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MSM
HISTORICAL
COLLECTION

THE LITHIUM TUNGSTEN BRONZES

By

SHUN SHENG HSU

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THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

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MSM
HISTORICAL
COLLECTION

Approved by M. E. Straumanis

Research Professor of Metallurgy

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INTRODUCTION

The "tungsten bronzes" are a series of anionic substitutional solid solutions of alkali or alkaline earth metal metatungstates and tungstic oxide. They are neither alloys or intermetallic compounds, the term "tungsten bronzes" was adopted because of their remarkable metallic properties -- e.g., high electrical conductivity, metallic luster on the crystal, and high specific gravity. Also owing to their intense and vivid colors and chemical inactivity it was possible to use them in the paint industry as a substitute for the so-called "bronze powders", the latter term is applied to the finely divided metal powders, such as aluminum, copper, brass, and bronze powders. The paint made of these tungsten bronzes with some binding materials are used to protect metal surfaces and for ornamental purpose.

The properties and structure of some of those tungsten bronzes are still unknown; in the last two decades, no published investigation about lithium tungsten bronzes has been made.(1)

The present work is intended to find out the structure and some other properties of the lithium tungsten bronzes, the solubility of tungstic oxide in the bronzes,

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(1) Am. Chem. Soc., Chemical Abstracts, 1926 - April 1949.

and the lattice changes with increasing amount of WO_3 in such a solid solution series. These points have not been reported by previous workers. Some chemical and metallurgical processes are involved in this investigation; theories and technique of x-ray diffraction are applied, the samples are identified, and the structure and lattice constants of lithium tungsten bronzes are found from x-ray powder photographs applying "Straumanis' technique".(2)

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(2) Straumanis, M. and A. Ievinš, "Die Präzisionbestimmung von Gitterkonstanten nach der asymmetrischen Methode", Springer, Berlin, 1940; Edwards, Ann Arbor, Michigan, 1948.

REVIEW OF LITERATURE

The tungsten bronzes were first prepared by F. Wohler in 1824 by reducing acid sodium tungstate with hydrogen.(3) Later, some other investigators also reported the preparation of tungsten bronzes of various alkali and alkaline earth metals, the methods of preparation may be classified into the following three types:(4)

1. Reduction of an acid tungstate with hydrogen, coal gas, tin, zinc, or iron at a high temperature --- F. Wohler and H. Wright.

2. The electrolytic reduction of a fused polytungstate or a fused mixture of tungstic acid with a metallic tungstate or of a solution of tungstic acid in a fused mixture of alkali chlorides --- C. Scheiber, A. Stayenhagen, E. Engels, L. H. and H. H. Kahlenbert and E. Zettnow.

3. Melting mixtures of normal or acid tungstates with tungsten dioxide in absence of air --- O. Brunner.

The exact formulas and structure of those tungsten bronzes were not known to the early workers; different formulas have been applied to the products of apparently

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(3) Wöhler, F., Pogg. Ann., Vol. 2, 1824, p. 350; Phil. Mag., Vol. 66, 1825, p. 263.

(4) Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. 11, London, 1931, pp. 750-751.

similar reactions. Some thought that these bronzes possess several sexivalent tungsten atoms and one quadrivalent tungsten atom and that their formula could generally be represented by $mR_2O.nWO_3.WO_2$. W. F. de Jong first reported that the crystal structure of these bronzes is the same as that of perovskite ($CaTiO_3$), so that the formula of the bright yellow sodium tungsten bronze must be $NaWO_3$.(5) G. Hägg then confirmed it and showed that the tungsten in the yellow Na-W-bronze is pentavalent.(6)

A recent investigation of the structure and chemical properties, the electrical conductivity of sodium tungsten bronzes, the maximum solid solubility of WO_3 in Na-W-bronzes, and the lattice changes with increasing amount of tungstic oxide in the bronzes have been made by M. E. Straumanis.(7)

The lithium tungsten bronzes were prepared by reducing fused lithium paratungstate with tin or by electrolysis of fused lithium paratungstate by L. A. Hallo-

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(5) de Jong, W. F., Zeit. Krist., Vol. 81, 1932, p. 314. de Jong, W. F. and H. Stek, ibid, Vol. 83, 1932, p. 496.

(6) Hägg, G., Zeit. Physik. Chem., (B) Vol. 29, 1935, p. 192.

(7) Straumanis, M. E., Journ. Am. Chem. Soc., Vol. 71, 1949, pp. 679-683. Straumanis, M. E. and A. Dravnieks, ibid, pp. 683-687.

peau,(8) O. Brunner(9) and others. The products have dark blue and steel blue colors; and the crystal forms are microscopic plates and prisms. These bronzes were assumed to have the formulas $Li_2W_4O_{12}$ and $Li_2W_5O_{15}$ respectively.

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(8) Hallopeau, L. A., Ann. Chim. Phys., Vol. 19, 1900, p. 117.

(9) Brunner, O., "Bertrage zur Kenntnis der Wolframbronzen", dissertation, Zurich, 1903.

THE PREPARATION OF LITHIUM TUNGSTEN BRONZES

1. The Starting Materials.

The lithium tungsten bronzes were prepared by reducing a mixture of lithium tungstate and tungstic oxide with metallic tungsten at high temperature in vacuum.

The lithium tungstate was made from lithium carbonate and tungstic acid by fusing at about 750°C in air for a half hour in a platinum crucible.

$$Li_2CO_3 + WO_3 \cdot H_2O \longrightarrow Li_2WO_4 + CO_2\uparrow + H_2O\uparrow \quad . \; . \; (1)$$

The tungstic oxide was prepared by heating tungstic acid in air to 900°C and keeping it at that temperature for two hours.

$$WO_3 \cdot H_2O \longrightarrow WO_3 + H_2O\uparrow \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \; (2)$$

The metallic tungsten is the finely divided c. p. powder.

2. Equipments for Preparing Li-W-Bronzes.

The samples were placed in either a silica bulb or a combusion boat and heated in an electric tube furnace with chromel wire windings; the highest temperature available is about 1100°C. The temperature in the center of the furnace was measured by a chromel-alumel thermocouple and read directly from a Brown potentiometer. The arrangement of the heating system is shown in Figure 1.

The bronzes were prepared in vacuum, the vacuum assembly includes a mercury diffusion pump, a mechanical vacuum pump and the tubing, valves, gages and a driving motor. Ordinarily, only the mechanical pump was used, a pressure as low as one micron Hg could be obtained. When silica bulb was used to hold the sample, it was evacuated, after the sample had been filled into it, and then sealed off with an oxy-gas flame.

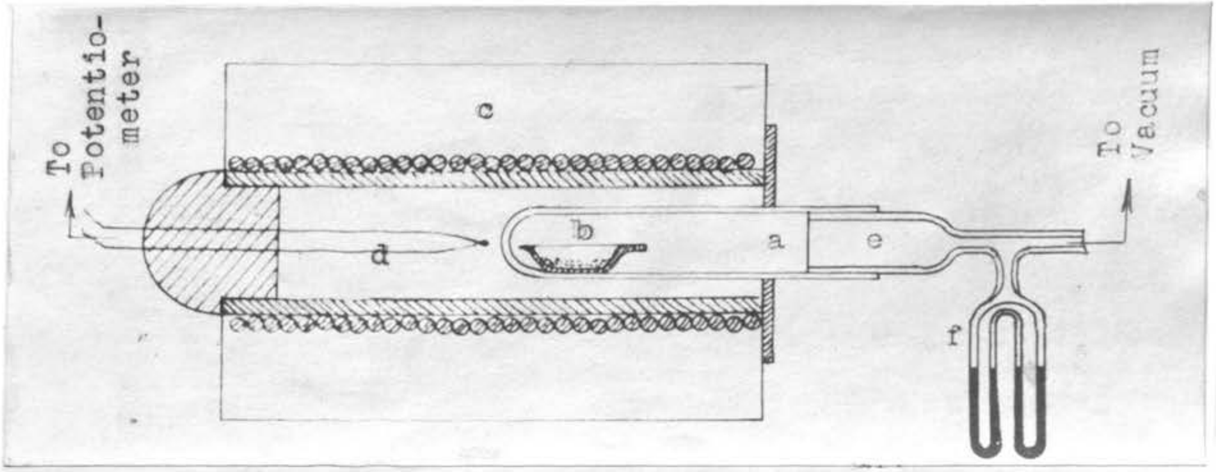

Figure 1. The Schematic Arrangement of the Heating System.
a. silica tube, b. combustion boat with sample, c. electric tube furnace,
d. thermocouple, e. glass joint,
f. manometer.

3. The Attempt to Make Pure Lithium Tungsten Bronzes

Nineteen experiments were made; in every case, the starting materials were weighed, intimately mixed, ground and then put into a porcelain or platinum combustion boat. The boat and its contents was pushed into a silica tube and heated in a tube furnace in absence of air as shown in Figure 1.

The products were taken out, ground, washed with water to remove the unreacted lithium tungstate, treated with NaOH solution to get rid of the excess free tungstic oxide, then washed with water again, neutralized with one or two drops of HCl, rewashed thoroughly, and dried on a hot plate. After drying, they were examined under microscope to observe the crystal form and the homogenity of the products. X-ray powder photographs were made for qualitative identification.

The x-ray machine used in this investigation has a demountable, self-rectifying, water-cooled gas type tube, with the target changeable, and is satisfactory for diffraction work.

Experiment 1

An attempt was made to prepare some pure $LiWO_3$ according to the equation,

$$\underset{785.4}{3Li_2WO_4} + \underset{462.8}{2WO_3} + \underset{183.9}{W} = 6LiWO_3 . \; . \; . \; . \; . \; . \quad (3)$$

The charge consisted of:
W --- 0.46 gram
WO_3 --- 1.16 grams
Li_2WO_4 --- 1.97 grams
Total --- 3.59 grams

The mixture was heated slowly in a porcelain boat to 750°C and kept at that temperature for 20 minutes then cooled gradually.

The product (S-1) was mainly brown powder with very few violet blue crystals. This brown powder has been proven to be tungsten dioxide by chemical analysis. L. A. Hallopeau in his work to prepare lithium tungsten bronzes also obtained such result.

An x-ray photograph (F.53) has been made for further identification of the product.

Experiment 2

The same conditions were used as in experiment 1, except the highest temperature was 800°C instead of 750°C.

