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Rice University, Ph.D., 1972
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THE ELASTIC CONSTANTS AND INTERATOMIC FORCE
CONSTANTS OF NIOBIUM-MOLYBDENUM ALLOYS

by

Wayne C. Hubbell

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

DOCTOR OF PHILOSOPHY

Thesis Director's signature:

Houston, Texas

May, 1972
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First, I wish to thank Dr. Franz R. Brotzen for suggesting this project and, above all, for his continued support and guidance through difficult times. I also wish to thank Al Ehlert and Don Hayes for assistance in preparing the crystals. A special note of thanks goes to Don Hayes for his many helpful discussions. Finally, I wish to thank Rick Offeman for his invaluable help in writing the computer programs.

The financial support of the National Aeronautics and Space Administration and the National Science Foundation is gratefully acknowledged.
PROLOGUE

The research reported in this thesis was designed to gain further insight into the basic mechanisms governing the mechanical properties of bcc metals, a subject of continuing research at Rice for the past twelve years. Alloys of niobium and molybdenum were chosen because of the complete solid solubility across the phase diagram and because of the extensive work on molybdenum and molybdenum-rhenium alloys already completed at Rice.

Underlying the mechanisms which control mechanical properties are the details of atomic bonding. Measurements of the adiabatic elastic constants were made to help provide some information about this bonding. Knowledge of these constants is also necessary to the calculations of elasticity, which is the basis of dislocation mechanics.

Some insight into the details of atomic bonding can be gained through calculation of the central interatomic force constants for nearest and next-nearest neighbors. This is made possible through knowledge of the elastic constants. An alternate approach, utilizing the published lattice-dispersion curves for the metals of interest, was used to calculate the general interatomic force constants out to seven nearest neighbors.

This thesis is divided into two parts. The first contains the results of the elastic constant measurements along with the results of the central force calculation. The second part contains the calculation and results for the general interatomic force constants.

It is hoped that through this work further knowledge of the physics of bcc transition metals has been gained.
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## PART II  CALCULATION OF THE GENERAL FORCE CONSTANTS

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PART I

THE MEASUREMENT OF THE ELASTIC CONSTANTS AND

THE CALCULATION OF THE CENTRAL FORCE CONSTANTS
INTRODUCTION

In the solid state the transition metals niobium and molybdenum are completely soluble in each other, and the melting point of the solution has a minimum at the compositions between 20 and 30% molybdenum.¹ The electronic configuration of the niobium atom is \(4d^4(5s^1)\) and that of molybdenum, \(4d^5(5s^1)\), so that the addition of molybdenum to niobium has the effect of increasing the electron/atom ratio of the alloy. The crystal structure of these alloys, like that of the two component metals, is body-centered cubic at all temperatures. The stability of the bcc structure in transition metals is dependent on a short range ion-ion interaction, which is particularly sensitive to the configuration of the \(d\)-electrons and which affects their elastic constants. This aspect was discussed first by Fuchs² for the hypothetical case of bcc copper, subsequently by Zener³ for the case of beta brass, and then by different investigators for a number of transition metals.⁴-⁶

An analysis of the elastic constants of molybdenum-rhenium alloys by Davidson and Brotzen⁷ revealed that the addition of rhenium to molybdenum tended to raise the central interatomic force constant for nearest atomic neighbors but lowered it for second-nearest neighbors. They attributed this to the splitting of the \(d\)-band into subbands of directional character, one of which is filled near the composition of pure molybdenum. Alloying molybdenum with niobium, rather than with rhenium, would tend to remove electrons from the filled subband and
can be expected to affect the interatomic force constants in a manner different from that of rhenium additions. The lowering of the force constant for second-nearest neighbors is accompanied by a decrease of the shear constant \( C' = \frac{1}{2}(c_{11} - c_{12}) \). A well defined relationship between \( C' \) and the electron/atom ratio was observed by Fisher and Dever, which applied to bcc transition metals. Ducastelle attempted to compute the elastic constants of transition elements from the crystal energy, which was assumed to consist of the contribution of the \( d \)-electrons and of a repulsive potential. This approach led to satisfactory results for fcc crystals, but proved inadequate for bcc transition metals, probably because details of the \( d \)-subbands had not been taken into consideration. Fischer et al. noted a correlation between the isotropic elastic moduli and the paramagnetic susceptibility of transition metals. They were able to present a theoretical justification for this relation, thereby establishing a direct link between the elastic behavior and the electron configuration of these materials. Bernstein showed that the electronic contribution to the temperature dependence of the elastic constants gives rise to a \( T^2 \) behavior. These studies suggest that knowledge of the elastic constants of transition metal alloys, such as niobium-molybdenum, can contribute to the understanding of the electronic structure of these solid solutions and to alloy theory in general.

It is not yet fully understood why the addition of rhenium to moly-
bdenum tends to produce solution softening, while the addition of niobium to molybdenum causes pronounced solution hardening. It has been suggested that this effect may have its cause in the modification of the electronic structure of the metal by the alloy addition. A change in the electronic structure, in turn, would alter the directional interatomic forces with the result of varying the Peierls stress of the dislocations. It is also likely that the stacking-fault energy, because of its dependence on the interatomic forces, is influenced by the electron configuration. Since the mechanical properties of transition-metal alloys are affected by the same interatomic forces that control the elastic constants, a better understanding of these forces would contribute significantly to the study of mechanical properties.

Once the elastic constants are known, the Debye temperature can be computed and compared with experimental determinations. Since the Debye temperatures of niobium-molybdenum alloys have been determined calorimetrically by Morin and Maita, this correlation can be readily made. Furthermore, the comparison of ultrasonic velocities obtained in this investigation with the initial slopes of phonon-dispersion curves determined by neutron diffraction by Powell et al. is a worthwhile undertaking.

The above considerations add to the significance of the study of elastic properties of niobium-molybdenum alloys. In this section the
results of adiabatic elastic-constant measurements by the pulse-echo technique of the complete series of these alloys are presented. Following this are the results of 1st and 2nd nearest-neighbor central force constants.
SAMPLE PREPARATION AND EXPERIMENTAL PROCEDURE

The specimens were prepared in this Laboratory from powders by compacting and subsequent electron-beam floating-zone melting. The starting materials for the alloys were reactor-grade niobium and molybdenum powders, which were mixed and compacted into 6.2 mm rounds, approximately 200 mm long with nominal molybdenum contents of 15, 25, 35, 50, 75, and 90 weight %. Two rods of each alloy were made and subjected to an initial pass in the electron-beam floating-zone melter to transform the powder compacts into solid solutions. In general, four additional passes were used for each specimen in an ultimate vacuum of $10^{-6}$ Torr, beginning with a seed crystal to obtain axial orientations of [100] and [110]. In the case of niobium metal, the starting material was 1/4" metallurgical-grade niobium rod (99.98%), from which single crystals were grown by the same electron-beam melting process used for the alloys. Cylinders, about 10 mm long, were spark sliced from all rods and their end faces spark-polished parallel to each other within $10^{-3}$ cm. The crystal axes were determined to be within 2° of the desired orientation by the Laue back-reflection method.

The actual composition of each sample was established by density measurements, with the assumption that the density was a linear function of composition. The density was determined reproducibly within $10^{-4}$ g cm$^{-3}$ by the Archimedean method, using a Mettler microbalance and benzene as a medium. The determination of compositions was corroborated by standard powder-pattern lattice-parameter measurements (Table I), which agreed with published values. For the computation of elastic constants from the sound velocities for different temperatures, the
Table I. Densities, thermal expansion coefficients and lattice parameters of niobium-molybdenum alloys.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Density at 25°C (gm-cm$^{-3} \pm 0.003$)</th>
<th>Expansion Coefficient (10$^{-6}$ per °C ± 1.5)</th>
<th>Lattice Parameter (Å ± 0.02)</th>
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</thead>
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<tr>
<td>Nb</td>
<td>8.569</td>
<td>8.6</td>
<td>3.31</td>
</tr>
<tr>
<td>Nb - 16.8% Mo</td>
<td>8.860</td>
<td>7.6</td>
<td>3.27</td>
</tr>
<tr>
<td>Nb - 23.3% Mo</td>
<td>8.968</td>
<td>7.3</td>
<td>3.25</td>
</tr>
<tr>
<td>Nb - 33.9% Mo</td>
<td>9.127</td>
<td>7.0</td>
<td>3.23</td>
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<tr>
<td>Nb - 51.6% Mo</td>
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<td>Nb - 75.2% Mo</td>
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<td>Nb - 92.1% Mo</td>
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<td>3.15</td>
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<tr>
<td>Mo</td>
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<td>3.15</td>
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Table II. The relations between the acoustic wave velocities and the elastic constants.

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

$v_i$ = wave velocity, $c_{ij}$ = elastic constant and $\rho$ = density.
Fig. 1 Pulse Superposition Instrumentation.
thermal expansion had to be determined. These thermal expansion coefficients were obtained from linear-dilatation measurements carried out with a displacement transducer (Appendix I). This equipment was tested for its accuracy by measuring the thermal expansion of high-purity polycrystalline copper; the results were in very good agreement with the data of Nix and MacNair. The expansion curves for niobium and the niobium-molybdenum alloys were found to be linear over the range from -190 to +100°C. Table I lists the expansion coefficients \( \alpha = \frac{1}{L} \frac{dL}{dT} \). Differences of the expansion coefficients for the two orientations of the individual alloys were not detected.

