RICE UNIVERSITY

ELECTRICAL RESISTIVITY MEASUREMENTS
OF DEFORMED MOLYBDENUM CRYSTALS

by

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ABSTRACT

Single crystals of molybdenum were deformed in tension at 195°K, 273°K, 373°K and 473°K. The influence of deformation temperature and intermediate annealing treatments at 473°K and 422°K on the electrical resistivity was investigated. All resistivity measurements were made at 4.2°K. The results indicated that:

(1) Point defects are created during deformation at 195°K and 273°K,

(2) The rate with respect to strain at which these defects are produced is an inverse function of the deformation temperature,

(3) Some or all of the point defects are mobile at 422°K and either diffuse together or to dislocations, and

(4) This movement of the point defects does not affect the flow stress.

No definite conclusion was reached on the dislocation model responsible for the results.
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INTRODUCTION

The total electrical resistivity of a metal can be conveniently separated into three components:

\[ \rho_{\text{total}} = \rho_{\text{thermal}} + \rho_{\text{physical}} + \rho_{\text{chemical}} \]

where \( \rho_{\text{thermal}} \) is the resistivity due to scattering of conduction electrons by the lattice vibrations or phonons, \( \rho_{\text{physical}} \) is the contribution due to physical defects, and \( \rho_{\text{chemical}} \) is the contribution due to chemical impurities in the metal. Except for the very purest metals containing no physical defects, \( \rho_{\text{thermal}} \) is negligible compared with \( \rho_{\text{physical}} \) and \( \rho_{\text{chemical}} \) at liquid helium temperatures so that \( \rho_{\text{He}} \approx \rho_{\text{physical}} + \rho_{\text{chemical}} \). In determining the relative magnitudes of \( \rho_{\text{physical}} \) and \( \rho_{\text{chemical}} \), the internal structure and chemical content of the metal must be known. For test specimens which were prepared under similar conditions, the internal structure should be approximately the same. With this assumption, the \( \rho_{\text{He}} \) of the specimens in the undeformed state should vary only with the chemical content. This assumption is usually made when \( \rho_{\text{He}} \) is used to investigate purity.

When a test specimen is subjected to mechanical and/or thermal treatments, variations in \( \rho_{\text{He}} \) are a measure of the change in the internal structure of the specimen. By simple resistivity measurements alone it is not possible to determine whether the change in \( \rho_{\text{He}} \) is due to:

1. Change in dislocation structure, or
2. Change in vacancy and/or interstitial concentration and arrangement, or
3. Combination of (1) and (2).
Normally the increase of $\rho_{He}$ during deformation is assumed to be a combination of (1) and (2), while the explanation for any change in $\rho_{He}$ during a thermal treatment depends upon the temperature of the treatment. When the thermal treatment does not change the mechanical properties of the material, the change in $\rho_{He}$ is usually assumed to be due to (2). If the thermal treatment changes the mechanical properties, the change in $\rho_{He}$ is considered due to a combination of (1) and (2).

With the above considerations and limitations in mind, the electrical resistivity of deformed molybdenum single crystals has been investigated. It was hoped that this investigation would be of help in determining the mechanism controlling the low-temperature plastic flow of molybdenum and BCC materials in general. Deformation temperatures of 195°K, 273°K, 373°K and 473°K and annealing temperatures of 300°K, 422°K and 473°K were used in this investigation.
SURVEY OF PREVIOUS INVESTIGATIONS

There have been many investigations into the controlling mechanism in the plastic flow of metals. Gregory and Rowe (1962) have an excellent review of the literature on the work hardening mechanisms in metal crystal and conclude that specific hardening mechanisms reported in the literature can be divided into three general classifications:

I. Interaction between stress fields of dislocations as the dislocation density increases with strain,

II. Dislocation intersection mechanisms, as dislocation density increases with strain, and

III. Exhausion of sources.

Conrad (1961) evaluated the activation energy $h^*$, activation volume $v^*$ and the frequency factor $\dot{\sigma}_0$ for various irons and steels from data in the literature. The activation volume $v^*$ represents the product of the three quantities, $b$, $t$ and $g$, where $b$ is the Burgers vector, $t$ is the average distance between pinning points, and $g$ is the activation distance. He considered as possible controlling mechanisms:

1. Breaking away from a Cottrell atmosphere,
2. Overcoming the Peierls Stress,
3. Intersection of dislocations (cutting the forest),
4. Cross slip, and
5. Production of vacancies or interstitials at jogs in dislocation with screw components.

He concluded that the dislocation mechanisms for which there was closest agreement between theoretical calculations and experimental data was overcoming the Peierls Stress. Conrad eliminated the production
of vacancies or interstitials at jogs in dislocations with screw components as a source of hardening because of three main reasons:

1. Experimentally determined activation energy is only 1/3 the value expected,
2. Dislocations in silicon-iron lie along close-packed directions, suggesting a high Peierls stress, and
3. No change in $\nu^*$ with strain was observed.

