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Solid solubility of sulfur, selenium, and tellurium in molybdenum at 1100°C, lattice constants thermal expansion coefficients, and densities of molybdenum and the molybdenum-base alloys

Ramesh Purushottamdas Shodhan

Recommended Citation

SOLID SOLUBILITY OF SULFUR, SELENIUM, AND TELLURIUM IN

MOLYBDENUM AT 1100°C, LATTICE CONSTANTS, THERMAL

EXPANSION COEFFICIENTS, AND DENSITIES OF

MOLYBDENUM AND THE

MOLYBDENUM-BASE ALLOYS

BY

RAMESH PURUSHOTTAMDAS SHODHAN, 1937   78p

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A

THESIS

submitted to the faculty of the

UNIVERSITY OF MISSOURI AT ROLLA

in partial fulfillment of the requirements for the

Degree of

MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

Rolla, Missouri

1965

———

Approved by

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ABSTRACT

The lattice constant of Hilger molybdenum (99.9935%) at 25° C is 3.14700 Å and that of Sylvania molybdenum at 25° C is 3.14696 Å. The coefficient of thermal expansion of Hilger Mo is 4.89×10^{-6} °C^{-1}.

The coefficient of thermal expansion of the Mo alloy with 2.0 at. % S is 5.02×10^{-6} °C^{-1}, with 2.0 at. % Se - 5.16×10^{-6} °C^{-1}, and with 2.0 at. % Te - 5.15×10^{-6} °C^{-1}.

The solid solubility limit of S in Mo at 1100° C is estimated to be in the vicinity of 2.0 atomic per cent and that of Se and Te in the vicinity of 1.5 atomic per cent.

The density of Hilger Mo, as received, is found to be 9.843 gm/cc, and that of the Sylvania sample to be 10.222 gm/cc.

The density of Hilger Mo after heating in vacuum at 700° C for 2 hours is found to be 9.973 gm/cc, while that of the Sylvania sample is 10.074 gm/cc.

The density of a Westinghouse Mo sheet is found to be 10.237 gm/cc.

Also the density of the Mo-S alloys containing S upto 5.0 atomic per cent are determined. They are much lower than that of the pure Mo.

Using the respective measured densities and lattice constants, the number of atoms per unit cell are calculated for each sample of pure Mo. They are:

Hilger Mo: as received - 1.9261; after heating - 1.9516,

Sylvania Mo: as received - 2.0003; after heating - 1.9713,

Westinghouse Mo sheet - 2.0033.

ACKNOWLEDGEMENTS

The author wishes to express his sincere appreciation and gratitude to Dr. M. E. Straumanis, Professor of Metallurgical Engineering and Research Professor of Materials, for his guidance and assistance during this research work.

Sincere thanks to Mr. C. D. Kim for his assistance and to various members of the faculty for their help and suggestions in the present investigation.

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CHAPTER I

INTRODUCTION

There is an almost universal trend today toward
higher operating temperatures in military applications and
commercial industries. There can be no doubt that improved
high-temperature materials are one of the important keys to
the development of advanced military aircraft, weapons,
missiles and satellites. An intensive search is, therefore,
now underway for new and improved materials.

With the ever increasing requirement for engineering
materials having adequate mechanical properties at ever
higher temperatures there has been, in quite recent years,
a considerable increase in the study of molybdenum and
molybdenum-rich alloys. Since 1945 extensive information
on the engineering properties of molybdenum and molybdenum-
base alloys has gradually become more available.

The studies into the physical metallurgy of molybdenum
have made a rapid progress. A large number of binary phase
diagrams have been investigated and many are still under
investigation. Many phase diagrams could not be established
previously because of the limited efficiency of the old
methods of thermal analysis and microscopic examination.

How x-ray diffraction methods have greatly extended the field of investigation.

The present work involves the determination of solid solubility of elements with large atoms such as sulfur, selenium, and tellurium in molybdenum at 1100° C using the parametric method. Furthermore, the thermal expansion co-efficients of pure molybdenum and of molybdenum-base solid solutions containing the elements just mentioned were of interest. In addition the densities of pure molybdenum and of some of the molybdenum-base chalcogenide alloys were also determined.

CHAPTER II

REVIEW OF LITERATURE

The survey of literature revealed no published studies on the solid solubility of sulfur, selenium, and tellurium in molybdenum.

Many authors have investigated the Mo-S, Mo-Se, and Mo-Te systems. However, their work mainly deals with the study of the intermediate compounds of molybdenum with sulfur, selenium, and tellurium.

In the chemical literature (1) the existence of Mo_2S_3, MoS_2, Mo_2S_5, MoS_3, and MoS_4 is reported. The work by Ehrlich (2) has shown that synthetic preparations can be obtained which contain only the phase of MoS_2 in the presence of metallic Mo. MoS_3 can be prepared (3) by decomposition of complex thiomolybdates. McCabe (4) obtained a sulfide by thermal decomposition of MoS_2 at approximately $1100°$ C which was identified by x-ray and chemical analysis as Mo_2S_3.

Stubbles and Richardson (5), in 1957, made an extensive study of the molybdenum-sulfur system using a radiochemical method to determine the equilibria which exist between the lower sulfides of molybdenum and hydrogen and hydrogen

sulfide. Mo_2S_3 and MoS_2 were identified by chemical analysis and x-ray diffraction. The unit cell of Mo_2S_3 is tetragonal and that of MoS_2 hexagonal.

However, there are also studies which show that S has some solubility in Mo. Schaefer (6) in a thermodynamic study of the Mo-S system at 1100° C found the extent of solid solubility in molybdenum to be approximately 1.5 atomic per cent sulfur at 1100° C.

There were no data concerning the solid solubility of Se and Te in Mo.

In the Mo-Se system, the existence of Mo_2Se_3, $MoSe_2$, Mo_2Se_5 and of $MoSe_3$, prepared in chemical reactions, is reported by Wendehorst (7).

Morette (8) identified the synthetically prepared phases Mo_2Te_3 (66.61 wt. % Te) and $MoTe_2$ (72.68 wt. % Te).

A considerable amount of work has been done to determine the lattice spacing, coefficient of thermal expansion, and density of molybdenum.

Among those who have made lattice spacing determination are:

1. Jette and Foote (9) found, in 1935, for hydrogen-reduced Mo, a = 3.1410 kX at 25° C. Photographs were taken

in a 10 cm. diameter symmetrical focusing camera.

2. Lu and Chang (10) found, in 1941, for Hilger Mo powder, a = 3.1403 kX at 20° C, using an improved back reflection method claimed to be accurate to 1 part in 50,000.

3. Swanson and Tatge (11) found, in 1953, for a sample prepared by fused salt electrolysis, a = 3.1472 Å at 25° C.

For the purpose of comparison, the values given in kX units are converted into Å units, using the factor 1.00202, and then reduced to one standard temperature (25° C), using the coefficient of thermal expansion 5.00×10^{-6} °C^{-1} . Table I lists these reduced values of the lattice parameter of molybdenum.

The results of determining the coefficient of thermal expansion of molybdenum are given in Table II.

The density of molybdenum is listed in the Handbook of Chemistry and Physics (15) as 10.20 gm/cc. In an NBS circular, "Standard X-ray Diffraction Powder Patterns", Swanson and Tatge (11) give the calculated value of density of molybdenum as 10.220 gm/cc at 25° C.

TABLE   I

Lattice Parameters Reported for Pure Mo at 25° C

Reference	Year	a, Å
Jette and Foote (9)	1935	3.1474
Lu and Chang (10)	1941	3.1467
Swanson and Tatge (11)	1953	3.1472

TABLE II

Coefficient of Thermal Expansion of Pure Mo

Reference	Year	Temp. Range	Coefficient of Thermal Exp. per °C
Hidnert and Gero (12)	1924	25° - 100°C	4.90×10^{-6}
Michel (13)	1938	–	5.00×10^{-6}
Nix and MacNair (14)	1942	-187° - +25°C	5.20×10^{-6}

CHAPTER III

EXPERIMENTAL PROCEDURE

A. Materials Used

1. **Molybdenum.** The molybdenum (99.9935 %) was sup-
plied by Hilger Co. in the form of a very fine powder
having the following analysis:

Element	Estimate of Quantity Present-%
Iron	0.0015
Silica	0.0050
	Traces only of other elements

Another sample from Sylvania Electric Products Inc. con-
tained 99.95 % molybdenum having the following analysis:

Element	Estimate of Quantity Present ppm, max.
Al	10
Ca	10
Cr	50
Cu	10
Fe	50
Pb	10
Mg	10
Mn	10
Ni	50
Si	50
Sn	50
C	50

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2. <u>Sulfur</u>. The sulfur in a sublimed form or very fine powder was from Fisher Scientific Co.

3. <u>Selenium</u>. The sample of granular selenium (99.999 %) was obtained from ASARCO.

4. <u>Tellurium</u>. The sample of large polycrystalline tellurium (99.999 %) was also supplied by ASARCO.

B. Preparation of the Alloys

The calculated amount of the Hilger molybdenum and the alloying element (S, Se or Te) was weighed on an analytical balance with an accuracy of $\pm$ 0.00005 gm and then the powders were ground intimately in a mortar. The mixture was placed into a clean, dry fused quartz tube closed at one end. The tube with its contents was evacuated using a mechanical vacuum pump and the tube was sealed off.

The mixture of the elements inside the evacuated, sealed tube was then placed in a horizontal tube furnace connected with a temperature controller. The temperature of the furnace was measured with a thermocouple calibrated against the melting points of pure copper, antimony and zinc. Each Mo mixture was heated at 1100° C for 144 hours. Then the tubes were quenched in ice water, assuming thereby

that the chalcogenes, dissolved in the Mo at 1100° C, would not segregate at room temperature.

C.   The Lattice Parameter Method for Solubility Determination

Since the lattice parameter of a solid solution varies with the concentration of the solute, the composition of a given solution can be determined from a measurement of its lattice parameter. Thermal expansion coefficients can also be determined by measurements of lattice parameter as a function of temperature. Since, in general, a change in solute concentration or temperature produces only a small change in lattice parameter, rather precise parameter measurements must be made in order to measure accurately the small changes.

In the present investigation, the solvent metal, molybdenum, has a body centered cubic crystal structure while the solute elements, S, Se, and Te, are noncubic. In comparison with the Mo atoms, the atoms of S, Se, and Te are rather large. Because of these reasons, a very low solubility of S, Se, and Te in Mo has to be expected. With the low solubility, a very small change in the lattice parameter of Mo will result. Therefore, it becomes necessary

to use a lattice parameter determination method of highest precision.

The process of measuring a lattice parameter is a very indirect one. The parameter 'a' of a cubic substance is directly proportional to the spacing 'd' of any particular set of lattice planes. If we measure the Bragg angle θ for this set of planes, we can use the Bragg law ($\lambda = 2 d \sin\theta$ where λ is the wavelength of the radiation, d is the spacing of the lattice planes and θ is the angle of reflection) to determine d and, knowing d, we can calculate a. But it is $\sin\theta$, not θ, which appears in the Bragg law. Precision in d, or a, therefore depends on the precision with which $\sin\theta$ is determined. The value of $\sin\theta$ changes very slowly with θ in the neighborhood of $90°$. For this reason, a very accurate value of $\sin\theta$ can be obtained from a measurement of θ near $90°$.

The Debye-Scherrer method of diffraction of x-rays by powders is most useful for the determination of the lattice parameters of a tremendous number of materials which can easily be obtained in powder form. But the Debye-Scherrer method is subject to a group of errors. The chief sources of error in θ are film shrinkage, incorrect camera radius,

off-centering of the specimen, absorption by the specimen and lack of temperature control.

The asymmetric method for precision determination of lattice constants eliminates all these errors. In this method a precisely built cylindrical camera is used. The film is loaded in the camera in such a way that the ends of the film are placed at an angle of about 90° with respect to the primary beam. This method permits not only determining the reflection angles but also the diameter of the developed and dry film cylinder very precisely. Therefore, using the asymmetric method, the error due to film shrinkage is eliminated. A knowledge of the camera radius becomes unnecessary.

The error due to the eccentricity of the sample is eliminated in this method as the camera is designed in such a way that it is possible to adjust the specimen exactly in the center.

To reduce the absorption error the thinnest possible sample is used.

