thermal and electrical equilibrium to be attained in general; this was checked from time to time by allowing longer periods to elapse and noting any change in resistance that might occur. Heating was carried out by permitting the apparatus to stand, or, if an accelerated rate were required, a copper heat sink was introduced into the petroleum ether.

It was found that unstable thermal conditions were obtained when the compressive load bearing members were made from mild steel rod. These were removed and hollow pillars of stainless steel substituted which reduced heat conduction to a fraction of its former value.

(ii) Vanadium

Cooling was by conduction, the specimen being in air. Adding liquid nitrogen to the vacuum flask resulted in a fast initial rate of cooling which soon slowed to a reasonably steady rate but subsequently virtually ceased. This was a far from ideal method. A temperature differential of as much as 2-3°C.
existed between ends of the specimen at times.

Allowing the apparatus to stand produced an acceptable heating rate which could be accelerated by partial removal of the polystyrene plug from the top of the flask.

(iii) Temperature Measurement.

In both instances the temperature was measured by means of a copper-constantan thermocouple using a melting ice cold junction. The e.m.f. generated was measured on a Pye portable potentiometer.

Winding the thermocouple around the middle of the specimen was found completely satisfactory.

H. Ultrasonic Preparation

1. Specimen Preparation

Parallelism in ultrasonic testing poses a serious mechanical problem in that very close tolerances are required - .0001" per inch being stipulated. For a ferromagnetic material which can be held in a magnetic chuck the problem is not serious. Neither Nb nor V is ferromagnetic, however, so an alternative procedure was devised.

Five slugs of V, all just under 0.5" in length, were mounted in bakelite. One was placed in the middle with the other four radially surrounding it with their nearest point of approach to the edge of the bakelite mount being 1/16" from its circumference.

Thus mounted the specimens were machined in a specially manufactured collet. One side was machined very carefully, the final cut being .0005" deep. Reversing the bakelite mount the other face was machined in the same manner.
Careful micrometer application showed the high spots. The mounted specimens were then polished on a coarse alumina wheel with the high spots held always furthest from the centre. This subjected the high spots to the increased cutting action of the faster portion of the wheel. This was continued until parallel faces were obtained to within the limits of accuracy imposed by the micrometer.

The slugs were cut from the mould, the saw cuts being so positioned that a part of the slug side was exposed, the rest remaining in the bakelite.

Having filed a groove in the bakelite a thermocouple was placed in the groove and secured in such a manner that the junction rested against the slug.

2. Specimen Mounting

Ultrasonic testing requires the use of a quartz transducer coupled by some means to the specimen and usually to a brass cylinder 1" deep and ½" in diameter which transmits the pulse from the generator to the transducer and also receives the reflected pulse back from the transducer, which signal then appears on an oscilloscope screen. This was modified by evaporating a film of copper onto the back of the transducer and soldering a very fine gold wire to this coating.

Fisher "Nonaq" grease or Dow-Corning High Vacuum grease was used as a couplant and the transducer was wrung on to the V slug. This was placed in a hollow copper cylinder, being held firmly against the grounded base by means of a wad of tissue and a cork in the end of the cylinder. Cotton batting was wrapped around the cylinder and it was placed in a can which in turn was
placed in a Dewar flask and surrounded by liquid nitrogen.

3. Procedure

A Sperry ultrasonic amplifier was used which was equipped with a pulse comparator so that when the wave form from the specimen matched the internally generated envelope on the screen the dial reading gave a direct measure of the wave attenuation.

Cooling was very rapid but adjustment of the pulse comparator was also rapid so that with assistance to continuously measure the temperature it was possible to obtain attenuation versus temperature curves.
Figure 15: Variation of Electrical Resistance with Temperature for High Purity Single Crystals of Nicotum under Load. (Specimen 1)
IV EXPERIMENTAL OBSERVATIONS AND RESULTS

The variation of electrical resistance with temperature has been observed for high purity single crystals of Nb and V at low temperatures. The effect upon resistance of adding hydrogen to Nb has been noted between -30°C. and -145°C.

A. High Purity Niobium Specimens

1. Mechanical Polish Only.

Initial testing of the variation of electrical resistance with temperature was carried out on specimens which had been carefully turned on a lathe and polished down to 0000 emery paper. As resistance is a bulk property it was not deemed necessary to electropolish them. They thus possessed a thin deformed surface layer, in all probability less than .001".

It was hoped to detect a resistance effect arising from dislocation movement and to this end a stress was applied to the specimen, usually after a test under no load. The load was not constant but was a given percentage of the yield stress at the test temperature, as previously measured.

Figure 11 shows curves 1, 2, and 3 for specimen 1. These were obtained after the specimen had been rapidly cooled to -146°C. As the specimen heated slowly back towards room temperature electrical resistance measurements were made.

A pronounced anomaly in the region of -120°C. occurs in 1 on the first test under load (70% yield stress). Below the anomaly a change in slope occurred.

Curve 2 shows a repeat of the test with the direction
of current flow reversed. No anomaly is observed and the slope change is in the opposite direction and of comparable magnitude, thus indicating the slope change to be an extrinsic effect. An overall increase in resistance is observed in spite of the apparatus having been completely undisturbed between tests.

Curve 3 was conducted with the current in the original direction and with the stress up to 90% of the yield stress. Again an anomaly was observed, but at a slightly higher temperature and of smaller magnitude. The slope change was as in 1 but the overall value of resistance was higher than 1 and 2, indicating that the increase in resistance upon standing is a genuine effect. Curve 3 commenced to rise quite sharply above $-105^\circ C$. and fractured at $-100^\circ C$.

Figures 12 and 13 relate to specimen No.2 but the tests were conducted during the cooling portion of the cycle i.e. cooling was accomplished slowly and in a uniform manner below $-90^\circ C$. Curves 4 to 8 were all conducted under no load.

Curve 4 showed a pronounced slope change and no anomaly, unless it was of such size that the limited temperature range of the curve did not reveal it.

Curve 5 also exhibited a slope change of smaller magnitude but accompanied by an anomaly in the region of $-110^\circ C$.

An anomaly is also seen on curve 6 but of apparently different character and smaller magnitude. The temperature of occurrence is $5^\circ$ lower at $-115^\circ C$. These anomalies are approximately $3\%$ of the total resistance at the temperature of occurrence.

No slope change occurs in 7 where the current has been reversed; a small anomaly in the form of a blip appears.
In curve 8 with the current flowing in the original direction and the resistance measured on the heating cycle a very small slope change appears at about -125°C.