Gregory and Rowe (1962) investigated the strain hardening of commercially pure polycrystalline niobium (columbium) in the temperature range 77°K to 373°K. Tensile tests were used to evaluate the activation volume by incremental strain rate changes at constant temperature and the activation energy by temperature changes at constant strain rate. Dislocation structures in the deformed niobium were examined by electron microscopy. The activation volume was found to decrease with strain and increase rapidly with temperature near 300°K. These activation-volume changes with temperature and strain were attributed to $l$, the average distance between pinning points, and $g$, the activation distance. They concluded that their results suggested a specific work-hardening mechanism of nonconservative motion of vacancy jogs in screw dislocations combined with a "debris" mechanism.

Gregory and Stroh (1963) in a continuing study on niobium determined the internal stress from electron microscopy of pure niobium sheet by the formula

$$\tau_g = 0.2 \ G b (\rho)^{1/2}$$

where $G$ is the shear modulus, $b$ is the Burgers vector, and $\rho$ is density of dislocations which are roughly parallel to the mobile dislocation held up at the energy barrier. Using values of $\tau_g$ obtained in this
manner, they found the activation energy to have values roughly 3.5 times greater than the value of the activation energy determined in the manner suggested by Conrad (1961). Their data indicated no reason to change their conclusion (1962) on the rate controlling mechanism.

Youngblood (1963) used the activation \( v^* \) as a parameter to investigate the mechanism governing the plastic flow of molybdenum single crystals over the temperature range 120°K to 500°K. To eliminate any uncertainty in the slip plane or direction, Youngblood tested in direct shear on the (110) plane in the [\( 1\bar{1}1 \)] direction. The measurement of \( v^* \) was made by changing strain rate incrementally and observing the stress change in accordance with

\[
v^* = kT \left( \partial \ln \sigma / \partial T \right)_T,
\]

Youngblood found that \( v^* \) decreased with increasing strain (Fig. 1) and that \( v^* \) increased drastically with temperature above approximately 300°K (Fig. 2). Decreases in \( v^* \) were attributed to decreases in \( l \), the distance between pinning points. Broad yield points (Fig. 3) were also observed when the temperature was suddenly changed from below 300°K to above 300°K. From these results, Youngblood concluded that the rate-controlling process at low temperature is the addition of a new vacancy, by thermally-activated, non-conservative movement of a jog, onto a string of vacancies (produced by previous non-conservative jumps of the same jog). In determining the activation energy, Youngblood, following the procedure used by Conrad (1961), found that it was smaller than expected for this type of mechanism. When determining the activation energy in this manner, the internal stress is assumed to be independent of temperature, except through small changes of the shear modulus. Youngblood points out that the broad yield points (Fig. 3), indicate
that the internal stress may change greatly with temperature. This would give an erroneous value for the activation energy calculated with the internal stress assumed to remain constant. If one were to assume that the internal stress does change with temperature, and the results obtained by Youngblood using the method suggested by Conrad are in error by the same factor as Gregory and Stroh (1963) found for niobium, the activation energy would be in close agreement with the energy required to form a vacancy. The only justification for this analogy is the similar behavior of the activation volume with temperature in both Mo and Nb. Youngblood postulated that the dramatic rise of the flow stress at low temperature is due to the lack of nonconservative motion of jogs in screw dislocations. The rapid rise in $v^*$ about $300^\circ$K was attributed to the jogs beginning to move conservatively and thereby increasing $v^*$ by increasing $l$, the average distance between pinning points.

Buehler and Kunzler (1961) investigated the change in $\frac{R_{4.2}}{R_{273}}$, which is proportional to the $\rho_{He}$, during zone-refining and thermal treatment of molybdenum. Samples of high-purity molybdenum of known mechanical history were heated to various temperatures between $800^\circ$C and their melting point. For thermal treatments below $800^\circ$C, they could detect little changes in resistance. This suggested that the original material was annealed free of most strains, as might be expected from the method of its preparation. An increase in the number of passes of zone refining was found to increase the purity of the material with a minimum $\frac{R_{4.2}}{R_{273}}$ ratio of .0003 for four passes. One pass of zone refining produced a ratio of about .001 at the lead end and .0015 at the tail end of the samples.
Martin (1957) investigated the annealing of cold worked polycrystalline molybdenum by measuring changes in the resistance at liquid nitrogen temperature. Evidence that a large decrease of resistance occurred between 100°C and 180°C with a constant activation energy, suggested that the annihilation of a fundamental imperfection, such as a certain kind of point defect, was being observed. Makin, in a private communication to Martin, has shown that there is no measurable change in the yield point at room temperature when heavily cold-worked wires have been annealed for 280 min at 175°C. Furthermore, the greater the degree of cold-work the larger was the 100-180°C step compared with the rest of the annealing curve.