The product (S-2) was similar to S-1.

An x-ray powder photograph (F. 54) shows the same pattern as that on F. 53.

Experiment 3

The same conditions were used as in Experiment 2, except that the sample container was not a porcelain boat but a platinum one.

The product (S-3) had the same appearance as S-2. An x-ray powder photograph (F. 56) is the same as F. 54.

Experiment 4

The reactants were those of reaction (3) but WO_3 was in excess:

W --- 0.24 gram

WO_3 --- 1.00 grams

Li_2WO_4 --- 1.00 grams

Total --- 2.24 grams

other conditions were the same as those in Experiment 3.

The product (S-4) was only brown powder.

An x-ray powder photograph (F. 62) has the WO_2 pattern.

Experiment 5

Reaction (3) was used, the sample was heated to 700°C and kept at that temperature for 4 hours, then cooled down slowly. All further experiments, including this one, were made in a porcelain boat.

The products were divided according to their color as follows:

a. Yellow powder with metallic luster (S-5a). X-ray photograph (F. 60) shows that it is metallic tungsten.

b. Violet blue crystals (S-5b) in cube form. The x-ray photograph shows a diffraction pattern quite different from those of WO_2, WO_3, W, and Li_2WO_4, but closely resembling that of sodium tungsten bronze; it shows the same structure but with a different lattice constant (see Fig. 2). Apparently it is one of the Li-W-bronzes.

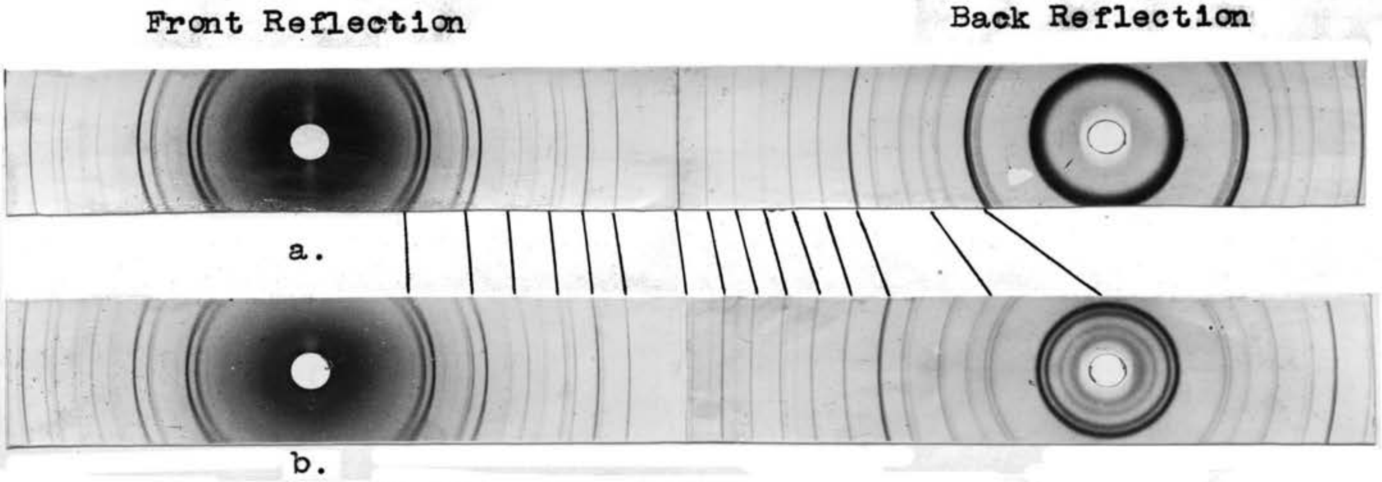

Figure 2. Comparison of the X-ray Diffraction Patterns of Li-W-Bronze and Na-W-Bronze. (Co-radiation).
a. Na-W-Bronze b. Li-W-Bronze

c. Reddish crystals (s-5c)

An x-ray photograph shows that it is the same substance as S-5b. Since these crystals are very thin, the reddish color due to the transmitted light may be a complement to those due to the reflected light; the latter is blue as is the color of S-5b.

Experiment 6

Similar to experiment 5 but the temperature was raised to 710°C and kept there for 4 hours.

The product (S-6) was mainly brown powder, presumably WO_2. An x-ray photograph (F. 63) showed the WO_2 pattern.

Experiment 7

An excess of W was used;

W --- 0.30 g.
WO_3 --- 0.58 g.
Li_2WO_4 --- 0.95 g.

Total --- 1.73 g.

The mixture was heated 4 hours at 750°C.

The product (S-7) was brown powder.

An x-ray photograph (F. 64) shows that it is a mixture of WO_2 and metallic tungsten.

Experiment 8

The same conditions as in Experiment 7, but the sample was heated to 690°C.

The product (S-8) was separated according to the specific gravities into three parts:

a. The light portion (S-8a) was composed of blue crystals.

The x-ray photograph (F. 66) shows the same pattern as that of S-5b (the bronze pattern).

b. The medium portion (S-8b), a mixture of blue and brown powders.

The x-ray photograph (F. 67) shows the mixed patterns of WO_2 and Li-W-bronze.

c. The heavy portion (S-8c), a brown powder.

The x-ray photograph (F.68) shows the WO_2 pattern.

Experiment 9

The same conditions as in Experiment 8, but the reaction was kept longer (15 hours) at maximum temperature.

The product (S-9) was a homogeneous brown powder.

X-ray photograph (F.69) proves that it is WO_2

Experiment 10

The sample was made according to the following reaction (WO_3 in excess):

$$3Li_2WO_4 + 8WO_3 + W = 6\,(LiWO_3 \cdot WO_3) \quad . . . (4)$$

W ---	0.092 g.
WO_3 ---	0.927 g.
Li_2WO_4 ---	0.373 g.
Total ---	1.392 g.

The mixture was heated to 700°C for 4 hours.

The product (S-10) was dark blue crystals that were not very homogeneous.

X-ray powder photograph (F. 70)gives the bronze pattern, with a greater lattice constant that that of S-5b.

Experiments 11-17

These experiments were carried out by keeping the WO_3 at 0.58 g. with gradually decreasing amounts of W (from 0.12 g. to 0.06 g.) and Li_2WO_4 (from 0.90 to 0.80 g.) The maximum temperatures which were kept at 4 hours were 700, 750, 700, 800, 850, 900, 800°C respectively.

The products (S-11 to S-17) all appear to contain a little brown WO_2 together with the blue bronzes.

X-ray photographs of these samples (F. 73, F. 74, F. 75, F. 76, F. 78, F. 82) have been made.

Experiment 18

The following starting materials were used:

W ---	0.05 g.
WO_3 ---	0.58 g.
Li_2WO_4 ---	0.80 g.
Total ---	1.43 g.

The mixture was heated to 800°C for 4 hours and cooled down slowly to room temperature.

The product (S-18) was composed of pure blue crystals without any WO_2 present.

X-ray powder photograph (F. 91) has sharp diffraction lines of the bronze pattern.

Experiment 19

The same as Experiment 18, but only half the quantity of Li_2WO_4 was used.

The product (S-19) was the same as S-18.

X-ray photograph (F.106) was the same as F. 91 in structure and lattice but was taken with Co-radiation. (Previous x-ray powder photographs were taken with Cu-radiation).

Several other samples were also made under the same conditions, but in larger quantities; the products (S-19b, S-19c, S-19d) have the same appearance and same x-ray diffraction pattern (with very small change in lattice constant) as those of S-19.

4. Conclusion and Discussion.

From the previous experiments, it can be seen that Experiment 19 was the most satisfactory way to prepare pure Li-W-bronze. In Experiment 18, though the product is as pure as that obtained from Experiment 19, but the Li_2WO_4 used was more than necessary. The blue Li-W-bronze, S-19, was taken as a starting material for further study.

The WO_3 (W in sexivalent form) content in such a blue bronze is approximately 50% by weight, as computed from the reactants used; its formula is approximately $LiWO_3 \cdot WO_3$.

The pure $LiWO_3$ cannot be obtained by using reaction (3) at various temperatures; this means that the $LiWO_3$ is not a stable compound; reaction (3) will not go to the right. In the case of Na-W-bronzes the pure $NaWO_3$ can be obtained without much difficulty.

In each of the first 17 experiments (Experiment 1 to Experiment 17) WO_2 is present more or less; it is a result of too much metallic tungsten, which reduced WO_3 to WO_2. The WO_2 does not react with Li_2WO_4 at that temperature.

THE CHEMICAL AND OTHER PROPERTIES OF LITHIUM TUNGSTEN BRONZES

The color of lithium tungsten bronzes is generally blue with variations from violet blue to dark blue; in thin plates they may show reddish or yellowish color, this is by transmitted light, and has been explained in Experiment 3 of the previous chapter.

The chemical activity of these bronzes is very poor; all of the common acids and bases do not attack them, even at an elevated temperature.

The WO_3 may absorb lithium vapor to form $LiWO_3$ (usually $LiWO_3$ is not stable, it absorbs more WO_3 to form solid solution), and to a certain extent, the $LiWO_3$ again dissociates into Li and WO_3; the equation:

$$LiWO_3 \rightleftharpoons Li + WO_3 \text{. . . . . .} \quad (5)$$

is a reversible one, this has been proven by the following experiment:

Pure WO_3 and blue Li-W-bronze were put into separate partitions of a combustion boat, and heated to 900°C for 2 hours. After the heating, the WO_3 and the bronze both have the same blue color, indicating the equilibrium of reaction (5).

Another experiment was made by reducing the blue bronze with metallic lithium; the bronze and a piece of metallic lithium was put together into a small iron crucible, and heated to 700°C for 2 hours in absence of air. The products included some metallic tungsten powder, white lithium tungstate, and blue crystals. The x-ray photograph of the blue crystals shows the same pattern with very small change in lattice constant as the original blue bronze. In the case of Na-W-bronze, pure $NaWO_3$ can be obtained by reducing red or blue Na-W-bronze with metallic sodium according to the reaction: (7)

$$NaWO_3 \cdot xWO_3 + xNa = (x+1)NaWO_3$$

The formation of metallic tungsten and lithium tungstate is supposed to occur by the following reaction:

$$LiWO_3 \cdot WO_3 + Li = 2LiWO_3 \cdot \; . \; . \; . \; . (6)$$

$$2LiWO_3 = Li_2WO_4 + WO_2 \; . \; . \; . \; . \; . (7)$$

Evidently $LiWO_3$ in reaction (6) is not stable, it again decomposes into lithium tungstate and tungsten dioxide.

