THE TEMPERATURE SCALE AND THE MELTING POINT OF MOLYBDENUM

By A. G. Worthing

Abstract

Spectral emissivities and temperature scales of Mo from 300° to 2900°K. A tubular filament of pure Mo was made by winding ribbon in a close helix about 15 mm long and 1 mm in diam. Spectral emissivities were then obtained by observing the ratio of the outer surface brightness to the interior brightness as seen through small holes in the wall. The results were checked by two other methods. At room temperature the spectral reflectivities were determined and found to be independent of previous heat treatment. For 0.665μ the emissivities at 300°, 1500° and 2800°K are 0.419, 0.371 and 0.331; for .475μ, 0.424, 0.390 and 0.365 each within $\pm$.007. These values are all lower than those reported by others, probably because of the greater purity of the Mo or of the better black body conditions. Hence these are believed more reliable. These emissivities lead to a difference between true temperature and brightness temperature as a function of the brightness temperature of 46° at 1000°, 113° at 1500°, 217° at 2000°, and 370° at 2500°K.

Melting point of Mo has been obtained by observing the brightness temperature of a Mo V-filament at melt and applying the correction to true temperature, and by two other methods. The rounded average of 97 readings yields 2895°K$\pm$10 ($c_2=14{,}330\mu$ deg., $T_{Au}=1336$°K). This value is higher than most of the results of others.

Introduction

ESTABLISHING the true temperature scale for a substance at incandescence consists in determining the relation between some conveniently chosen physical property of the substance and temperature. For substances which can be operated as lamp filaments at incandescent temperature, a convenient property is a spectral emissivity. This property has been chosen in this case.

Previously published works on the spectral emissivity and the melting point of molybdenum will be noted later.

Spectral Emissivities

Spectral emissivities obtained directly. For the most part, the spectral emissivities of molybdenum have been obtained with tubular filaments which possessed small openings through their side walls. With such a tube uniformly heated, a spectral emissivity may be obtained directly from the ratio of surface brightness to interior (hole) or black body brightness corresponding to the same temperature. In case of a small tem-

perature gradient along the tube, as will be shown later, it is necessary to measure the interior brightness in a plane nearly normal to the axis of the tube.

In the present case the tubes were formed by winding molybdenum ribbon into closed helixes (Fig. 1). The holes through the side walls were small notches which had been filed in the edge of the ribbon previous to coiling. Molybdenum was found very satisfactory for this treatment, and little trouble was experienced in obtaining finished tubes which on heating showed a satisfactorily uniform brightness for a considerable length of tube. These tubes were usually about 15 mm long. The supports used were tungsten wires chosen of such size that their junctions with the molybdenum tube were of about the same temperature as the central parts of the tube. Current conduction along these tubes was largely

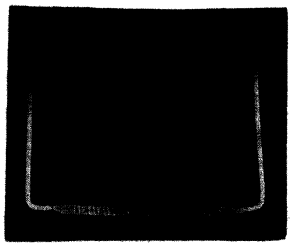

Fig. 1A Fig. 1B

A. Photograph (natural size) showing mounting of molybdenum tube.
B. Photograph (magnified) showing detail of molybdenum tube.

parallel to the axis. Any loose contact between turns was made evident by the localized high temperature in that vicinity. When using a tube it was necessary to keep at a distance from such a hot spot. While this type of tube is not as satisfactory as the type with a continuous wall, such as was used in a study of tungsten,[1] just as reliable results can be obtained.

Previous to employing any particular hole for spectral emissivity determinations, the uniformity in temperature along the filament for several diameters was studied, and the need of precautions as to direction of viewing the interior brightness was considered. Black body brightnesses in uniformly heated enclosures result from a building up by reflection both diffuse and specular. In the tubes used in this work, the building up was very largely due to specular reflection. The evidence was the appearance within the holes, on proper orientation of tube with

[1] A. G. Worthing, Phys. Rev. **10**, 377 (1917)

respect to the line of sight, of dark patches of nearly surface brightness. Just how black body brightnesses were assumed to build up in the interior of the tubes used is indicated in Fig. 2. Where r is the reflectivity of the material, B_a, B_b, B_c etc. the natural brightnesses of the material at points a, b, c etc., and B_o the brightness of the hole, it follows that in the direction OP

$$B_0 = B_a + rB_b + r^2B_c + r^3B_d + \cdots\cdots\cdots$$

In case B_a, B_b, B_c etc. are equal this becomes

$$B_0 = B_a/(1-r) = B_a/e$$

where e is the emissivity. In this case, except for a slight difference in temperature between inside and outside of tube, B_a is also the brightness