Lawley, Van den Sype and Maddin (1962) investigated the tensile properties of zone-refined molybdenum crystals in the temperature range 4.2-373°K. Their Knoop hardness results indicated that the impurity content of the material decreased with the number of passes during zone refining, while spectrographic analysis indicated no systematic difference in impurity content after 1 and 6 passes. It was concluded that spectrographic analysis was not sensitive to variations in the very low impurity content. Considering the work of Buehler and Kunzler (1961), both the vaporization of impurities and true zone refining occur during zone-refining. Lawley, Van den Sype and Maddin also point out that the observed variation with strain in the reversible flow stress, which is the change in flow stress with an abrupt change in temperature, is inconsistent with the idea of a temperature-dependent flow stress based on an intrinsic lattice friction.
Seitz (1952) has reviewed the way point defects may be generated by moving dislocations. According to Seitz, vacancies and interstitials may be created in four ways:

(1) By local heating of the lattice in the immediate vicinity of the dislocation as it moves through the lattice and absorbs energy from the applied stress field.

(2) By purely geometrical means in which dislocations of opposite sign move in neighboring planes annihilate one another and produce a row of vacancies. The nonconservative motion of a jog, which would produce either vacancies or interstitials, would be another geometrical means of creating point defects.

(3) As a result of instability of the in-phase motion of atoms during passage of a dislocation.

(4) As a result of large, transient thermal pulses in regions where dislocations annihilate one another and produce a large lattice disturbance.

It should be noted that these methods of generation do not necessarily lead to the effective dispersal of single vacancies or interstitials. Intense local heating in the lattice, due to shortening of a dislocation line in a high stress field or to annihilation of pairs of dislocations of opposite sign, can cause dispersion of the defects produced.

Broom (1954) has reviewed lattice defects and the electrical resistivity of metals. He discusses the effect of various lattice defects on the electrical resistivity and the various experimental methods (quenching, irradiation, deformation) used to introduce lattice defects into the material being investigated.
Molenaar and Aarts (1950) measured the relative change of resistivity ($\frac{\Delta \rho}{\rho}$) with plastic deformation at liquid air temperature, with an intermediate anneal at room temperature or above, for copper, silver and aluminum. The principal qualitative results were:

1. The increase in resistivity produced during the initial deformation is at least partly eliminated by the annealing treatment.
2. The stress-strain curve does not appear to be altered by the annealing treatments.

They concluded that the mechanism producing hardening by cold work was at least in part different from that producing the change in resistivity during the anneals.

Pry and Hennig (1954) showed that the increase in resistivity that remains in deformed copper after a room temperature anneal is closely related to the dislocation structure and therefore to the stress which must be applied to continue the deformation, and that within certain limitations, the stress during deformation is determined, independent of previous deformation history, by the instantaneous measurement of electrical resistivity, temperature and strain rate. Their results varied from those of Molenaar and Aarts (1950) in that the stress-strain curves were appreciably altered by the room temperature anneal. Pry and Hennig concluded that either some dislocation annealing takes place in copper at room temperature, or the defects which decay at this temperature do affect the strength, at least indirectly.

Berghout (1956) also investigated the relation between the electrical resistivity and the yield strength of deformed copper. He concluded that the single-valued relation between the extra resistivity due to dislocation and yield stress suggested by Pry and Hennig (1954) does not exist in the general case.
Blewitt (1953) found that when copper, which had been deformed at 78°K, was annealed at 300°K for 16 hours, the electrical resistivity was reduced by an amount which was dependent on the amount of deformation. Upon reloading the sample, a small but detectable increase in the yield point was observed which suggested a definite strain aging phenomena. This phenomenon was observed only in those regions where a recovery of electrical resistance was observed.

Makin and Gillies (1956) found that annealing neutron-irradiated molybdenum in the temperature range where vacancies are expected to become mobile leads to a slight increase in the hardness of the irradiated metal. Annealing at 473°K caused the yield stress of a specimen deformed at room temperature to be increased by about 2% (i.e. by about 2000 psi) and produced a yield point with a stress drop of about 1000 psi.

Aust and Maddin (1956) measured changes in the resistivity of single crystals of molybdenum due to bending through various angles. The resistance measurements were made at room temperature. Crystals which were bent at room temperature showed a rapid increase in resistivity after about a 12° bend. The beginning of this rapid rise in resistivity was found to coincide with the first appearance of intersecting slip bands. They interpreted this result in terms of a high concentration of "frozen-in" vacancies and piled up groups of dislocations formed by crossing dislocations.

Lawley and Gaigher (1963) examined zone-melted single crystals of molybdenum by thinfilm electron-transmission microscopy. The dislocation density was observed to be higher and more uniformly distributed for deformation at lower temperatures. They suggested that movement of
screw dislocations is controlled by a thermally-activated conservative
movement of jogs.