For the temperature control of the sample the entire camera is placed in a thermostat with a precision of $\pm 0.01 - 0.02°$ C.

The asymmetric method for the precision determination of lattice constants is explained below.

D.   The Asymmetric Diffraction Powder Patterns

By loading the powder camera with a film in the asymmetric position, the circumference of the film can be exactly determined without knowing the diameter of the camera or the amount of film shrinkage after its development. Careful sample mounting, centering and maintenance of a constant and known temperature of the sample make it possible to measure the lattice parameters of crystalline powders with high precision. A detailed description of the experimental method and the necessary equipment is given in the literature (16, 17, 18).

1.   Sample mounting. In order to get sharp diffraction lines, it is necessary to have a well-centered, thin, uniform and undistorted crystalline sample.

In order to adjust the sample in the center of the camera, the following procedure was carried out. A lithium-boron glass fiber (0.05 mm in diameter and 5-8 mm in length) was glued to the fiber groove on a tip of a small centering head which was screwed to a sample holder. The

sample holder was fastened permanently with screws to the camera shaft. The camera cover was put under a microscope in such a position that the glass fiber was horizontal. By looking in the microscope, the fiber was moved back and forth and up and down till its rotation axis coincided with the camera cover axis. Then the cover with the powder mount was put on the camera. The centering was checked further by examining the fiber in the camera under a microscope and observing the exactly centered fiber while rotating the cover of the camera around its axis. If the position of the fiber, which was visible in the microscope through the collimator, did not move from the center then the fiber was accurately located on the rotation axis of the camera cover. After the sample holder assembly had been properly centered in the camera cover, it was however necessary to screw it down tightly so that it was not possible to mis-center it accidently. When this was done, the camera was ready for use.

All the samples for x-ray diffraction were ground to a fine powder and sieved through a 325 mesh screen. The powder was spread over the surface of a fiber coated with a thin layer of oil. The powder was uniformly spread over

2 - 3 mm length of the fiber. The powder mount was then checked again for centering.

When it was necessary to remove the powder from the glass fiber, a small amount of acetone was applied to the oil on the glass fiber with a thin and narrow strip of aluminum foil. The acetone dissolved the oil which held the powder particles. The oil with the powder particles was scraped off the fiber with the strip of aluminum foil. The clean glass fiber was then ready for another powder mount. All of these operations were performed under a microscope.

2. <u>X-ray diffraction patterns</u>. The film was loaded asymmetrically in the powder camera (64 mm diameter), so that both front and back reflections could appear uninterrupted on one film. Then the two holes were carefully drilled in the film to admit the collimator and beam stopper, as it was reported that punching of holes causes an uneven local shrinkage of the film (19).

In order to get the lattice constant results at a known and constant temperature, the loaded camera was mounted in the thermostat until thermal equilibrium was established.

For the solubility determinations, the photographs of the alloys were taken at 25° C and for the thermal expansion coefficient determinations at 15°, 25°, 35°, 45°, 55°, and 65° C. After a 30 minute exposure, each film was developed, fixed, washed 20 minutes in running water and dried. The same film processing was maintained for all films throughout this work.

3. **Film measurement.** A comparator with a precision of 0.001 mm was used to measure the diffraction lines on the film. The film was placed between two glass plates of the comparator and was so adjusted that the intersection of the cross hair of the microscope traveled along the equator of the diffraction pattern.

Two sets of lines in the front reflection region and three sets of lines in the back reflection region were measured by superimposing the intersection of the cross hair in the eyepiece of the microscope with the maximum density of the line. From these measurements the effective film circumference, the conversion factor (from mm to degrees) and back reflection Bragg-angles were calculated as shown in section 8 on page 24.

4. <u>Indexing of the patterns and the selection of a proper radiation.</u> The diffraction patterns were indexed by a graphical method based on the reciprocal lattice. This method is simple and convenient for indexing patterns of the cubic system. At the same time the proper radiation for a certain sample can be selected to give the highest back reflection angles which are necessary to achieve highest precision in lattice constant measurement. The theory and procedures are described in detail in the literature (20).

The 2θ angles found from a molybdenum film were plotted on the circle of reflection and the intersections with the circle projected on the diameter as shown in Figures 1 and 2. From the missing reflections it can be shown that molybdenum has the body centered cubic structure and the last line originates from the (420) plane if Cu-radiation is used.

In order to select the radiation giving the best reflection angle, different radiations were used to obtain the diffraction patterns. The change in radiation from copper to another radiation will change the diameter of the reflection circle. The relation between the wavelength and

the radius of the circle is given by

$$r_2 = r_1 \lambda_1^2 / \lambda_2^2 \qquad (1)$$

where r_1 is the radius of Cu-Kα_1 radiation reflection circle and r_2 is that of the new radiation reflection circle. λ_1 is the wavelength of the Cu-Kα_1 radiation and λ_2 is that of the new radiation.

If the radius of the Cu Kα_1 radiation reflection circle is taken as 100 mm, the radii of the reflection circles for other radiations become as follows:

Cu Kα_1	100 mm	Cu Kβ	121.3 mm
Co Kα_1	74.1 mm	Co Kβ	90.4 mm
Fe Kα_1	63.4 mm	Fe Kβ	76.9 mm
Cr Kα_1	45.3 mm	Cr Kβ	54.6 mm

Reflection circles representing Co Kα_1 and Cr Kα_1 were drawn in Figure 1 and those representing Co Kβ and Cr Kβ were drawn in Figure 2.

Cu Kβ radiation gave the highest back reflection line (420), $\theta \cong 81°$. Accordingly, Cu Kβ radiation was selected for powder diffraction patterns of molybdenum and molybdenum-base alloys.
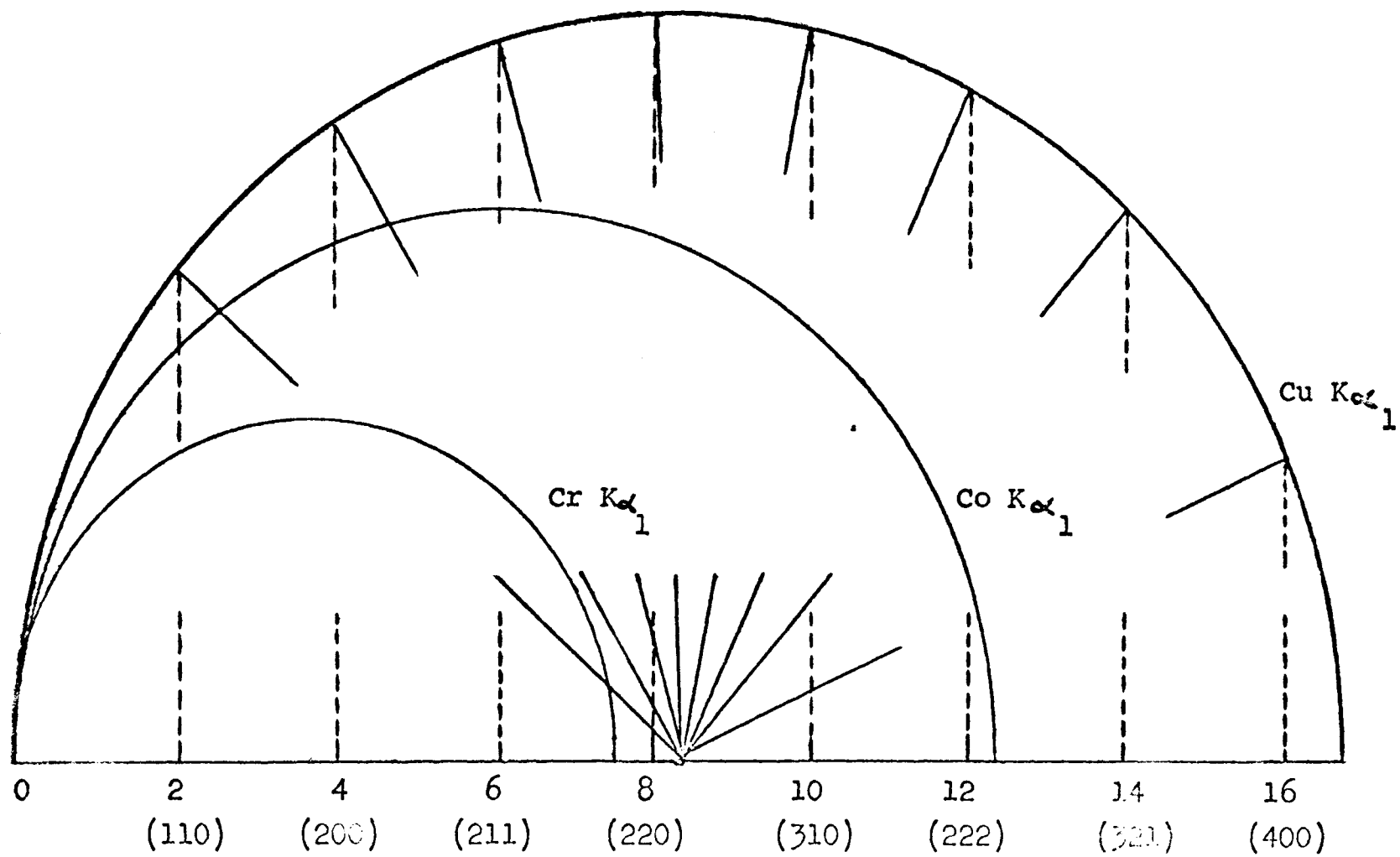
Figure 1. Graphical indexing of a powder pattern of pure Mo.

Cr Kα₁

Co Kα₁

Cu Kα₁

0	2	4	6	8	10	12	14	16
	(110)	(200)	(211)	(220)	(310)	(222)	(321)	(400)
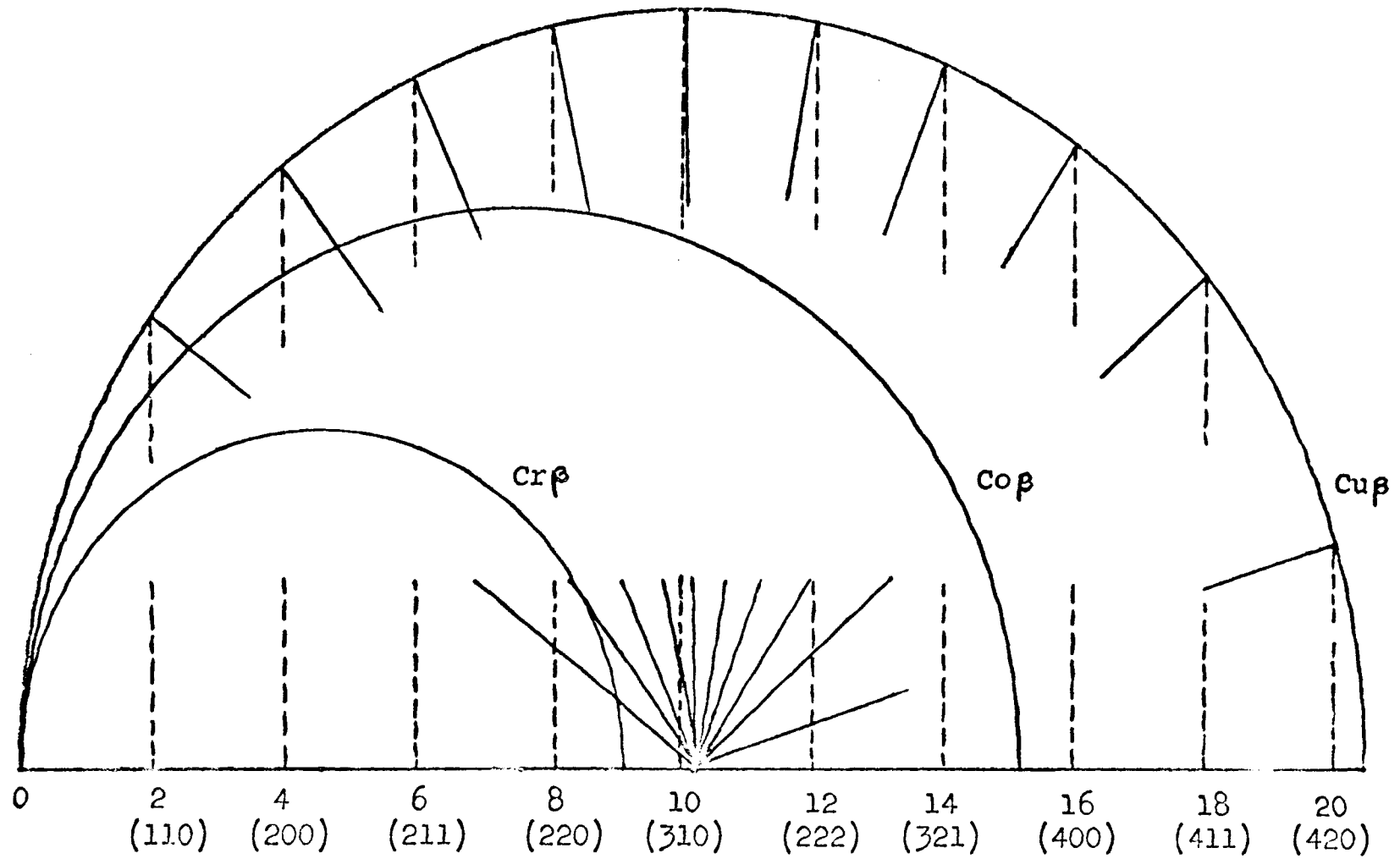
Figure 2. Graphical indexing of a powder pattern of pure Mo.