Sound velocities were determined by the pulse-superposition method, using equipment similar to that described by McSkimin (Fig. 1). Measurements were made principally with 20 MHz X-cut and Y-cut transducers using Dow-Corning Resin 276-V9 as a bonding agent. With crystals of two orientations, i.e., [100] and [110], five sound velocities can be obtained which permit computation of the elastic constants as shown in Table II. All five velocities were determined at 25°C for all the alloys and for niobium. Only the velocities \( v_1, v_2, \) and \( v_3 \) were determined over the entire range from -190 to +100°C. This made possible the computation of the three independent elastic constants for all the temperatures and, at the same time, provided a cross check between the elastic constants obtained from different velocities at room temperature. The actual molybdenum content of crystals of the same nominal composition but of different orientation was usually not quite the same. Thus, computation of \( c_{12} \), was possible only from the velocity \( v_3 \) after \( c_{11} \) and \( c_{44} \) obtained from the [100] crystals were adjusted by
interpolation to the actual compositions of the [110] crystals. The elastic constants were calculated for each composition at 10°C intervals over the above temperature range by a computer (Appendix II) utilizing the measured temperature variations of the acoustic wave "time of flight" and the expansion coefficient.
RESULTS

The elastic constants of the niobium-molybdenum alloys obtained in this investigation are listed in Table III, and the constants for niobium, in Table IV. The accuracy of these results can be estimated from the limitations of length and density measurements of the crystals and from the reproducibility of readings after transducer removal and reattachment to the specimen. The accuracy for the absolute values of the directly measured constants, $c_{11}$ and $c_{44}$, is then estimated to be within ± 0.1% and that of the indirectly determined constant $c_{12}$, to be within ± 0.2%. The accuracy for the relative changes with temperature is higher by about one order of magnitude.

A comparison of the data for niobium at room temperature with those of other investigators is shown in Table V. The agreement of the present data with those by Jones et al.\textsuperscript{32} is particularly good and extends over the entire temperature range.

The phonon dispersion curves for a series of niobium-molybdenum alloys were obtained from neutron diffraction data by Powell et al.\textsuperscript{19} At the continuum limit, i.e., as the reduced wave vector approaches zero, the slope of the curves of the $\Delta_5$ branch correspond to $v_2/a$ where $v_2$ is the sound velocity of a transverse wave propagated in the [100] direction and $a$ is the lattice parameter. Good agreement was obtained when the values of $v_2/a$ obtained from the present investigation were plotted as solid lines in Fig. 2 along with the $\Delta_5$ branches of the dispersion curves. Similar good agreement was noted for the other branches.

The constant $c_{44}$ rises substantially with increasing molybdenum content (Fig. 3), and the effect of composition on this constant is far greater than that of temperature. The other shear constant follows
Table III. The elastic constants of the niobium-molybdenum alloys.

<table>
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<tr>
<th>T(°C)</th>
<th>16.8% Mo</th>
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<td>T(°C)</td>
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Table V. Comparison of elastic constants of niobium at room temperature.

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<th>Investigators</th>
<th>$c_{11}$</th>
<th>$c_{12}$</th>
<th>$c_{44}$</th>
<th>$C'$</th>
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<th>$\rho$</th>
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<td>Bolef $^5$</td>
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<td>0.5604</td>
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<td>Carroll $^{28}$</td>
<td>2.456</td>
<td>1.387</td>
<td>0.2903</td>
<td>0.5345</td>
<td>1.743</td>
<td>8.560</td>
</tr>
<tr>
<td>Wasilewski $^{29}$</td>
<td>2.34</td>
<td>1.21</td>
<td>0.2821</td>
<td>0.571</td>
<td>1.59</td>
<td>8.578</td>
</tr>
<tr>
<td>Armstrong et al. $^{30}$</td>
<td>2.40</td>
<td>1.26</td>
<td>0.2809</td>
<td>0.57</td>
<td>1.64</td>
<td></td>
</tr>
<tr>
<td>Grahm et al. $^{31}$</td>
<td>2.465</td>
<td>1.333</td>
<td>0.2840</td>
<td>0.5661</td>
<td>1.710</td>
<td>8.578</td>
</tr>
<tr>
<td>Jones et al. $^{32}$</td>
<td>2.4674</td>
<td>1.3324</td>
<td>0.2808</td>
<td>0.5675</td>
<td>1.7107</td>
<td>8.567</td>
</tr>
<tr>
<td>Present Work</td>
<td>2.472</td>
<td>1.331</td>
<td>0.2823</td>
<td>0.5705</td>
<td>1.711</td>
<td>8.569</td>
</tr>
</tbody>
</table>

The elastic constants are given in units of $10^{12}$ dynes/cm$^2$.

$C' = \frac{1}{2}(c_{11} - c_{12})$, $B = \text{bulk modulus} = \frac{1}{3}(c_{11} + 2c_{12})$, $\rho = \text{density}$.

Table VI. Contribution of dimensional effects to the change in elastic constants as a result of alloying. ($10^{12}$ dyn/cm$^2$)

<table>
<thead>
<tr>
<th>Metal</th>
<th>Solute</th>
<th>$\Delta \frac{\partial c_{11}}{\partial x}$</th>
<th>$\Delta \frac{\partial c'}{\partial x}$</th>
<th>$\Delta \frac{\partial c_{44}}{\partial x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Niobium</td>
<td>Molybdenum</td>
<td>$-2.39$</td>
<td>$-0.26$</td>
<td>$-0.07$</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Niobium</td>
<td>$+1.22$</td>
<td>$+0.35$</td>
<td>$+0.38$</td>
</tr>
</tbody>
</table>
Fig. 2. The Λ branches of the dispersion curves.
Fig. 3 The $c_{44}$ elastic constant for the niobium-molybdenum alloy system at 25°C.
Fig. 4 The $C'$ elastic constant of the niobium-molybdenum alloy system at 25°C.
Fig. 5 The temperature dependence of the $c_{44}$ elastic constant for the niobium-molybdenum alloy system.
Fig. 6 The bulk modulus for the niobium-molybdenum alloy system at 25°C.
a trend similar to that of \( c_{44} \) (Fig. 4). It is noteworthy that \( C' \) tends to reach a maximum near the composition of 100% molybdenum, as discussed by Davidson and Brotzen\(^7\) and by Fisher and Dever.\(^8\)

The temperature dependence of \( c_{44} \) in the niobium-rich alloys is anomalous, (Fig. 5), as they become elastically softer as the temperature is lowered. This anomalous effect is strongest in the 33.9% molybdenum alloy and diminishes gradually as the molybdenum content decreases. In unalloyed niobium, \( c_{44} \) seems to rise at an increasing rate as the temperature is decreased below room temperature. Several investigators\(^{28,30,32}\) have observed a broad minimum in the values of \( c_{44} \) in niobium near 50°C, and their results are in very good agreement with the measurements of this investigation. The temperature dependence of \( C' \) is normal in the temperature region studied, although in the alloys containing 23.3 and 33.9% molybdenum, \( C' \) remains virtually unaffected by temperature changes above -100°C and tends to decrease very slightly at lower temperatures.

The bulk modulus, \( B = \frac{1}{3}(c_{11}+c_{12}) \), was calculated from the elastic constants listed in Table III. It increases with the addition of molybdenum to niobium, (Fig. 6), in agreement with the rising trend of the isotropic bulk modulus of the transition metals of the 4d-series with increasing atomic numbers from yttrium to ruthenium.\(^{33}\) In the temperature range studied, the bulk modulus of the alloys displays generally a monotonically decreasing behavior with temperature. Pronounced deviations from this norm, such as those reported for niobium and molybdenum,\(^6\) were not observed.
Fig. 7 The dispersion curve slope, v/a, for a niobium-rich and a molybdenum-rich niobium-molybdenum alloy.
DISCUSSION

The observation of a positive temperature coefficients of the elastic constant $c_{44}$ in niobium-rich molybdenum alloys is likely to be associated with certain features of the Fermi surface of these alloys. This view appears to be corroborated by results of neutron-diffraction and low temperature calorimetric investigations.

A possible explanation of the anomalous temperature dependence of the elastic constants was suggested by Bernstein,\textsuperscript{11} who considered the contribution from the displacement of the Fermi surface during strain and the attendant transfer of electrons across the Brillouin-zone boundaries. Bernstein noted that the magnitude and algebraic sign of the temperature variation of the elastic constants depend sensitively on the shape of the Fermi surface and the electron-density distribution. Rayne and his coworkers\textsuperscript{34} suggested an explanation similar to this based on the work of Leigh\textsuperscript{35} for the anomalous temperature variation of the elastic constants for platinum and palladium. It is noteworthy that the details of the dispersion curves of the niobium-rich alloys differ greatly from the details of the other alloys. This is illustrated in Fig. 7 by an example obtained from the aforementioned neutron diffraction data. The niobium-rich alloy in this diagram exhibits the unusual temperature dependence of $c_{44}$, while the molybdenum-rich alloy has a normal temperature behavior. There is a strong indication that the anomalies in the dispersion curves are related to certain features of the Fermi surface,\textsuperscript{36,37} the details of which are still to be explored.

An anomaly in the temperature dependence of the specific heat at low temperature in niobium-rich molybdenum alloys was observed by Morin and Maita.\textsuperscript{18} These investigators concluded from results of low-tempera-
Fig. 8 The central first and second-nearest neighbor force constants for the niobium-molybdenum and molybdenum-rhenium alloy systems.
ture calorimetry that niobium-rich molybdenum alloys undergo a rapid change of the density of electron states at the Fermi level with temperature. They attributed this to a relative shift in the band edges with temperature and a consequent redistribution of the electrons.