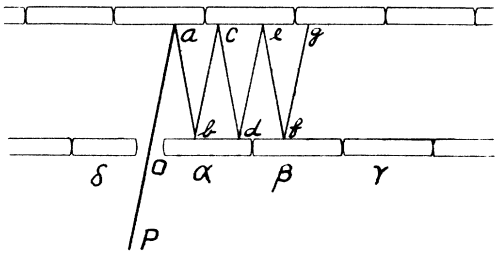

Fig. 2. Illustrating building up of black body radiation and method of taking into account a temperature gradient along the tube.

of the outside of the tube next to the opening; and the emissivity may be obtained by comparing a surface brightness next to the hole with the hole brightness. In this work, however, differences in B_a, B_b, B_c etc. were taken into account by taking as the surface brightness a weighted average of B_α, B_β, B_γ, and B_δ. While the weighting varied somewhat, generally they were weighted in order about as 5, 3, 1, and 3. B_δ was included partly to yield with B_α the average B_a and partly to take account of some diffuse reflection. As used the line of sight OP did not pass through the axis of the tube and there were usually two or three reflections between two such points as a and c. Usually the brightnesses B_a to B_δ varied less than 3 or 4 per cent over all.

The results obtained by this method for wave-lengths 0.665μ and 0.475μ are plotted as circles and crosses in Fig. 3. As the question of the true temperature scale, which was of most interest, required emissivities at only one wave-length, many more determinations were made for the more convenient wave-length .665μ. In going from the dashed curves representing observed results to the full line curves representing final results, a correction was applied for the difference in temperature between

the interior and the exterior of the hollow tube. The correction applied assumed the difference in temperature to be the same as if tungsten were used instead of molybdenum.[2]

Spectral emissivities from reflectivity data. Spectral emissivities at room temperature and at 1080°K were obtained from spectral reflectivities according to a method described elsewhere.[3] Results obtained for two wave-lengths $\lambda = 0.665\mu$ and $\lambda = 0.475\mu$ are shown in Fig. 3. The values

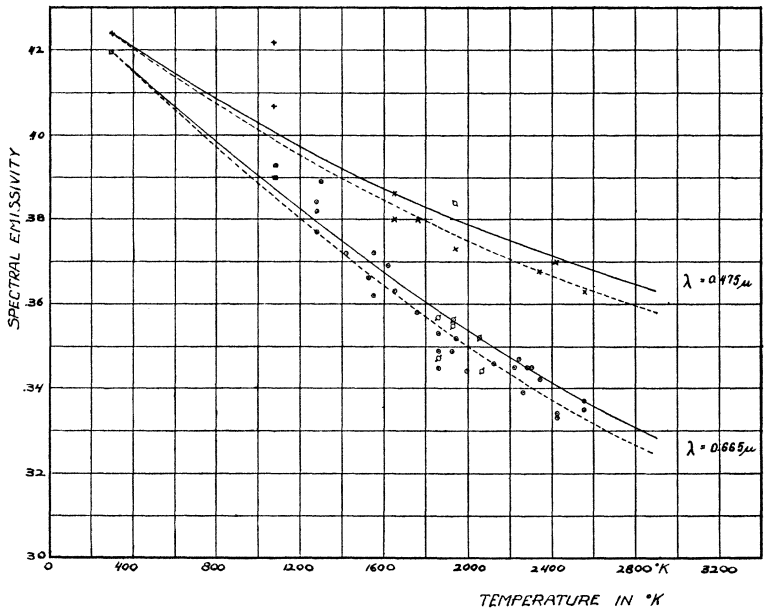

Fig. 3. Spectral emissivities of molybdenum as a function of temperature obtained by three methods.

at room temperature obtained from reflectivity measurements are believed quite accurate since they represent the average of a large number of determinations, many of which were undertaken expressly to see whether or not there was a change of reflectivity with heat treatment. (None was found.) The single values plotted at 1080°K were obtained under unfavorable circumstances and are to be given little weight.