Keh (1962) found that the total number of dislocations was, for
decarburized vacuum-melted iron, a function only of the strain. He
concluded that the dislocation arrangement and not the number of disloca-
tions was a function of the deformation temperature.
EXPERIMENTAL PROCEDURE

A. General

All tests were conducted on single crystals of molybdenum grown in an electron beam melting apparatus built by Youngblood (1963). Test crystals were oriented as closely as possible to a tensile axis which gave maximum resolved shear stress on the (110) plane in the [111] direction.

The resistances, diameters and gauge lengths of all the crystals were determined before and after deformation. All resistance measurements were made at 4.2°K.

The first series of tests consisted of measuring the resistance after various amounts of deformation at 195°K, 273°K, 373°K and 473°K. In a second series of tests, the crystals were deformed at 195°K and 273°K, annealed at 423°K and 473°K, and deformed again at 195°K and 273°K with the resistances being measured before and after each deformation and annealing treatment. During the third series of tests, the crystals were deformed at 195°K, annealed at 473°K and then deformed at 473°K with the resistance being measured before and after each deformation and anneal.

B. Impurity Determination

Starting material for all crystals was obtained from General Electric Company, Lamp Metals and Components Department, Dover, Ohio. This material was purchased in the form of 1/16" diameter rods under the same specifications used by Youngblood (1963) for 1/8" diameter rods. No effort was made to determine if there was any variation in the
impurity content between the two different diameter rods. The impurity analysis furnished with the 1/8" diameter rods is as follows:

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<tr>
<td>A1 .001</td>
<td>Ni &lt; .001 Sn &lt; .001 Oxygen 12 ± 5 ppm</td>
</tr>
<tr>
<td>Ca .002</td>
<td>Cu &lt; .001 Co ND Nitrogen 4 ± 4 ppm</td>
</tr>
<tr>
<td>Se .002</td>
<td>W .004 Ag ND Hydrogen 2 ± 2 ppm</td>
</tr>
<tr>
<td>Fe .001</td>
<td>Mn &lt; .001 Pb ND</td>
</tr>
<tr>
<td>Cr &lt; .001</td>
<td>Mg &lt; .001 Zr ND</td>
</tr>
</tbody>
</table>

Due to the inconclusive results obtained by Youngblood (1963) and by Lawley, Van der Sype and Maddin (1962), the impurity content of the single crystals, as given by spectrographic analysis or hardness tests, was not determined.

The effect on the electrical resistivity of the number of passes when zone refining a single crystal was investigated by measuring the resistance of one, two, three, four and five pass 1/8" diameter crystals.

All of the 1/16" diameter crystals tested were subjected to 5 passes in the electron beam melter, at a vacuum less than 3 x 10^-5 mm Hg. The vacuum and travel rate for the last pass for all crystals tested is shown in Table I.
C. Diameter and Gauge Length

The diameters and gauge lengths of the crystals were measured optically with a Wilder Micro Projector. Measurements of the diameters were taken at 1/8" intervals along the length of the crystals with the procedure being repeated after rotating the crystals 90° about the tensile axis.

An error range of ±0.0005" on each measurement of the diameter and the gauge length yields an accuracy of approximately 2% on each measurement of the diameter and 0.05% on the gauge length measurement. Since the diameter was measured approximately fifty times on each specimen, the error in the determination of the average diameters should be less than 2%.

D. Strain

The crystals were strained in tension in an Instron Model TT-C-L tensile testing machine. Templin-type grips were used to hold the crystals while straining with the amount of elongation being determined by optical measurement of the distance between potential leads. The grips were spherically seated on the ends to prevent introduction of bending movements into the crystals.

E. Temperature Control

An isopentane bath with dry ice was used for the tests at 195°K, with an ice-water bath being used for the tests at 273°K. The temperature variation for the 195°K and 273°K tests was ±2°C. A Crisco oil bath and the heat exchanger developed by Youngblood (1963) were used in deforming the crystals at 373°K and 473°K with variations of ±2°C experienced during deformation at these temperatures.
For all the anneals, a Fisher Unified Constant Temperature Bath with a Halikainen Thermotrol Model 1053A controller was used with the oil in the bath being the same as above. It was possible to control the temperature to within ±0.5°C during the anneals.

F. Orientation

The orientation of all crystals was determined by taking Laue back-reflection x-ray photographs. From these photographs, the orientation could be determined within about 2°.

To eliminate some of the scatter in the results due to orientation effects, all crystals tested were grown with approximately the same orientation. The orientation chosen was the one with the normal to the (110) plane and the [1$\bar{1}$1] direction as close as possible to 45° from the tensile axis and in the same plane with the tensile axis as shown in Fig. 4. Fig. 5 shows the orientation of all crystals in the stereographic triangle.