5. _Lattice constant._ The lattice constant for the cubic system was obtained by combining the Bragg and interspacing equations:

$$a = \lambda \sqrt{h^2 + k^2 + l^2} / 2 \sin\theta \qquad (2)$$

where a is the lattice constant, λ the wavelength of the radiation used, θ the reflection (Bragg) angle and h, k, l are the Miller indices of the reflecting plane.

In the above equation (2), the wavelength, λ , and the Miller indices, h, k, l, are constant for a certain substance and reflecting plane. Thus a new constant, K_o can be introduced:

$$K_o = \lambda \sqrt{h^2 + k^2 + l^2} / 2 \qquad (3)$$

From equations (2) and (3) the following equation is then obtained:

$$a = K_o / \sin\theta \qquad (4)$$

For the present work, Cu K_β radiation of wavelength 1.389350 in kX units and the plane which gives the highest Bragg angle, namely 420, were used for all calculations of

lattice parameters. Therefore, the new constant, K_o, is calculated to be 3.106681.

6. <u>Refraction correction</u>. The wavelengths of the x-rays are altered when they pass from one medium to another. This phenomenon causes a deviation from the Bragg law which leads to slightly smaller lattice constant values. The corrected Bragg equation may be written as follows (21):

$$n\lambda = 2 d (1 - 5.40 \frac{\rho d^2}{n} 10^{-6}) \sin\theta \qquad (5)$$

where n is the order of diffraction, λ is the wavelength of the x-ray used, d is the interplanar spacing, ρ is the density of the crystal, and θ is the reflection angle.

Substituting the interplanar spacing, d, of the cubic system into equation (5) and equating equation (2), the following convenient form for the refraction correction is obtained:

$$a_{corr} = a + \frac{5.40 \rho a^3 10^{-6}}{h^2 + k^2 + l^2} \qquad (6)$$

where a_{corr} is the constant a corrected for refraction and ρ is the density of the substance.

Substituting the appropriate values for a, ρ , etc.
in equation (6) the value for the refraction correction of
the pure molybdenum and the molybdenum-base alloys is
0.00009 in Å units.

7. <u>Error Calculation</u>. Error calculations were
necessary in order to evaluate the precision of the lattice
constant determination. The values of the lattice constants
measured at different temperatures were reduced to 25° C,
using the following equation:

$$a_{25^\circ} = a_t \left[1 + \alpha (25 - t) \right] \tag{7}$$

where α is the coefficient of thermal expansion and a_t is
the lattice constant at t° C.

The mean value of these reduced constants was found
and the deviations from this average value were calculated.
The standard deviation and the probable error are given by
equations (8) and (9):

$$S = \sqrt{\Sigma (dx)^2/(n - 1)} \tag{8}$$

where S is standard deviation, $\Sigma (dx)^2$ is the sum of the
squares of the deviations from the average value and n is
the number of measurements or degrees of freedom.

If S is multiplied by 0.675, the probable error, S',
is obtained at a 50 per cent confidence limit:

$$s' = 0.675 \, s \tag{9}$$

8. <u>Sample calculation</u>. An example of the calcula-
tion of the lattice constant is given from Film No. 2638,
the essential pattern of which is shown in Figure 3. The
figure represents an x-ray diffraction pattern of pure Mo
at 25° C taken during an exposure of 30 minutes with Cu
radiation in a 64 mm circular camera.

Two sets of lines in the front reflection area and
three sets of lines in the back reflection area were mea-
sured with the comparator. The calculations and results
are as follows:

	Front Reflection		Back Reflection		
			α_1	α_2	β
Reading (in mm)	c 74.191	d 83.130	j 166.770	i 166.015	h 163.095
	b 33.734	a 24.793	e 140.723	f 141.482	g 144.400
Sum (in mm)	107.925	107.923	307.493	307.497	307.495
Average (in mm)	= 107.924		= 307.495		

Circumference of film cylinder = 307.495 - 107.924

= 199.571
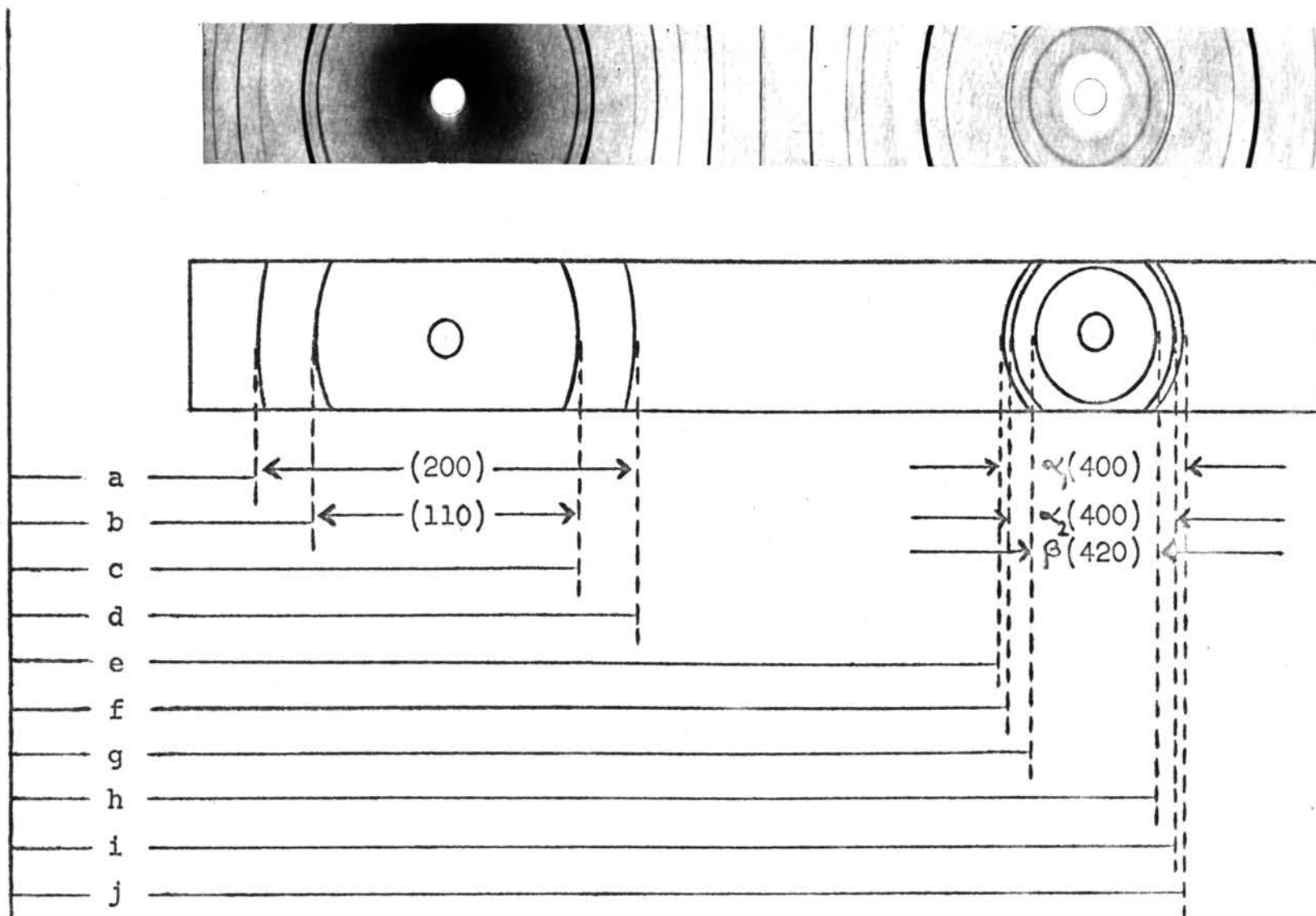
Figure 3. Asymmetric pattern of Mo taken with
Cu-radiation.

Conversion factor, $F = (360)/(4 \times 199.571) = 0.450967$

Back reflection angle, $\phi_\beta = (h - g) F$

$$= 18.695 \times 0.450967 = 8.4308$$

Front reflection angle, $\theta_\beta = (90 - \phi_\beta)$

$$= 90.0000 - 8.4308 = 81.5692$$

for the same line. Hence, $\sin\theta_\beta = 0.9891937$, and

the lattice constant, a, $= (3.106681/0.9891937) \times 1.00202$

$$= 3.14696 \text{ Å}$$

Refraction correction for pure Mo is 0.00009 Å and

$$a_{25°C} = 3.14705 \text{ Å}$$

9. **Coefficient of thermal expansion.** The coefficients
of thermal expansion were determined from the average lat-
tice constants obtained at different temperatures, using the
following equation:

$$\alpha = (a_t - a)/a (t - 25) \quad \text{or} \quad \Delta a/a \cdot \Delta t \quad (10)$$

where a_t is the lattice constant at temperature $t°$ C, a is
the lattice constant at a temperature of $25°$ C.

In equation (10), $\Delta a/\Delta t$ is the thermal expansion of
the unit cell and is represented by the slope of the
straight line in the plot of the lattice constant versus

temperature. From this and the lattice constant at 25° C, the coefficients of thermal expansion were calculated.

E. Density Measurements

The experimental density of a substance and its lattice constants are necessary in order to evaluate the perfection of the structure of a crystalline substance. For this purpose density measurements based on Archimedes principle were performed.

A small cup, which was suspended with a fine tungsten wire, was weighed in air and then in xylene. The sample in powder form was put in the cup which was then slowly immersed into xylene. The beaker, containing xylene and the cup, was put on an electric oscillator kept in a desiccator, which could be evacuated with a mechanical vacuum pump. First of all, the oscillator was started and immediately some air bubbles escaped. Then, while oscillating, the desiccator was evacuated so that all the air sticking to the sample left it in bubbles. After that the sample was suspended at the arm of the balance without taking it out from the liquid. The sample was weighed in the liquid and the temperature of the liquid was read simultaneously from a thermometer. The weighing was carried out to a

precision of ± 0.00005 gm on an analytical balance and the density of the liquid was read from a plot of density versus temperature.

The sample was taken out of the liquid very carefully and was placed in a metal box heated to about 80° C. The box was connected with a mechanical vacuum pump. After all the liquid in the cup had evaporated, the box was evacuated in order to remove the xylene completely. Then the sample was weighed in air on the analytical balance. The density of air was calculated from the temperature and the atmospheric pressure at the time of weighing the sample in air.

The density was calculated from equation (11):

$$d_t = (d_1 - d_a)\frac{W_a}{W_a - W_1} + d_a \tag{11}$$

where d_t is the density of the sample at the respective and known temperature t, d_a the density of the air, d_1 the density of the liquid, W_a the weight of the sample in the air, and W_1 the weight of the sample in the liquid. Addition of d_a reduced the density of the sample in air to that in vacuum.

The density measured at a temperature t was reduced
to the density at 25° C using equation (12):

$$d_{25} = d_t \left[1 + 3\alpha \ (t - 25) \right] \tag{12}$$

where d_{25} is the density of the sample at 25° C, d_t is the
density of the sample at the experimental temperature of
$t°$ C, and α is the thermal expansion coefficient.