Spectral emissivities obtained from comparisons with tungsten. Originally it was hoped that the spectral emissivity of molybdenum might be obtained by comparing its brightness with that of tungsten at the same temperature, and computing its emissivity from their ratio of brightnesses

[2] A. G. Worthing, l.c.[1] p. 382

[3] A. G. Worthing, Zeits. f. Phys. **22**, 9 (1924)

and the previously determined spectral emissivity of tungsten. By tapering bluntly the end of a tungsten filament, indenting slightly the end of a molybdenum filament, mounting the filaments end to end in a lamp, heating the combination carefully until the molybdenum just melted at the junction, and then cooling quickly, a lamp was obtained which made emissivity comparisons between the two metals possible. Due to alloying action, there was at the junction a boundary line which was brighter than either the tungsten or the molybdenum adjacent. However, as long as the temperature was maintained sufficiently low so as not to cause appreciable further alloying, this line of demarcation did not trouble. Assuming the temperature at the opposite sides of a junction to be the same, it was a simple matter to obtain relative brightnesses of tungsten and molybdenum corresponding to the same temperature and then to compute the emissivity of molybdenum. Unfortunately, neither of the two lamps obtained in the above described fashion was used very long before it was spoiled by the spread of the alloying action due to operation at too high temperatures. However, some spectral emissivity determinations, as shown in Fig. 3, were obtained by this method at about 2000°K.

Except, perhaps, that they indicate the plotted curve for $\lambda = 0.475\mu$ to be somewhat low, the results obtained by these comparisons with tungsten agree very well with the directly observed values. This fact is quite gratifying and lends increased confidence to both sets of emissivities.

Previously published spectral emissivities. But few published values for spectral reflectivities and emissivities for molybdenum in the visible region are to be found. Insofar as they well can be, these together with some comparative values obtained in the present investigation are shown in Table I. Considerable variations both at room and at incandescent temperatures are shown. However, as one general observation, it is to be noted that at all temperatures the emissivities obtained by the present writer are lower than those obtained by the other workers.

In explaining the differences of Table I, there are at least three general considerations that must be taken into account: (a) The use of rough or poorly polished surfaces leads to too low reflectivities and thus to too high emissivities. (b) The imperfect realization of black body conditions leads to too high emissivities. (c) The use of impure specimens, especially if the impurity consists of a tungsten-molybdenum alloy, will result in too high emissivities. In a lamp with a filament composed of a piece of tungsten wire and a piece of molybdenum wire butt-welded, the alloy formed at the junction when heated to incandescence is noticeably brighter than either unalloyed component. Since all three factors tend toward too

high emissivities, the lower experimental values, other things being the same, are to be regarded as the more nearly correct.

Coblentz states that his specimen of molybdenum had a very good polish, so, in his case at least, the difference must be explained otherwise than as due to a lack of polish. Also it hardly seems possible to ascribe the differences to method since using the same methods gave very good agreement in the case of tungsten.[3] The most probable source of difference

TABLE I

Comparative values of spectral emissivities of Mo as obtained by different experimenters

Observers	At 300°K		At high temperatures		
	λ	e_λ	T	λ	e_λ
Coblentz[4]	.46μ	.554			
	.665μ	.510			
Mendenhall and Forsythe[5]			1300°K	.658μ	.44
			2000	"	.38
			2750	"	.39*
Burgess and Waltenberg[6]			2273	0.65μ	.43
			2773	"	.40 (liquid)
Worthing (this paper)	0.475μ	.424 ± .007	1300	.665μ	.378
	0.665μ	.419 ± .006	2000	"	.353
			2750	"	.332

* The value 0.63 for the reflectivity quoted in table by Mendenhall and Forsythe for 2400°C seems to have been a misprint. Their Fig. 5 shows that it should have been 0.61.

is the difference in purity of the metals used. Tungsten is a material that is difficult to separate from molybdenum, and their alloy has a higher spectral emissivity at incandescence, and also probably at room temperature, than either component. Now, it seems not improbable that Coblentz's specimen may have contained some tungsten, having been prepared at a time when the metallurgy of tungsten and molybdenum was not as advanced as when the present writer's specimens were prepared. In fact, the Wire Division of the National Lamp Works, which furnished the writer with wire, states that the wire used in the room temperature measurements was obtained from slugs of exceptionally high purity. A determination of the temperature coefficient of resistance to be presented in a forthcoming paper bears out this statement.