The lithium tungsten bronzes react with iodine or lithium iodide by the following reversible reaction:

$$nLiWO_3 \cdot mWO_3 + I = (n-1)LiWO_3 \cdot (m+1)WO_3 + LiI \; . \; . \; . \; . (8)$$

The following two experiments were made to prove the above reaction:

a. Blue bronze (S-19) and iodine were mixed and put into a silica bulb, evacuated and sealed off, and heated to 900°C for 2 hours. The product has been proven to contain lithium iodide.

b. Pure WO_3 and lithium iodide were put together into a silica tube, as shown in Figure 3 (at point "a"), evacuated and sealed off, and heated to 900°C for two hours. Iodine came off from the mixture as a sublimate and condensed at "b". The residue in the tube after heating was treated with NaOH solution and washed with water and dried; after drying, it has a yellowish brown color, and under microscope it appeared as both brown and yellow crystals. X-ray powder photographs show that it is a mixture of WO_2 and metallic tungsten. The reactions may be:

$$LiI = Li + I \quad \ldots\ldots\ldots\ldots \quad (9)$$

$$Li + WO_3 = LiWO_3 \quad \ldots\ldots\ldots\ldots \quad (5a)$$

$$2LiWO_3 + 6LiI = 4Li_2O + W + WO_2 + 6I \quad \ldots \quad (10)$$

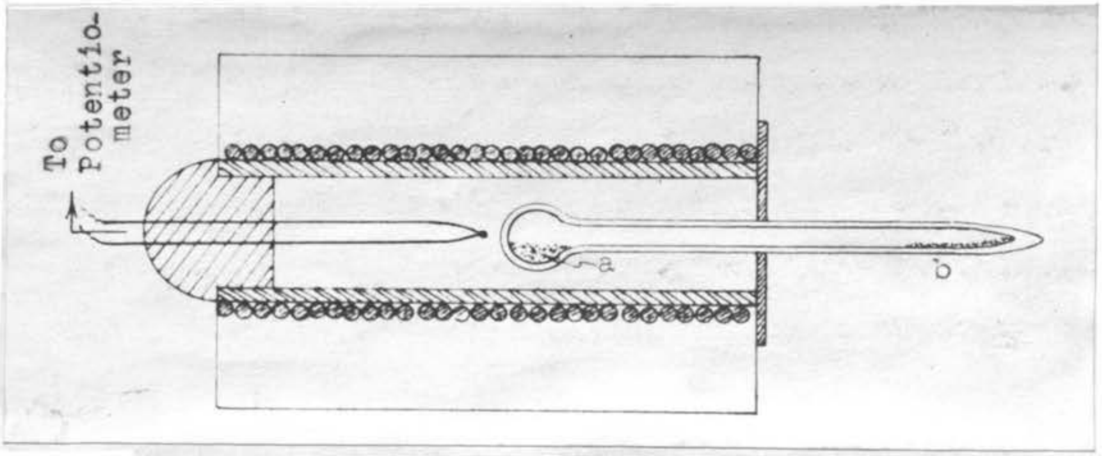

Figure 3. The Schematic Arrangement for the Reaction of Tungstic Oxide and Lithium Iodide.

The specific gravity of Li-W-bronzes is about 7.4.

The electric conductivity of these bronzes is high.

These lithium tungsten bronzes have the crystal forms of cubes and plates; the crystals are very brittle, and the cleavage plane parallel to the 100 direction is perfect.

THE STRUCTURE OF LITHIUM TUNGSTEN BRONZES

1. Indexing of the Film.

In order to find out the structure type and what the atomic positions of the lithium tungsten bronzes are, and to determine the lattice constants of such crystals, the films of the x-ray photographs of the bronze must be first indexed.

Films of pure lithium tungsten bronzes with Cu and Co radiations are indexed by the graphic method for indexing cubic crystal using the principles of reciprocal lattice.(10)

For the Cu-$K_{\alpha 1}$ radiation, the radius of the reflecting circle is taken as 10 cm, for other radiations the radii of the reflecting circle are determined from the wave length of the new radiation using the following equations:

$$a_0 = \lambda_1 \sqrt{\frac{r1}{2p}} \quad . . . . (a)$$

$$a_0 = \lambda_2 \sqrt{\frac{r2}{2p}} \quad . . . . (b)$$

where a_0 is the lattice constant; it is constant for a

λ_1 is the wave length of the Cu-$K_{\alpha 1}$ radiation

= 1.5374 kX.

r_1 is the radius of Cu-K_1 reflecting circle.

p is the equidivision on the diameter of the re-

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(10) Straumanis, M., Zeit. Krist. (A) Vol. 104, 1942, pp. 167 - 177.

flecting circle. For a given sample, it is constant for any kind of radiation.

λ_2 is the wave length of the new radiation to be used.

r_2 is the radius of reflecting circle for the new radiation.

From (a) and (b),

$$r_2 = r_1 \frac{\lambda_1^2}{\lambda_2^2} \quad \ldots\ldots\ldots\ldots\ldots\ldots . (c)$$

If the radius of the Cu-$K_{\alpha 1}$ reflecting circle, r_1, is taken as 10 cm,

For Cu-K_β radiation,

$$r_{Cu-K_\beta} = 10 \times \frac{(1.5374)^2}{(1.3894)^2} = 12.245 \text{ cm.}$$

For Co-$K_{\alpha 1}$ radiation,

$$r_{Co-K_{\alpha 1}} = 10 \times \frac{(1.5374)^2}{(1.7853)^2} = 7.416 \text{ cm.}$$

For Co-K_β radiation,

$$r_{Co-K_\beta} = 10 \times \frac{(1.5374)^2}{(1.6174)^2} = 9.035 \text{ cm.}$$

Examples for indexing F.60 (S-5b) (Cu-radiations) and F.107 (S19b) (Co-radiations) are given in Figure 4 and Figure 5 respectively; the 2 values used for constructing these two figures are listed in Table I.

In these figures, when all of the possible diffraction lines present are projected exactly at equidivisions,

TABLE I

2 VALUES OF THE DIFFRACTION LINES ON F. 60 and F. 107 (Cu and Co Radiations Respectively)

No. of Lines	2θ , in Degree	
	F.60	F.107
1	21.61	25.78
2	23.89	27.89
3	30.75	36.98
4	34.07	39.86
5	42.11	49.38
6	44.01	54.81
7	49.06	57.56
8	55.29	65.12
9	61.00	72.30
10	71.79	84.90
11	76.81	92.42
12	81.89	99.08
13	86.84	105.84
14	91.65	112.99
15	96.57	120.11
16	101.30	121.05
17	111.40	128.13
18	117.09	148.04
19	122.76	153.31
20	128.85	164.33
21	135.47	169.58
22	142.89	------
23	144.88	------
24	152.92	------