To check the method, the density of a silver single
crystal was determined. The results of 10 determinations
are given in Table III. In Table IV, the result of the
density determination of silver by the present author is
compared with the results of the density determination of
silver by other authors. From the Table IV it is seen that
the density of silver, as determined by this method, com-
pares favorably with that determined by other authors.

As a further check of this method, the density of
silver is compared with the x-ray density of silver which
is given by equation (13):

$$\rho = \frac{A \cdot n}{v \cdot N_0} \tag{13}$$

where ρ is the x-ray density, A the atomic weight of
silver (107.870), v the volume of the unit cell of silver

TABLE III

Density of Silver in Vacuum

Run No.	Pressure (mm Hg)	Temp. (°C)	d_t (gm/cc)	d_{25} (gm/cc)	$\Delta d_{25} \times 10^{+4}$
1	731.0	28.8	10.4893	10.4915	21
2	729.7	27.3	10.4905	10.4918	18
3	731.3	28.1	10.4914	10.4932	4
4	732.4	28.6	10.4912	10.4933	3
5	733.1	28.5	10.4917	10.4938	2
6	733.5	25.6	10.4943	10.4946	10
7	733.3	24.7	10.4942	10.4940	4
8	733.0	24.6	10.4935	10.4933	3
9	733.6	24.5	10.4956	10.4953	17
10	734.7	24.4	10.4954	10.4951	15

Average $d_{25°C}$ = 10.4936 ± 0.0009 gm/cc

$\Sigma (\Delta d_{25})^2$ = 1433 × 10^{-8}

S = ± 12.62 × 10^{-4}

S' = ± 0.0009

α = 18.73 × 10^{-6} °C^{-1} was used for the reduction of d_t to d_{25}.

TABLE IV

Density of Pure Silver at 25° C

Reference	Year	Density (gm/cc)	Remarks for Ag
Kahlbaum (22)	1902	10.4891	Vacuo-distilled
Kahlbaum (22)	1902	10.5000	Compressed
International Critical Tables II (23)	1926	10.4914	Electrolytic
Igata (24)	1937	10.4973	Cold worked and annealed
Riad (25)	1964	10.4904	Polycrystal
Present work	1965	10.4936	Single crystal

(for F.C.C. silver $v = a^3$; $a = 4.08626$ Å), n the ideal number of atoms per unit cell (4 for F.C.C. silver) and N_O, Avogadro's number (6.0240×10^{23} mole^{-1}). The measured density of silver, 10.4936 gm/cc, compares favorably with the calculated x-ray density of silver, 10.4978 gm/cc.

As a further check of this method, equation (13) was used to find out the number of atoms per unit cell of silver using the measured density of silver - 10.4936 gm per cc. The calculated number of atoms per unit cell for silver is 3.9984 which compares favorably with 4 atoms per unit cell for an F.C.C. silver.

From the above comparisons, it can be concluded that the present method can be relied upon for accurate density determinations.

CHAPTER IV

EXPERIMENTAL RESULTS

A. Lattice Constants

1. Pure molybdenum. Eight x-ray diffraction patterns of Hilger molybdenum of 99.9935 per cent purity and six x-ray diffraction patterns of Sylvania molybdenum of 99.95 per cent purity were made. The temperature of the camera was controlled at 25° ± 0.05° C.

As mentioned in the previous chapter, Cu K_β radiation and the (420) line were used for the precision determinations. The lattice constants of Hilger molybdenum are listed in Table V while those of Sylvania molybdenum are listed in Table VI. The average value of the lattice constant of the Hilger molybdenum is 3.14700 ± 0.00001 Å and that of the Sylvania product 3.14696 ± 0.00003 Å both at 25° C.

2. Molybdenum-sulfur alloys. Seven Mo-S alloys containing 0.5, 1.0, 1.5, 2.0, 2.5, 3.0, and 5.0 atomic per cent sulfur were prepared as described in the previous chapter. The alloys were obtained in a powder form and were sieved through a 325 mesh screen.

TABLE V

Lattice constant of Hilger Mo, 99.9935%, at 25°C.

Copper radiation; refraction correction of 0.00009 Å

included.

Film No.	Sample	θ (deg.)	$a_{25°C}$ (Å)	Mean $a_{25°C}$ (Å)	$\Delta a_{25°C} \times 10^5$
2636	A	81.5822	3.14694		
2637	A	81.5746	3.14701	3.14698	2
2638	B	81.5692	3.14705		
2639	B	81.5764	3.14699	3.14702	2
2640	C	81.5792	3.14697		
2641	C	81.5743	3.14701	3.14699	1
2572	D	81.5653	3.14708		
2573	D	81.5863	3.14691	3.14700	0

Average $a_{25°C}$ = 3.14700 ± 0.00001 Å

$\Sigma (\Delta a_{25°C})^2$ = 9.0 x 10^{-10}

s = ± 1.73 x 10^{-5}

s' = ± 1.17 x 10^{-5}

TABLE VI

Lattice constant of Sylvania Mo, 99.95%, at 25°C.

Copper radiation; refraction correction of 0.00009 Å

included.

Film No.	Sample	θ (deg.)	$a_{25°C}$ (Å)	Mean $a_{25°C}$ (Å)	$\Delta a_{25°C} \times 10^5$
2720	A	81.5764	3.14699		
2721	A	81.5688	3.14705	3.14702	6
2722	B	81.5841	3.14693		
2723	B	81.5791	3.14697	3.14695	1
2724	C	81.5887	3.14689		
2725	C	81.5814	3.14695	3.14692	4

Average $a_{25°C}$ = 3.14696 ± 0.00003 Å

$\Sigma (\Delta a_{25°C})^2$ = 53.0 x 10^{-10}

s = ± 5.15 x 10^{-5}

s' = ± 3.48 x 10^{-5}

X-ray diffraction patterns of three samples of each alloy were made at 25° C. Cu K_β radiation and the (420) line were used for the precision determination of the lattice constants. They are listed in Table VII.

3. <u>Molybdenum-selenium alloys</u>. Four Mo-Se alloys containing 0.5, 1.0, 1.5, and 2.0 atomic per cent selenium were prepared as described in the previous chapter. The alloys were obtained in a powder form and were sieved through a 325 mesh screen.

X-ray diffraction patterns of three samples of each alloy were made at 25° C. Cu K_β radiation and the (420) line were used for the determination. The lattice constants are listed in Table VIII.

4. <u>Molybdenum-tellurium alloys</u>. Four Mo-Te alloys containing 0.5, 1.0, 1.5, and 2.0 atomic per cent tellurium were prepared as described previously. The alloys were obtained in a powder from and were sieved through a 325 mesh screen.

X-ray diffraction patterns of three samples of each alloy were made at 25° C. Cu K_β radiation and the (420) line were used for the determination. The lattice constants are listed in Table IX.

TABLE VII

Lattice constants of Mo-S alloys at 25°C. Copper

radiation; refraction correction of 0.00009 Å

included.

Film No.	Sample	At.% S	θ (deg.)	$a_{25°C}$ (Å)	Average $a_{25°C}$ (Å)
2642	A	0.5	81.5718	3.14703	
2643	B	0.5	81.5729	3.14702	
2644	C	0.5	81.5741	3.14701	3.14702 ± 0.00001
2645	A	1.0	81.5667	3.14707	
2646	B	1.0	81.5733	3.14702	
2647	C	1.0	81.5753	3.14700	3.14703 ± 0.00002
2648	A	1.5	81.5757	3.14700	
2649	B	1.5	81.5638	3.14709	
2650	C	1.5	81.5662	3.14707	3.14705 ± 0.00003
2651	A	2.0	81.5604	3.14712	
2652	B	2.0	81.5652	3.14708	
2653	C	2.0	81.5738	3.14701	3.14707 ± 0.00004
2654	A	2.5	81.5666	3.14707	
2655	B	2.5	81.5707	3.14704	
2656	C	2.5	81.5621	3.14711	3.14707 ± 0.00002
2657	A	3.0	81.5656	3.14708	
2658	B	3.0	81.5680	3.14706	
2659	C	3.0	81.5656	3.14708	3.14707 ± 0.00001
2660	A	5.0	81.5678	3.14706	
2661	B	5.0	81.5627	3.14710	
2662	C	5.0	81.5698	3.14704	3.14707 ± 0.00002

TABLE VIII

Lattice constants of Mo-Se alloys at 25° C. Copper radiation; refraction correction of 0.00009 Å included.

Film No.	Sample	At.% Se	θ (deg.)	$a_{25°C}$ (Å)	Average $a_{25°C}$ (Å)
2663	A	0.5	81.5691	3.14705	
2664	B	0.5	81.5655	3.14708	
2665	C	0.5	81.5604	3.14712	3.14708 ± 0.00002
2666	A	1.0	81.5601	3.14712	
2667	B	1.0	81.5643	3.14709	
2668	C	1.0	81.5598	3.14713	3.14711 ± 0.00001
2669	A	1.5	81.5606	3.14712	
2670	B	1.5	81.5632	3.14710	
2671	C	1.5	81.5581	3.14714	3.14712 ± 0.00001
2672	A	2.0	81.5545	3.14717	
2673	B	2.0	81.5643	3.14709	
2674	C	2.0	81.5620	3.14711	3.14712 ± 0.00003

TABLE IX

Lattice constants of Mo–Te alloys at 25°C. Copper radiation; refraction correction of 0.00009 Å included.

Film No.	Sample	At.% Te	θ (deg.)	$a_{25°C}$ (Å)	Average $a_{25°C}$ (Å)
2675	A	0.5	81.5631	3.14710	
2676	B	0.5	81.5644	3.14709	
2677	C	0.5	81.5578	3.14714	3.14711 ± 0.00002
2678	A	1.0	81.5542	3.14717	
2679	B	1.0	81.5632	3.14710	
2680	C	1.0	81.5603	3.14712	3.14713 ± 0.00002
2681	A	1.5	81.5557	3.14716	
2682	B	1.5	81.5643	3.14709	
2683	C	1.5	81.5519	3.14719	3.14715 ± 0.00003
2684	A	2.0	81.5507	3.14720	
2685	B	2.0	81.5583	3.14714	
2686	C	2.0	81.5609	3.14712	3.14715 ± 0.00003

B. Coefficients of Thermal Expansion

The linear thermal expansion coefficient of pure molybdenum and molybdenum alloys containing 2 atomic per cent alloying elements was determined by preparing a powder sample of the substance in question and making x-ray diffraction patterns at six different levels of temperature, ranging from 15° to 65° C as mentioned before. The average lattice parameters obtained at each temperature were then plotted against the temperature. In all cases, this relationship was very close to a linear function and it was therefore possible to draw a straight line passing through these points. From the slope of these lines, the corresponding linear thermal expansion coefficients were calculated using equation (10).