Loading to 90% of the yield stress produced 9 wherein a reverse blip appears just prior to fracture as in 3, but no untoward increase in resistance appears unless it is manifested in the anomaly.

Curves 7 and 9 appear to have slope changes at -80°C but this may be the usual overall curve of the resistance versus temperature curve.

Specimen 2 showed the same overall increase in resistance upon standing as specimen 1, the resistance increasing approximately 2% on standing for 24 hours. The increase on successive days is of smaller magnitude.

2. Electropolished Specimens

Specimens which had been mechanically polished were electropolished to remove the deformed surface layer.

Figure 14 shows R vs. T for specimen 3. This specimen was deformed torsionally quite severely during machining and thus possessed a distorted lattice structure.

Curve 10 shows the first cooling of this specimen. An anomaly occurs in the region of -122°C which is about 0.6% of the total resistance at -120°C. Subsequently a slope change appears. The heating cycle shows an increase in resistance but no anomaly.

Curve 11 shows what appears to be slightly anomalous behaviour from -110°C to -120°C. (See enlarged portion of the curve in Figure 15A). There is no slope change. The curve
Figure 15: Enlarged Sections of Figures 14 and 15
obtained as the specimen slowly heats showed instability in the region of -120°C.

The anomaly persists in curve 12 (See Figure 15A) but is now approximately 0.1% of the total resistance, as opposed to 0.4% in 10. The heating curve for 12 shows no anomalies of any description and is only very slightly higher than the cooling curve. Repeated cooling appears to enable the specimen to approach some form of equilibrium.

Specimen 4 was deep machined without being subject to a deep electropolish, as was specimen 3. X-ray examination did not indicate a deformed layer, but sub-boundaries of 3-4° misorientation were present. The single crystal from which this specimen was produced was not of as high a purity as usual due to defective sealing of the zone refining apparatus leading to a poorer vacuum being obtained than was customary. Operation was usually at 4.5 x 10^-6 mm. of Hg, in this case it was 10^-5 mm. of Hg.

Experimental difficulties were encountered in the testing of specimen 4 so that curve 13 is the third cooling. Two small blips (approximately 0.2%) were observed at -108°C. and -116°C. (See Figure 16A). Little overall increase in resistance is observed in the heating cycle but some trace of the cooling anomalies appears to persist. The cooling cycle was accomplished in two parts on different days, thus its validity is somewhat suspect.

Specimen 4 was removed from the apparatus and annealed in a vacuum furnace for 24 hours at 1050°C. and 5 x 10^-6 mm. of Hg after which it was cooled quite rapidly by rolling back the furnace to achieve an air cool.
Figure 16 Electrical Resistance Versus Temperature (Specimen 4)
Curve 14 shows the behaviour of the annealed specimen. A very large blip (3\%) in the curve appeared in the vicinity of $-133^\circ C$.

On repeating the test (15) an overall increase in resistance occurred and possible anomalous behaviour in the region of $-120^\circ C$.

Re-annealing the specimen produced curve 16 which exhibited no slope changes or anomalies. The heating cycle was commenced on the same day but only completed as far as $-125^\circ C$, whereupon the specimen stood overnight, heating very slowly to $-40^\circ C$. Re-cooling the following day to complete the curve produced appreciably higher resistance. The first part (April 17th.) of the heating curve diverged from the cooling curve, whilst the second part (April 18th.) had a slope very nearly parallel to the cooling curve, again indicating that some sort of equilibrium is being approached as the specimen is left standing.

Curves 14, 15 and 16 exhibit a step in the R vs. T curve in the region of $-97^\circ C$, similar to that reported by Rostoker et al\textsuperscript{27}.

Specimen 5 was of exceptionally high purity as the re-built apparatus produced a vacuum of $10^{-6}$ mm. of Hg. A possible very small anomaly and a slight slope change at $-124^\circ C$ were the only departures from linearity. Figure 17 also shows curve 18 which was determined from specimen 6. Specimen 6 was made from the extreme end of a single crystal and is thus of doubtful purity. Two steps or possibly very long blips were noted at $-123^\circ C$ and $-133^\circ C$. These were .5 and .6\% increases respectively.
in total resistance.

Specimen 7 was from the same crystal as specimen 5 and thus very pure. It was, however, heavily deformed during machining. Small twin blips were found in the region of -120°C. followed by a long blip or it may be the curve is straight to -128°C. and then takes a downward step of about .5%. A virtually coincident curve (not shown) but with no anomalies, is obtained from the heating cycle.

Specimen 8 was also of high purity. Testing over a wide range of temperature produced only the previously observed slight slope change in the vicinity of -90°C.


Hydrogen doping was carried out on the specimen to an estimated content of 3-400 p.p.m. of hydrogen. This produced an increase in resistance at -120°C. of 25% approximately. A definite figure cannot be stated as the doping process necessitated the removal of the contacts and contact resistance would probably change significantly upon their replacement.

Testing this doped specimen produced curve 21. Heating to repeat a cooling range from -40 to -50°C. produced the effect shown, once more indicating an unstable equilibrium. A pronounced slope change at -75°C. is noted. From -101°C to -126°C a long reverse blip (3%) occurs. The end of this is seen more clearly in the curve at the right of Figure 19 which is plotted on double scale and also has the heating cycle plotted. A slope change but no other anomalies was noted for the heating cycle.
Figure 21 shows the results of repeating the experiment with Specimen 8 a week later. A slope change and small reverse blip was noted at -65°C. This was followed by a loop and discontinuity at -100°C. The anomalies in the lower section of the curve are shown at the right of Figure 20 on double scale. The one occurring at -120°C could be a reverse blip or a step and is 1.1% of the total resistance. A step anomaly occurs at -125°C. The two anomalies are possibly part of a long reverse blip.

4. Summary of Results on Niobium

(1) No effect ascribable to dislocation movement was observed.

(2) Relatively pronounced anomalies occur in the temperature range -110 to 130°C.

(3) Other anomalies such as steps and slope changes, occur at other temperatures in various specimens but not consistently.

(4) Pronounced slope changes seem to be associated with a deformed surface layer.

(5) Of the specimens exhibiting anomalies in the vicinity of -120°C, blips tend to be found in deformed specimens and steps in undeformed specimens.

(6) Specimens prepared under high vacuum, which it is reasonable to suppose would be of high purity, exhibit little or no anomalous behaviour.