G. Resistance

An a.c. bridge was used to measure the resistance of the single crystals. The circuit diagram of this bridge is shown in Figs. 6a, 6b, and a parts list is given in the Appendix. By determining the ratio of the voltage drop across the test specimen to the voltage drop across the calibrated shunt, the resistance of the test specimen could be determined. Since the same current passes through both the test specimen and shunt, this voltage ratio was independent of the current. The voltage ratio was determined by comparing the test specimen voltage drop to some fraction of the voltage drop across the shunt, with the
fraction of the shunt voltage drop used in this comparison being determined by the position of the Helipot slide wire. These two voltage drops were used as the input to a low noise solid-state differential amplifier.

By putting the output from this amplifier on the vertical plates of an oscilloscope and line voltage on the horizontal plates, the balance point could be detected as a horizontal trace on the oscilloscope. At balance the resistance of the test specimen was given by the following formula:

$$R_{test} = \frac{\text{Dial Reading on Helipot}}{25} \times \frac{1}{10} \times R_{shunt}$$

A change in the resistance of $5 \times 10^{-8}$ ohms could be easily detected.

All resistance measurements were made with test crystals at liquid helium temperature. In order to conserve liquid helium, a lucite crystal holder was designed which allowed the test specimen to be lowered into the liquid helium storage dewar. This eliminated any helium loss due to transferring helium from one container to another.

The crystal holder for lowering the crystal into the helium was designed so that a dummy sample could be held at the same time (Fig. 7). This allowed the resistance of the dummy sample to be measured concurrently with each crystals. This arrangement provided a check on the constancy of the measuring conditions. Twisted 30 gauge teflon-coated wire was used for the potential and current leads on the crystals holder. The leads were brought to the center of the crystals before being untwisted. By using four potential leads, two to each end, with the two leads going to the same end of the crystal on opposite sides of the crystal, the amount of spurious potential could be reduced. Twisted 22 gauge teflon-coated wire was used throughout the rest of the circuit
to eliminate spurious readings and noise. A filter was also used to reduce noise, and the circuit diagram for it is shown in Fig. 8.

To aid in the detection of the balance point on the oscilloscope, a "phase compensator" was used in the circuit. This "phase compensator" consisted of two concentric lucite rings with the current leads to the specimen on one ring and the potential leads to the specimen on the other ring. By changing the relative position of the two rings, the shunt and test specimen voltage drops could be brought into phase. It was found that this "phase compensator" introduced no detectable error.

Potential leads were attached to the specimen by spot welding a short length of nickel wire to the single crystal and soldering the copper wires to the nickel. The current leads were incorporated into the clamps which held the specimen in the holder.

The change in the resistance due to geometrical changes during strain were compensated for by assuming constant volume with deformation of the test specimens.
EXPERIMENTAL RESULTS

The resistivity of all the crystals tested in the undeformed state is given in Table II. It will be noticed that there is a variation in the resistivity by a factor of about three. Since all crystals were 5-pass zone-refined crystals and should, therefore, be of about the same impurity content, this variation in the resistivity was unexpected. When growing 1/16" diameter crystals, it is very difficult to see clearly the molten zone, referred to by Youngblood (1963), and still produce a crystal of uniform cross-section. If the molten zone on the 1/16" diameter crystal becomes large enough to be easily detected, the probability of melting through or of developing a nonuniform crystal becomes very great. Due to this difficulty and in view of the wide variation in the resistivities of the crystals produced, the crystals may not have been heated to liquefaction and melted during all passes in the zone-refining equipment. To check this explanation, five 1/8" diameter crystals were grown with from 1 to 5 zone passes. With the 1/8" crystals the molten zone can be seen easily, and the number of passes during which the crystal is actually molten can be determined with certainty. The resistivity of the 1/8" crystals is given in Table III. It shows that the resistivity varies by about a factor of three from the crystal with the least number of passes to the crystal with the greatest number of zone passes. It would seem that the most logical reason for the variation in the resistivity of the undeformed 1/16" diameter crystals is that the crystals were not completely molten during every pass in the zone refining equipment.
In Fig. 9, the ratio of the resistivity after deformation to the resistivity before deformation is plotted versus \( \frac{\Delta L}{L} \) for deformation temperatures of 195°K, 273°K, 373°K and 473°K. From these curves it can be seen that the rate of increase of the resistivity is greater, the lower the temperature of deformation.

Although a linear relation between \( \frac{\Delta \rho}{\rho} \) and strain was considered to describe the experimental results best, this conclusion may be in error. Examination of Fig. 9 indicates that:

1. A curve with positive curvature would fit the data points of MO 269 and MO 276 deformed at 195°K, and
2. A curve with negative curvature would fit the data points of MO 261 deformed at 273°K.

Since the same curvature was expected for both deformation temperatures, a linear relation between \( \frac{\Delta \rho}{\rho} \) and strain was assumed correct; the deviation from this linear relation was attributed to scatter in the data.