Compositional changes affect the elastic constants and the outer-electron configurations of the alloys. The manner in which the elastic properties vary with composition, therefore, sheds some light on the relation between the electronic structure and the interatomic forces of the alloys. Using the Born-von Kármán lattice theory, de Launay\textsuperscript{38} derived expressions for the interatomic force constants in cubic metals in terms of their elastic coefficients. Applying these expressions to the niobium-molybdenum system, the central-force interactions between nearest atomic neighbors, $\alpha_1$, as well as those including the binding due to the electron gas, $\alpha_1'$, were computed (Fig. 8a). Similarly, Fig. 8b illustrates these interactions for the second-nearest neighbors in the niobium-molybdenum alloys ($\alpha_2$, $\alpha_2'$). For purposes of comparison, the corresponding interatomic force constants for molybdenum-rhenium alloys\textsuperscript{7} were included in these figures. Niu and Shimizu\textsuperscript{39} proposed a method for computing the force constants, which takes angular forces between nearest atomic neighbors into account. The central-force constants for nearest and second-nearest neighbors obtained by the latter method followed closely the curves in Fig. 8a and 8b and were therefore omitted in these figures. The angular force constant between nearest neighbors represents the non-central force contribution and shows, therefore, the deviation from the Cauchy relation, viz., $c_{44} = c_{12}$ (Fig. 8c).

An expression for the interatomic force constants can be obtained by a method proposed by Bolef\textsuperscript{5}, which follows earlier work by
Fuchs and Isenberg. The analysis is relatively simple and makes possible estimates of the short-range forces between transition element atoms. These forces have their origin in the "overlap energy", which consists of the Coulomb interaction of overlapping charge distributions of the ions and, in addition, of the exchange energy resulting from this overlap. This approach, which assumes monovalency of the elements, leads to expressions for the second derivatives of the overlap energy. These were calculated for nearest and second nearest-neighbors and denoted by $W''_1$ and $W''_2$, respectively (Figs. 8a and 8b). The first derivatives of the overlap energy for the nearest-neighbor interaction have negative values and, as expected, are so small that their variations with composition fall within the experimental error. The first derivatives for second-nearest neighbors were assumed to be zero.

The procedures of computing the force constants leading to the results illustrated in Fig. 8 are, at best, approximate and require further scrutiny. They are generally based on the assumption that the effective interatomic forces are of short extension. Yet, by an analysis of the frequency/wave-vector dispersion curves measured by inelastic neutron diffraction, Nakagawa and Woods concluded that the long-range forces in niobium are by no means negligible.

Upon closer examination we find that de Launay's two approaches make essentially the same assumptions:

1) only nearest and next-nearest neighbor forces are important,
2) the interactions are central in nature.

The first assumption, of course, is contrary to the findings of Woods and his coworkers from neutron diffraction studies. This objection is present in both of de Launay's approaches.
Objections to the second assumption are present in differing degrees for the two approaches. This assumption seems to fail for the first approach when one considers the Cauchy relation \((c_{12} = c_{44})\) which is a consequence of central force interactions. The ratio, \(c_{12}/c_{44}\), for the metals in question varies from 4.71 for niobium to 1.56 for molybdenum. In the second approach, the inclusion of electron gas effects modifies the Cauchy relation so that it becomes \(c_{12} - c_{44} = 2(\alpha'_1 - \alpha_1)/a\). A rough calculation shows that the ratio

\[
\frac{c_{12} - c_{44}}{2(\alpha'_1 - \alpha_1)/a} \sim 1.5
\]

for the metals in question. Thus, the effect of the electron gas seems to take into account some of the non-central nature of the forces and hence removes the serious objections to that assumption.

Niu and Shimizu's method is essentially the same as de Launay's second approach and embodies the same sort of objections.

The Fuchs-Isenberg-Bolef approach assumes a localized model for the \(d\)-electrons with a strong repulsive force between the second nearest-neighbor in addition to an attractive force between first neighbors. Besides neglecting long range forces, this method, which predicts an antiferromagnetic structure, is inconsistent with neutron diffraction experiments. Furthermore, even the basic assumptions of Fuchs are questionable when applied to the present metals. In the first case, the metals are assumed to be monovalent which allows one to neglect the interaction of the Fermi surface with the Brillouin zone. Secondly, Fuchs assumes that the ion core shells are closed which allows one to treat the ion-ion interactions from the standpoint of central forces.

Because of the shortcomings inherent in the various analyses used
to find the force constants, the conclusions that can be drawn from them are in some measure conjectural. Yet, certain trends can be clearly discerned from the curves in Fig. 8. The force constants for the nearest neighbors (Fig. 8a) have a tendency to rise as molybdenum is added to niobium, i.e., as the electron concentration increases. The rise is slow up to about 30% molybdenum and accelerates rapidly at higher molybdenum concentrations. This trend clearly continues as the curves are followed into the molybdenum-rhenium system. The difference between the force constants for nearest neighbors, \( \alpha'_1 - \alpha_1 \), which is attributed to the binding force of the electron gas, is considerably larger in niobium than in molybdenum. The force constants for second-nearest neighbors also rise as the molybdenum content of the alloys is increased (Fig. 8b), but do so at a decreasing rate as 100% molybdenum is approached. This behavior was to be expected, since further increase of the electron concentration by the addition of rhenium to molybdenum caused these force constants to decrease. On the basis of their investigation of the elastic properties of molybdenum-rhenium alloys, Davidson and Brotzen speculated that the latter effect was associated with a filled \( d \)-subband near the 100% molybdenum concentration. It is noteworthy that the force constant for nearest neighbors does not reach a maximum near the molybdenum composition (Fig. 8a), corroborating the concept that the various \( d \)-subbands are highly directional. The results presented here may suggest that nearest neighbor interactions are largely associated with the bonding states in the triply degenerate \( t_{2g} \) level, the electron distribution of which favors the nearest neighbor bonds. The interaction between second-nearest neighbors, on the other hand, depends primarily on the electrons in the doubly degenerate \( e_g \) level, which is generally
thought to have a parallel spin correlation$^{42}$ The maximum of the force constant for second-nearest neighbors near the molybdenum composition also coincides roughly with a minimum in the density of states$^{18}$.

The analysis of the results obtained in this investigation could be advanced by a study of third order elastic constants of transition-metal alloys. Such a study would provide information on the relative contribution to the elastic constants of the dimensional changes of the lattice that result from alloying. It would be of special value in the case of the niobium-molybdenum system, because it appears that dimensional changes affect the elastic constants of niobium quite differently from those of molybdenum. This assertion is supported by the results of rough calculations made for these metals (Table VI) based on third-order elastic constant data for niobium by Grahm et al.$^{31}$ and the isotropic pressure derivatives of the elastic constants of molybdenum by Smith et al.$^{43}$ The results in Table VI were then obtained by converting the third-order elastic constants into pressure derivatives$^{44}$ and by using the formulation for the volume-dependent term derived from classical thermodynamics:

$$
\frac{d c_{ij}}{dx} - \left[ \frac{\partial c_{ij}}{\partial x} \right]_v = \Delta \frac{\partial c_{ij}}{\partial x} = -3B \left[ \frac{\partial c_{ij}}{\partial P} \right]_a \frac{d \ln a}{dx},
$$

where $c_{ij}$ = elastic constant under consideration, $x$ = mole fraction of the solute, $B$ = bulk modulus of the metal, $\left[ \frac{\partial c_{ij}}{\partial P} \right]_a$ = pressure derivative of the elastic constant evaluated at zero deformation, and $a$ = the lattice parameter shown in Table I. The contribution of the dimensional changes to the alloying effect, $\Delta \frac{\partial c_{ij}}{\partial x}$, is larger for $c_{11}$ than for the shear constants, reflecting the considerable influence of the electron gas on $c_{11}$.
Fig. 9 The anisotropy factor $A$ for the niobium-molybdenum alloy system at 25°C.
Fig. 10 The Debye temperatures of the niobium-molybdenum alloy system. ◊ calculated from elastic constants, x's are experimental data of Morin and Maita.18
The anisotropy factor \( A = \frac{2c_{44}}{c_{11} - c_{12}} \) is much lower for niobium than in molybdenum (Fig. 9). It forms a distinct minimum between the compositions of 20 and 30% molybdenum, that is, in a region in which the anomalous temperature behavior of \( c_{44} \) was observed to be most prominent. It appears that the two phenomena are linked and may be attributed to particular features of the Fermi surface, which are still to be explored.

The Debye temperatures of the alloys were computed from the elastic constants at 77 K (Fig. 10), using Marcus' method. The figure also includes the experimental data by Morin and Maita. The correlation is quite satisfactory, especially if the unusual low-temperature behavior of the specific heat of the niobium-rich alloys is taken into consideration. This anomaly led Morin and Maita to list two possible values of the Debye temperatures, which were included in the aforementioned figure. A number of other investigators have seen similar anomalies in pure niobium. A comparison of their calorimetrically determined Debye temperatures, along with those of Morin and Maita, with that calculated from the present work is presented in Table VII.
Table VII. The Debye temperature of niobium.

<table>
<thead>
<tr>
<th>Investigators</th>
<th>$\Theta_D$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>upper value</td>
</tr>
<tr>
<td>Da Silva et al. $^{46}$</td>
<td>276</td>
</tr>
<tr>
<td>Da Silva et al. $^{46}$ (unannealed)</td>
<td>250</td>
</tr>
<tr>
<td>Leupold and Boorse $^{47}$</td>
<td>275</td>
</tr>
<tr>
<td>Van der Hoeven and Keesom $^{48}$</td>
<td>275</td>
</tr>
<tr>
<td>Heiniger et al. $^{49}$</td>
<td>278</td>
</tr>
<tr>
<td>Shen et al. $^{50}$</td>
<td>277</td>
</tr>
<tr>
<td>Morin and Maita $^{18}$</td>
<td>260</td>
</tr>
<tr>
<td>Present Work (calculated)</td>
<td>267</td>
</tr>
</tbody>
</table>
CONCLUSIONS

(1) The addition of molybdenum to niobium strengthens the interactions between nearest and second-nearest atomic neighbors. The central interatomic force constant for second-nearest neighbors tends to reach a maximum near the composition of 100% molybdenum.