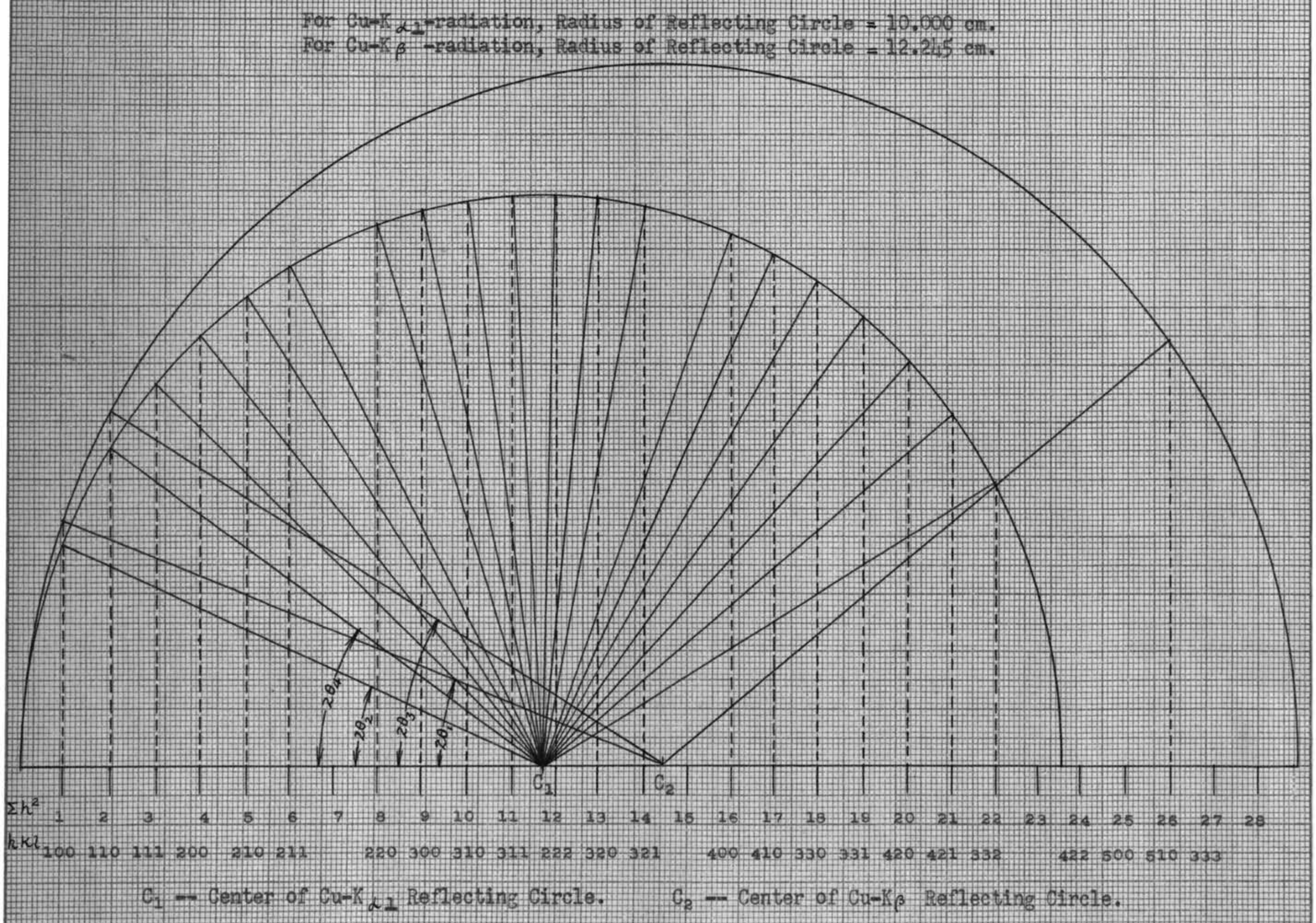
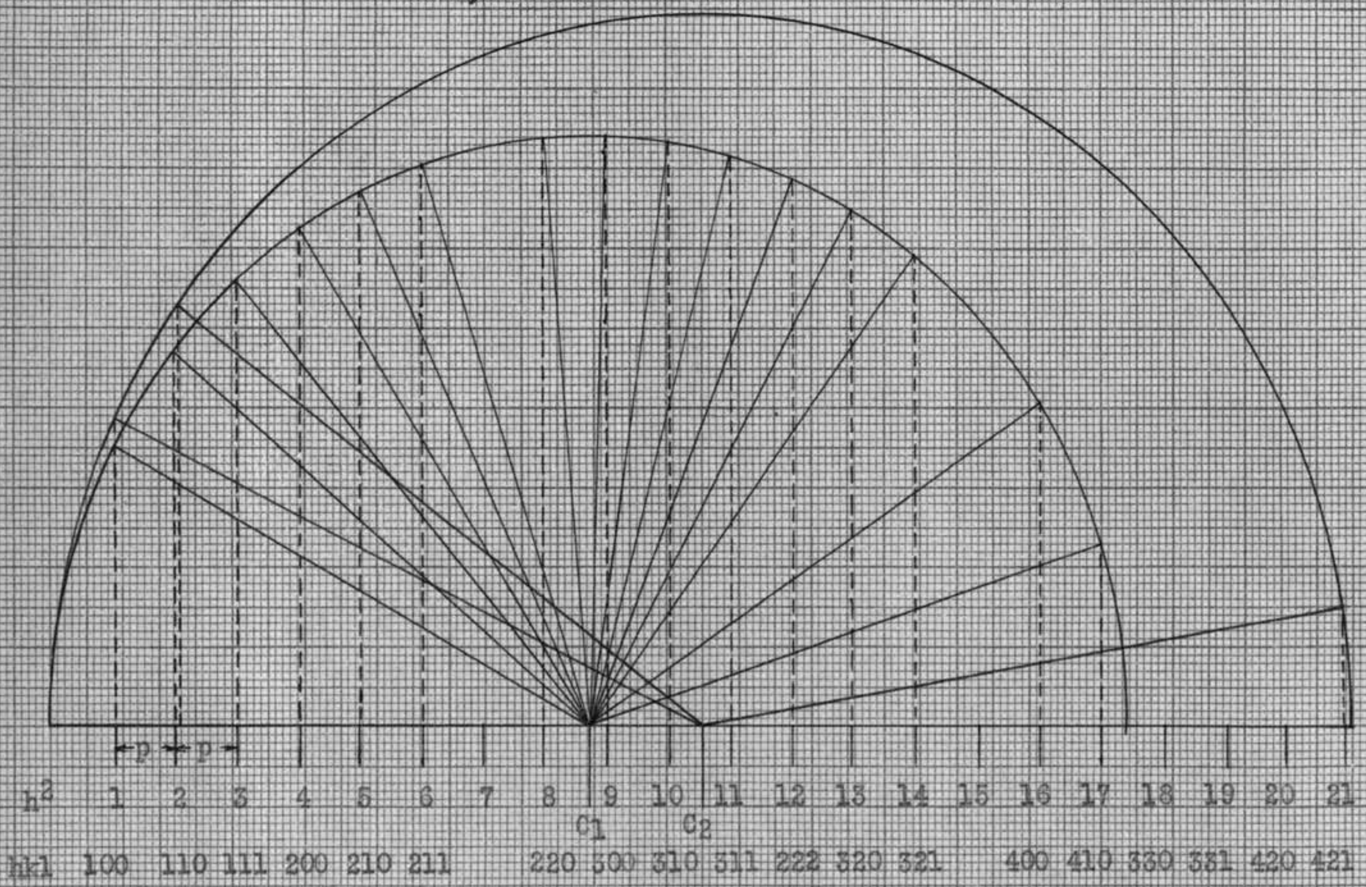


Figure 4. The Graphic Method for Indexing X-ray Powder Photographs of Cubic Crystals Using Cu-radiation.

For Co-K_{α_1}-radiation, Radius of Reflecting Circle = 7.416 cm.
For Co-K_β -radiation, Radius of Reflecting Circle = 9.035 cm.



C_1 -- Center of Co-K_{α_1} Reflecting Circle.
C_2 -- Center of Co-K_β Reflecting Circle.

Figure 5. The Graphic Method for Indexing X-ray Powder Photographs of Cubic Crystals Using Co-radiation.

it indicates that these bronzes have a simple cubic crystal structure.

The indexed films are shown in Figure 9.

2. Determining the Atomic Positions in the Li-W-Bronzes Crystals by Trial.

The atomic positions in an ideal $LiWO_3$ crystal are determined by trial. First some possible positions are assumed and the theoretical intensities of the diffraction lines are calculated, applying the molecular structure and other factors. Then the calculated results are checked with the observed result to see whether the assumption is correct or not.(11)

Since the lithium tungsten bronze crystals have the same structure as that of the sodium tungsten bronzes, the lithium tungsten metatungstate crystal is also assumed to have the perovskite structure with the atomic positions.

Li --- 000
W --- $\frac{1}{2}\frac{1}{2}\frac{1}{2}$
O --- $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}0\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}0$ (12)

The theoretical intensities are obtained by the fol-

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(11) Bunn, C. W., "Chemical Crystallography", London, Oxford University Press, 1948, pp. 190-273. Hermann, C., "Internationale Tabellen", Erster Band, Berlin, 1935, pp. 353-355; ibid, Zweiter Band, pp. 556-585.

(12) Barth, T., Strukturbericht, Zeit. Krist, Erganzungsband, 1913-1928, pp. 331-332.

lowing formula:

$$I\ (\text{Theor.}) = F_1 \times F_2 \times F_5 \times F_6 \quad \ldots\ldots\ldots (c)$$

where

$$F_6 = \{F_3[F_{4(Li)} \times A_{(Li)} + F_{4(W)} \times A_{(W)} + F_{4(O)} \times A_{(O)}]\}^2 + \{F_3[F_{4(Li)} \times B_{(Li)} + F_{4(W)} \times B_{(W)} + F_{4(O)} \times B_{(O)}]\}^2 \quad \ldots\ldots (d)$$

a. F_1 (Laue-Lorentz Factor) to correct the polarization of x-rays coming from the sample.

$$F_1 = \frac{1 - \cos 2\theta}{\sin^2\theta \cdot \cos\theta} \quad \ldots\ldots\ldots\ldots (e)$$

Values of F_1 at various angle of θ can be interpolated from the curve in Figure 6.

b. F_2 (Multiplicity Factor) This takes into account the strength of diffraction from all possible faces encountered in a certain hkl.

c. F_3 (Debye-Waller Temperature Factor) This compensates for the activity of the electrons in the atoms, and depends on the strength of bond between atoms.

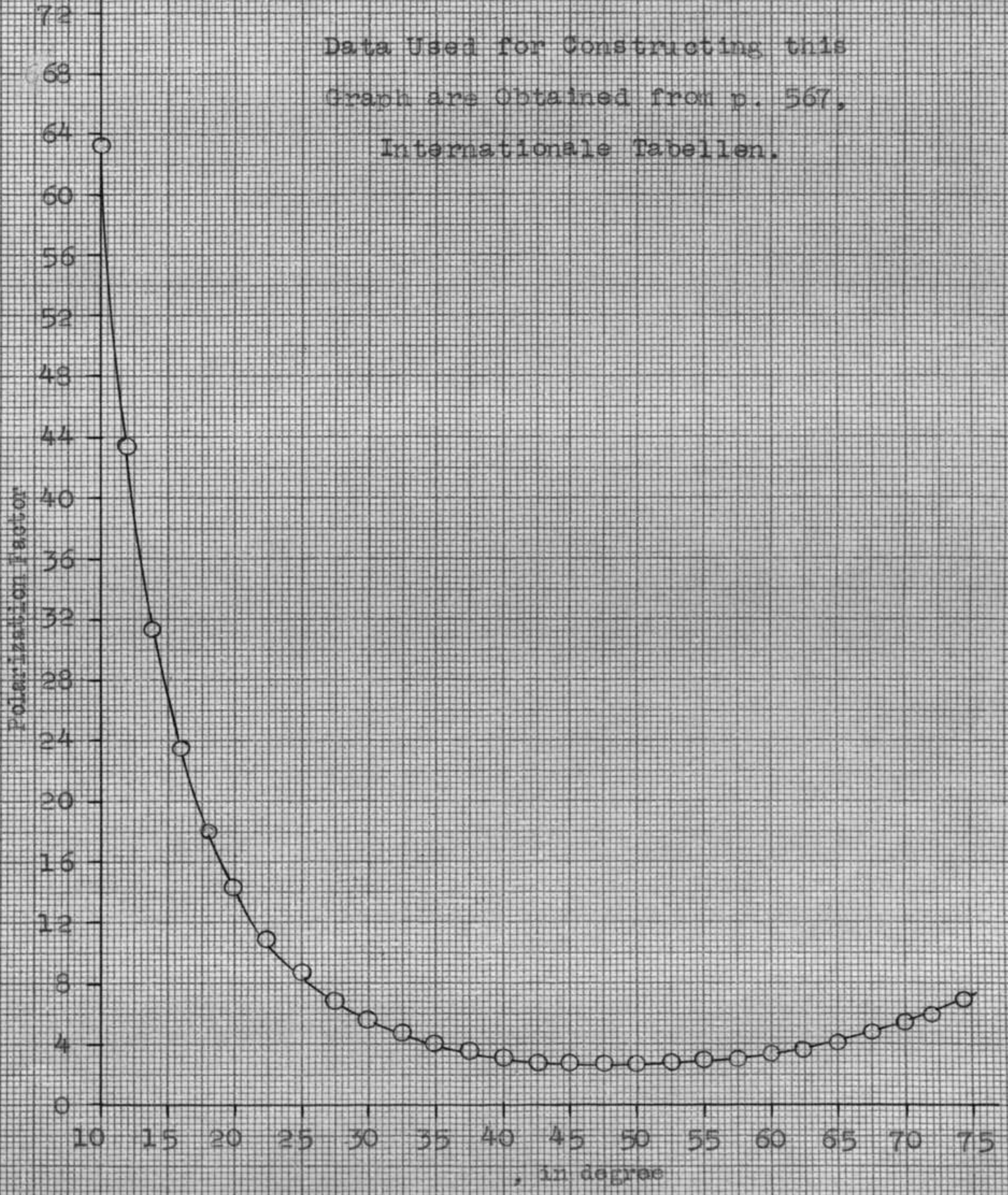
$$F_3 = e^{-B\left(\frac{\sin\theta}{\lambda}\right)^2} \quad \ldots\ldots\ldots\ldots\ldots (f)$$

and

$$B = \frac{6h^2}{mk\alpha}\left\{\frac{\Phi(x)}{x} + \frac{1}{4}\right\} \quad \ldots\ldots (g)$$

where m is the mass of atom = atomic weight x 1.6488 x 10^{-24} g.

h is Planck Constant = 6.547 x 10^{-27} erg-sec.