1. Pure molybdenum. The lattice constants obtained at various temperatures are summarized in Table X. The lattice constant versus temperature plot is shown in Figure 4. The coefficient of thermal expansion and the lattice constant calculated are:

$$\alpha = 4.89 \times 10^{-6} \ °C^{-1} \ , \ a_{25°C} = 3.14700 \pm 0.00001 \ \overset{o}{A}.$$

TABLE X

Lattice constant of Hilger Mo, 99.9935%, at different temperatures. Copper radiation; refraction correction of 0.00009 Å included

Film No.	Temp. (°C)	θ (deg.)	a (Å)	Mean a (Å)	$a_{25°C}$ (Å)	$\Delta a_{25°C}$ x 10^5
2574	15	81.5962	3.14683			
2575	15	81.5943	3.14684	3.14684	3.14699	1
2572	25	81.5653	3.14708			
2573	25	81.5863	3.14691	3.14700	3.14700	0
2576	35	81.5567	3.14715			
2577	35	81.5544	3.14717	3.14716	3.14701	1
2584	45	81.5348	3.14733			
2585	45	81.5422	3.14727	3.14730	3.14699	1
2596	55	81.5272	3.14739			
2597	55	81.5126	3.14751	3.14745	3.14699	1
2598	65	81.5005	3.14761			
2599	65	81.5030	3.14760	3.14761	3.14699	1

Average $a_{25°C}$ = 3.14700 ± 0.00001 Å

$\Sigma (\Delta a_{25°C})^2$ = 5.0 x 10^{-10}

s = ± 1.0 x 10^{-5}

s' = ± 0.68 x 10^{-5}
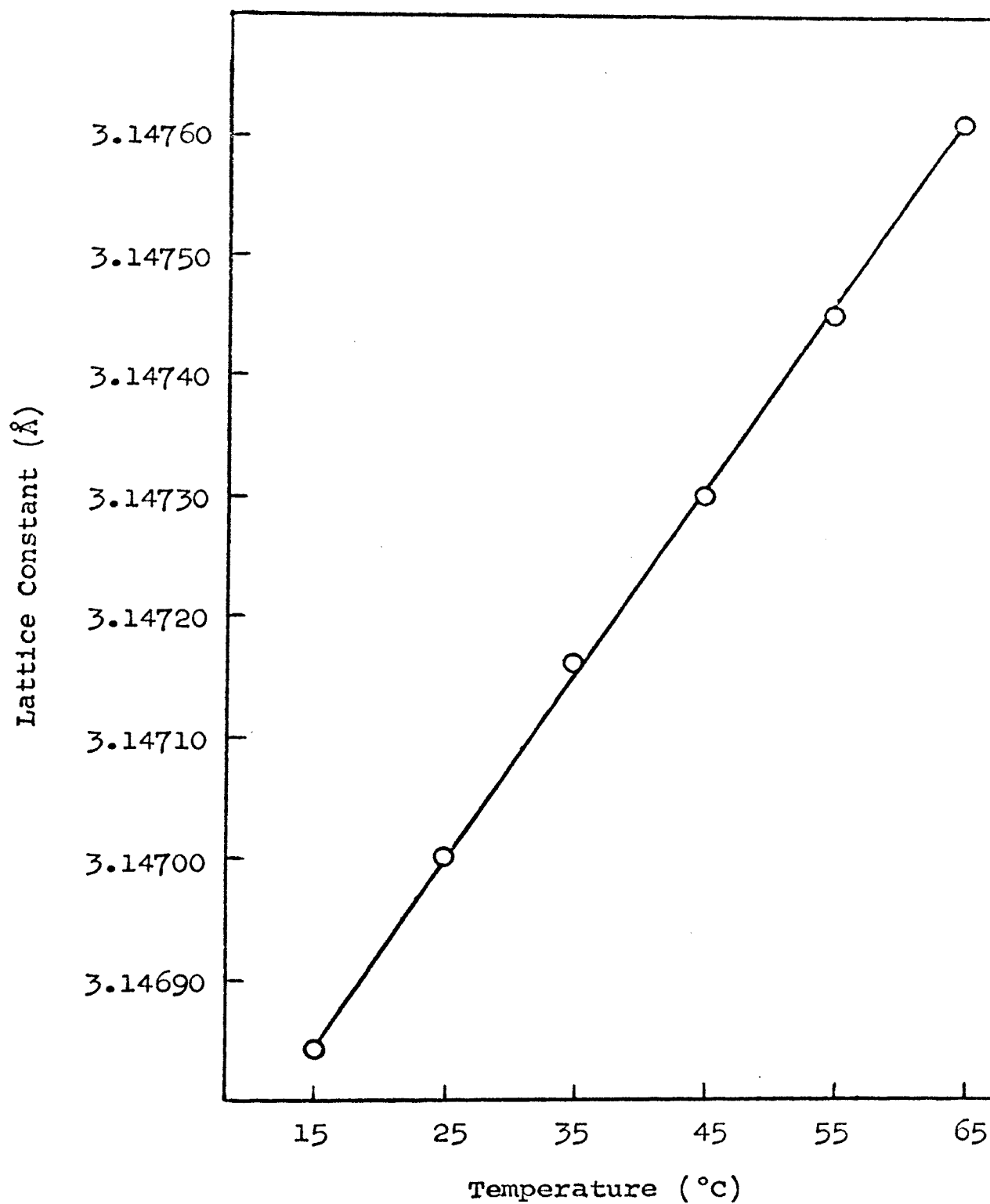
Figure 4. Lattice constant versus temperature for
Hilger Mo.

2.   <u>98.0 at. % Mo - 2.0 at. % S alloy</u>. The lattice constants obtained at various temperatures are summarized in Table XI. The lattice constant versus temperature plot is shown in Figure 5. The coefficient of thermal expansion and the lattice constant calculated are:

$$\alpha = 5.02 \times 10^{-6} \, °C^{-1}, \quad a_{25°C} = 3.14707 \pm 0.00001 \, \overset{\circ}{A}.$$

3.   <u>98.0 at. % Mo - 2.0 at. % Se alloy</u>. The lattice constants obtained at various temperatures are summarized in Table XII and plotted in Figure 6. The coefficient of thermal expansion and the lattice constant calculated are:

$$\alpha = 5.16 \times 10^{-6} \, °C^{-1}, \quad a_{25°C} = 3.14714 \pm 0.00001 \, \overset{\circ}{A}.$$

4.   <u>98.0 at. % Mo - 2.0 at. % Te alloy</u>. The lattice constants obtained at various temperatures are summarized in Table XIII and are plotted in Figure 7. The coefficient of thermal expansion and the lattice constant calculated are:

$$\alpha = 5.15 \times 10^{-6} \, °C^{-1}, \quad a_{25°C} = 3.14716 \pm 0.00001 \, \overset{\circ}{A}.$$

For the sake of comparison, the linear thermal expansion coefficient of pure molybdenum as found by other

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TABLE XI

Lattice constant of 98.0 at.% Mo - 2.0 at.% S alloy

at different temperatures. Copper radiation; refraction

correction of 0.00009 Å included.

Film No.	Temp. (°C)	θ (deg.)	a (Å)	Mean a (Å)	$a_{25°C}$ (Å)	$\Delta a_{25°C}$ x 10^5
2608	15	81.5937	3.14685			
2609	15	81.5825	3.14694	3.14690	3.14706	1
2606	25	81.5738	3.14701			
2607	25	81.5616	3.14711	3.14706	3.14706	1
2628	35	81.5436	3.14726			
2629	35	81.5481	3.14722	3.14724	3.14708	2
2630	45	81.5287	3.14738			
2631	45	81.5263	3.14740	3.14739	3.14707	0
2632	55	81.5080	3.14756			
2633	55	81.5138	3.14750	3.14753	3.14706	1
2634	65	81.4872	3.14773			
2635	65	81.4970	3.14765	3.14769	3.14706	1

Average $a_{25°C}$ = 3.14707 ± 0.00001 Å

$\Sigma (\Delta a_{25°C})^2$ = 8.0 x 10^{-10}

s = ±1.26 x 10^{-5}

s' = ± 0.85 x 10^{-5}

Figure 5. Lattice constant versus temperature for
98.0 at.% Mo - 2.0 at.% S alloy.

TABLE XII

Lattice constant of 98.0 at.% Mo - 2.0 at.% Se alloy
at different temperatures. Copper radiation; refraction
correction of 0.00009 Å included.

Film No.	Temp. (°C)	θ (deg.)	a (Å)	Mean a (Å)	$a_{25°C}$ (Å)	$\Delta a_{25°C}$ x 10^5
2687	15	81.5780	3.14698			
2688	15	81.5803	3.14696	3.14697	3.14713	1
2689	25	81.5557	3.14716			
2690	25	81.5629	3.14710	3.14713	3.14713	1
2691	35	81.5348	3.14733			
2692	35	81.5409	3.14728	3.14731	3.14715	2
2693	45	81.5236	3.14742			
2694	45	81.5142	3.14750	3.14746	3.14714	0
2695	55	81.4955	3.14766			
2696	55	81.5006	3.14762	3.14764	3.14715	2
2697	63	81.4873	3.14773			
2698	63	81.4822	3.14777	3.14775	3.14713	1