(2) The shear constant $C' = \frac{1}{2}(c_{11} - c_{12})$ rises with the addition of molybdenum to niobium, pointing towards an increased stability of the bcc structure with increasing molybdenum content.

(3) The shear constant $c_{44}$ displays an anomalous temperature dependence in the niobium-rich alloys. The same alloys also show a distinct minimum in the anisotropy coefficient $A = \frac{c_{44}}{c^2}$. This behavior is tentatively attributed to particular features of the Fermi surface of these alloys.

(4) The Debye temperature is raised by the addition of molybdenum to niobium. Debye temperatures computed from the elastic constants agree rather well with those determined by calorimetry.
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PART II

CALCULATION OF THE GENERAL FORCE CONSTANTS
INTRODUCTION

Phonon dispersion curves depend rather directly on the harmonic forces existing between the ion cores in metal crystals.\(^1\) For sufficiently simple crystals, it is possible to deduce the harmonic forces from the dispersion curves by use of the Born-von Karmán theory of lattice dynamics.\(^2\)

In the Born-von Karmán theory, the atomic motions in a crystal are described by lattice waves which are considered to be uncoupled harmonic oscillators (normal modes). The frequencies of the oscillators are related to the wave vector \(\mathbf{q}\) by the dispersion relation

\[ \nu = \nu(\mathbf{q}). \]  \hspace{1cm} (1)

The interatomic force constants can be determined by equating the Fourier coefficients of the dispersion curves, i.e., the interplanar force constants, to a linear combination of interatomic force constants and solving the resulting set of simultaneous equations. The linear combinations are determined according to the method of Squires.\(^3\)

The dispersion relations can be determined directly by neutron spectrometry (inelastic scattering of neutrons), by study of the processes in which neutrons interact with the crystal by creation or annihilation of a single phonon (quantum of a normal mode). The frequency and wave vector of the particular normal mode are determined from conservation of energy and momentum between the neutron and the phonon. The incoming and outgoing wave vectors, \((\mathbf{k}_0, \mathbf{k}'),\) and energies, \((E_0, E'),\) are related to the phonon wave vector and energy by means of the equations\(^4\)
\[ \mathbf{\tau} = \mathbf{k}_0 - \mathbf{k}' = 2\pi \mathbf{\tau} - \mathbf{q} \]
\[ E_0 - E' = \pm \hbar \nu \]  
\hspace{1cm} (2)

where \( \mathbf{\tau} \) is a reciprocal lattice vector. Thus, scattering of neutrons occurs as groups in the energy distribution which, neglecting resolution, are ideally sharp.\(^1\) The centers of the neutron groups, when used with the above equation gives values of the frequency \( \nu \) and the wave vector \( \mathbf{q} \) of the phonons with which the neutrons interact.

The phonon dispersion curves for a number of metals including niobium, molybdenum and a series of six niobium-molybdenum alloys have been determined by A. D. B. Woods and his colleagues\(^5\)\(^-\)\(^9\) at the Chalk River nuclear facility of Canada. They used the crystal spectrometer method as described by Brockhouse\(^5\) operating in a constant momentum transfer mode.

The phonon dispersion curves for niobium and molybdenum were found to be very different from each other,\(^7\) and furthermore, the variation of the dispersion curves with composition was complicated, involving changes in the shape as well as general frequency level. The levels of the niobium-rich alloys increased significantly with increasing molybdenum content while their shapes remained substantially unchanged. On the other hand, the molybdenum-rich alloys maintained a nearly constant level of frequencies while the shapes were found to be very sensitive to alloy composition.

The Fourier analyses of the various branches of the dispersion curves involved non-negligible contributions from distant planes. This was a consequence of the rather intricate shapes of some of the curves. In principle, this implies that rather long-range interatomic forces are operative in these metals. However, according to Nakagawa and Woods\(^6\)
this does not necessarily imply the existence of direct distant-neighbor interactions. They speculate that indirect interactions may account for the long range forces, e.g., indirect interactions between sixth neighbors, $a/2(400)$, is possible through the medium of a second neighbor, $a/2(200)$; when the ion at $a/2(400)$ is displaced, the $d$-electron shell belonging to the ion at $a/2(200)$ is deformed so that the force exerted on the ion at the origin is changed.

Thus, it seems that the calculation of the general interatomic force constants for the series of alloys could possibly lead to a better understanding of the complex nature of the basic interactions which determine the properties and behavior of these metals.
DETERMINATION OF INTERPLANAR FORCE CONSTANTS
FROM PHONON DISPERSION CURVES

When the phonon wave vectors lie in one of the symmetry directions, [100], [110] or [111], the displacement of the atoms corresponds to motions in which all of the atoms in a plane perpendicular to the symmetry axis move as a whole. The motion is therefore equivalent to that of a one dimensional lattice in which each point represents a plane of atoms in the three dimensional lattice. The force on a point, \( \mathbf{p} \), in such an array is related to the displacements of the other points by the expression \(^{10}\)

\[
M \ddot{u}_s = \sum_{p} C_p (u_{s+p} - u_s)
\]  

(1)

The \( C_p \)'s are the force constants between points in the linear chain- or in this case interplanar constants. This equation is solved as usual by substituting a traveling wave solution of the form

\[
u_{s+p} = u_o \exp[i(s+p)q \alpha - i\omega t].
\]  

(2)

After simplification we arrive at the expression

\[
4\pi^2 v^2 = (2/M) \sum_{p=1} C_p (1 - \cos pq \alpha)
\]

(3)

which is the familiar form of the Fourier series with coefficients \( C_p \).

Inelastic scattering of neutrons provides us with the exact form of the \( v \) vs. \( q \) curves (and thus \( v^2 \) vs. \( q \)). Thus, by Fourier analyzing these curves, we get the coefficients \( C_p \) - or in other words the interplanar force constants.
INTERATOMIC FORCE CONSTANTS

In the Born-von Karmán theory of lattice dynamics, the equation of motion of the \( K \) th atom in the \( l \) th unit cell is given by

\[
M_K \ddot{u}_x(K,l) = \sum_y \sum_{K'} \Phi_{xy}(KK',ll') u_y(K',l).
\]  

(4)

In this equation, \( M_K \) is the mass of the atom, \( u_x \) is the displacement of the atom from equilibrium in the \( x \)-direction, \( l \) indicates the unit cell position and \( \Phi_{xy}(KK',ll') \) is the force in the \( x \)-direction on the \( K \) th atom in the \( l \) th cell when the \( K' \) th atom in the \( l' \) th cell is moved unit distance in the \( y \)-direction. These \( \Phi_{xy} \)'s are the general interatomic force constants. At this point we introduce the following notation of Squires for the force constants between an atom at the origin and, say, its \( s \) th nearest neighbor (\( s = 1,2,3,\ldots \)):

\[
\begin{align*}
\Phi_{xx} & \quad \Phi_{xy} \quad \Phi_{xz} \quad \alpha_1^s \quad \beta_1^s \quad \beta_2^s \\
\Phi_{yx} & \quad \Phi_{yy} \quad \Phi_{yz} \quad \beta_3^s \quad \alpha_2^s \quad \beta_1^s \\
\Phi_{zx} & \quad \Phi_{zy} \quad \Phi_{zz} \quad \beta_2^s \quad \beta_1^s \quad \alpha_3^s
\end{align*}
\]

The solution of the equation of motion can again be written in terms of plane waves. In general the solution for the eigenfunctions is very involved but for symmetry directions in a cubic crystal, the expression for \( v^2 \) reduces to a simple linear equation. This equation can be written as

\[
4\pi^2 v^2 = \sum_{p=1} C_p (1 - \cos \pi pq/q_m)
\]

(5)

which is essentially the same as Eq.(3). These Fourier coefficients, i.e., the interplanar force constants, are linear combinations of the Born-von Karmán interatomic force constants. The linear combinations are determined by summing the forces between the constituent atoms on
a given plane, $p$, and an atom at the origin. Squires\textsuperscript{3} has compiled a set of general formulas which give the proper relationships between the interatomic force constants and the interplanar constants. These are given below.

[100] axis

Consider a phonon with $\vec{q}$ lying along the [100] axis. Label the origin point in the one dimensional lattice zero, and successive points 1, 2, 3, ..., $n$. A longitudinal interplanar force constant $\eta_{L}^{n}$ is defined so that when the point $n$ moves unit distance along the [100] axis, the force on the origin point in the same direction is $N\eta_{L}^{n}$, where $N$ is the number of atoms in the plane in the three dimensional lattice. The transverse interplanar force constant $\eta_{t}^{n}$ is defined similarly.

These two force constants are related to the interatomic force constants by

$$\eta_{L}^{n} = \sum_{S} m^{S} \alpha_{1}^{S}$$

$$\eta_{t}^{n} = \frac{1}{2} \sum_{S} m^{S} (\alpha_{j}^{S} + \alpha_{k}^{S})$$

(6)

The coefficients $m^{S}$ are zero unless one of the integers $h_{1}^{S}, h_{2}^{S}, h_{3}^{S}$ is equal to $n$. In that case put $n = h_{1}^{S}$. This gives the value of $i$ equal 1, 2, or 3; $j$ and $k$ are the remaining pair. If $h_{j}^{S} = h_{k}^{S} = 0$, $m^{S} = 1$; if one of $h_{j}^{S}, h_{k}^{S}$ is zero and the other not zero, $m^{S} = 4$; if $h_{j}^{S} = h_{k}^{S} \neq 0$, $m^{S} = 4$. In all other cases, $m^{S} = 8$.