Data Used for Constructing this Graph are Obtained from p. 567, Internationale Tabellen.

Figure 6. Polarization Factor versus Bragg Angle .

k is Boltzmann's Constant $= 1.3709 \times 10^{-16}$ erg/deg.

α is the characteristic temperature of the crystal, for the ideal $LiWO_3$ crystal, taken as 600°C.

$x = \alpha/T$, where T is the absolute temperature of the sample in °C.

$\Phi(x)$ is data from p. 574, Table IV, Int. Tab. (Internationale Tabellen)

$$B = \frac{6 \times (6.548 \times 10^{-27})^2}{\left(\frac{6.94 + 184 + 48}{5}\right) 1.6489 \times 10^{-24} \times 1.3709 \times 10^{-16} \times 600} \times \left\{ \frac{0.607 \times 300}{600} + \frac{1}{4} \right\}$$

$$= 0.244 \times 10^{-16}$$

$$\frac{\sin\theta}{\lambda} = 1/(2d) \quad . . . . (h)$$

F_3 can be found from p. 574, Table III, Int. Tab. with the proper B and $\frac{\sin\theta}{\lambda}$ values.

d. F_4 (Atomic Structure Factor) Expresses the scattering produced by each atom in the crystal. F_4 can be obtained by interpolation the data given on Tables I and II, p. 571-573, Int. Tab.

e. F_5 (Absorption Factor) To correct the absorption of x-ray by the sample at different positions.

$$\mu = 7.4 \left(\frac{20.5}{100} \times 12.7 + \frac{77}{100} \times 171 \right)$$

$$= 1170$$

$R =$ radius of sample $= 0.0032$ cm.

$$\mu R = 1170 \times 0.0032 = 3.7$$

F_5 can be found from Figure 7.

f. F_6 (Molecular Structure Factor) To correct density of each plane.

The ideal $LiWO_3$ is assumed to be a simple cubic substance having the structure type O^1_h with the atomic positions as mentioned above. A and B in Equation (d) can be obtained from p. 355, Int. Tab. as:

$$\begin{aligned} A = 8\{ & \cos 2\pi hx \cos 2\pi ky \cos 2\pi lz + \\ & + \cos 2\pi hy \cos 2\pi kz \cos 2\pi lx + \\ & + \cos 2\pi kx \cos 2\pi ly \cos 2\pi hz + \\ & + \cos 2\pi kx \cos 2\pi hy \cos 2\pi lz + \\ & + \cos 2\pi hx \cos 2\pi ly \cos 2\pi kz + \\ & + \cos 2\pi lx \cos 2\pi ky \cos 2\pi hz \} \end{aligned}$$

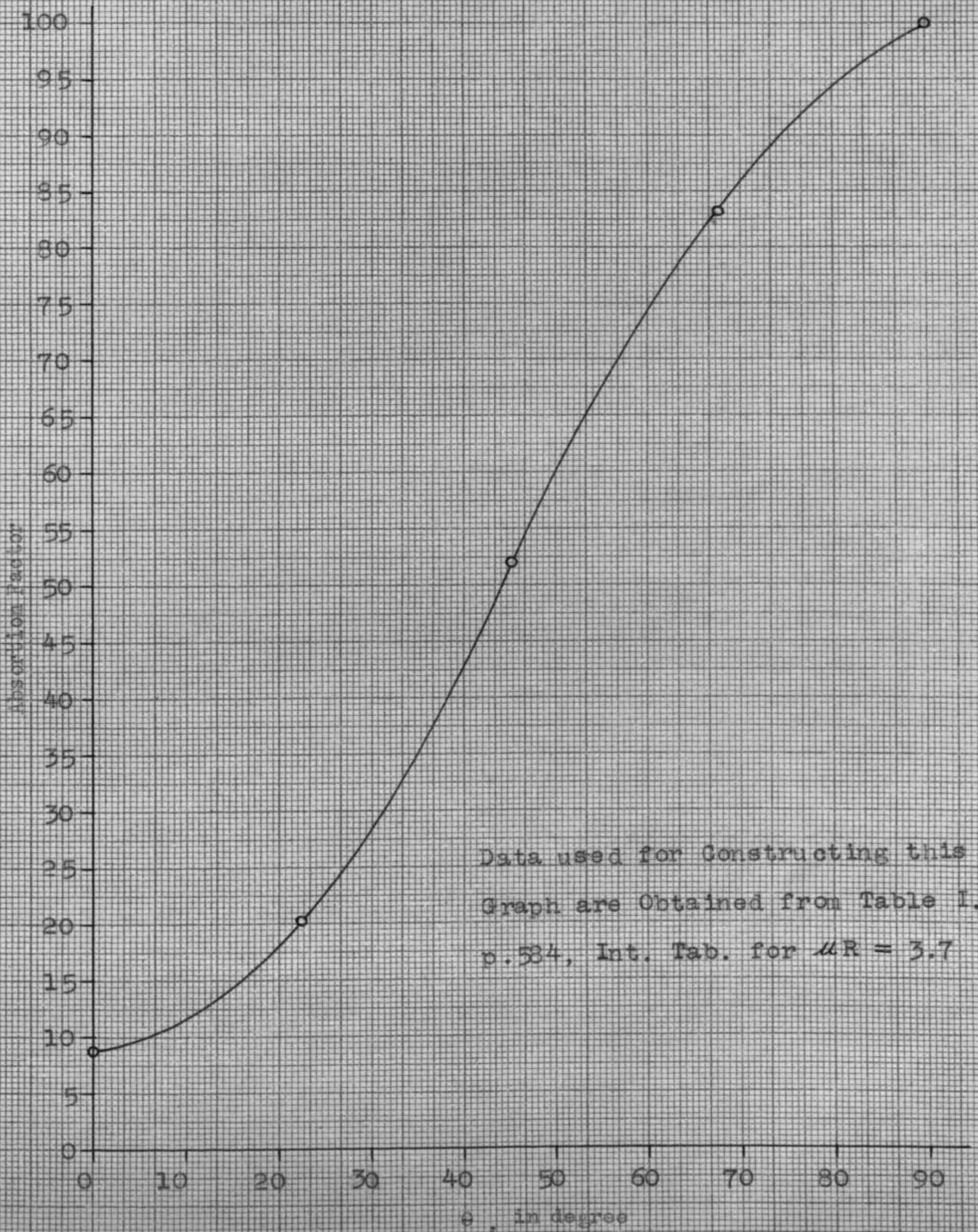
$$B = 0 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (i)$$

The calculated intensities and the observed ones are listed in Table II.

The crystal structure of the ideal $LiWO_3$ is illustrated in Figure 8.

3. Conclusion and Discussion.

The graphic method for indexing the x-ray films of cubic crystals is very satisfactory for the lithium tungsten bronze pattern with Cu-$K_{\alpha 1}$, Cu-K_β, and Co-$K_{\alpha 1}$ radiations, but the lines from the Co-K_β radiation do not give very good results. This is possibly because the wave



Data used for Constructing this Graph are Obtained from Table I. p.584, Int. Tab. for $\mu R = 3.7$

Figure 7. Absorption Factor versus Bragg Angle θ .

Table II.

The Theoretical and Observed Intensities of Lithium Metatunstate Crystals (Cu-radiation)

hkl	d kX.	1/2d	θ	F_1	F_2	F_3	F4			F_5	$F_6 \times 10^5$	(calc) $I \times 10^9$	(Calc) Rela. I	(Observ.) I
							Li+1	W+5	0-2					
100	3.7155	0.1346	11.95	43.8	6	0.995	1.91	65.90	7.15	14.1	72.9	27.1	42.3	strong
110	2.6277	0.1903	17.04	20.9	12	0.991	1.82	61.24	5.75	18.0	74.5	33.6	52.4	strong
111	2.1452	0.2331	21.06	13.1	8	0.986	1.70	57.87	4.98	21.5	38.5	8.7	13.6	Weak
200	1.8578	0.2691	24.53	9.2	6	0.982	1.59	55.10	4.30	24.3	107.2	14.4	22.4	medium
210	1.6616	0.3009	27.65	7.0	24	0.978	1.50	52.8	3.80	27.7	67.0	31.1	48.5	strong
211	1.5168	0.3296	30.50	5.3	24	0.973	1.44	50.8	3.47	31.0	51.0	20.1	31.4	strong
220	1.3136	0.3806	35.90	4.0	12	0.964	1.34	47.5	2.92	38.0	71.0	13.0	20.3	medium
300 221	1.2385	0.4037	38.41	3.5	6 24	0.960	1.29	45.9	2.68	42.0	47.5	4.2 21.0 16.8	32.8	strong
310	1.1749	0.4256	40.95	3.2	24	0.956	1.23	44.7	2.55	45.0	39.6	13.7	21.4	medium
311	1.1273	0.4440	43.42	3.0	24	0.952	1.17	43.6	2.43	49.0	26.0	11.8	18.4	weak
222	1.0726	0.4662	45.82	2.8	8	0.948	1.11	42.4	2.30	53.0	52.6	6.2	9.7	weak
320	1.0305	0.4852	48.29	2.7	24	0.943	1.05	41.3	2.19	57.0	37.0	13.7	21.4	medium
321	0.9930	0.5035	50.65	2.7	48	0.940	0.99	40.4	2.09	60.0	31.5	24.6	38.4	strong
400	0.9289	0.5383	55.70	2.9	6	0.930	0.92	39.1	1.98	68.0	23.0	2.7	4.2	very weak
410 322	0.9011	0.5552	58.55	3.2	24	0.926	0.89	38.4	1.93	71.8	30.6	16.9 33.8 16.9	52.7	strong
330 411	0.8758	0.5709	61.38	3.5	12 24	0.922	0.86	37.9	1.89	75.8	26.7	8.5 25.5 17.0	39.8	strong
331	0.8524	0.5866	64.43	4.0	24	0.918	0.83	37.3	1.84	79.1	8.6	14.1	22.0	medium
420	0.8308	0.6018	67.74	4.6	24	0.914	0.80	36.8	1.80	83.0	35.6	32.6	50.8	medium
421	0.8108	0.6167	71.45	5.8	48	0.910	0.77	36.3	1.75	86.5	26.6	64.1	100.0	very str.
332	0.7921	0.6312	74.46	7.9	24	0.906	0.74	35.8	1.71	91.3	22.8	39.5	61.6	strong