Average $a_{25°C}$ = 3.14714 ± 0.00001 Å

$\sum (\Delta a_{25°C})^2$ = 11.0 x 10^{-10}

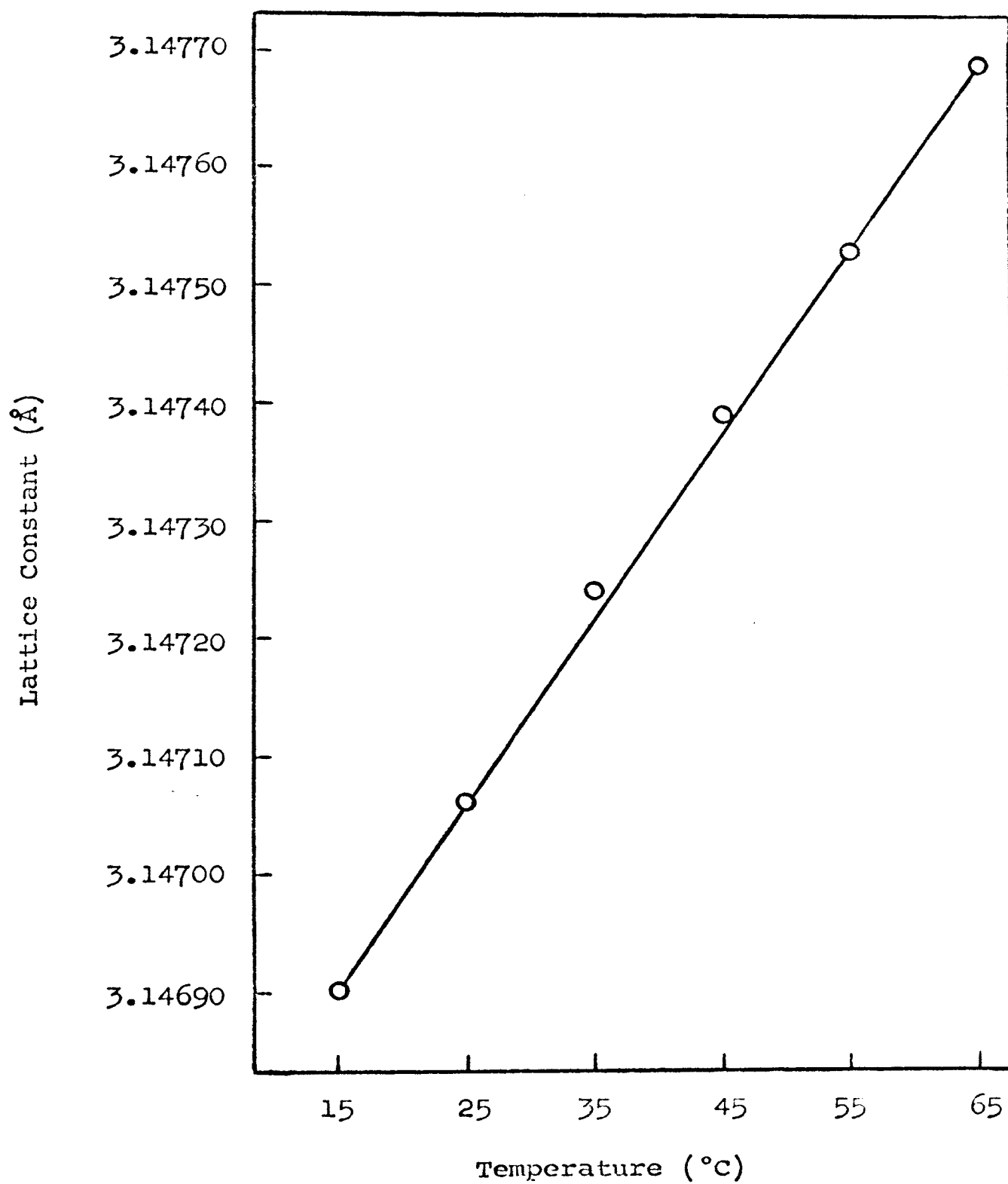s = ± 1.49 x 10^{-5}

s' = ± 1.00 x 10^{-5}
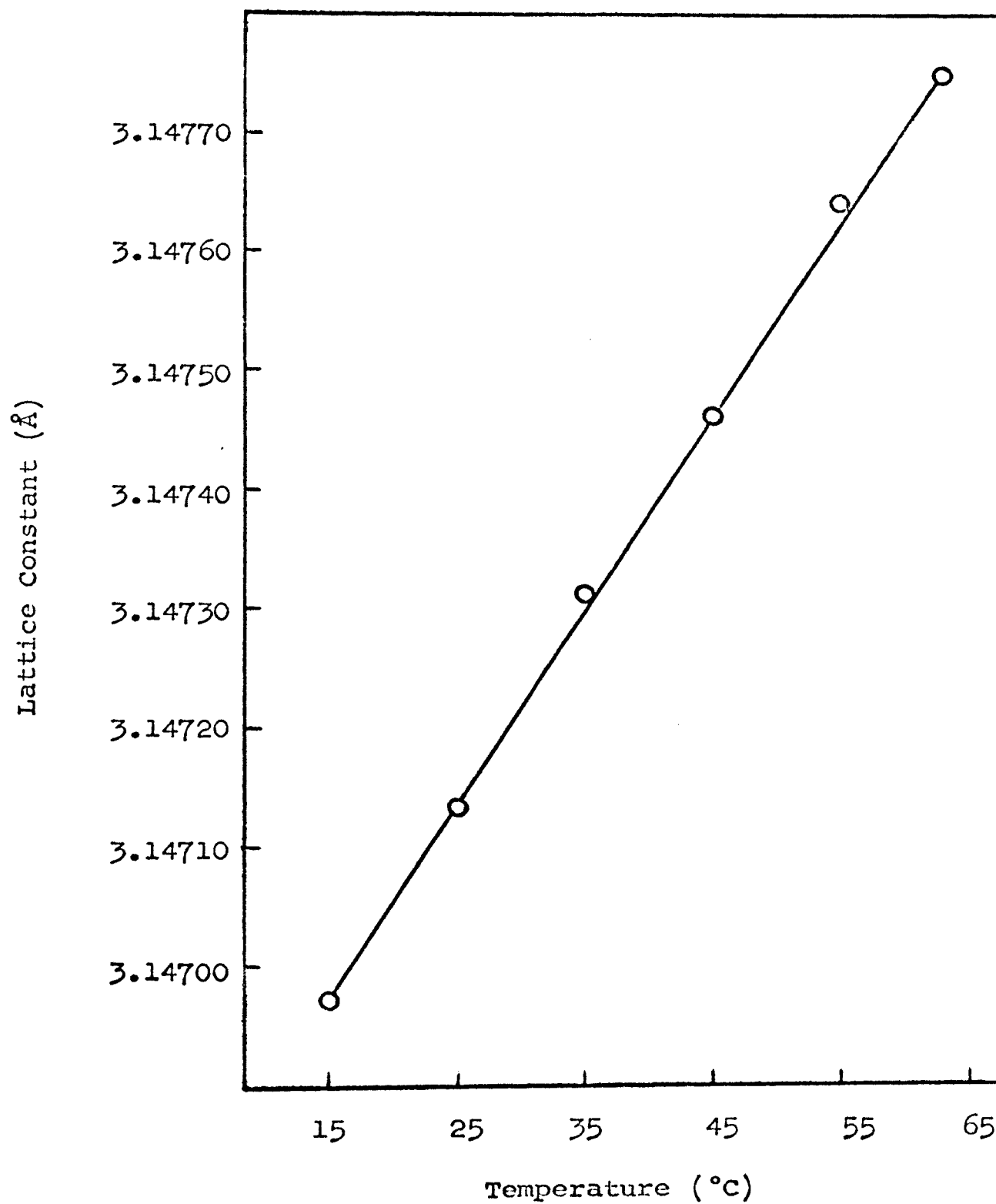
Figure 6. Lattice constant versus temperature for 98.0 at.% Mo - 2.0 at.% Se alloy.

TABLE XIII

Lattice constant of 98.0 at.% Mo- 2.0 at.% Te alloy

at different temperatures. Copper radiation; refraction

correction of 0.00009 Å included.

Film No.	Temp. (°C)	θ (deg.)	a (Å)	Mean a (Å)	$a_{25°C}$ (Å)	$\Delta a_{25°C}$ x 10^5
2699	15	81.5802	3.14696			
2700	15	81.5702	3.14704	3.14700	3.14716	0
2701	25	81.5628	3.14710			
2702	25	81.5505	3.14720	3.14715	3.14715	1
2703	35	81.5297	3.14737			
2704	35	81.5423	3.14727	3.14732	3.14716	0
2705	45	81.5126	3.14751			
2706	45	81.5175	3.14747	3.14749	3.14717	1
2707	55	81.5067	3.14757			
2708	55	81.4931	3.14768	3.14763	3.14714	2
2709	65	81.4702	3.14787			
2710	65	81.4845	3.14775	3.14781	3.14716	0

Average $a_{25°C}$ = 3.14716 ± 0.00001 Å

$\Sigma (\Delta a_{25°C})^2$ = 6.00 x 10^{-10}

S = ± 1.1 x 10^{-5}

S' = ± 0.74 x 10^{-5}
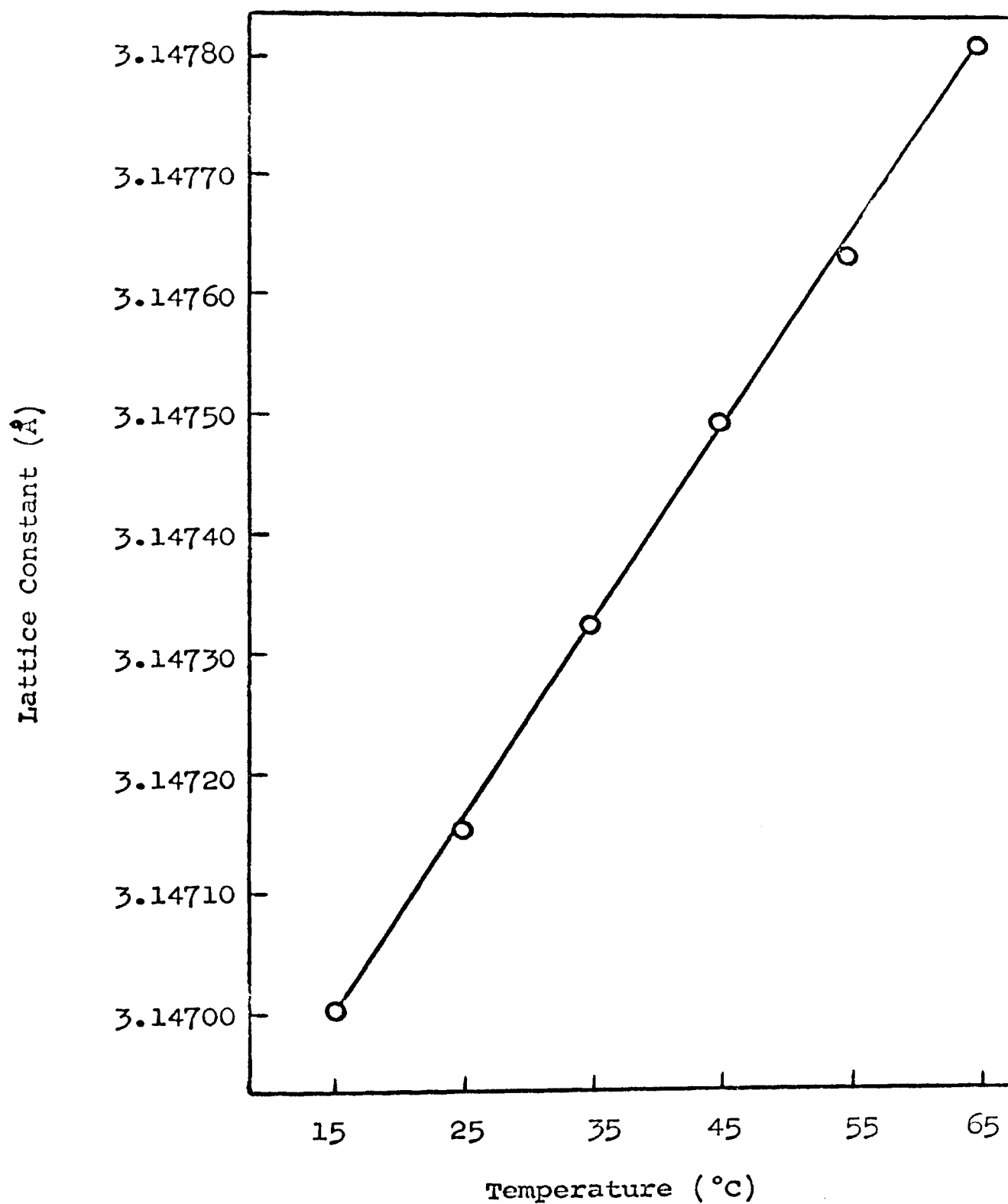
Figure 7. Lattice constant versus temperature for
98.0 at.% Mo — 2.0 at.% Te alloy.

authors and that found by the present author are grouped in Table XIV. In Table XV are grouped the linear thermal expansion coefficients of the molybdenum-based alloys containing 2 atomic per cent alloying elements.

C. Solid Solubility of S, Se, and Te in Molybdenum at 1100° C

In order to find out the solid solubility limit of S, Se, and Te in molybdenum at 1100° C, the lattice constants of the respective alloys are plotted against the atomic per cent of the alloying element in Figure 8. For the sake of comparison, the three systems are plotted in the same figure.

From the plot, it may be inferred that for sulfur the solid solubility limit may be in the vicinity of 2 atomic per cent and for selenium and tellurium it may be in the vicinity of 1.5 atomic per cent.

The x-ray diffraction films of the alloys were examined for the appearance of new lines due to formation of new phases formed beyond the solid solubility limit. No such new lines were found, evidently because of small amount of the new phase (below 3 % by weight).

TABLE XIV

Linear Thermal Expansion Coefficient of Pure Mo

Reference	Year	Temp. Range	Coeff. of Thermal Expansion
		$(^{\circ}c)$	$\propto \times 10^{6} \; ^{\circ}c^{-1}$
Hidnert and Gero (12)	1924	25 - 100	4.90
Michel (13)	1938		5.00
Nix and MacNair (14)	1942	-187 - +25	5.20
Present work	1965	15 - 65	4.89

TABLE XV

Linear Thermal Expansion Coefficients

of Mo-base Alloys

No.	Alloy	Coefficient of Thermal Expansion $\alpha \times 10^6 \, °C^{-1}$
1	98.0 at.% Mo–2.0 at.% S	5.02
2	98.0 at.% Mo–2.0 at.% Se	5.16
3	98.0 at.% Mo–2.0 at.% Te	5.15
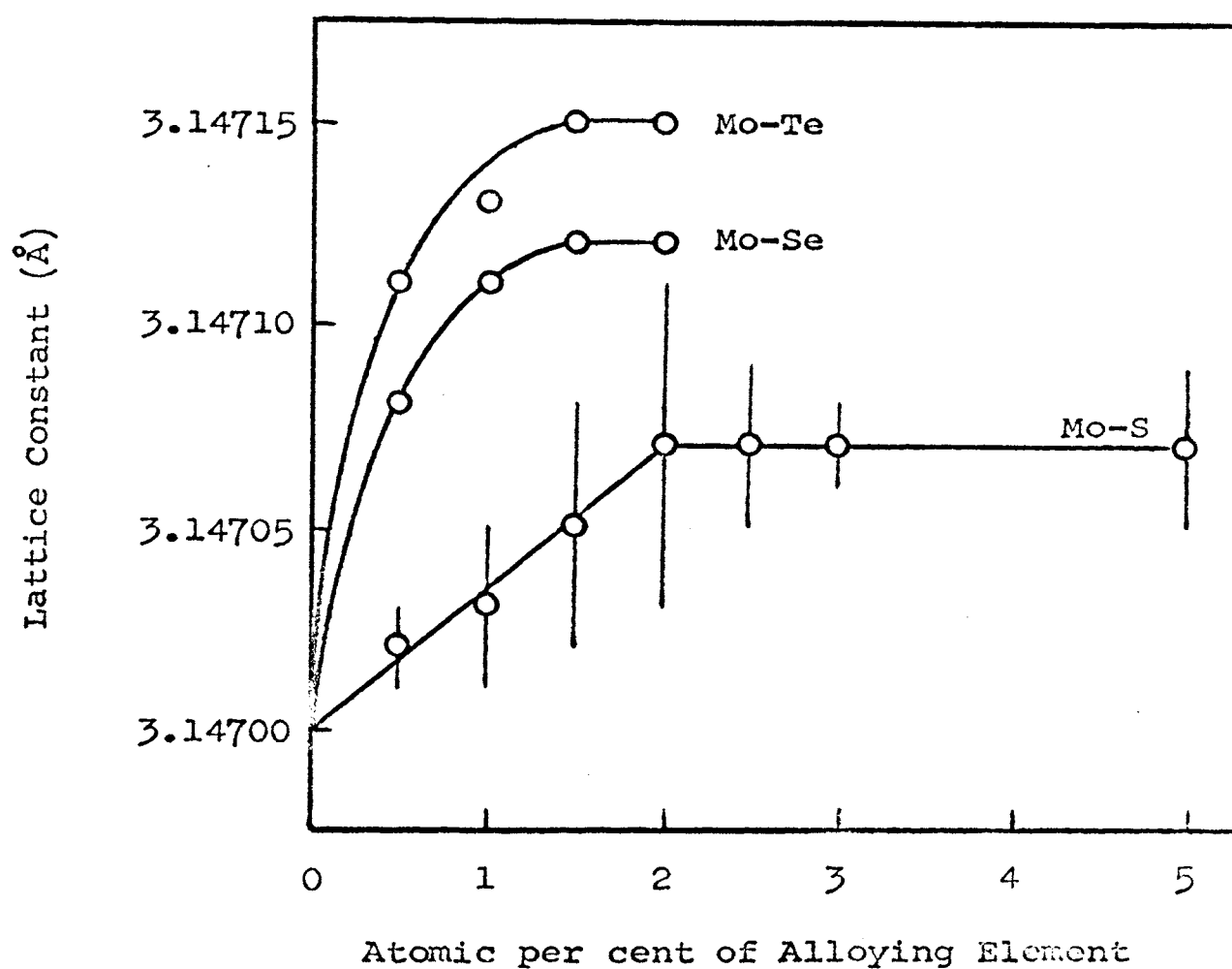
Figure 8. Lattice constant versus atomic per cent of the alloying element.