[110] axis

The frequencies of phonons with $\vec{q}$ lying along the [110] axis may be expressed in terms of three sets of force constants defined in a manner similar to that of the $\pi$'s. The force constants for longitudinal motion are denoted by $\rho_{L}^{n}$, for transverse motion parallel to a 2-fold symmetry axis by $\rho_{t2}^{n}$ and for transverse motion parallel to a 4-fold
symmetry axis by \( \rho^n_{t4} \). They are

\[
\rho^n_{t4} = \sum_s m^s \left[ \frac{1}{3}(\alpha^s_1 + \alpha^s_2 + \alpha^s_3) \pm \beta^s_3 \right]
\]

\[
\rho^n_{t2} = \sum_s m^s \left[ \frac{1}{3}(\alpha^s_1 + \alpha^s_2) \mp \beta^s_3 \right]
\]

\[
\rho^n_t = \sum_s m^s \alpha^s_3.
\]

The coefficient \( m^s \) is zero unless two of the integers \( h^s_1, h^s_2, h^s_3 \) add or subtract to \( n \). In that case denote the third integer by \( h^s_k \). This gives the integer \( k = 1, 2, \) or \( 3 \); \( i \) and \( j \) are the remaining pair. The upper or lower sign is to be taken according to whether the two integers \( h^s_i \) and \( h^s_j \) add or subtract to \( n \). If \( h^s_i = h^s_j \), \( m^s \) is one or two depending on whether the third integer \( h^s_k \) is zero or not. If \( h^s_i \neq h^s_j \), \( m^s \) is 2 or 4 depending on whether \( h^s_k \) is zero or not.

[111] axis

The interplanar force constants are denoted by \( \sigma^n_{t4} \) and \( \sigma^n_{t2} \). They are given in terms of the interatomic force constants by

\[
\sigma^n_{t4} = \sum_s m^s \left[ \frac{1}{3}(\alpha^s_1 + \alpha^s_2 + \alpha^s_3) + \frac{2}{3} (\pm \beta^s_1 \pm \beta^s_2 \pm \beta^s_3) \right]
\]

\[
\sigma^n_{t2} = \sum_s m^s \left[ \frac{1}{3}(\alpha^s_1 + \alpha^s_2 + \alpha^s_3) - \frac{1}{3} (\pm \beta^s_1 \pm \beta^s_2 \pm \beta^s_3) \right]
\]

The coefficient \( m^s \) is zero unless the three integers \( h^s_1, h^s_2, h^s_3 \) satisfy the equation

\[
\pm h^s_1 \pm h^s_2 \pm h^s_3 = n
\]

for some combination of the + and - signs. If the three signs in Eq. (9) are the same, take the upper sign in Eq. (8). If the sign of \( h^s_1 \) is opposite to that of the other two integers, take the upper sign for \( \beta^s_1 \) and the lower sign for the other two \( \beta \)'s. If all three integers are equal and add up to \( n \), \( m^s = 1 \); if two of them are equal and have the same sign in Eq. (9), \( m^s = 3 \); in all other cases \( m^s = 6 \).
In order to set up the simultaneous equations relating the interatomic force constants to the interplanar force constants, one only need know the positions of the various neighbor atoms relative to a reference atom at the origin of the coordinate system. For a bcc lattice the positions of the eight closest neighbors, \( a/2(h_i^S, h_j^S, h_k^S) \), are given in Table I.

In general each neighbor has associated with it six interatomic force constants; however, owing to symmetry, the actual number of constants is usually somewhat less than six. The resulting set of force constant matrices out to eight nearest neighbors is given in Table II.

It is now possible to write sets of simultaneous equations to include interactions out to eight nearest neighbors. However, for dispersion curve measurements along the three symmetry axes, one can only determine force constants out to the seventh neighbor \(^4\) (although there are 31 equations and 23 unknowns out to eight-nearest neighbors, there are at least seven relations between the interplanar force constants. Four arise from the slopes of the dispersion curves at the origin and three from the fact that the points \((1/a,1/a,1/a)\) and \((1/a,0,0)\) represent equivalent waves).

The same equations (Table III) apply, with appropriate terms dropped, to calculate the force constants when considering less than seven neighbor interactions. Thus one can have up to seven different sets of equations; the first set includes only the first-nearest neighbor, the second set includes only first and second-nearest neighbor interactions, the third set includes first, second and third-nearest neighbor interactions, etc.
Table I. Position of neighbor atoms relative to origin and associated force constants.

<table>
<thead>
<tr>
<th>s</th>
<th>( h_1, h_2, h_3 )</th>
<th>n</th>
<th>Force Constants</th>
<th>number of constants</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,1,1</td>
<td>8</td>
<td>( \alpha^1_1, \beta^1_1 )</td>
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<tr>
<td>2</td>
<td>2,0,0</td>
<td>6</td>
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<tr>
<td>3</td>
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<td>12</td>
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</tr>
<tr>
<td>4</td>
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</tr>
<tr>
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<td>2,2,2</td>
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<tr>
<td>6</td>
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<td>( \alpha^6_1, \alpha^6_2 )</td>
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<tr>
<td>7</td>
<td>3,3,1</td>
<td>24</td>
<td>( \alpha^7_1, \alpha^7_3, \beta^7_1, \beta^7_3 )</td>
<td>19</td>
</tr>
<tr>
<td>8</td>
<td>4,2,0</td>
<td>24</td>
<td>( \alpha^8_1, \alpha^8_3, \beta^8_3 )</td>
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Table II. The interatomic force constant matrices.

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<th></th>
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<td>$\alpha_3^3$</td>
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Table III. Equations relating interatomic force constants to interplanar force constants.

| \( n^1_t \) | \( = 4\alpha_1^1 + 8\alpha_2^4 + 4\alpha_3^7 \) |
| \( n^2_t \) | \( = \alpha_1^2 + 4\alpha_2^3 + 4\alpha_1^5 + 4\alpha_2^8 \) |
| \( n^3_t \) | \( = 4\alpha_1^4 + 8\alpha_2^7 \) |
| \( n^4_t \) | \( = \alpha_1^6 + 4\alpha_1^8 \) |

| \( n^1_t \) | \( = 4\alpha_1^1 + 4\alpha_2^4 + 4\alpha_2^4 + 4\alpha_1^7 \) |
| \( n^2_t \) | \( = \alpha_2^2 + 2\alpha_1^3 + 2\alpha_3^5 + 4\alpha_1^5 + 2\alpha_2^8 + 2\alpha_3^8 \) |
| \( n^3_t \) | \( = 4\alpha_2^4 + 4\alpha_1^7 + 4\alpha_2^7 \) |
| \( n^4_t \) | \( = \alpha_2^6 + 2\alpha_2^8 + 2\alpha_3^8 \) |

| \( \rho^1_t \) | \( = 2\alpha_1^1 + 2\beta_1^1 + \alpha_2^1 + \alpha_2^2 + 2\alpha_3^3 + 2\alpha_1^4 + 2\alpha_2^4 + 4\alpha_2^4 + 2\beta_1^4 - 4\beta_2^4 + \alpha_1^8 + 3\alpha_2^8 + 2\alpha_3^8 - 2\beta_3^8 \) |
| \( \rho^2_t \) | \( = \alpha_3^3 + \beta_3^3 + 2\alpha_1^4 + 2\alpha_2^4 + 4\beta_2^4 + 2\alpha_1^5 + 2\beta_1^5 + \alpha_1^6 + \alpha_2^6 + 2\alpha_1^7 + 2\alpha_3^7 \) |
| \( \rho^3_t \) | \( = 4\beta_1^7 + 2\alpha_1^8 + 2\alpha_3^8 \) |
| \( \rho^4_t \) | \( = \alpha_1^7 + 2\beta_3^7 + \alpha_3^8 + \alpha_2^8 + 2\beta_3^8 \) |

| \( \rho^1_t \) | \( = 2\alpha_1^1 + 2\alpha_2^2 + 4\alpha_1^4 + 2\alpha_1^4 + 4\alpha_2^4 + 4\alpha_1^8 + 2\alpha_3^8 \) |
| \( \rho^2_t \) | \( = \alpha_3^3 + 4\alpha_2^4 + 2\alpha_1^5 + 2\alpha_2^6 + 4\alpha_1^7 + 4\alpha_2^8 \) |
| \( \rho^3_t \) | \( = 2\alpha_3^7 + 2\alpha_3^8 \) |

| \( \sigma^1_t \) | \( = 3\alpha_1^1 - 2\beta_1^1 + \alpha_2^4 + 2\alpha_2^4 + 2\beta_1^4 - 4\beta_2^4 + 4\alpha_1^7 + 2\alpha_3^7 - 4\beta_3^7 \) |
| \( \sigma^2_t \) | \( = \alpha_1^2 + 2\alpha_2^2 + 3\alpha_1^5 - 2\beta_1^5 + 2\alpha_2^5 + 2\alpha_3^5 + 2\alpha_3^8 - 4\beta_3^8 \) |
| \( \sigma^3_t \) | \( = \alpha_1^3 + 2\beta_1^1 + 2\alpha_1^4 + 4\alpha_2^4 - 4\beta_1^4 \) |
| \( \sigma^4_t \) | \( = 2\alpha_3^3 + \alpha_3^3 + 2\beta_3^3 + \alpha_1^6 + 2\alpha_2^6 \) |
| \( \sigma^5_t \) | \( = \alpha_1^4 + 2\alpha_2^4 + 2\beta_1^4 + 4\beta_2^4 + 2\alpha_1^7 + \alpha_3^7 - 4\beta_1^7 + 2\beta_3^7 \) |
| \( \sigma^6_t \) | \( = \alpha_1^5 + 2\alpha_1^5 + 2\alpha_2^8 + 2\alpha_3^8 + 4\beta_3^8 \) |
| \( \sigma^7_t \) | \( = 2\alpha_1^7 + \alpha_3^7 + 4\beta_1^7 + 2\beta_3^7 \) |
\[
\begin{align*}
\sigma_1' &= 3\alpha_1' + \beta_1' + \alpha_4' + 2\alpha_2' - \beta_1' + 2\beta_2' + 4\alpha_1' + 2\alpha_3' + 2\beta_3' \\
\sigma_2' &= \alpha_1' + 2\alpha_2' + 3\alpha_1' + \beta_1' + 2\alpha_2' + 2\alpha_8' + 2\alpha_2' + 2\beta_3' \\
\sigma_3' &= \alpha_1' - \beta_1' + 2\alpha_1' + 4\alpha_1' + 2\beta_1' \\
\sigma_4' &= 2\alpha_1' + \alpha_3' - \beta_3' + \alpha_1' + 2\alpha_3' \\
\sigma_5' &= \alpha_1' + 2\alpha_2' - \beta_1' - 2\beta_2' + 2\alpha_1' + \alpha_3' + 2\beta_1' - \beta_3' \\
\sigma_6' &= \alpha_1' - \beta_1' + 2\alpha_1' + 2\alpha_2' + 2\alpha_8' - 2\beta_3' \\
\sigma_7' &= 2\alpha_1' + \alpha_3' - 2\beta_1' - \beta_3'
\end{align*}
\]
With a knowledge of the interatomic force constants, it is possible to calculate the elastic constants from the following equations of Squires\textsuperscript{3}