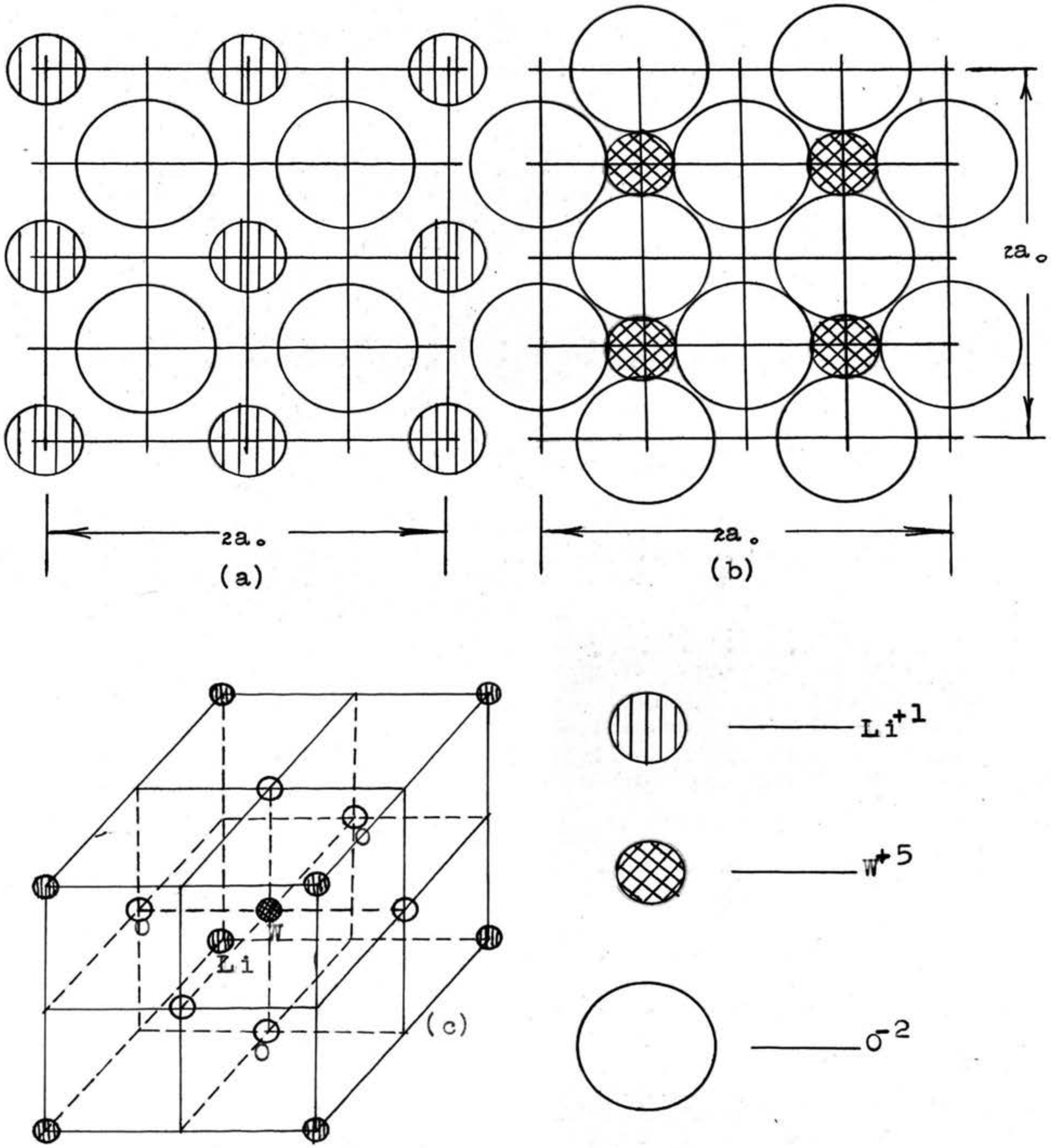


Figure 8. The Crystal Structure of the Ideal $LiWO_3$
(a). The First Layer of the Crystal.
(b). The Second Layer of the Crystal.
The 3rd Layer is Identical with the First One.
(c). The Unit Cell of The Crystal. Showing Atomic Positions: Li(000); W($\frac{1}{2}\frac{1}{2}\frac{1}{2}$); O(0$\frac{1}{2}\frac{1}{2}$,$\frac{1}{2}0\frac{1}{2}$,$\frac{1}{2}\frac{1}{2}$0).
Ionic Radii in (c) not in Proportion.

length of the Co-K_β radiation was not accurately determined by previous workers.

The crystal of the lithium tungsten bronzes is found to be a simple cubic one, all the possible hkl are present on the films.

The atomic positions in the ideal $LiWO_3$ crystal are determined from the intensity calculation to be: Li (000); W ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$); O ($0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$). Though the blue bronze which contains not only the lithium metatungstate molecules but also the tungstic oxide molecules in solid solution, is taken as a base to calculate the theoretical intensities of the diffraction lines of the ideal $LiWO_3$ crystal, the deviation of the results may be neglected; because when a $W^{+6}O_3$ molecule goes into the $LiWO_3$ molecules forming anionic substitutional solid solution $Li_{(1-x)}(W^{+5}O_3)_{(1-x)}\cdot(W^{+6}O_3)_x$, the oxygen atoms will occupy their original positions --- i. e., the corners of the octahedron, A W^{+5} atom will be substituted by a W^{+6} atom with the escape of a lithium atom to keep the total charge at zero. Since the lithium atoms are so light, their ability to diffract x-ray is very small as compared with those of tungsten and oxygen atoms. The ionic radii of W^{+5} and W^{+6} are nearly the same(13); the effect of the intensities due to the

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(13) Wyckoff, R.W.G., "Crystal Structures", Interscience Publishers, Inc., New York, 1948, Chap. III, Table p. 15. In this table, the ionic radii of W^{+4} and W^{+6} are given as 0.68 and 0.65°Å respectively, since the ionic radius of W^{+5} is not known at the present time, it is assumed to 0.665 Å, the middle value of 0.68 and 0.65 Å, so the difference between the ionic radii of W^{+5} and W^{+6} is only 0.015 Å.

substitution of W^{+5} and W^{+6} should be very small, and may be ignored in the calculation.

THE SOLID SOLUTIONS OF $LiWO_3$ AND WO_3 SERIES

In order to determine the lattice constant of each of these solid solutions exactly, the following apparatus and technique have been used:

1. The Precise X-ray Camera and the Sample Mounting Method.

The camera was designed by Dr. M. E. Straumanis; it is a modified Debye-Scherrer type cylindrical camera with a diameter of 64 mm. The sample to be diffracted is mounted on a thin Lindemann glass (B-Li-glass) wire, which has been adjusted exactly to coincide with the axis of the camera; the diameter of the glass wire is about 0.08 mm. The diameter of the sample including the glass wire is about 0.15 mm. The sample must be very fine and stuck uniformly on the glass wire with the help of very small amount of glue. All the sample mounting and the adjustment of the glass wire position are done under a microscope. The glass rotates with the goniometer head of the camera during the time of exposure.

2. Straumanis' Technique.

The x-ray film 3 x 7 cm is loaded into the camera according to "Straumanis' technique", (2) which has the following advantages:

a. Both front reflections and back reflections are recorded on the same film at same time.

b. The sample coincides exactly with the axis of the camera, as mentioned above; the error due to eccentricity is greatly reduced.

c. The effective circumference of the camera is measured and counted from the film in each instance, the errors due to the diameter of the camera and shrinkage of the film are eliminated.

d. The sample is so fine that the error due to absorption of x-rays is reduced to a negligible extent, if the "last lines" in the back reflection region ($80 - 87^{\circ}$) are used for calculation.

3. <u>The Comparator.</u>

The comparator used to measure the films has a fixed carriage and a microscope travels over it on ways. The screw has a pitch of 1 mm; the micrometer drum has 1000 divisions, so that the least count is 0.001 mm while fractions of this unit can be estimated. The film on the carriage can be adjusted to the desired position with two screws. The traveling microscope has a low magnification combination of eye-piece and objective.

A record of measurement and calculation of certain x-ray powder photographic film is given in Table III as an example.

Table III.

Example of Film Measurement and Calculation

F. 70, Li-W-Bronze, blue (S-11),

Cu-radiation

Front ref.

Intensity		M.	V.S.	W.	M.	V.S.
Comp.Read.	R.	60.667	62.004	64.775	65.708	67.563
Comp.Read.	L.	36.744	35.427	32.685	31.722	29.842
Total R. and L.		97.401	97.431	97.460	97.430	97.405

97.425 (Average total R & L)

Back ref.