<u>Microscopic examination of pure Mo and Mo-base alloys</u>.

From Figure 8, one can expect a formation of a new phase

beyond the solid solubility limit of 2 atomic per cent for

S and 1.5 atomic per cent for Se and Te. To determine the

existence of the new phase, the pure Mo and the Mo-base

alloys were examined under an optical microscope (Reichert-

Austria). An oil immersion objective and a yellow filter

were used. The total magnification was 1430X.

Under the microscope, the Hilger Mo consisted of very

small shiny metallic particles, single or in aggregates

having frequently a cubic or octahedral shape. There was

no deposit on the surface of the particles.

In some samples a reddish discoloration of particle

groups was observed.

The second phase could be recognized by the presence

of noncubic particles, of irregular or hexagonal shape.

However, on some shiny faces a few black dots of unknown

origin were observed as shown in Figure 9.

The results of the microscopic examination of all the

samples are presented in a tabular form in Table XVI.

Figure 9. Black dots on a shiny face of a crystal of a Mo alloy with 2.0 at.% Te, Mag. 1800X.

TABLE XVI

Results of the Microscopic Examination of Pure Mo and Mo-base Alloys

No.	Sample	Particles			Black Dots on Surface of Particles	Second Phase	
		Cubic	Octa-hedral	Reddish		Irregular Platelets	Hexagonal Platelets
1	Hilger Mo*	X	X				
2	Hilger Mo**	X	X		X		
3	0.5 at.% S + 99.5 at.% Mo	X	X	X			
4	1.0 at.% S + 99.0 at.% Mo	X	X	X #			
5	1.5 at.% S + 98.5 at.% Mo	X	X	X #			
6	2.0 at.% S + 98.0 at.% Mo	X	X	X #			
7	2.5 at.% S + 97.5 at.% Mo	X	X	X #		X Elongated	
8	3.0 at.% S + 97.0 at.% Mo	X	X	X		X Elongated	
9	5.0 at.% S + 95.0 at.% Mo	X	X	X		X Elongated and striped	
10	Excess S + Mo	X		Rare		X Elongated (Mo sulfide)	

* As received.   ** Heated in vacuum at 700°C for 2 hours.
X indicates presence of particles.   # (see footnote on page 56A).

TABLE XVI (Continued)

Results of the Microscopic Examination of Pure Mo and Mo-base Alloys

No.	Sample	Particles			Black Dots on Surface of Particles	Second Phase	
		Cubic	Octa-hedral	Reddish		Irregular Platelets	Hexagonal Platelets
11	0.5 at.% Se + 99.5 at.% Mo	X	X		X		
12	1.0 at.% Se + 99.0 at.% Mo	X	X	X			
13	1.5 at.% Se + 98.5 at.% Mo	X	X	X			X
14	2.0 at.% Se + 98.0 at.% Mo	X	X	X			X #
15	0.5 at.% Te + 99.5 at.% Mo	X	X		X		
16	1.0 at.% Te + 99.0 at.% Mo	X	X	X		X Nearly round	
17	1.5 at.% Te + 98.5 at.% Mo	X	X	X Quite a few	X	X	
18	2.0 at.% Te + 98.0 at.% Mo	X	X		X	X	

X indicates presence of particles.
# indicates more particles than in the previous sample.

D. Density

1. Pure molybdenum. The density measurements of
Hilger, of Sylvania Mo powders and of Mo sheet were made
using the method described in the previous chapter. First
the densities were measured at the experimental tempera-
tures, and then these values were reduced to the density at
25° C using equation (12).

The densities of Hilger and Sylvania powders were
determined first without heating and then after heating in
vacuum at 700° C for 2 hours.

In Table XVII are summarized the density measurements
of the Hilger Mo powder without heating and of the
Sylvania sample, as received, and after heating in vacuum
at 700° C for 2 hours. The results of the measurements
of the Hilger Mo powder after heating in vacuum at 700° C
for 2 hours and of the Mo sheet are given in Tables XVIII
and XIX, respectively.

From equation (13), the x-ray density of pure molyb-
denum is calculated to be 10.220 gm/cc. Also from equa-
tion (13) the number of atoms per unit cell for molybdenum
can be obtained using the experimental density. The
results are summarized in Table XX.

TABLE XVII

Densities of Molybdenum Powders at 25° C

Run No.	Hilger Mo as received (gm/cc)	Sylvania Mo as received (gm/cc)	Sylvania Mo heated* (gm/cc)
1	9.825	10.267	10.179
2	9.821	10.156	10.128
3	9.846	10.206	10.111
4	9.871	10.308	10.135
5	9.844	10.238	10.158
6	9.790	10.140	10.088
7	9.844	10.228	9.953
8	9.876	10.234	9.972
9	9.854	–	10.035
10	9.854	–	9.982
Average Density (gm/cc)	9.843 ± 0.017	10.222 ± 0.036	10.074 ± 0.056

* In vacuum at 700° C for 2 hours

TABLE XVIII

Density of Hilger Molybdenum Powder Heated

at 700°C for 2 Hours in Vacuum

Run No.	Pressure (mm Hg)	Temp. (°C)	d_t (gm/cc)	d_{25} (gm/cc)	$\Delta d_{25} \times 10^3$
1	734.0	27.9	9.998	9.998	25
2	734.3	28.0	10.019	10.019	46
3	730.5	26.6	9.964	9.964	9
4	730.3	27.3	9.997	9.997	24
5	728.7	27.6	10.061	10.061	88
6	729.3	26.0	9.920	9.920	53
7	726.3	26.6	9.942	9.942	31
8	727.3	25.6	9.931	9.931	42
9	728.7	26.0	9.910	9.910	63
10	729.8	26.6	9.983	9.983	10

Average $d_{25°C}$ = 9.973 ± 0.032 gm/cc

$\Sigma (\Delta d_{25})^2$ = 20,745 x 10^{-6}

s = ± 0.048

s' = ± 0.032

α = 4.89 x 10^{-6} °C^{-1} was used for the reduction of d_t to d_{25}.

TABLE XIX

Density of Pure Molybdenum Sheet

Run No.	Pressure (mm Hg)	Temp. (°C)	d_t (gm/cc)	d_{25} (gm/cc)	$\Delta d_{25} \times 10^3$
1	732.6	26.0	10.234	10.234	3
2	732.8	26.0	10.234	10.234	3
3	733.5	25.6	10.235	10.235	2
4	733.5	25.4	10.239	10.239	2
5	733.0	25.8	10.232	10.233	4
6	733.6	26.8	10.238	10.239	2
7	734.1	27.0	10.239	10.240	3
8	734.5	25.8	10.239	10.239	2
9	735.1	25.3	10.234	10.234	3
10	736.0	26.7	10.243	10.243	6

$$\text{Average } d_{25°C} = 10.237 \pm 0.002 \text{ gm/cc}$$

$$\Sigma (\Delta d_{25})^2 = 104 \times 10^{-6}$$

$$s = \pm 0.003$$

$$s' = \pm 0.002$$

$\alpha = 4.89 \times 10^{-6} \ °C^{-1}$ was used for the reduction of d_t to d_{25}.

TABLE XX

Densities and Number of Atoms per Unit Cell

of Pure Molybdenum

Sample	Density at 25°C (gm/cc)	No. of Atoms per Unit Cell
Hilger Mo powder as received	9.843 ± 0.017	1.9261
Hilger Mo powder heated*	9.973 ± 0.032	1.9516
Sylvania Mo powder as received	10.222 ± 0.036	2.0003
Sylvania Mo powder heated*	10.074 ± 0.056	1.9713
Westinghouse Mo sheet	10.237 ± 0.002	2.0033

* In vacuum at 700°C for 2 hours. Air cooled.

2. <u>Mo-S alloys.</u> Density measurements were made of the Mo-S powdered alloys containing 0.5, 1.0, 1.5, 2.0, and 5.0 atomic per cent sulfur using the method described in the previous chapter. The densities were measured at the experimental temperatures, and then these values were reduced to the density at 25° C using equation (12).

In Table XXI are summarized the results of the density measurements at 25° C of the five Mo-S alloys. In Figure 10 the densities of these alloys are plotted against their sulfur content.

TABLE XXI

Densities of Mo-S Alloys at 25° C

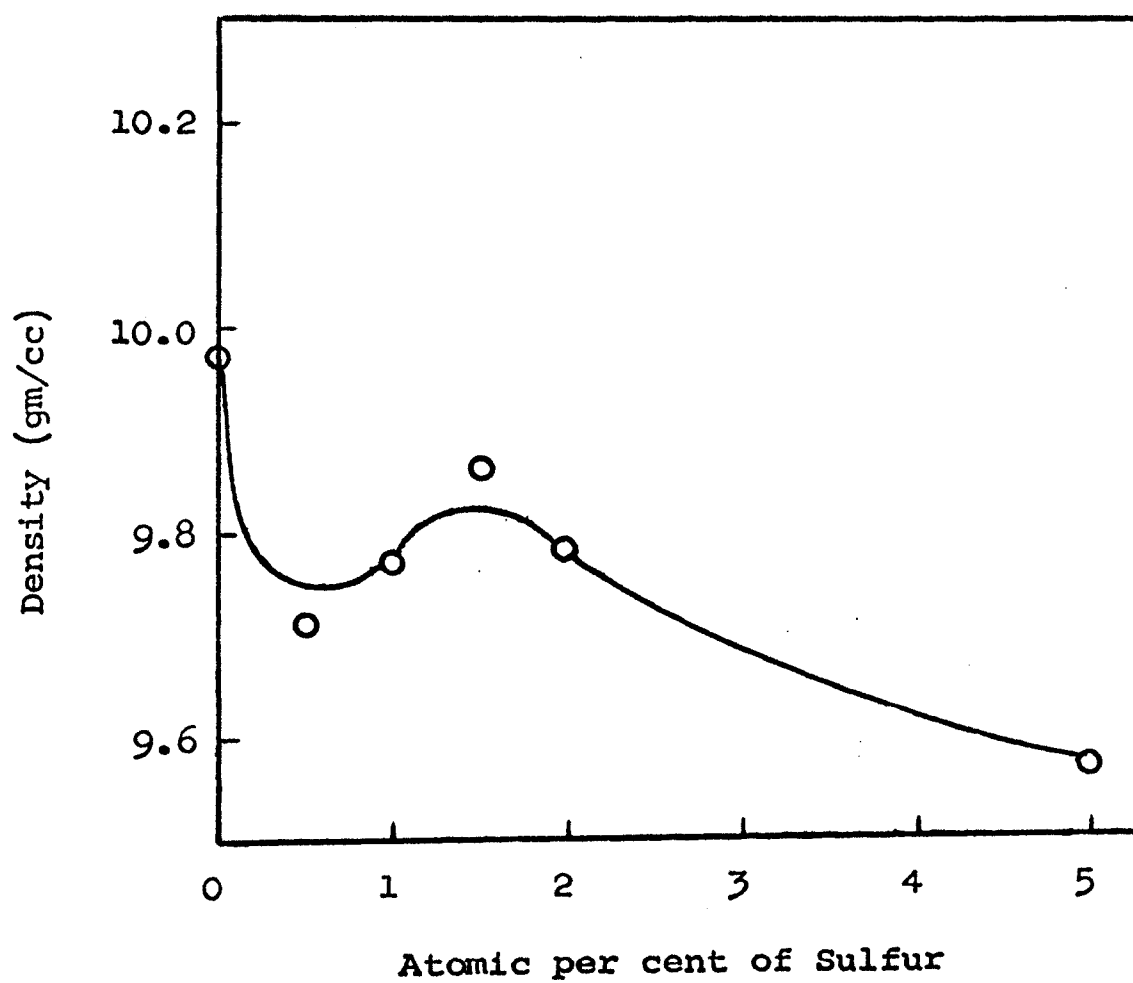| Run No.	0.5 at.% S (gm/cc)	1.0 at.% S (gm/cc)	1.5 at.% S (gm/cc)	2.0 at.% S (gm/cc)	5.0 at.% S (gm/cc)
1	9.690	9.772	9.806	9.722	9.599
2	9.678	9.773	9.829	9.747	9.593
3	9.733	9.791	9.884	9.805	9.552
4	9.757	9.772	9.831	9.818	9.523
5	9.687	9.734	9.896	9.753	9.557
6	9.754	9.765	9.886	9.776	9.591
7	9.704	9.808	9.873	9.830	9.586
8	9.672	9.793	9.857	9.794	9.575
Average Density (gm/cc)	9.709 ± 0.022	9.771 ± 0.018	9.858 ± 0.022	9.781 ± 0.026	9.572 ± 0.018