[4] Coblentz, Bull. Bur. Stds. **7**, 197 (1911)
[5] Mendenhall, and Forsythe, Astrophys. J. **37**, 380 (1913)
[6] Burgess and Waltenberg, Bull. Bur. Stds. **11**, 591 (1914)

In the writer's opinion, this question of alloying with tungsten probably also explains why the writer's results differ from those of Burgess and Waltenberg. They obtained their emissivities of molybdenum by comparing the brightness of a speck of Mo which had previously been melted on a strip presumably of tungsten in order to bring the two in good thermal contact, with that of the strip. To check the alloying action, they cooled their strip as soon as the melt occurred, but the question arises, especially since such small amounts of molybdenum were actually used, whether the damage had not already been done.

It might be argued that the writer's results are subject to errors of alloying resulting from the use of tungsten wire to support the Mo tube. The answer is that the surfaces observed were too far from the tungsten for alloying to occur at the temperatures and in the time involved. Moreover, if the writer's results are thus in error, the discrepancies shown in Table I must be increased rather than diminished.

With regard to the work of Mendenhall and Forsythe, the present writer is inclined to regard the possibility of a failure to get black body conditions as the explanation. They used V-shaped strips with a 10° opening. And, while it may be shown that, if a V is perfectly knife-edged, the radiation from the V will be very nearly black, it may also be shown that, if the junction of the two sides is slightly rounded and particularly if also the optical pyrometer is so used that its object glass subtends an angle of several degrees at the V, there will be a failure to obtain black body radiation which may be appreciable. Other work with tungsten lends credence to this view.

While it may seem unreasonable to entirely disregard the earlier results on the spectral emissivities ofmolybdenum, the present writer feels justified in so doing, particularly (a) since the direction of difference points to his having had purer material and better black body conditions, and (b) since his results obtained by three different methods are in very good agreement with one another.

Relations between True, Brightness and Color Temperatures

Brightness temperature S_λ, true temperature T, and spectral emissivity e_λ are related by Wien's equation as follows

$$\log_e e_\lambda = \frac{c_2}{\lambda}\left(\frac{1}{T} - \frac{1}{S_\lambda}\right)$$

where c_2 is the Wien constant. For use with the disappearing filament pyrometer, a curve showing $(T-S)$ as a function of S is the most con-

venient method of expressing the true temperature scale. Curve *a*, Fig. 4, shows such relation for $\lambda = 0.665\mu$.

Another method of representing the true temperature scale consists in giving the relation between color temperature T_c and true temperature. When, as with molybdenum, an accurate color match with a black body

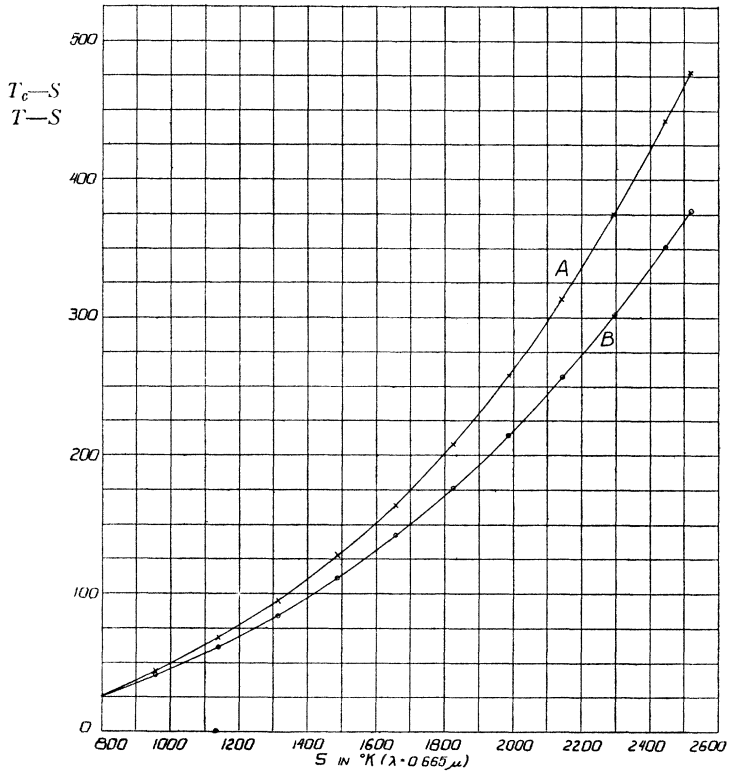

Fig. 4. Showing relations (A) between the color temperature T_c the brightness temperature S (0.665μ), and (B) between the true temperature T and S. The ordinates are T_c—S and T—S, respectively.