Intensity		W.	W.	M.	V.W.	
hkl		$331_{\alpha 1}$	$420_{\alpha 1}$	$421_{\alpha 1}$	$421_{\alpha 2}$	
Comp.Read.	R.	175.984	174.160	170.089	169.667	
Comp.Read.	L.	121.661	123.468	127.556	127.964	
Total R. and L.		297.645	297.628	297.649	297.631	**297**.639 (ave.)
R. minus L.		54.323	50.692	42.533	41.703	
(R-L) x f = φ in degree		24.419	22.758	19.119	18.746	297.639
cos φ		.910547	.922147	.944840	.946952	- 97.425
$\lambda/2 \times \sqrt{\Sigma h^2}$		3.42076	3.43773	3.52263	3.53141	200.214
a_o in kX		3.7283	3.7292	3.7283	3.7280	f = 90/200.214

a_o = 3.7284 kX (Average)

= 0.44952 deg/mm

4. Determine the Lattice Constants by Using Back Reflection Technique.

The lattice constant:

$$a_o = \frac{d}{\sqrt{h^2 + k^2 + l^2}} \quad \ldots\ldots\ldots\ldots (j)$$

where hkl are the Miller indices of any set of atomic planes in a crystal, and d is the interplanar spacing of this hkl.

From Bragg's equation

$$\lambda = 2d \sin\theta \quad \ldots\ldots\ldots\ldots (k)$$

$$d = \frac{\lambda/2}{\sin\theta} \quad \ldots\ldots\ldots\ldots (l)$$

from (k) and (l),

$$a_o = \frac{\lambda/2}{\sin\theta\sqrt{h^2 + k^2 + l^2}} \quad \ldots\ldots\ldots\ldots (m)$$

or,

$$a_o = \frac{\lambda/2}{\cos\varphi\sqrt{h^2 + k^2 + l^2}} \quad \ldots\ldots\ldots\ldots (n)$$

where $\varphi = 90^\circ - \theta$

The Bragg angle θ of any plane hkl can be found from the film measurement record. When θ is very large, that is, nearly 90°, a small error of measuring only gives a very small deviation of the $\sin\theta$ value; it will not effect the precision of the lattice constant determination too much. This large Bragg angle is found in the back reflection region.

Another reason for using back reflection technique appears on differentiating Bragg's equation (k), while d is regarded as constant and λ as a variable.

$$d\lambda = 2d \cos\theta \, d\theta$$

$$d\theta / d\lambda = 1/ (2d \cos\theta), \text{ or } (\sec\theta) / (2d) \ldots (o)$$

Equation (o) shows that a doublet, such as Co $K_{\alpha 1}$-$K_{\alpha 2}$ (λ equal to 1.7853 and 1.7892 kX respectively, $d\lambda$ = 0.041 kX) will be resolved much more readily in the Bragg reflection from any given set of planes with spacing d for large value of θ than for small ones, because the angular separation for any given wave length separation $d\lambda$ and interplanar spacing d varies as sec θ . Such doublets can be seen in Figure 2 and Figure 9.

Also at large θ, the error due to absorption is much reduced.

5. Choice of Radiation.

From the preceeding statement, it is understood that the back reflection technique is very valuable for determining lattice constants, and the choice of a proper radiation becomes important. In this investigation Cu-radiaiation was first used for qualitative identification of the prepared samples; for the quantitative work, Co-radiation was selected. Since, from the above statement, a large θ approaching 90° for some diffraction lines is desirable; and from Equation (k).

$$\lambda = 2d \sin \ ,$$

when θ approaches 90°, sin θ is slightly smaller than one, so that a λ slightly smaller than 2d of a prominent line in the back reflection region is required to obtain satisfactory result.

Table IV gives the 2d values of some prominent lines of a blue lithium tungsten bronze sample having a large Bragg angle. (see also Table II.)

Table V gives the wave lengths of the $K_{\alpha 1}$ radiation of common target elements using for diffraction work.

From Tables IV and V, one can predict that both the Co and Ni targets will give desirable results for this bronze sample. The selected Co-radiation will give a very large θ for the (411,322) line.

Figure 9 shows the x-ray diffraction patterns of the same sample (blue lithium tungsten bronze) with different radiations (Cu and CO).

Bronzes containing more than 50% (by weight) of WO_3 were made by mixing S-19 with the exact amount of WO_3 required, the WO_3 added was computed from the following formulas:

Let x be the % (by weight) of free WO_3 required, and y be the final % (by weight) of WO_3 in sample. Since the S-19 contains 50% of WO_3, therefore,

$$y = 50/100\ (100 - x) + x$$

$$x = 2(y - 50)\ .\ .\ .\ .\ .\ .\ .\ .\ .\ .\ .\ .\ (p)$$

For instance, if a sample containing 75% WO_3 is required,

Table IV.

The 2d Values and the Corresponding Intensities of the More Intense Reflections From Li-W-Bronze Crystals

Indices hkl	d kX	2d kX	I, Relative, Calc. %
321	0.9930	1.9860	38.4
410 322	0.9011	1.8022	52.7
330 411	0.8758	1.7516	39.8
331	0.8524	1.7048	22.0
420	0.8308	1.6616	50.8
421	0.8108	1.6216	100.0
332	0.7921	1.5842	61.6

Table V.

The Wave Length of $K_{\alpha 1}$ Radiation for the Common Target Elements Using for Diffraction

Target Metal	Atomic No.	Wave Length of $K_{\alpha 1}$ kX
Cr	24	2.2850
Fe	26	1.9321
Co	27	1.7853
Ni	28	1.6545
Cu	29	1.5373
Zn	30	1.4322
Mo	42	0.7078

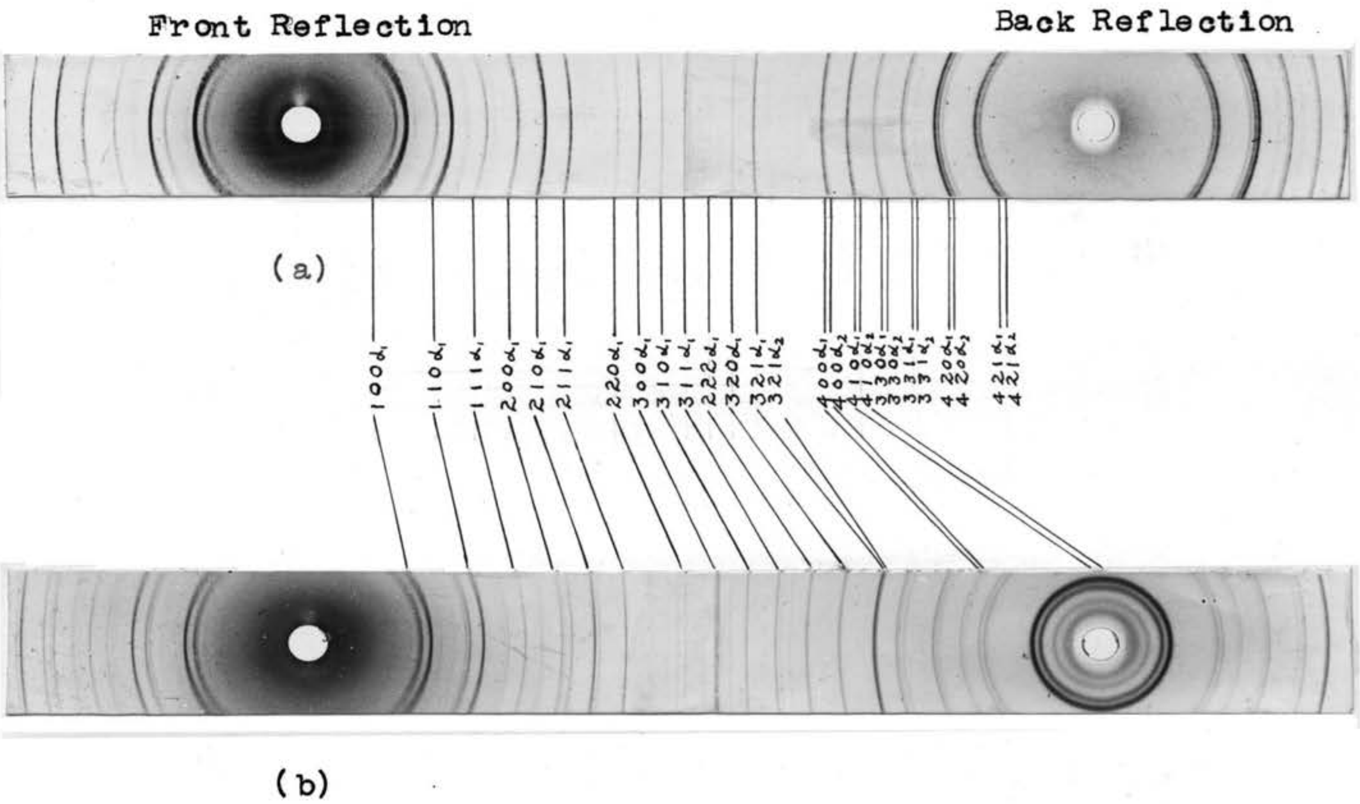


Figure 9. X-ray Powder Photographs of Same Li-W-Bronze Sample with Cu and Co Radiations.

(a). Cu-radiation.
(b). Co-radiation.

Numeral between (a) and (b) Indicates Miller Indices of the Lines on the Photographs.

and the weight of the sample is 0.5 g. then the free WO_3 required to add into S-19 equals 2(75 - 50) x 0.5 = 0.25 g. and the S-19 required = 0.5 - 0.25 = 0.25 g.

The mixture was ground, put into a quartz bulb, evacuated, sealed off and heated to 800 C to 900 C, according to the WO_3 content in the sample. After 2 hours heating, the sample was taken out and cooled quickly. X-ray powder photograph of each of these samples was made, the film measured, and the lattice constant computed. A sample containing WO_3 as high as 99.9% has been made, the color, phase and lattice changes of these samples are tabulated in Table VI.

The lattice changes with increasing amount of WO_3 in samples are shown in Figure 10.

Conclusion and Discussion.

The nature of the anionic substitutional solid solution series of $LiWO_3$ and WO_3 has been explained in the Chapter V, The Structure of Li-W-Bronzes.

The lattice constant increases with the increasing amount of WO_3 in the solid solution, the reason for this lattice expansion cannot be explained at the present time. The relationship between the lattice constant and the WO_3 content is shown in Figure 11. In this figure, the first three points are on a straight line. For samples containing more than 68% WO_3, the lattice change becomes more rapid; the 5 points, F. 162 (58.3% WO_3), F.127 (60.0% WO_3),

F. 159 (63.3% WO_3), F. 128 (65.0% WO_3), F. 160 (68.2% WO_3) are on another straight line which intersects the first line at about 58% WO_3 on the abscissa.