Figs. 10 through 14 show the variation of the resistivity ratio versus strain with intermediate anneals of 473°K for deformation temperatures of 195°K and 273°K. It is evident from these curves that annealing at 473°K lowers the resistivity of the crystals but does not seem to change the rate at which the resistivity changes with strain.

The variation of \( \rho_{\text{strained}}/\rho_{\text{unstrained}} \) with strain at a deformation temperature of 195°K is represented in Fig. 15, with an anneal at 422°K.

Two crystals were partially deformed at 195°K, annealed at 473°K until the resistivity ceased to decrease with time, then deformed at 473°K. The results of these tests are shown in Figs. 16 and 17.

When a deformed crystal is annealed and the resistivity decreases the cause of this decrease in resistivity is usually attributed to the
annihilation of the point defects if the mechanical properties of the metal are not changed. To determine if the flow stress of a single crystal of molybdenum deformed at 195°K is changed by an anneal at 473°K, the stress-strain curve for deformation at 195°K with intermediate anneals at 473°K was determined (Fig. 18). It can be seen from this curve that there was no noticeable change in flow stress after the anneal. This agrees with the results reported by Martin (1957) for polycrystalline molybdenum after anneals at 448°K.
DISCUSSION OF RESULTS

The decrease in the resistivity for annealing treatments at 473°K without a change in the flow stress indicates that:

(1) The structural defects being annealed out are point defects which do not affect the flow stress, and

(2) The dislocation structure is not changed by these annealing treatments.

This decrease in resistivity without a change in the flow stress is in agreement with the results obtained by Martin (1957) for polycrystalline molybdenum and is analogous to the results of Molenaar and Aarts (1950) for polycrystalline copper.

The reason for measuring the resistivity of molybdenum was to find how its internal structure changed during deformation and low temperature annealing. This was done to compare the results to the predictions of various proposed models for the controlling mechanism in the low temperature deformation of molybdenum and BCC metals in general. Since the correct model is generally believed to be one of the five discussed by Conrad (1961), mentioned earlier, only these models will be considered here.

The Cottrell atmosphere model fails to prescribe the movement of the dislocations after they break away from their "clouds"; therefore, no useful comparison between the results of these resistivity tests and predictions based on the Cottrell atmosphere model can be made.

Consider then the mechanism suggested by Youngblood (1963), where the flow stress at low temperature is controlled by the nonconservative motion of the vacancy-producing jogs in screw dislocations. In this
model the amount of conservative movement of jogs is very small below 300°K, but increases rapidly above 300°K. In this way Youngblood accounted for the behavior of the activation volume with temperature shown in Fig. 2. The factor in the activation volume \( V^* = b\gamma \) that increases with temperature is assumed to be \( \ell \). With this model the resistivity due to vacancies should increase more rapidly with strain as the deformation temperature is lowered, since the number of vacancies produced per unit strain is proportional to \( 1/\ell \). From Fig. 9 it is evident that the total resistivity did increase more rapidly with strain as the deformation temperature was lowered. Considering the electron-microscopy work of Lawley and Gaigher (1963) on the deformed structure of molybdenum, it could be argued that the more rapid increase of resistivity at the lower temperatures is due to the more dense distribution of dislocations throughout the bulk of the material. It is generally accepted that the resistivity will be greater with an increased number of dislocations, and this might explain the inability to reduce, by annealing at 473°K the resistivity ratio of a crystal deformed at 195°K to the value of a crystal deformed at 473°K. The above resistivity results could support the argument that the internal stress at high temperature is not characteristic of the internal stress at low temperature. Even if one assumes that part of the increased resistivity for the lower deformation temperature is due to the denser dislocation arrangement, the decrease in the resistivity during the anneals should still vary inversely with the deformation temperature for this model. This would be the case because a larger number of vacancies is produced during deformation at lower temperature, and there would, therefore, be more defects to be eliminated during the anneals. The dislocation
structure did not change during the anneals, and any drop in the resistivity during this process can be attributed to the migration of the vacancies. Fig. 14 shows that the amount of resistivity eliminated is greater after deformation at 195°K than after deformation at 273°K. These results are, therefore, in agreement with the above predictions for this model.