source is possible, the equation, deducible from Wien's equation, which shows how T_c may be computed as a function of T, is

$$\log_e \frac{e_1}{e_2} = c_2\left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right) \quad \left(\frac{1}{T} - \frac{1}{T_c}\right),$$

where e_1 and e_2 are spectral emissivities corresponding to λ_1, and λ_2. T_c as thus defined may be related to S by

$$\log_e e_c = \frac{c_2}{\lambda}\left(\frac{1}{T_c} - \frac{1}{S_\lambda}\right)$$

where e_c is the color emissivity and represents the brightness of the

molybdenum relative to that of a black body at color match. For simplicity this latter relation has been selected for curve *b*, Fig. 3.

Melting-Point

Three methods have been employed in obtaining the temperature of molybdenum at its melting point. The first, or filament-melt method, employed a short, narrow, V-shaped filament with a reduced cross-section at the point of the V, which was gradually heated electrically in a commercial argon atmosphere until it was seen to melt. At the same time, the brightness of the reduced segment was followed with a disappearing filament pyrometer, and the brightness temperature of the filament at melt noted. Thereafter, the true temperature was obtained with the aid of the spectral emissivity and Wien's equation. A lamp with such a filament mounted as stated and burned with the point of the V upward served generally for four or five melts, it being usually possible several times in succession to cool the filament so quickly after melting started that the filament did not separate. After the filament did break, it was still possible to use it for the second type of melting point determination. Frequent bulb transmission measurements were needed to take account of blackening due to vaporization of material. Pyrometer filters corresponding to 0.665μ and 0.462μ were used.

The second, or arc method, of determining the melting-point, usually made use of lamps previously used in the filament-melt method. When the filament once separated, ball terminals formed on the remaining stubs of the filament. The pyrometer was sighted on the positive terminal at the junction of the ball terminal and the filament stub. There was always some detail visible there, though usually no detail was visible on the ball itself. As the current through the arc was increased, the ball finally melted, but no criterion as to when melting started at any particular point was ever visible on the face of the ball. In fact, for the portion opposite to the negative terminal, the first indication of melt often consisted of a sputtering and a swaying of the ball as if it were yielding considerable amounts of gas. But the rear of the ball where the pyrometer was sighted gave no evidence of any such disturbances. Moreover, it furnished a good criterion of melting in the shift of the line which marked the disappearance of detail at the junction of ball and filament stub. So far as the pyrometering and the determining of the true temperature were concerned the procedure was the same as in the filament-melt method. One arc lamp of the type described usually served for about 10 or 15 determinations. Throughout all, the brightness temperatures measured were uninfluenced by the brightness of the arc proper,

a condition which has not always been attained heretofore in arc method measurements. To eliminate effects arising from deviations from Lambert's cosine law, the pyrometer was always sighted at a spot where the surface was nearly normal to the line of vision. Pyrometer filters corresponding to 0.665μ and 0.462μ were used.

The third, or tungsten-molybdenum contact method of determining the melting point employed a lamp with a piece of tungsten and a piece of molybdenum wire mounted end to end. The end of the tungsten wire was bluntly tapered and the end of the molybdenum wire slightly hollowed so that during the building of the lamp there might not be excessive trouble experienced in keeping the wires end to end. As in the other methods, the wires were electrically heated by a current, in this case so directed as to insure a positive Peltier heating and hence a temperature of the molybdenum filament definitely hotter at the junction than elsewhere. With the pyrometer sighted on the tungsten close to the junction the current was increased until melting occurred. Application of the previously determined emissivity of tungsten to the brightness temperature found gave the melting point of molybdenum. Only one determination with a pyrometer filter corresponding to 0.665μ was secured by this method.

Melting-point results. A summary of results obtained by these methods just described is given in Table II. For both wave-lengths the arc method yielded values about 20° higher than the filament-melt method. The

TABLE II

Results obtained for the melting point of molybdenum
($c_2 = 14330\mu$ deg., $T_{Au} = 1336°K$)

Method	No. of readings	Wave-length λ	Brightness temperature S_λ	Spectral emissivity e_λ	True temperature T
Filament-melt	23	0.664μ	2518°K ± 6°*	.328	2894°K
Arc	47	.664	2531 ±11	.328	2911
Filament-melt	10	.462	2647 ± 5	.363	2890
Arc	16	.462	2666 ±10	.363	2915
W-Mo contact	1	.664			2912
				Weighted average	2895° ± 10°

* Average deviation in S_λ, observed or estimated.

assumption that the emissivity of molybdenum at the melting point suddenly increases on melting, requires about a 5 percent change to account for the magnitude of the change observed. While the filament-melt method might naturally be expected to yield too low a result, and the arc method as carried out too high a result, a difference on this account of more than 1 or 2 percent (4° or 8°) was not anticipated. In

fact, work on tungsten[3] showed no certain change. While it seems very doubtful that an increase in emissivity of from 3 to 5 percent on melting could have escaped detection, some such change may actually have occurred.