\[ c_{11} = \frac{4}{a} \sum_{s} \frac{n_{s}}{48} \sum_{j} (h_{j}^{s})^{2} \alpha_{j}^{s} \]

\[ c_{44} = \frac{2}{a} \sum_{s} \frac{n_{s}}{48} \sum_{j} [(h_{j+1}^{s})^{2} + (h_{j+2}^{s})^{2}] \alpha_{j}^{s} \]  

(10)

In these equations \( a \) is the lattice parameter and \( n_{s} \) is given in Table I.
RESULTS

The phonon dispersion curves for niobium, molybdenum, and a series of six niobium-molybdenum alloys were published by Powell et al.\textsuperscript{7} These curves are reproduced in Fig. 1 for niobium and molybdenum and in Appendix III for the alloys. Data are presented for the following branches: $\Delta_1$, $\Delta_5$, $\Sigma_1$, $\Sigma_3$, $\Lambda_1$, and $\Lambda_3$. The $\Delta_1$ and $\Delta_5$ branches correspond respectively to longitudinal and transverse modes for phonon wave vectors parallel to the [100] axis. Similarly, the $\Sigma_1$ and $\Sigma_3$ branches correspond to longitudinal and transverse modes for phonon wave vectors parallel to the [110] axis. In the case of $\Sigma_3$, the displacement is in a direction parallel to the 4-fold symmetry axis. Finally, the $\Lambda_1$ and the $\Lambda_3$ are respectively longitudinal and transverse modes for $\vec{q}$ parallel to the [111] direction. For each of the branches, a Fourier analysis was carried out by the above authors. The resulting Fourier coefficients, i.e., the interplanar force constants, are found in Table IV.

Six sets of simultaneous equations were then solved. The simplest set included only first and second-nearest neighbors. The most complex set included interactions out to seven nearest neighbors. The other sets of equations correspond to the remaining intermediate possibilities.

The sets including interactions out to third and seventh-nearest neighbors yielded force constants which corresponded most closely to the published values for pure niobium\textsuperscript{8} and pure molybdenum.\textsuperscript{9} It is assumed that these were also the "best fits" (obtainable with the present data) for the six alloys. A comparison of the interatomic force constants determined by the aforementioned methods with those in the literature for niobium and molybdenum is given in Table V.
Table IV. The interplanar force constants for the niobium-molybdenum alloys.

<table>
<thead>
<tr>
<th>Nb</th>
<th>Mo</th>
<th>Nb-Mo</th>
<th>Mo-Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1</td>
<td>0.1</td>
<td>1.0</td>
</tr>
<tr>
<td>0</td>
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</tr>
<tr>
<td>0</td>
<td>3</td>
<td>0.3</td>
<td>3.0</td>
</tr>
<tr>
<td>0</td>
<td>4</td>
<td>0.4</td>
<td>4.0</td>
</tr>
</tbody>
</table>

**Notes:**
- The values are given in units of 10^-12 dyne cm.
- The Nb-Mo and Mo-Nb force constants are given for the equilibrium position.
Fig. 1 Dispersion curves for a) niobium and b) molybdenum.
Table V. First and second-nearest neighbor interatomic force constants for niobium and molybdenum.

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<tr>
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<th>$a_1^1$</th>
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<th>$a_1^2$</th>
<th>$a_2^2$</th>
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<td>Nb$^b$</td>
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<td>8.84</td>
<td>14.16</td>
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<tr>
<td>Nb$^c$</td>
<td>12.60</td>
<td>9.93</td>
<td>14.99</td>
<td>4.91</td>
</tr>
<tr>
<td>Nb$^7$</td>
<td>14.09</td>
<td>10.50</td>
<td>9.59</td>
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<tr>
<td>Mo$^c$</td>
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<tr>
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<td>Mo$^7$</td>
<td>16.67</td>
<td>11.37</td>
<td>45.55</td>
<td>-1.71</td>
</tr>
</tbody>
</table>

Nb$^a$ - R. I. Sharp$^{11}$  
Nb$^b$ - Nakagawa and Woods$^8$  
Mo$^c$ - Woods and Chen$^9$  

$\text{Nb}^3$ and $\text{Mo}^3$ are calculated from a third neighbor fit.  
$\text{Nb}^7$ and $\text{Mo}^7$ are calculated from a seventh neighbor fit.
Table VI. Calculated interatomic force constants.

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<tr>
<th></th>
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<th>35% Mo</th>
<th>41% Mo</th>
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<td>18.71</td>
<td>17.57</td>
<td>16.67</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>10.50</td>
<td>11.25</td>
<td>5.69</td>
<td>12.87</td>
<td>11.00</td>
<td>8.49</td>
<td>8.70</td>
<td>11.37</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>9.59</td>
<td>16.37</td>
<td>31.29</td>
<td>30.69</td>
<td>36.98</td>
<td>46.54</td>
<td>48.25</td>
<td>45.55</td>
</tr>
<tr>
<td>$\alpha_3$</td>
<td>-1.87</td>
<td>-2.43</td>
<td>-7.99</td>
<td>-4.11</td>
<td>-4.80</td>
<td>-3.94</td>
<td>-2.74</td>
<td>-1.71</td>
</tr>
<tr>
<td>$\alpha_4$</td>
<td>2.10</td>
<td>2.21</td>
<td>5.06</td>
<td>2.45</td>
<td>2.86</td>
<td>3.16</td>
<td>3.43</td>
<td>3.57</td>
</tr>
<tr>
<td>$\alpha_5$</td>
<td>-8.12</td>
<td>-8.71</td>
<td>1.47</td>
<td>-6.31</td>
<td>-3.53</td>
<td>2.38</td>
<td>3.03</td>
<td>0.96</td>
</tr>
<tr>
<td>$\beta_3$</td>
<td>0.97</td>
<td>0.74</td>
<td>1.79</td>
<td>1.76</td>
<td>2.06</td>
<td>2.02</td>
<td>2.73</td>
<td>1.11</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>0.32</td>
<td>-0.08</td>
<td>-0.01</td>
<td>0.08</td>
<td>-0.53</td>
<td>-0.69</td>
<td>-0.67</td>
<td>-0.55</td>
</tr>
<tr>
<td>$\beta_2$</td>
<td>1.04</td>
<td>1.12</td>
<td>1.12</td>
<td>0.74</td>
<td>1.20</td>
<td>0.39</td>
<td>-0.34</td>
<td>-1.22</td>
</tr>
<tr>
<td>$\beta_1$</td>
<td>-0.25</td>
<td>-0.30</td>
<td>-3.14</td>
<td>0.19</td>
<td>-0.01</td>
<td>-1.51</td>
<td>-0.96</td>
<td>0.37</td>
</tr>
<tr>
<td>$\alpha_5$</td>
<td>0.87</td>
<td>-0.02</td>
<td>1.58</td>
<td>0.21</td>
<td>-0.26</td>
<td>1.42</td>
<td>1.28</td>
<td>0.88</td>
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<tr>
<td>$\beta_1$</td>
<td>-0.07</td>
<td>-0.18</td>
<td>-4.81</td>
<td>-0.90</td>
<td>-1.96</td>
<td>-3.34</td>
<td>-2.12</td>
<td>-0.03</td>
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<tr>
<td>$\beta_1$</td>
<td>-1.72</td>
<td>-1.67</td>
<td>5.28</td>
<td>-1.18</td>
<td>-1.26</td>
<td>-0.32</td>
<td>0.27</td>
<td>0.76</td>
</tr>
</tbody>
</table>
Table VI. Continued

<table>
<thead>
<tr>
<th></th>
<th>Nb</th>
<th>15% Mo</th>
<th>35% Mo</th>
<th>41% Mo</th>
<th>56% Mo</th>
<th>75% Mo</th>
<th>91% Mo</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha_1^6$</td>
<td>10.34</td>
<td>13.87</td>
<td>-0.71</td>
<td>8.90</td>
<td>8.51</td>
<td>-1.46</td>
<td>-4.64</td>
<td>-5.15</td>
</tr>
<tr>
<td>$\alpha_2^6$</td>
<td>-6.34</td>
<td>-7.30</td>
<td>-6.24</td>
<td>-4.84</td>
<td>-4.49</td>
<td>-0.92</td>
<td>2.46</td>
<td>4.70</td>
</tr>
<tr>
<td>$\alpha_1^7$</td>
<td>1.50</td>
<td>1.65</td>
<td>1.51</td>
<td>1.37</td>
<td>1.03</td>
<td>0.47</td>
<td>-0.46</td>
<td>-0.74</td>
</tr>
<tr>
<td>$\alpha_3^7$</td>
<td>-3.50</td>
<td>-3.68</td>
<td>-3.35</td>
<td>-2.30</td>
<td>-1.75</td>
<td>-0.24</td>
<td>0.47</td>
<td>0.66</td>
</tr>
<tr>
<td>$\beta_1^7$</td>
<td>-0.12</td>
<td>-0.82</td>
<td>-0.15</td>
<td>-0.02</td>
<td>-0.14</td>
<td>0.78</td>
<td>0.32</td>
<td>-0.12</td>
</tr>
<tr>
<td>$\beta_3^7$</td>
<td>0.19</td>
<td>1.14</td>
<td>1.02</td>
<td>-0.16</td>
<td>1.69</td>
<td>-0.85</td>
<td>-0.62</td>
<td>-0.78</td>
</tr>
</tbody>
</table>
The seventh-nearest neighbor interaction fit has average deviations of $0.84 \times 10^3$ for niobium and $0.53 \times 10^3$ dynes/cm for molybdenum while the third neighbor fit has values of $1.51 \times 10^3$ and $1.07 \times 10^3$ respectively.