(7) Hydrogen doping produces a long reverse blip, or slope change and step.
(8) On being allowed to stand after the first cooling the resistance of the specimen increases.

B. High Purity Vanadium Specimens.

Electropolished single crystals of vanadium were tested between -130° and -200°C. to determine the variation of electrical resistance with temperature in this range.

Owing to the temperature range employed the specimen was mounted in air leading to the presence of thermal gradients. It was thus necessary to measure the electrical resistance with the current flowing both from right to left and left to right in the specimen. On the curves an arrow pointing upwards denotes a current flow from right to left and a downward pointing arrow from left to right.

Curve 23 in Figure 21 shows the results of cooling from -145°C. to -185°C. Between -165 and -170°C. an apparent slope change is observed and possibly a blip anomaly also. Curve 24 was obtained whilst heating the specimen and no apparent anomaly of any description appeared, though the scatter of points was wider than for the cooling curve.

Figure 22 shows curve 25 which owing to mechanical problems was obtained in two parts, the second of which exhibited greater thermal gradient effect. The average curve (broken line) exhibits a slight slope change at -168°C.

Specimen 10 was re-tested over a more comprehensive range, the results of which are shown in Figure 23. Curve 26 was obtained by cooling from -140 to -196°C. A large blip
(2.5% of the total resistance) extending over approximately 10° from -162°C was observed, which was accompanied by a change of slope. Cooling specimen 10 for the third time (Figure 24) produced no anomaly and a barely detectable slope change.

Specimen 11 produced a definite slope change and a large (4%) blip.

No doping was attempted on Vanadium.

Vanadium thus appears similar to Niobium in that anomalous behaviour is encountered to a more marked degree on the first cooling that on subsequent ones; these effects would probably disappear after 4 or more cycles. The effects are not observed for the heating curves.

C. Ultrasonic Testing of High Purity Vanadium.

Single crystal slugs of V were tested between -30° and -196°C using a Sperry Ultrasonic Comparator operating at a frequency of 3.5 megacycles. Two types of couplant were used - Fisher Scientific Co's Nonaq grease and Dow-Corning's Hi-Vac grease.

Figure 26 shows the results obtained using Nonaq. Curve 29 is the first cooling and the attenuation reaches a minimum at or about -173°C. At -196°C the curve goes off the scale. Allowing the specimen to heat up produced curve 30 which followed 29 in form, reaching a minimum at -175°C but on extending the temperature range another minimum was observed in the vicinity of 90°C. Immediate re-cooling to give curve 31 gave minima about -103°C and -176°C. Thus it would appear that the cause
of the resistance anomaly is also the cause of the attenuation minimum occurring about -170°C. The fact that another minimum appears above -100°C. indicates the advisability of extending the temperature range of the resistance measurements on V.

The results using Hi-Vac grease were a little more ambiguous. The first cooling of specimen 13 (Figure 27, curve 32) reveals no minimum in the vicinity of -100°C. but the curve appears to be dropping towards a minimum of -170°C. when contact was lost. A second attempt (curve 33) produced a not very distinct minimum about -100°C. followed by a peak which is probably not, from its appearance, the result of the intrinsic properties of V. A minimum at -170°C. is followed by an increase in attenuation to such an extent that the waveform amplitude had to be re-set. Heating gave no minimum in this region and a very diffuse one at -110°C.

Figure 28 shows the continued work. A third cooling of the same specimen (curve 35) shows a minimum in the vicinity of -80°C. and another at -193°C; the heating which followed (curve 36) showed minima about -165°C. and -110°C. Curve 37 was taken immediately, showing a broad minimum at -110°C and a much sharper one at -170°C.

In general Hi-Vac does not seem to give results of as satisfactory reproducibility as does Nonaq, but both indicate that the physical behaviour which gives rise to the resistance anomaly also affects internal friction and that there is another
change of this nature in the vicinity of -100 C. which should have been investigated electrically. Repeated cooling and heating do not remove the minima
A. **High Purity Niobium**

1. **Electrical Resistance Anomalies**

The experimental results on the variation of electrical resistivity of Nb with temperature indicate that some form of anomalous behaviour of this property occurs in the vicinity of \(-120^\circ\text{C}\). In non-electropolished specimens having a deformed surface layer it appears to be a slope change, sometimes associated with a blip (Figures 11, 12). In electropolished specimens it is a step in undeformed specimens (Figures 17, 18); in deformed specimens it is a blip (Figures 14, 15, 18).

Energy level splitting of electrons and changes in magnetic ordering which are held accountable for many resistance anomalies would be revealed in magnetic susceptibility versus temperature curves. The uniform behaviour of these plots indicates that the effect does not originate in these phenomena.

Hume-Rothery and Coles\(^3\) report no antiferromagnetic Curie temperature or antiferromagnetic behaviour of magnetic susceptibility or of specific heat for either Nb or V.

Successive runs exhibit smaller anomalies and heating curves rarely show any effect. In view of this and the preceding any change in electronic structure, energy level splitting or effects involving electrons must be ruled out as the hysteresis involved in such changes with temperature is negligible. Thus it would appear that some form of equilibrium is involved.
Preparation of the single crystals removes only O, N and H. Substitutional impurities remain and C is virtually unaffected i.e. the refining process is one of out-gassing. Anomaly magnitude appears to be critically dependent upon the efficiency of this process. Running the zone-refiner at a higher vacuum than usual results in no anomaly in the curve (Figures 17,19). Thus the anomaly appears to be associated with the presence of O, N and H in the material.

Precipitation of a second phase in Nb of this purity has not been reported. Concentrations orders of magnitude higher are required\(^{34,35}\). In any event, the precipitation of a second phase requires that the resistance decrease, not increase.

It is assumed, therefore, that C, O, N and H are all interstitially dissolved. There are two positions that an interstitial may adopt in a b.c.c. lattice; it may enter the octahedral "O" site or the tetrahedral "T" site.

\[ O - \left(\frac{1}{2}, \frac{1}{2}, 0\right) \]
\[ T - \left(\frac{1}{2}, \frac{1}{4}, 0\right) \]

**Figure 29**

The T position is considerably larger than the O, but with the possible exception of H considerable lattice strain is involved in either. Interstitials are therefore stress centres in the lattice and a change of position of interstitials could be responsible for anomalies in the resistance versus temperature...
Calculations of the stress arising from the occupancy of a site by an interstitial are rendered difficult because of the impossibility of assigning an exact radius to the interstitial atom (if it is indeed an atom at all in lattice; this is open to question). Barrett gives approximate values of $r$ in Table V. These values are based on half the single bond lengths of the atoms involved.

\begin{tabular}{|c|c|c|c|}
\hline
 & O & N & C & H \\
\hline
$r$ (kX) & 0.74 & 0.74 & 0.77 & 0.46 \\
\hline
\end{tabular}

It has been shown that the scattering of conduction electrons resulting from lattice distortions surrounding imperfections is an order of magnitude greater than that due to the imperfection itself. Thus comparatively large effects are to be expected from low concentrations of interstitials if they are in positions of high strain energy.