In arriving at an average for the melting point temperature, the possibility of such a change in emissivity at melt justifies giving the filament-melt values considerably greater weight. This has been done. Everything considered, a rounded average of 2895°K ± 10° as the melting point of molybdenum seems the most justifiable conclusion.

Comparison of melting-point determinations with results of others. All available data on the melting point of Mo which the writer has found are summarized in Table III. The results of Ruff and Goecke are obviously in error. The others reduced to a common temperature scale

TABLE III

Summary of determinations of the melting point of Mo

Author	Method of producing melt	Values used in published results for c_2	λ	e_λ	S_λ	T	T†
Wartenberg[7]	Tungsten furnace	14,600				2800°K	2870°K
Ruff and Goecke[8]	Furnace					2380°	
Pirani and Meyer[9]	Hg vapor arc	14,200	0.64μ	0.51		2725° ± 30	2850° ± 30
Mendenhall and Forsythe[10]	Filament	14,500	.658	0.390	2510°K	2808°	(S)2935* (T)2870*
Pirani and Althertum[11]	Tube	14,300	.545-548 .580-591			2840 ± 40	2835 ± 40
Worthing	Filament	14,330	0.462	.363	2651°	See Table II	2895° ± 10
	Arc terminal W-Mo junction		0.664	.328	2519°		

* In transferring the published results, the S and T values which were obtained separately were transferred separately. Due to the change in spectral emissivity the transfer from S gives the higher temperature. Account was taken of a change in effective wave-length (Hyde, Cady, and Forsythe, Astrophys. J., **42**, 294, 1915) from 0.658μ to 0.664μ. These relative values are independent of any measured emissivities.

† Computed assuming $c_2 = 14330\mu$ deg., $T_{Au} = 1336$°K, $e(.665\mu) = .328$.

vary from 2835°K to 2935°K. The cause for this wide range may perhaps be linked up with the discussion given above regarding the great range

[7] Wartenberg, Verh. Deutsch. Phys. Gesell. **12**, 121 (1910)

[8] Ruff and Goecke, Z. angew. Chem. **24**, 1459 (1911)

[9] Pirani and Meyer, Verh. Deutsch. Phys. Gesell. **14**, 426 (1912)

[10] Mendenhall and Forsythe, Astrophys. J. **38**, 196 (1913)

[11] Pirani and Althertum, Z. Electrochem. **29**, 5 (1923)

to be found in recorded spectral emissivities. The discussion there given does not, of course, concern the results of Pirani and Althertum. Perhaps more may be said following an international intercomparison of temperature scales which the writer's colleague Dr. W. E. Forsythe has now under way.

For efficient aid throughout the progress of this work, which was largely performed two years ago, the writer is greatly indebted to Kenneth Moorhead, Charlotte Skinner, Lester Boss, Ruth Sublett, and C. H. Prescott, Jr.

NELA RESEARCH LABORATORY,
March 13, 1925.

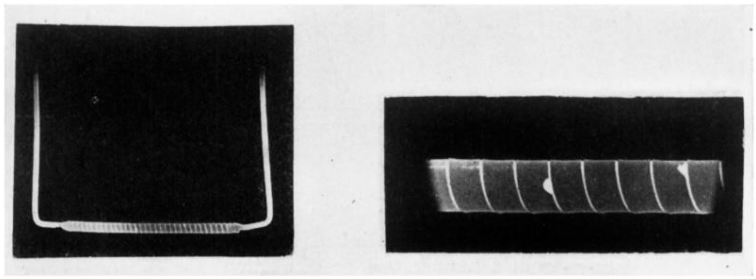

Fig. 1A Fig. 1B

A. Photograph (natural size) showing mounting of molybdenum tube.
B. Photograph (magnified) showing detail of molybdenum tube.