The computed values of the resulting interatomic force constants for third and seventh neighbor interactions are given in Table VI. The behavior of the first and second-nearest neighbor force constants for both cases is plotted in Figs. 2-5. The force constants associated with atoms beyond second neighbor positions are roughly one or two orders of magnitude smaller than those associated with first and second-nearest neighbors. Furthermore, the larger of them ($\alpha_3^3, \alpha_1^6, \alpha_2^6, \alpha_3^7$) decrease in magnitude with increasing molybdenum content while the remainder seem to have a uniformly smaller magnitude across the range of compositions.

The theoretical values of the $c_{11}$ and $c_{44}$ elastic constants were then calculated from the interatomic force constants using Eqs. (10). A comparison of results of third and seventh-nearest neighbor calculations is given in Figs. 6 and 7.
Fig. 2 The general interatomic force constant $\alpha_1$ for the niobium-molybdenum alloy system.
Fig. 3 The general interatomic force constant $\beta_1$ for the niobium-molybdenum alloy system.
Fig. 4 The general interatomic force constant $a_1^2$ for the niobium-molybdenum alloy system.
Fig. 5 The general interatomic force constant $\alpha^2$ for the niobium-molybdenum alloy system.
Fig. 6 The elastic constant $c_{11}$ calculated from the interatomic force constants for the niobium-molybdenum alloy system.
Fig. 7 The elastic constant $c_{44}$ calculated from the interatomic force constants for the niobium-molybdenum alloys.
DISCUSSION

On comparing the present results for the interatomic force constants for niobium and molybdenum with those reported in the literature (Table V), it appears that the seventh-neighbor fit is better than the third-neighbor fit for both pure metals. Thus one would assume the same to be true for the alloys.

On the other hand, the calculated elastic constants (Figs. 7 and 8) for the third-neighbor fit agree well with the measured values while the corresponding values for the seventh-neighbor fit differ considerably. The results of the third-neighbor fit follow the observed trends as the concentration of molybdenum is increased.

Because the two checks yield contradictory results, it is not possible to conclude that the results of either of the two methods are intrinsically better than the other. One would expect that the seventh-neighbor fit would be more successful in reproducing the details of the dispersion curves and in general give better results for the elastic constants. It appears, however, that the slopes as $q \to 0$, i.e., the elastic constants, are more faithfully reproduced by the third-neighbor fit.

It is possible that the gross features of the dispersion curves are adequately accounted for by the interactions only out to third-nearest neighbor. In fact, it is well known that the presence of distant neighbor forces is only necessitated by the fine structure in the dispersion curves.

There was an implicit assumption in this analysis that the interplanar force constants beyond those needed for the various fits could
taken as zero. An obvious corollary to this statement is that the remaining interplanar force constants should have been modified after dropping those distant plane terms. These factors could be responsible for the disparity in the present results, however, Brockhouse et al.\textsuperscript{1} have shown that the relevant \( \Phi_n \)'s do not change significantly when considering more than third-neighbor interactions. Furthermore, the distant neighbor \( \Phi_n \)'s are found in general to oscillate about zero with relatively small magnitude. Thus, by assuming them to be zero, one is effectively taking the "average", thereby neglecting the effects which produce the fine structure in the dispersion curves.

In any case neither of the two best-fits produces exactly the same trends in first and second-nearest neighbor force constants as the central force approach generated in Part I. In particular, the general force constants \( \alpha_1^1, \beta_1^1, \alpha_1^2, \) and \( \alpha_2^2 \) all have the same general behavior (Figs. 2-5) as a function of molybdenum concentration. They all have a broad maximum (minimum for \( \alpha_2^2 \) from seventh-neighbor calculation) near the 50% composition. This is, of course, contrary to the monotonically increasing behavior of the general force constants seen in part I. There is, however, still a net increase in all but the \( \alpha_2^2 \) from niobium to molybdenum in agreement with the results of part I.

In addition, one can see that although the force constants associated with those atoms beyond the second neighbor are certainly not negligible, in most cases they are considerably smaller. Furthermore those which are not initially small tend to decrease in magnitude with increasing molybdenum content. Thus, the distant neighbor forces seem to be significantly weaker for the molybdenum-rich alloys.

Because of the nature of the force constant curves referred to above,
it seems rather difficult to draw any valid conclusions about the band structure from them.
CONCLUSIONS

1) The first and second-nearest neighbor force constants increase as molybdenum is added to niobium.

2) Forces for atoms beyond second-nearest neighbors are generally smaller than those of first and second-nearest neighbors, however, they are not negligible.

3) The importance of the distant neighbor forces decreases as molybdenum is added to niobium.
REFERENCES


APPENDIX I

Determination of Linear Expansion Coefficients

The method of measurement made use of an electromechanical displacement transducer. The instrumentation is depicted in Fig. A-1. Single crystal rods about 5 cm in length were connected to the transducer via a quartz rod, Fig. A-2. The lower part of this apparatus was housed in a heater can which was immersed in liquid nitrogen. This enabled the temperature to be varied over the range of interest (−190°C to +100°C). As the temperature was varied, the calibrated output of the displacement transducer, corresponding to the associated expansion and contraction of the sample, was plotted on the Y-axis of an X-Y recorder. The copper-constantan thermocouple voltage, i.e. the temperature, was plotted on the X-axis of the recorder.

In order to check the method, the thermal expansion of a pure copper rod was measured. The results were found to be in excellent agreement with the work of NIX and MacNair¹ as is shown in Fig. A-3.

Over the temperature range of interest, the expansion curves for the various alloys were found to be linear. Thus, the expansion can be characterized, in the present case, by the equation

\[ \frac{\Delta l}{l_o} = \alpha(T - 25^\circ) \]

(1)

where \( l_o \) is the length measured at 25°C and \( T \) is the temperature in °C.
INSTRUMENTATION FOR LINEAR EXPANSION MEASUREMENTS

![Diagram of instrumentation for linear expansion measurements](image)

Fig. A-1.
Fig. A-2 Sample holder for determination of expansion coefficients.
APPENDIX II

Computational Programs

Three programs were written utilizing Basic computer language. They were used on the time-sharing terminal of the Rice B5500 Borroughs computer.

Program I, CURVE

This program was used to provide an \( n \)th order polynomial curve fit for the "time of flight" measurements as a function of temperature. It required the operator to supply:

a) the number of data points \((X,Y)\),

b) the values of the corresponding \( X \)'s and \( Y \)'s, and

c) the desired degree of the polynomial.

In turn, the computer calculated the \( n + 1 \) constants for an \( n \)th order polynomial. It also computed the standard deviation which allowed one to judge how good of a fit was obtained.

This program was equipped to determine the polynomial fit for either linear-linear, linear-log, log-linear or log-log plots. It also had provisions for listing the input \( X \) and \( Y \) values along with the \( Y \) values as calculated from the polynomial for comparison.

Program II, ELAST

This program was used to calculate the elastic constants from the "time of flight" polynomial function, the thermal expansion function, \( \Delta l/l_0(T) \), and room temperature values of the density and length, \( \rho_0 \) and \( l_0 \). The actual equation which the program evaluated is derived below.

The elastic constant of a crystal is related to its density and
the velocity of an appropriate acoustic wave by the equation

\[ c_{ij} = \rho v_k^2 \]  

(2)

where \( c_{ij} \) is the elastic constant, \( \rho \) the density and \( v_k \) the velocity.

Now, in a cylindrical sample of length \( l \) and diameter \( d \), the acoustic wave velocity is related to the pulse superposition frequency, \( f \), by the relation

\[ v_k = 2lf. \]  

(3)

Also, for this geometry we have \( \rho = m/V \) where \( V = \pi d^2 l/4 \) and \( m \) is the mass of the cylinder. If we assume that the thermal expansion is isotropic, then by substuting in for \( \rho \) and \( V \), the following equation will result

\[ c = 4\rho_o l_o^3 f^2 / l \]  

(4)

Finally, \( l \) is related to the measured thermal expansion by the relation

\[ l(T) = l_o \left( 1 + \Delta l(T)/l_o \right). \]

Upon substitution, we arrive at the final expression for the elastic constants

\[ c(T) = \frac{4\rho_o l_o^2 l_o^2(T)}{1 + \Delta l(T)/l_o }. \]  

(5)

This program evaluated the elastic constants as a function of temperature between upper and lower temperature extremes at fixed temperature increments.