Van Buren gives a method for calculating the stress due to dissolving a substitutional atom in a lattice which has been modified slightly to and applied to interstitially dissolved impurities. The use of this is further complicated by the fact that the O site is not spherically symmetrical whilst the T site is. The formula gives the hydrostatic stress $\sigma_{rr}$ arising at a distance from the substitutional atom. Thus the value calculated for the O position will be too large.
\[
\sigma_{rr} = \frac{\varepsilon_0}{r} \left( \frac{1-2\nu}{1-\nu} \right) \frac{1}{r^3}
\]

where \( \nu \) = Poisson's ratio

and \( \varepsilon_0 \) = constant

\( r \) = distance from the stress centre

Addition of an interstitial brings about a change in volume given by

\[
\Delta V = \frac{\varepsilon_0}{2G} \left( \frac{1-2\nu}{1+\nu} \right)
\]

where \( G \) = Young's modulus

In order to find \( \Delta V \) it is necessary to know the size of the interstitial site. The radius, \( r \), of the largest sphere to fit in an O site is given by \( 0.154 \, R \), where \( R \) is the atomic radius of Nb. The distance from the centre of the site to the next nearest neighbours is given by \( 0.633 \, R \). T holes are \( 0.291 \, R \) in radius.

\[
\begin{align*}
\text{O site} & \quad 0.154 \, R = 0.154 \times 1.426 = 0.202 \, \text{kX} \\
& \quad 0.633 \, R = 0.633 \times 1.426 = 0.903 \, \text{kX} \\
\text{T site} & \quad 0.291 \, R = 0.291 \times 1.426 = 0.415 \, \text{kX}
\end{align*}
\]

1. Stress Arising from the Presence of Interstitials

(1) H on O sites
\[ \Delta V = \frac{4}{3} \pi (0.46^3 - 0.202^3) \]
\[ = 0.374 \text{ kx}^3 \]
\[ \Delta V = \frac{g_0}{6.76 \times 10^6} \cdot \frac{28}{1.36} \]
\[ g_0 = \Delta V \times 6.76 \times 10^6 \times \frac{1.26}{28} = 1.27 \times 10^7 \]
\[ \sigma_{rr} = \frac{28}{64} \cdot \frac{g_0}{\pi} \cdot \frac{1}{r^3} \]
\[ = 1.78 \times 10^6 \times \frac{1}{r^3} \]

(ii) H on T sites
\[ \Delta V = \frac{4}{3} \pi (0.46^3 - 0.383^3) \]
\[ = 17.3 \times 10^{-2} \text{ kx}^3 \]
\[ g_0 = \Delta V \times 3.28 \times 10^7 \]
\[ \sigma_{rr} = \frac{28}{64} \cdot \frac{g_0}{\pi} \cdot \frac{1}{r^3} \]
\[ = 7.9 \times 10^5 \times \frac{1}{r^3} \]

Similarly
(iii) C on O Sites
\[ \sigma_{rr} = 8.51 \times 10^6 \times \frac{1}{r^3} \]

(iv) C on T Sites
\[ \sigma_{rr} = 7.76 \times 10^6 \times \frac{1}{r^3} \]
(v) O and N on O Sites

\[ \sigma_{rr} = 7.62 \times 10^6 \times \frac{1}{r^3} \]

(vi) O and N on T Sites

\[ \sigma_{rr} = 6.7 \times 10^6 \times \frac{1}{r^3} \]

The maximum value of \( \sigma_{rr} \) will occur at the minimum value of \( r \) which is the radius of the interstitial.

Thus it is seen that distortions of high strain energy are produced.

With regard to the distortion on O sites, with the next nearest neighbour 0.903 kX from the stress centre it is obvious that even the largest interstitial, C, of radius .77 kX, will touch the next nearest neighbours. Thus on O sites distortion to a first approximation is only of one row of atoms along the cube edge. On T sites the distortion is spherically symmetrical, so that distortion of the O site might in fact be more easily accomplished than the distortion of a T site.

It might be thought that thermal contraction of the lattice would result in an increase in stress to such a point that the interstitial, if on an unfavourable site, would move to one of lower strain energy. It may be seen from Figure 29 that on the hard sphere atomic model there is no energy barrier to prevent an interstitial from moving from an O site to a T should strain energy render the original
site unfavourable. Such a movement would, however, result in a decrease in the size of the stress centre, whereas the anomaly noted is an increase in resistance. It may be argued that a re-distribution of stress could occur in such a manner as to increase the scattering effect even though the stress is smaller. It is possible that a high stress spread over a small area could result in a stress centre which was too small to be an effective scattering agent if it were smaller than the wave length of the conduction electrons. However, as it is found that dislocation cores scatter very effectively\(^{37}\), interstitials in either position should also be capable of scattering conduction electrons as the stress distribution could not be concentrated in an area less than that of a dislocation core.

Bonding is postulated as being the cause of interstitial movement from one site to another; the movement is such as to increase the strain energy, the increase in strain energy being offset by a decrease in the energy required for bonding to give a decrease in total energy.

There is considerable evidence to indicate that bonding occurs between the interstitial and the solvent atoms.

Hume-Rothery and Coles\(^{33}\) point out that it is possible to calculate the size of the holes in a b.c.c. lattice available for interstitial occupation but when it is occupied by the interstitial bonding will occur altering the effective size of the hole. It is concluded from this that the more bonding that occurs the larger the size of interstitial which can be accommodated without excessive lattice strain. It is
therefore fruitless to place any great emphasis upon the preceding stress calculations other than to give a rough estimate of orders of magnitude.

In discussing interstitial structures Kiessling\textsuperscript{39} states that interstitial compounds are true compounds stabilized by electron transfer from the interstitial to the metal lattice. The ratio of electron concentration to coordination number is stated to be of fundamental importance in determining lattice structure and that donor capacity increases from O to N to C.