Samples contain WO_3 beyond 72%, a new phase appears and the old pattern (the cubic bronze pattern) becomes weaker and weaker with the increase of WO_3, and the lattice constant stays at about 3.7291 kX without change as shown by the last three points in Figure 11. The maximum solid solubility of tungstic oxide in the Li-W-bronzes is about 72%, where the last two straight lines intersect.

The new phase, as shown in Figure 12, does not belong to the cubic Li-W-bronzes series, no further investigation of it has been made.

For samples containing more than 99.0% WO_3 the x-ray diffraction pattern is the same as that of the pure WO_3. The x-ray photograph of pure WO_3 is shown in Figure 13.

The coloring effect of the blue Li-W-bronzes on the WO_3 is very remarkable, even 0.1% bronze gives the WO_3 a darker color as described in Table V.

Though the exact percentage of WO_3 in the blue bronze S-19 has not been analyzed, the straight line relationship will not be effected, since the relative composition will be the same after the amount of WO_3 in the S-19 has been redetermined.

Table VI.

The Color and Lattice Changes of the $LiWO_3$ - WO_3 Series

% WO_3	Color	a_0, kX.	Remark
50.0	dark violet blue	3.7145	S-19, made at 800°C.
52.5	dark violet blue	3.7148	S-19b & WO_3, 800°C.
55.0	dark violet blue	3.7153	S-19b & WO_3, 800°C.
58.3	dark violet blue	3.7166	S-19d & WO_3, 800°C.
60.0	dark violet blue	3.7172	S-19b & WO_3, 800°C.
63.3	dark violet blue	3.7204	S-19d & WO_3, 800°C.
65.0	dark violet blue	3.7227	S-19b & WO_3, 800°C.
68.2	dark violet blue	3.7258	S-19d & WO_3, 800°C.
75.0	blue	3.7290	S-19b & WO_3, 800°C. New phase appear
86.2	blue	3.7291	S-19c & WO_3, 800°C. Old pattern weaker
90.0	greyish blue	3.7291	S-19c & WO_3, 850°C. Old pattern very weak
95.0	greyish, greenish blue	------	S-19c & WO_3, 850°C. Free WO_3 present. Old pattern disappeared
97.0	greenish, blusih grey	------	S-19c & WO_3, 850°C.
99.0	dark olive green	------	S-19c & WO_3, 900°C.
99.5	dark olive green	------	S-19c & WO_3, 900°C.
99.7	olive green	------	S-19c & WO_3, 900°C.
99.9	olive green	------	S-19c & WO_3, 900°C.
100.0	greenish yellow	------	Pure WO_3, annealed at 1000°C.

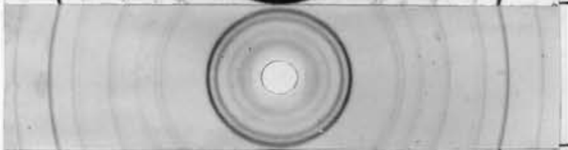
Back Reflection	No. of film	WO$_3$ % wt.	a. kX.
	107	50.0	3.7145
	121	52.5	3.7148
	125	55.0	3.7153
	162	58.3	3.7166
	127	60.0	3.7172
	159	63.3	3.7204
	128	65.0	3.7227
	160	68.2	3.7258
	133	75.0	3.7290

Figure 10. X-ray Powder Photographs Showing the Lattice Changes of Li-W-Bronzes with Increasing Amount of WO$_3$ in Solid Solution.

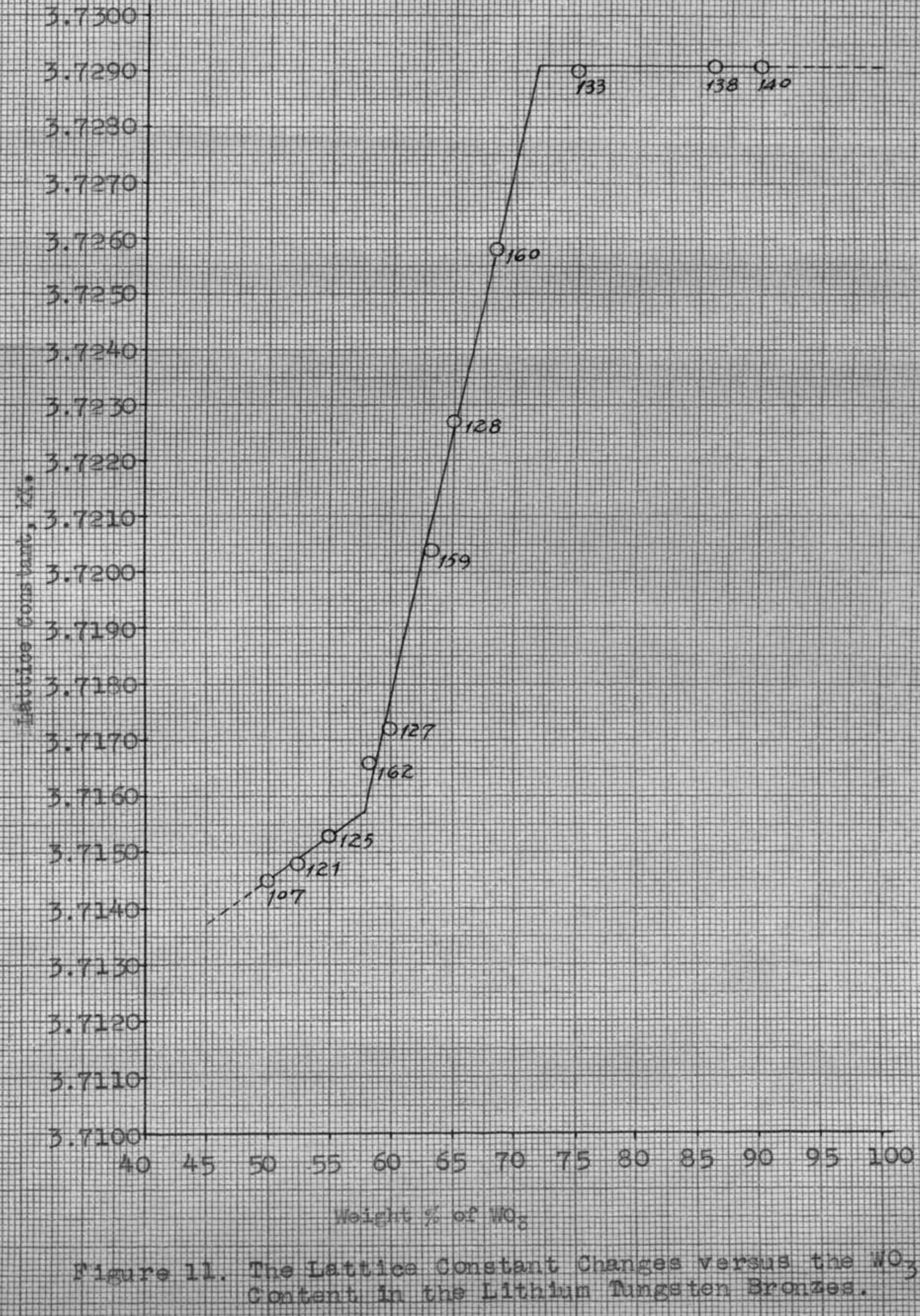


Figure 11. The Lattice Constant Changes versus the WO_3 Content in the Lithium Tungsten Bronzes.

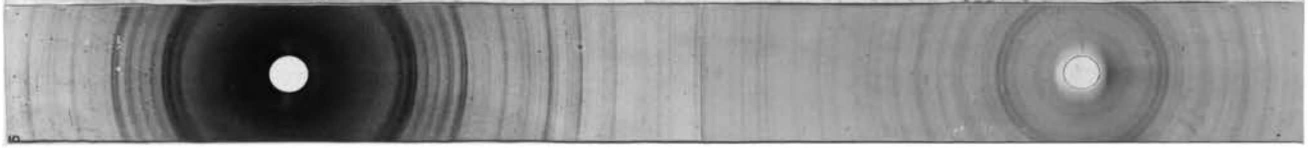


Figure 12. (above) The X-ray Powder Photograph of the Sample Contains 80% WO_3. Showing the Formation of a New Phase. (Co-radiation).

Figure 13. (below) The X-ray Powder Photograph of Pure WO_3 (Annealed at 1000°C) (Co-radiation).

SUMMARY

1. The lithium tungsten bronzes have been prepared by reducing lithium tungstate and tungstic oxide with metallic tungsten at 800°C in vacuum.

2. The bronze containing the least amount of WO_3 in solid solution has the formula approximately of $LiWO_3 \cdot WO_3$.

3. The pure $LiWO_3$ is not stable, and cannot be obtained.

4. Metallic lithium reacts with tungstic oxide very violently, and cannot be used to prepare $LiWO_3$; but WO_3 can absorb Li vapor from lithium tungsten bronzes at high temperature in vacuum. The reaction between Li vapor and WO_3 is a reversible one.

$$Li + WO_3 \rightleftharpoons LiWO_3 . \quad \ldots\ldots\ldots\ldots \quad (5)$$

5. The equilibrium of the above equation can be influenced by:

   a. Reducing Li-W-bronze with metallic lithium, equations (6), (7).

   b. Bringing the Li-W-bronze to react with iodine, Equation (8).

   c. Bringing the WO_3 to react with lithium iodide, Equations (9), (5), (10).

6. Some chemical and other properties of Li-W-bronzes have been observed.

7. The li-W-bronzes have simple cubic crystal struc-

ture. The atomic positions of the ideal $LiWO_3$ crystal have been found to be: Li (000); W ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$); O ($0\frac{1}{2}\frac{1}{2}$, $\frac{1}{2}0\frac{1}{2}$, $\frac{1}{2}\frac{1}{2}0$).

8. The Li-W-bronzes have no definite formula, WO_3 forms anionic substitutional solid solutions with $LiWO_3$.

9. The lattice of the lithium tungsten bronze expands with the increasing solid solubility of WO_3, the maximum solid solubility of WO_3 in these bronzes is found to be 72%.

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