Youngblood also attributes the decrease in the activation volume with strain to a decrease in $t$. If $t$ decreases with strain, the rate at which vacancies are produced with strain should increase. Therefore, at higher strain, a more rapid increase of the resistivity due to vacancies should occur. As can be seen from Fig. 9, the total resistivity exhibits a linear increase with strain. It is quite possible that the rate of resistivity change with strain due to vacancies (does increase with deformation, but the magnitude of this increase) is small and overshadowed by the resistivity change due to the dislocations. This possibility cannot be disregarded, since the resistivity due to vacancies, after deforming about 4 per cent at 195°K, is only 40 per cent of the resistivity increase caused by dislocations. The relative values are illustrated in Figs. 16 and 17. With about 40 per cent of the increase in resistivity due to vacancies, a higher rate of production of vacancies by jogs could be nullified by a lower rate of resistivity change due to dislocations. In fact, it seems reasonable that the resistivity due to N dislocations would not be N times the resistivity due to one dislocation, and the rate of resistivity change due to dislocations would decrease with increasing strain. Considering this possibility, the linear increase in resistivity with strain cannot be considered as strong evidence against the model proposed by Youngblood.
In Youngblood's model the flow stress is inversely proportional to the activation volume. There is no change in the activation volume during the low-temperature annealing treatments, since there is no change in the flow stress. It is generally assumed that dislocations act as sinks for mobile vacancies, and when a vacancy diffuses to an edge dislocation, it forms a jog in the dislocation. If this vacancy-formed jog is considered a pinning point, the distance between pinning points will be reduced by this vacancy-to-dislocation diffusion, and the activation volume will be decreased. This would contradict the above results. With more jogs on the dislocations after an anneal, the rate at which the resistivity increases with strain would be greater just after an anneal than just before. Figs. 10 through 13 indicate that this behavior was not observed. It is possible that the vacancy-formed jogs are not structurally identical to the intersection formed jogs, and the vacancies diffuse down the core of the dislocation to the surface of the crystal. If such core diffusion occurs, no change in the flow stress or in the slope of resistivity versus strain curve would be expected.

There is also the possibility that the vacancies do not diffuse to the dislocations, but, instead, migrate together to form clusters. By creating larger but fewer clusters, the resistivity could be lowered. This would not affect the density of jogs. Therefore, the flow stress, according to this model, would be unaltered. It seems reasonable, nevertheless, that there would be some hardening effect when the dislocations move through these clusters. However, if this hardening takes place, the effect is small and undetected. Vacancies could diffuse to, and annihilate, interstitials, but because of the low concentration of interstitials, the effect would be of no consequence.
by Pearce. A Fortran II program for the solution to the set of equations (30) for a 25 step distribution is given in Appendix A.
In the Peierls model, the flow stress is directly determined by the crystal lattice, rather than the dislocation structure. This model assumes that the effective stress, plus the thermal energy, must supply sufficient energy to allow the dislocations to overcome the Peierls energy barriers and thus enter the next equilibrium positions. Movement of jogs in this model is considered an effect, instead of the cause, of the variation in the flow stress with temperature. At low temperature the flow stress increase is caused by the decrease in the thermal contribution in the energy required for pushing the dislocations over the Peierls energy barriers. This increased flow stress could also cause more dislocations to move nonconservatively, thereby creating vacancies and/or interstitials. Since more vacancies and/or interstitials could be produced, the rate of resistivity increase with strain could become greater as the deformation temperature is lowered. The results shown in Fig. 9 illustrate the above behavior. This model would then predict an inverse relation between deformation temperature and the decrease in resistivity during an anneal at 473°K. These predictions agree with the results shown in Fig. 14.

The Peierls stress model places the same restrictions on the vacancy-to-dislocation diffusion as was required for the two models discussed above. Vacancies could not diffuse to the dislocations and change the density of jogs without altering the rate of resistivity increase before and after an anneal. The vacancies and/or interstitials could still migrate together to form clusters or annihilate each other.

The flow stress in the cross-slip model is again a function of the crystal lattice, rather than the dislocation structure. Therefore, the same resistivity results would be expected for this model as for the previously discussed Peierls stress model.
CONCLUSIONS

The results indicated that:

(1) Point defects are created during deformation at 195°K and 273°K,

(2) The rate with respect to strain at which these defects are produced is an inverse function of the deformation temperature,

(3) Some or all of the point defects are mobile at 422°K and either diffuse together or to dislocations, and

(4) This movement of the point defects does not affect the flow stress.

No definite conclusion was reached on the dislocation model responsible for the results.
SUGGESTIONS FOR FURTHER WORK

This investigator intends to study the resistivity of molybdenum single crystals further. The procedure will be such as to determine the following:

(1) Is the linear $\Delta\rho \cdot \rho$ versus strain assumption valid, and

(2) What is the relative magnitude of resistivity due to vacancies and dislocations.
ACKNOWLEDGMENTS

The author wishes to acknowledge Dr. Franz R. Brotzen, Dean of Engineering, for suggesting the nature of this work and without whose guidance and assistance, this investigation could not have been undertaken or completed.

Helpful discussions with Dr. John M. Roberts, Associate Professor of Mechanical Engineering, and with Dr. Harold E. Rorschach, Professor of Physics, are also gratefully acknowledged.

Dr. Martin H. Graham, Professor of Electrical Engineering, designed and extended helpful consultations during the construction of the bridge used in measuring the resistance; his assistance is gratefully acknowledged.