However, Rundle's\textsuperscript{36} view of the bonding between interstitials and metals in the form of compounds MX, where M is the metal and X is H, C, O or N, is that the bonds are very strong, directional and the X component has strong acceptor properties.

Internal friction work by Powers and Doyle\textsuperscript{40} has shown that in Nb where Zr appears as an impurity, ZrN is formed as atom couples throughout the lattice.

Hydrogen is rather a unique case and deserves separate consideration. It is generally conceded that H in metals is in the atomic form\textsuperscript{41}. However, Smith in his "rift" theory suggests H may be present as protons and Isenberg\textsuperscript{42} purports to prove this. Whether this is valid or not H is the only interstitial to have appreciable mobility in the region of -100°C. and so it is necessary to afford it special attention, and will be treated later.

Considering the anomalies in the vicinity of -120°C. in electropolished specimens, undeformed specimens show a
step with the curve possessing the same slope prior to and after the discontinuity. This behaviour must be the result of an increase in the number of stress centres or their effectiveness. Precipitation, ordering, or the formation of a new phase would produce a slope change instead of or in addition to a step. Also a change of this nature would be slow to occur at these low temperatures.

To account for the change of position to one of higher strain energy an overall decrease in energy is envisaged, being due to the change in bond energy.

It is known that in Fe, with a lattice constant of 2.8606 kX the C atom normally i.e. at room temperature, occupies the smaller O site, producing very great strains. On the other hand, in Mo with a lattice constant of 3.140 kX, the C atoms occupy the T site. With the acceptor tendency of C in mind, it would seem that 4 electrons are required for each C atom. In the T position one electron would come from each of the four nearest neighbours. Fe is in a lower energy position with 2 electrons removed - its valency being 2 or 3, so that it is conceivable that even with the lower strain energy this is not a favourable position. In the O site each of the two nearest neighbours loses 2 electrons from the s shell and in consequence are in lower energy states.

As temperature decreases the p bonding orbitals of the interstitials become denser and more directional so that it is found that in spite of lattice contraction and the high strains produced the C remains in this position down to room
temperature.

In the case of Mo, with a valency of 4, no such favourable bonding exists in the 0 site, 2 electrons from each of two nearest neighbours being little different from an energy viewpoint from 4 electrons donated by each of 4 neighbours. Because of strain energy the C will go to the larger site.

In the case of Mo, with a valency of 4, no such favourable bonding exists in the 0 site, 2 electrons from each of two nearest neighbours being little different from an energy viewpoint from 4 electrons donated by each of 4 neighbours. Because of strain energy the C will go to the larger site.

In the case of Nb, with one 5 S electron, the T position is definitely favoured for C from strain energy and bonding considerations, removing one outer electron from each of the four tetrahedral atoms. Thus C in Nb will tend to occupy T sites and stay in them.

Oxygen has 6 outer electrons in its shell and therefore will require 2 more. At room temperature and above there will be a statistical distribution of 0 between 0 and T sites as one electron from each 0 nearest neighbour is desirable from a bonding viewpoint but the lesser strain energy of the larger T site offsets this. On cooling down below room temperatures some 0 will be on T sites and will remain there as 0 has lost its mobility at room temperature. As cooling progresses and the bonds become more directional the 0 atoms will reach a point where the higher bond energies involved offset the elastic strain energy and in spite of the lattice having contracted they will be pulled into an 0 site. It is found that
repeated cooling produces steps of smaller magnitude at slightly lower temperatures e.g. -115, -117, -116.5°C. This indicates that were the specimen held at the step temperature for a longer period of time than was usually the case under test conditions a larger step would result. In some cases the steps are quite gradual which bears this out. Eventually after several cycles steps no longer tend to occur as all interstitials have left the unfavourable sites. Steps do occur on heating, but are of smaller magnitude and at higher temperatures indicating elastic strain energy does force some reversibility in the process.

N has 5 outer electrons and thus will require 3 more. Because of the symmetry and the directional properties of the metallic bond it is probably energetically favourable to obtain these electrons in the form of covalent bonding with the 6 octahedral atoms.

The manner of functioning of the bonding mechanism is tentative. Were the interstitials to behave as acceptors a modified picture would result. It is quite conceivable that the interstitials could move from 0 to T at the anomaly temperature and that this could lead to a greater scattering of conduction electrons resulting from the spherical symmetry of the T site requiring more strain energy to accommodate an interstitial that the asymmetrical 0 site. Until more information is obtained with regard to the positions adopted by interstitials in b.c.c. lattice this must remain a moot point.

The foregoing leads to the basic hypothesis that some
form of non-equilibrium distribution of interstitials is obtained in Nb when it is cooled fairly rapidly from high temperature. Cycling between room temperature and low temperature gradually removes the anomalies as a pseudo equilibrium is attained by atoms on unfavourable sites moving to favourable ones due to the nature of the bond between the interstitial and the lattice. Marx finds a change in activation energy of diffusion of O and N in Nb. This could be attributed to a change in bonding.

It is noted (Figure 16) that an anneal followed by a rapid cool (at a greater rate than was obtained in the zone refiner) produced the largest anomaly. Re-annealing followed by a slow furnace cool produced no anomaly, but this could have been due to interstitial loss during annealing.

Experimental work thus seems to indicate that interstitials are frozen into non-equilibrium positions. Further support of this is lent by the formation of loops when the cooling curves are interrupted or reversed (Figures 14 and 20).

Deformed specimens which exhibit an anomaly do so in the form of a blip (Curves 1, 3, 7, 10 and 12). It is thought that this is a step initially but that the vacancies present in the specimen as a consequence of the deformation suffered may migrate into the vicinity of the interstitials and thus relieve some of the stress associated with the new position.

The magnitude of the blips seem to be larger than the steps when the specimens are of the same general level of purity. This could be due to deformation causing more interstitials to go to the lower strain energy sites so that upon reaching the anomaly temperature more interstitials are moved to the higher
strain energy positions, or it could be due to the bonding forces removing interstitials from the close proximity of vacancies with which they are associated, giving a larger increase in strain energy than would occur were vacancies absent. The vacancies quickly re-arrange themselves to again provide stress relief and in so doing change the step into a blip.

It has been noted that in some instances a step denoting a decrease in strain energy occurs (Figures 16 and 19). This suggests stress relief by an interstitial changing its position under the influence of thermally engendered stress.