Program III, EQN SOLVER

This program was used to solve a set of \( R \) simultaneous equations with \( C \) unknowns. After supplying the matrix of unknown coefficients along with the associated interplanar constants, the program computed the unknowns. It had a provision to check the interatomic constants by recalculating the interplanar constants.
PROGRAM I

CURVE
1000 DIM P(30,2), w(30,30), C(30,1), A(30,7), B(7,30), F(7,7)
1010 DIM G(7,1), H(7,7), T(7,1), U(30,7), V(30,1)
1020 PRINT "NO. PTS?"
1030 INPUT N
1040 PRINT "INPUT PTS: X, Y"
1050 MAT P = ZER(N, 2)
1060 FOR J = 1 TO N
1070 INPUT P(J, 1), P(J, 2)
1080 NEXT J
1090 PRINT "NO. TO CHANGE?"
1100 INPUT K
1110 IF K = 0 THEN 1180
1120 PRINT "INPUT LINE, X, Y"
1130 FOR J = 1 TO K
1140 INPUT L, X, Y
1150 P(L, 1) = X
1160 P(L, 2) = Y
1170 NEXT J
1180 PRINT "DEGREE?"
1190 INPUT a
1200 D = 3 + 1
1210 PRINT "NO. WTS?"
1220 INPUT N1
1230 MAT w = IDV(N1, N)
1240 IF N1 = 0 THEN 1300
1250 PRINT "INPUT LINE, WT"
1260 FOR J = 1 TO N1
1270 INPUT X1, X2
1280 w(X1, X1) = X2
1290 NEXT J
1300 MAT C = ZER(N1, 1)
1310 MAT A = ZER(N1, D)
1320 MAT B = ZER(D, N)
1330 MAT F = ZER(D, D)
1340 MAT G = ZER(D, 1)
1350 MAT H = ZER(D, D)
1360 MAT T = ZER(D, 1)
1370 MAT U = ZER(N1, D)
1380 MAT V = ZER(N1, 1)
1390 PRINT "TYPE 1,1 FOR LIN-LIN; 1,2 FOR LIN-LOG"
1400 PRINT "TYPE 2,1 FOR LOG-LIN; 2,2 FOR LOG-LOG"
1410 INPUT Z1, Z2
1420 FOR J = 1 TO N
1430 A(J, 1) = 1
1440 Z1 Z1 GOTO 1450, 1470
1450 A(J, 2) = P(J, 1)
CURVE CONTINUED
1460 G010 1480
1470 A(J,2) = LOG(P(J,1))
1480 FOR K = 3 TO D
1490 A(J,K) = A(J,2)**(K-1)
1500 NEXT K
1510 ON Z2 G010 1520,1540
1520 C(J,1) = P(J,2)
1530 G010 1550
1540 C(J,1) = LOG(P(J,2))
1550 NEXT J
1560 MAT U = W*A
1570 MAT V = W*C
1580 MAT B = TRV(A)
1590 MAT F = B*U
1600 MAT G = B*V
1610 MAT H = INV(F)
1620 MAT I = H*G
1630 MAT PRINT T
1625 Z = 1
1630 G0SUB 1730
1640 PRINT "AVE DEV =":R
1650 PRINT "1=LIS1, 2=NEW FN, 3=NEW DATA, 4=STOP"
1660 INPUT S
1670 ON S G010 1680,1180,1020,1710
1680 Z = 2
1690 G0SUB 1730
1700 G010 1650
1710 STOP
1730 R = 0
1740 FOR J = 1 TO N
1750 Y1 = 0
1760 FOR K = 1 TO D
1770 Y1 = Y1+R(K,1)*A(J,K)
1780 NEXT K
1790 ON Z1 G010 1800,1820
1800 X = A(J,2)
1810 G010 1830
1820 X = EXP(A(J,2))
1830 ON Z2 G010 1840,1860
1840 Y = C(J,1)
1850 G010 1880
1860 Y = EXP(C(J,1))
1870 Y1 = EXP(Y1)
1880 ON Z G010 1890,1910
1890 R = R+ABS(Y-Y1)
1900 G010 1920
1910 PRINT X,Y,Y1
1920 NEXT J
1930 R = N/N
1940 RETURN-
ELAST
1000 DIM F(7), L(7)-
1010 Z = 0-
1020 PRINT "INPUT DEN AT ROOM T"-
1030 INPUT P-
1040 PRINT "INPUT LENGTH AT ROOM T"-
1050 INPUT R-
1060 PRINT "INPUT DEGREE FOR FREQ"-
1070 INPUT Q1-
1080 PRINT "INPUT CONSTANTS"-
1090 FOR J = 1 TO Q1+1-
1100 INPUT F(J)-
1110 NEXT J-
1120 IF Z=0 THEN 1190-
1130 PRINT "INPUT DEGREE FOR LENGTH"-
1140 INPUT Q2-
1150 PRINT "INPUT CONSTANTS"-
1160 FOR J = 1 TO Q2+1-
1170 INPUT L(J)-
1180 NEXT J-
1190 PRINT "1=RESTAT"-
1190 PRINT "1=RESTART, 2=NEW FREQ, 3=NEW LENGTH, 4=RUN"-
1200 INPUT Z-
1210 ON Z GOTO 1010, 1060, 1130, 1220-
1220 PRINT "INPUT INITIAL T, INCREMENT, NUMBER"-
1230 INPUT T, I, N-
1240 PRINT-
1250 PRINT-
1260 T = T-I-
1270 FOR S = 1 TO N-
1280 T = T+I-
1290 G = 0-
1300 M = 0-
1310 FOR K = 1 TO Q1+1-
1320 G = G+F(K)*T**(K-1)-
1330 M = M+L(K)*T**(K-1)-
1340 NEXT T-
1340 NEXT K-
1350 L = 4*P*R*R*G/(1+M)-
1360 PRINT T, C-
1370 NEXT S-
1380 PRINT-
1390 PRINT-
1400 PRINT "1=CHANGE, 2=STOP"-
1410 INPUT Z-
1420 ON Z GOTO 1190, 1430-
1430 STOP-
1440 END-
1330 NEXT K-
1340 FOR K = 1 TO Q2+1-
1342 M = M+L(K)*T**(K-1)-
1344 NEXT K-
1350 C = 4*P*R*R*G*G/(1+M)-
PROGRAM III

EQN SOLVER
100 DIM A(35,35), B(35,1), D(35,35), E(35,35), F(35,1), H(35,1), I(35,1)
200 PRINT "NO MORE THAN 35 EQNS OR VARS"
300 X=0
400 PRINT "ROWS, COLS?"
500 INPUT R,C
600 PRINT "INPUT MAT"
700 MAT A=ZER(R,C)
800 MAT INPUT A
900 PRINT "NO. CHNGS MAT?"
1000 INPUT Z
1100 IF Z=0 THEN 1700
1200 PRINT "ROW, COL, VAR?"
1300 FOR J=1 TO Z
1400 INPUT B1, B2, B3
1500 A(B1, B2)=B3
1600 NEXT J
1700 IF X=0 THEN 1900
1800 GOTO 2200
1900 PRINT "INPUT CONS"
2000 MAT B=ZER(R,1)
2100 MAT INPUT B
2200 PRINT "NO. CHNGS CONS?"
2300 INPUT Z
2400 IF Z=0 THEN 3000
2500 PRINT "ROW, VAR?"
2600 FOR J=1 TO Z
2700 INPUT B1, B2
2800 B(B1,1)=B2
2900 NEXT J
3000 MAT D=ZER(C,R)
3100 MAT E=ZER(C,C)
3200 MAT F=ZER(C,1)
3300 MAT I=ZER(R,1)
3400 MAT H=ZER(C,1)
3500 MAT G=ZER(C,C)
3600 IF C=R THEN 4100
3700 MAT D=INV(A)
3800 MAT E=D*A
3900 MAT F=D*B
4000 GOTO 4300
4100 MAT E=A
4200 MAT F=B
4300 MAT D=ZER(C,C)
4400 MAT D=INV(E)
4500 MAT H=D*F
EDN SOLVER CONTINUED

4600 PRINT
4700 MAT PRINT H
4800 PRINT "1=CHK, 2=RESTART, 3=CHVG, 4=STOP"
4900 INPUT X
5000 ON X GOTO 5100, 300, 900, 5700
5100 MAT I=A*H
5200 PRINT "ACTUAL, COMPUTED CONSTANTS"
5300 FOR J=1 TO R
5400 PRINT B(J,J), I(J,J)
5500 NEXT J
5600 GOTO 4800
5700 STOP
5800 END
APPENDIX III

Phonon Dispersion Curves for Nb-Mo Alloys

The measurements were made by Powell, Martel and Woods\textsuperscript{2} on the triple-axis spectrometer\textsuperscript{3} at the Chalk River facility at a temperature of 296 K. The experiment was carried out using the spectrometer in its constant $\vec{Q}$ mode of operation with variable incident energy.

The niobium crystals were obtained from Metals Research Ltd., Cambridge England and the molybdenum crystals were supplied by the Linde Co. The alloy samples were produced by Materials Research Corp.

The alloy compositions were checked by measuring the lattice spacing with neutron diffraction methods, and comparing the measured spacings with the published values for this alloy system.\textsuperscript{4}
Fig. A-4 Dispersion curves of Nb$_{0.85}$Mo$_{0.15}$.

Fig. A-5 Dispersion curves of Nb$_{0.65}$Mo$_{0.35}$.

Fig. A-6 Dispersion curves of Nb$_{0.59}$Mo$_{0.41}$. 

Fig. A-7 Dispersion curves of $\text{Nb}_{0.44}\text{-Mo}_{0.56}$.

Fig. A-8 Dispersion curves for $\text{Nb}_{0.25}\text{-Mo}_{0.75}$.

Fig. A-9 Dispersion curves for $\text{Nb}_{0.09}\text{-Mo}_{0.91}$.
REFERENCES