Figure 10. Density versus atomic per cent of sulfur.

CHAPTER V

DISCUSSION

A. Lattice Constants and Coefficients of Thermal Expansion

The asymmetric film method for precision determination of lattice constants eliminates nearly completely the systematic errors caused by the partial absorption of the x-ray beam by the specimen, eccentricity of the specimen in the camera and divergence of the x-ray beam. Errors due to an inaccurate knowledge of the temperature of the sample were eliminated by holding the whole camera at a constant and known temperature. Therefore, using the high indexed lines (Bragg angle about $81.5°$), a precision of the order of $1 : 200,000$ and better is believed to have been reached (16) in measuring the lattice constants of molybdenum and the molybdenum-base alloys.

Table XXII lists the lattice constants of molybdenum that have been reported earlier, together with the results of this investigation. For the purpose of comparison, all these values have been reduced to the same temperature $(25.0°C)$ using the thermal expansion coefficient value of $4.89 \times 10^{-6} °C^{-1}$ and same units (Å) using the conversion

TABLE XXII

Lattice constants of molybdenum at 25° C. Refraction correction of 0.00009 Å added.

Reference	Year	Purity of Mo	a, Å	Probable Error, Å
Jette and Foote (9)	1935	99.5 %	3.1474	± 0.00004
Lu and Chang (10)	1941	Hilger (6422)	3.1467*	± 0.00006
Swanson and Tatge (11)	1953	High purity	3.1472*	?
Present work:	1965			
Hilger Mo		99.9935 %	3.14700	± 0.00001
Sylvania Mo		99.95 %	3.14696	± 0.00003

* Without refraction correction.

factor of 1.00202. The variations in these reported values may be explained in terms of unequal purity of the molybdenum samples being examined, as well as the variation in the precision of controlling and measuring temperature of the sample during the time of exposure. The temperature factor is believed to be more effective in causing such variations. The eccentric position of the sample mount in the x-ray camera may be a further reason. It should be remembered that the x-ray diffraction camera, used throughout this investigation, was so designed that it was possible to check and correct for eccentric position of the sample, if any.

Table XIV lists the linear thermal expansion coefficients of molybdenum that have been reported earlier, together with the result of this investigation. The present investigation is the only one where the thermal expansion coefficient of pure Mo was determined near the room temperature, between 15° and 65° C. The purity of the sample examined, the method of determination and the temperature range used may explain the differences between the present value and those reported in the literature.

The present investigation is also the first one to
determine the linear thermal expansion coefficients of
Mo-base alloys with 2.0 atomic per cent S, Se, and Te.
These values are listed in Table XV. It is observed that
the thermal expansion coefficients of the alloys are higher
than that of the pure Mo. The much higher thermal expan-
sion coefficients of the alloying elements may tend to
increase the thermal expansion coefficients of the Mo-base
alloys containing these elements.

B. Solid Solubility of S, Se, and Te in Mo at 1100° C

From Figure 8, in which a plot of lattice constant
versus atomic per cent of the alloying element is drawn,
it is seen that the addition of the alloying element ex-
pands the lattice spacing of molybdenum. From the plot it
seems that solid solubility limit for S in Mo at 1100° C
may be in the vicinity of 2.0 atomic per cent, while that
for Se and Te may be in the vicinity of 1.5 atomic per
cent.

This conclusion depends on the precision of determi-
nation of lattice constants. An average value of three
lattice constants obtained with three mounted samples of
each of the 15 alloys was taken as the final lattice

constant for that particular alloy. There was a slight variation between the three values of the lattice constants for the same alloy (Tables VII, VIII and IX) and the error was calculated by using equations (8) and (9). Although the error limits for each alloy partially cover each other (e.g. see Table VII and Figure 8), there is, nevertheless, an increasing trend (with increasing amount of S) in the lattice constants. Therefore, the conclusion that the solid solubility limit of S in Mo at 1100° C is at about 2.0 atomic per cent, is justified. The same concerns the solubility of Se and Te in Mo.

The existence of very low solid solubility limits may be explained on the basis of the Hume-Rothery principles (26). The atomic diameters of Mo and S differ by 22.20%, while those of Se and Te differ by 14.13% and 5.32%, respectively. All three alloying elements are noncubic in crystal structure. Even though the Se and Te atomic diameters differ within the limit of ±15 per cent of the atomic diameter of the solvent, Mo, extensive solid solutions are not expected because of the nonsimilarity of the crystal structures.

S, Se, and Te form, with Mo, stable sulfides, sele-
nides, and tellurides, respectively and consequently solid
solutions of these elements in Mo are usually, if not
always, very restricted.

The relative valency hypothesis, according to Hume-
Rothery (26) cannot be applied in the present case because
the elements of higher valency are involved.

C. Density

Densities are of extreme importance in the evaluation
of the perfection of the structure of crystals, as well as
in establishing whether the solid solution is interstitial
or substitutional in nature.

Table XX lists the densities and the number of atoms
per unit cell of different samples of pure Mo. Theoreti-
cally there should be two atoms per unit cell for a body-
centered cubic Mo crystal structure and the density should
be close to 10.220 gm/cc at 25° C as calculated from the
lattice constant of Mo (see equation (13)).

However, the density of the high purity Hilger Mo
samples, as received, was 9.843 gm/cc which is much below
the calculated x-ray density. After heating it in vacuum
at 700° C for 2 hours, the density increased to

9.973 gm/cc which is still below the calculated value. It may be suspected that, even after heating, the sample may have some gaseous elements occluded in it.

The density of the less pure Sylvania Mo sample, as received, was 10.222 gm/cc which is in excellent agreement with the calculated value. After heating it in vacuum at 700° C for 2 hours, the density, however, dropped to 10.074 gm/cc which is quite unusual. A probable explanation may be that during the heating, out of many impurities present in the sample (see page 8), some lighter compound might have been formed, which may have reduced the density.

The **density** of a Westinghouse Mo sheet was 10.237 gm/cc which is slightly higher than the calculated value. The reason may be that during the mechanical working the sample is compressed and consequently the density is higher. On the other hand, it is known that cold work reduces the density of some metals.

Table XXI lists the densities of the Mo-S alloys at 25° C. A plot of density versus atomic per cent sulfur is drawn in Figure 10. The overall trend of the curve indicates that there is a decrease in density with the addition of S to Mo. There is a strong drop at first (upto 0.5

atomic per cent S) which then decreases (upto 2.0 atomic per cent) and then continues to increase again. It is difficult to explain the hump created in the curve between 1.0 and 2.0 atomic per cent. The density should also not decrease as strongly if the sample would be regarded as a structure of Mo and Mo_2S_3 (or MoS_2). Therefore, we have to assume that the presence of sulfides in solid solution with Mo causes voids in the latter, which, during the density determination, could not be filled with the liquid (xylene).

CHAPTER VI

SUMMARY

1. The lattice constant of Hilger Mo, 99.9935%, at 25° C was determined to be 3.14700 ± 0.00001 Å and that of Sylvania Mo, 99.95% at 25° C to be 3.14696 ± 0.00003 Å.

2. The lattice constants of the Mo-S alloys at 25° C are:

0.5 at. % S	3.14702 ± 0.00001 Å
1.0 at. % S	3.14703 ± 0.00002 Å
1.5 at. % S	3.14705 ± 0.00003 Å
2.0 at. % S	3.14707 ± 0.00004 Å
2.5 at. % S	3.14707 ± 0.00002 Å
3.0 at. % S	3.14707 ± 0.00001 Å
5.0 at. % S	3.14707 ± 0.00002 Å

3. The lattice constants of the Mo-Se alloys at 25° C are:

0.5 at. % Se	3.14708 ± 0.00002 Å
1.0 at. % Se	3.14711 ± 0.00001 Å
1.5 at. % Se	3.14712 ± 0.00001 Å
2.0 at. % Se	3.14712 ± 0.00003 Å

4.   The lattice constants of the Mo-Te alloys at 25° C
are:

$$0.5 \text{ at. \% Te} \qquad 3.14711 \pm 0.00002 \text{ Å}$$

$$1.0 \text{ at. \% Te} \qquad 3.14713 \pm 0.00002 \text{ Å}$$

$$1.5 \text{ at. \% Te} \qquad 3.14715 \pm 0.00003 \text{ Å}$$

$$2.0 \text{ at. \% Te} \qquad 3.14715 \pm 0.00003 \text{ Å}$$

5.   The coefficient of thermal expansion of Hilger Mo
between 15° and 65° C is 4.89×10^{-6} °C^{-1}.

6.   The coefficients of thermal expansion of the Mo-
base alloys at about the solid solubility limits between
15° and 65° C are:

$$\text{with 2.0 at. \% S} \qquad 5.02 \times 10^{-6} \text{ °C}^{-1}$$

$$\text{with 2.0 at. \% Se} \qquad 5.16 \times 10^{-6} \text{ °C}^{-1}$$

$$\text{with 2.0 at. \% Te} \qquad 5.15 \times 10^{-6} \text{ °C}^{-1}$$

7.   The solid solubility limit of S in Mo at 1100° C
is estimated to be in the vicinity of 2.0 atomic per cent
and that of Se and Te in the vicinity of 1.5 atomic per
cent.

8.   The density of Hilger Mo, as received, was found
to be 9.843 ± 0.017 gm/cc and after heating in vacuum at

700° C for 2 hours was 9.973 ± 0.032 gm/cc.

9. The density of Sylvania Mo, as received, is found to be 10.222 ± 0.036 gm/cc and after heating in vacuum at 700° C for 2 hours is 10.074 ± 0.056 gm/cc.

10. The density of a Westinghouse Mo sheet is 10.237 ± 0.002 gm/cc.

11. The densities of the Mo-S alloys are:

0.5 at. % S	9.709 gm/cc
1.0 at. % S	9.771 gm/cc
1.5 at. % S	9.858 gm/cc
2.0 at. % S	9.781 gm/cc
5.0 at. % S	9.572 gm/cc

12. The number of atoms per unit cell of pure Mo samples are:

Hilger Mo, as received,	1.9261 atoms/u.c.
Hilger Mo, after heating,	1.9516 atoms/u.c.
Sylvania Mo, as received,	2.0003 atoms/u.c.
Sylvania Mo, after heating,	1.9713 atoms/u.c.
Westinghouse Mo sheet	2.0033 atoms/u.c.

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