2. Increase in Resistance during the Heating Cycle and on Standing at Room Temperature.

Because of the method employed of measuring the potential drop down the specimen there is a possibility that the effect is due to poor contact resulting from the variation in thermal expansion of the mild steel screws and the Nb. If this be the case, on reheating back to the starting point the resistance should return to the original value as the screws cannot turn and loosen mechanically owing to the wire soldered to the screw.
head.

The increase in resistance commences as soon as the specimen is on the heating portion of the cycle. This is due to hysteresis in the T → 0 transition. If the heating is carried out quickly the slope will continue with its increased value through the test range. Slower heating gives a curve which decreases its slope at some point. Above this point the heating curve remains parallel to the cooling curve. On even slower heating the stable slope value, parallel to the cooling curve, appears at a lower temperature.

On second cooling the effect is very much smaller but is usually present. A third cooling may produce little or no increase in resistance on heating.

On standing at room temperature an increase in resistance is observed, the rate of increase of which becomes progressively smaller. This and the above is thought to be due to the interstitials approaching equilibrium in their distribution. Cooling to -140°C. has the effect of changing the statistical distribution of interstitials on 0 and T sites. By the laws of probability some interstitial on 0 sites will not have received sufficient heat energy to break the bonds holding them to the 0 sites and so will remain there.

The effect is dependent upon impurity content, very pure specimens which show little or no anomaly also show almost identical heating and cooling curves. Normal specimens show increases of up to 2-3% of the total resistance on standing. Hydrogen doped specimens show increases up to 25%.

Specimen 3  Nov 3rd to Nov 7th  Nov 7th to Nov 9th
R inc. 3.0%  R inc. 0.8%
It is possible that precipitation on a micro scale or ordering of a certain type could increase the resistance. A study of the ordering processes in Cu₂Au has shown that during the initial stages of ordering electrical resistance does increase. Small unstable ordered regions—"embryos" are formed. It is likely that stable neighbouring embryos are antiphase.

Sykes and Jones⁴⁴ show that the presence of antiphase domains in a crystal destroys its homogeneity. When the domains are of a size comparable with the mean free path of conduction electrons, scattering will result. When the domains are sufficiently small the resistivity is the same as for a completely disordered material.

Small embryos initially present act as scattering centres. Nuclei of high order increase the inhomogeneity and thus increase resistivity. Subsequent nuclear growth removes disordered material and decreases the resistivity.

Nuclei are progressively smaller and their density in the metal larger as the temperature decreases.

It has also been proposed that a limitation of electron mean free path by internal boundaries could occur which would cause an increase in resistance. These boundaries are grain, mosaic or dislocation boundaries.

Seraphim⁴⁶ has reported the formation of a super-lattice
of N in Ta at a concentration of 65 p.p.m. At this low concentration to be meaningful the super-lattice would have to consist of domains of ordering. They would be antiphase in all probability and increase electrical resistance.

Thus the increase in resistance could be due to either an increase in strain energy due to the interstitial movement or to small domains of local order formed which reduce the lattice regularity. Micro-precipitation or coupling of the type Zr - N are other alternatives which could also be considered.

Before any mechanism could be chosen more work would be necessary.

B. Vanadium

The work done on V did not give results of comparable accuracy to those obtained from Nb. The method of testing was such as to give curves of differing slopes and positions with changing direction of current flow. An average of these provided an approximation to a curve representative of the true electrical properties of the material. From this it appeared that blips similar to those in Nb were found. Certainly a definite change in slope occurred. The magnitude of the slope change decreased with the number of cycles to which the specimen was subjected, also similar to the behaviour in Nb with regard to the change of position of the interstitial until some pseudo equilibrium is obtained. However, within the rather poor relative accuracy attained in this work there did not appear to be any increase in the resistance on standing.

With regard to the previously reported anomaly in the
vicinity of $-30$ to $-50^{\circ}C^{23-28}$, it would appear that this is accompanied by similar anomalies in other properties, mechanical and electrical, so that a second phase being precipitated is a possible explanation. The variation in temperature of the reported anomaly could be caused by varying purities, though it is unlikely this could be lowered to $-170^{\circ}C$ as the anomaly was reported at $-46^{\circ}C$ for electron beam refined material. No other reported magnetic susceptibility anomalies have been found.

As the anomaly is, or is accompanied by, a slope change, some change in lattice structure is to be held accountable. The slope change indicates an increased resistance and precipitation would cause a decrease. However, the previously mentioned arguments for Nb with regard to the increase in resistance on standing apply equally well here, noting that the lower the temperature the more nuclei there are and the smaller in size. The change of slope indicates continuous formation of these nuclei. Some reversibility is indicated in that Snowball obtained the effect on heating.

As with Nb, an equilibrium is attained after 3 or more cycles. Unfortunately the effect of H doping was not investigated.

The possibility that the slope change is due to change of interstitial site is an unlikely one in that a continuous change of site over a temperature range of at least $25^{\circ}C$ would be required and there is no obvious reason why this should occur.

Precipitation appears to be a reasonable supposition in vanadium as it has a higher impurity content than the Nb. Snowball$^3$ observed what he believed to be $V_{2}C$ in the as received
vanadium at an analysis of 314 p.p.m. In the purified condition 136 p.p.m. of C were found; thus it is not inconceivable that $V_2C$ precipitate.

Stanley and Werts\textsuperscript{29} reported that the damping peaks in vanadium ascribed to N decreased in height with time, which they took to indicate precipitation. This could also be explained by the N atoms taking up more stable positions in the lattice as the peak could be due only to N atoms on certain sites.

White and Woods\textsuperscript{47} did work on many transition metals and found a slope change for vanadium at about $-73^\circ C$ which they feel may be due to the presence of oxygen.

In recent work on $V$\textsuperscript{48} it was noted that 10 p.p.m. of H caused embrittlement in the vicinity of $-100^\circ C$. This could be linked with the attenuation minimum at this temperature. In doping with O it was found the yield load on bend tests was proportional to temperature down to about $-170^\circ C$, after which it became invariant with temperature. This was true for concentrations of O from 150 to 3100 p.p.m. This suggests again that there may be some connection between the slope change and the position of the interstitial on the lattice.

This investigation on vanadium suffered from too small a temperature range of testing. Ultrasonic testing revealed two minima in the attenuation vs. temperature curve, one in vicinity of $-170^\circ C$ and one in vicinity of $-100^\circ C$. As a slope change occurs at $-170^\circ C$ it would have been of interest to determine whether one also was to be found at $-100^\circ C$.