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TABLE I

<table>
<thead>
<tr>
<th>Crystal No.</th>
<th>No. of Zone Passes</th>
<th>Filament Feed Rate (mm/min.)</th>
<th>Vacuum Before Starting (mm Hg.)</th>
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TABLE I
RESISTIVITY OF 1/16" DIAMETER CRYSTALS BEFORE DEFORMATION

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TABLE II
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## APPENDIX

### PARTS LIST FOR RESISTANCE MEASURING CIRCUIT

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<td>1</td>
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<tr>
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<td>Shunt, Weston, 300 Amps.</td>
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<tr>
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<td>Ammeter (0-15)</td>
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<td>Oscilloscope, Tektronic Type 561</td>
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<td>1</td>
<td>Powerstat, Superior Type 117T</td>
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<td>1</td>
<td>Transformer, 50/1 Ratio</td>
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<td>1</td>
<td>Chassis, Aluminum, for mounting Helipot and UTC A-11 Transformer</td>
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Fig. 1. Effect of strain on the activation volume of specimen Mo 113.2, tested at 250 °K. From Youngblood (1963).
Fig. 2. Effect of temperature and strain rate on the activation volume at 60 per cent strain. From Youngblood (1963).

- Strain rate: $10^{-4}$ sec$^{-1}$
- Strain rate: $10^{-2}$ sec$^{-1}$
Fig. 3. Broad yield points due to incremental temperature changes.

From Youngblood (1963).
Fig. 4. Normal to (110) plane and 111 direction are 45° from tensile axis and are coplanar with it.
Fig. 5. Orientation of the tensile axis in the stereographic triangle.

- MO 283
- MO 280
- MO 282
- MO 278
- MO 269
- MO 272
- MO 276
- MO 274
- MO 281
- MO 262
- MO 261
- MO 273
- MO 284
Fig. 6a. Resistance measuring circuit.
Fig. 6b. Resistance measuring circuit.
Fig. 7. Lucite crystal holder for use in helium storage dewar.
Fig. 8. Filter circuit diagram.
Fig. 9. Effect of deformation temperature on the resistivity increase with strain.

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<td>Mo 269</td>
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<td>Mo 284</td>
<td>195 °K</td>
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<td>Mo 276</td>
<td>195 °K</td>
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<tr>
<td>Mo 278</td>
<td>273 °K</td>
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<td>Mo 261</td>
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<tr>
<td>Mo 272</td>
<td>373 °K</td>
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<tr>
<td>Mo 273</td>
<td>473 °K</td>
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Fig. 10. Effect of strain and anneal on the resistivity of Mo 261.

Deformation temperature: 273 °K.
Strain rate: $8.7 \times 10^{-5}$ sec$^{-1}$

ANNEAL AT 
473 °K 3 33 MIN.
Fig. 11. Effect of strain and anneal on the resistivity of Mo 278

Deformation temperature: 273 °K

Strain rate: \(5.5 \times 10^{-5}\) sec\(^{-1}\)
Fig. 12. Effect of strain and anneal on the resistivity of Mo 262.

Deformation temperature: $195^\circ K$

Strain rate: $4.3 \times 10^{-5}$ sec$^{-1}$

Anneal at $473^\circ K$

1900 MIN.

Anneal at $473^\circ K$

2110 MIN.
Fig. 13. Effect of strain and anneal on the resistivity of Mo 282.

Anneal at 473 °K 2605 min.
Anneal at 473 °K 1038 min.

Deformation temperature: 195 °K
Strain rate: 4.4 x 10^-5 sec^-1

$\frac{\Delta L}{L} \sim \text{per cent}$
Fig. 14. Effect of deformation temperature on the resistivity decrease for anneals at 473 °K.

<table>
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<th>Specimen number</th>
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<td>273 °K</td>
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<td>▽ Mo 261</td>
<td>273 °K</td>
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Fig. 15. Effect of strain and anneal on the resistivity of Mo 283.

Deformation temperature: 195 °K
Strain rate: $4.6 \times 10^{-5}$ sec $^{-1}$
Effect of deformation temperature on the resistivity change due to strain for No 276.
Fig. 17. Effect of deformation on the resistivity change due to strain for MO 284.

$\frac{\Delta L}{L} \sim \text{per cent}$

Strain rate: $3.9 \times 10^{-5} \text{ sec}^{-1}$
Fig. 18. Stress versus strain for No 278.

Load: $4 \times 10^{-5}$ sec$^{-1}$

Deformation temperature: 273 $^\circ$K

Strain rate: $4 \times 10^{-5}$ sec$^{-1}$

- A - UNLOAD & RELOAD IMMEDIATELY
- B - UNLOAD & ANNEAL AT 473 $^\circ$K FOR 75 MIN.
- C - UNLOAD & ANNEAL AT 473 $^\circ$K FOR 330 MIN.
- D - UNLOAD & RELOAD IMMEDIATELY

$\frac{\Delta L}{L}$ ~ per cent

$2 \times \text{ORIGINAL AREA}$

$\sigma \times 10^3$ psi

LOAD