Changes in the depths of these minima did occur but
owing to the limited time available it was not possible to attain sufficient proficiency in the technique for even qualitative comparisons to be made.

It is of interest to note that the slope change noted by previous workers is an increase in slope, this investigation reports a decrease in slope at a lower temperature. Combined, the two would give a long and large reverse blip of the type reported in H doped Nb and to be discussed in the next section. Its size could be readily explained by the much higher interstitial content present in Nb.

C. The Hydrogen Anomaly in Nb.

Hydrogen is unique among the interstitials in that it retains its mobility down to very low temperatures. This is due in part to its small size but also the fact that it does not bond as the other interstitials do. Both Nb and V are exothermic occluders forming psuedo-metallic hydrides. In the concentrations involved in the high purity specimen H will be in solid solution. In the doped specimens H will still be in solution but a portion of it may be in the form of a psuedohydride which may be regarded as a loosely bonded compound.

H on O and T sites will be subject to stress, though at room temperature it is doubtful if those H atoms on T sites will be greatly stressed. As the specimen is cooled H, which will diffuse in any case, is losing thermal energy but gaining stress energy. As the temperature is approached at which H undergoes the O to T transition, some atoms will make the transition at a higher temperature due to having acquired sufficient
thermal energy. This gives stress relief and an attendant lowering of resistance. Thus it is found that the anomaly commences below about -100°C. and continues down to below -120°C. In this range the resistance is falling steadily to a maximum of about 1% below the extrapolated to the temperature. This may occur because H on T sites has commenced to strain the lattice. While the T site is larger, it is also spherically symmetrical and there are four atoms to be strained instead of two in the 0 site so the value of R rises quickly. Heating does not show the effect. This increase in R is more probably due to the previously noted step occurring due to other interstitials making the T→0 transition which occurs in this region.

D. Correspondence of Mechanical and Thermal Strain

It was noted the difference in temperature that the anomalies occurred in the yield point resistance curves could be possibly accounted for by corresponding thermal and mechanical strains.

1. Vanadium

Yield Point anomaly - -125°C.
Resistance anomaly - -170°C.

The hypothesis is that the effects occur each time at equivalent strains.
Mechanical:

Yield Point stress = 6.5 x 10^4 p.s.i.

At right angles to axis

Yield Point stress = 6.5 x 10^4 x .36

Strain = \frac{6.5 \times .36 \times 10^4}{1.9 \times 10^7} = 12.3 \times 10^{-4}

Thermal:

\alpha = 7 \times 10^{-6} \text{ inch/inch/°C.}

\Delta T = 45^\circ C

Strain = 7 \times 10^{-6} \times 45 = 3.15 \times 10^{-4}

Temperature would also be expected to have an effect - at the higher temperature less strain would be expected to affect the transition as greater thermal energy is available. However, the higher temperature anomaly is the mechanical one where the strain is approximately four times the thermal strain.

2. Niobium

Mechanical:

Yield Point stress = 4.2 \times 10^4 \text{ p.s.i.}

Young's Modulus = 1.85 \times 10^7 \text{ p.s.i.}

Strain = \frac{4.2 \times 10^4 \times .33}{1.85 \times 10^7} = \frac{1.4 \times 10^{-3}}{1.85} = 7.55 \times 10^{-4}

Thermal:

\alpha = 6.9 \times 10^{-6} \text{ inch/inch/°C.}

Strain = 1.38 \times 10^{-4}
The difference could be explained by a decrease in compressibility of the atoms as the temperature decreases.

This correspondence is possibly of significance but the discrepancy appears rather too large to be tolerated.

E. Hydrogen Embrittlement

Recent work by Baldwin and Adenis upon the effect of H on pure Fe has shown that when Fe containing H is quenched from the austenitic region it is subject to time dependent fracture. When H was in the state to produce this effect it was termed "noxious". In the absence of H (less than 1 p.p.m.) or when a H containing specimen had been slow furnace cooled no such effect was observed. H after the slow furnace cool was said to be innocuous. A ductile to brittle to ductile transition was obtained with H in the noxious state.

Figure 31. Percentage Reduction in Area versus Temperature for Fe containing H in the Two States.
After quenching H into position an anneal of one hour at 315°C was sufficient to render the H innocuous.

Rapid fracture of Fe containing noxious H produced the same strength as Fe containing no H. Slow testing in a tensile machine of the same material produced a reduction in area of only 27% whereas H free Fe had a value of 61.5% under the same circumstances.

This suggests the H is quenched onto O sites and occupies only T sites when allowed to come to equilibrium. The internal stresses arising from H occupying O sites results in hydrogen embrittlement. H doped Nb shows exactly the same behaviour, as does V. The brittle area shows an increase in yield stress corresponding to decrease in ductility. H present on O sites, straining the lattice, would undoubtedly increase the yield stress and decrease the ductility. As it leaves the O sites and occupies the larger T sites an increase in ductility and decrease in strength would come about.

To explain time dependent fracture on this model the diffusion of H must be invoked, particularly since the process occurring during annealing has an activation energy close to that of H diffusion in Fe.

Baldwin and Adenis propose the mechanism of Zapffe and Sims, or of Petch. The formation of voids near the fracture surface seems to bear this out, but it is not explained why they only occur there; on the mechanism of Zapffe and Sims one would expect voids throughout the specimen.

On the H leaving O sites mechanism it is proposed that
as the lattice undergoes thermal contraction there will come a point when the H becomes unstable in the 0 site and vacates it. It may then seek a T site or a dislocation array or some type of lattice imperfection. In the latter cases the presence of H is sufficient to cause microcracking. As the crack enlarges more H will find low energy accommodation in it and lead to increased cracking. This may be accomplished in the manner proposed by Petch. H on T sites, where the interstitial is under less strain and is symmetrically surrounded by lattice atoms, is under less pressure to move and tends to remain where it is.

When a stress is applied to a b.c.c. metal containing H in the 0 sites stress activated diffusion will cause H movement to occur at higher temperatures and to move faster. Also microcracks will enlarge and be more numerous so that the H will have a shorter distance to cover before helping to initiate the spread of the crack. If the deformation is accomplished sufficiently rapidly H will not have time to diffuse to the microcrack areas and thus a ductile fracture will occur.

As H diffuses towards the cracks and becomes absorbed therein there will be left in the lattice regions of metal comparatively free of H which will deform plastically as the cracks open on failure of the specimen. In this manner the voids found in the fracture region are formed. Although H will diffuse to microcracks in regions away from the fracture the vigorous deformation accompanying fracture is required to pull the cracks into voids.
F. Application to the Results of Harding on High Purity and Doped Single Crystals of Niobium


These showed an anomaly in the yield stress versus temperature curve at about $-105^\circ C$ which indicate an increase in strength of the material. This is considered due to the interstitials O and N making the $T \rightarrow 0$ transition in this vicinity and the resulting increase in the associated stress centre providing greater dislocation locking.

Ductility versus temperature curves do not show any appreciable effect at these low concentrations of interstitials.


These exhibited a yield stress anomaly around $-120^\circ C$, again due to O and N. The temperature is lowered because of interference with the $T \rightarrow 0$ transition from H already present on O sites.

![Figure 32](image_url)  
**Figure 32.** Recovery of Ductility of H doped Nb at Low Temperatures.

![Figure 33](image_url)  
**Figure 33.** Resistance vs. Temperature for N doped Nb.
The recovery of ductility demonstrated by H doped material is due to thermal contraction and probably stress inducing H to leave O sites. The R. vs. T. curve for H doped Nb (Figure 33) shows stress relief beginning about -100°C, at which temperature recovery of ductility commences and continues to -170°C. when presumably all, or nearly all, H has left the O sites and the curve follows the form which it would possess were no H present.

3. **Oxygen Doped Specimens**

The yield stress anomaly occurs at -110°C for 800 and 2000 p.p.m. O, and at 2000 p.p.m. of O a ductility minimum occurs at -140°C. This indicates that strain energies at this high concentration of O are so great that the bond energy is overcome and some O leaves the O site. Alternatively, at the high lattice strains involved precipitation may occur.

At 800 p.p.m. the % Reduction in Area commences to decrease sharply at -100°C. At lower concentrations this would occur at lower temperatures, say about -110° to -120°C., indicating the O anomaly should occur hereabouts.

4. **Nitrogen Doped Specimens**

The yield stress anomaly occurs at -110°C for 70 and 85 p.p.m. of N. In both instances ductility falls off at -100° to -110°C. This implies that the higher temperature step or blip is due to N and lower to O.

Harding also reported that on quickly warming a specimen from liquid N₂ temperature to -146°C and allowing thermal
equilibrium to be established a yield stress value 17% higher than was usual was obtained. This is thought due to the fact that always there is a statistical distribution of interstitials between 0 and T sites. The rapid heating disturbed the equilibrium and some interstitials are left on 0 sites which would occupy T sites at equilibrium. The resulting hardening effect increases the strength of the material.
VI CONCLUSIONS

1. No effect attributable to dislocation movement was found in measurements of electrical resistance.

2. Anomalies in the region of $-120^\circ C$ were found which were ascribed to $O$ and $N$; the anomalies were indicative of an increase in resistance.

3. Anomalies were found in cooling curves, rarely in heating curves and tended to decrease in magnitude on cycling, indicating some sort of equilibrium was concerned.

4. Hydrogen doping showed hydrogen to behave differently, producing anomalous behaviour commencing at about $-100^\circ C$ and indicating a decrease in resistance occurred.

5. The mechanism proposed concerned the occupancy of the two available interstitial sites, $O$ and $T$, by oxygen, nitrogen and hydrogen. The mechanism was capable of explaining the mechanical phenomena of hydrogen embrittlement, time dependent fracture, low temperature recovery of ductility and the yield stress anomaly.

6. An increase in resistance occurred on the heating portion of the cycle and when the specimen was left to stand overnight. This could have been due to the $T \rightarrow O$ mechanism or to others such as micro-precipitation or small domains of high order.

7. High purity single crystals of vanadium exhibited a change in slope in the electrical resistance versus curve
temperature curve at \(-170^\circ C\) and was more in evidence on cooling rather than on heating. The effect was not explainable on the basis of this investigation.

8. Ultrasonic testing of single crystals of high purity vanadium showed minima in the attenuation curves in the vicinity of \(-100^\circ C\) and \(-170^\circ C\).
VII  RECOMMENDATIONS FOR FUTURE WORK

It is felt that this work should be repeated measuring resistivity rather than resistance; an extended temperature range would also be advantageous - below $-140^\circ C$ for Nb and above $-100^\circ C$ for V.

The effect of doping with oxygen, nitrogen and carbon should be determined, including measurement of residual resistance.

Extended work in the ultrasonic field is also recommended, particularly as it could be put on a quantitative basis.

Other b.c.c. metals tested in this manner would provide valuable comparative data.
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IX. APPENDIX
APPENDIX

I  Change in Resistance of Specimen due to Thermal Contraction

\[ \text{Nb - Specimen 8} \]

\[
\text{Length} = 1.304''
\]

\[
\text{Radius} = .0475''
\]

\[
\alpha = 7.1 \times 10^{-6} / ^\circ C
\]

Temperature drop -90 to -145\(^\circ\)C = 55\(^\circ\)C

\[
R = .0475 \times 55 \times 7.1 \times 10^{-6} \approx 19.25 \times 10^{-6}
\]

Increase in R = \( \frac{.0475^2 - \frac{.0475 - 19.25 \times 10^{-6}}{.0475^2}}{100\%} \)

\[= .09\%
\]

Considering the Length - R decreases.

\[
\Delta l = 1.304 \times 55 \times 7.1 \times 10^{-6}
\]

\[= 71.5 \times 10^{-6}
\]

R decreases \(71.5 \times 10^{-4}\)%

\[= .006\%
\]

Thus thermal contraction as such may be regarded as having negligible effect upon the electrical over the temperature range considered.
II Estimated Experimental Error

A. Niobium

Relative accuracy of temperature measurement = ± .2°C

Equivalent error in R

\[ \frac{.2 \times 1 \times 100}{2.0 \times 5} = .200\% \]

Error in current measurement:

Error in standard resistance ≈ 0

"" potential measurement = \[ \frac{\pm 4 \times 100}{6500} = .060\% \]

Error in measurement of potential drop across specimen

\[ \frac{1 \times 100}{2000} = .050\% \]

Total Error

\[ = .31\% \]

The actual relative error will be considerably smaller as compensation will occur.

B. Vanadium

An accurate estimate is not possible, scatter of points on the curves is the only indication which can be used.