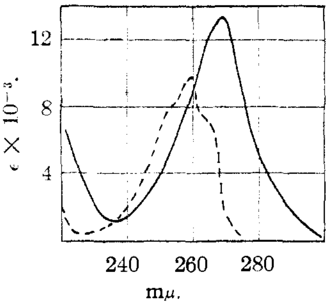

Fig. 14.— —, bis-N-methyl-α,α′-dipyridylium chloride; – – –, N-methylpyridinium chloride.

In the α-substituted compounds the A band of the univalent ions as compared with the free bases is increased in intensity and shifted to longer wave lengths, whereas the B band is strongly suppressed. In the β-derivates the predominant B band of the bases is split in the ions into two distinct absorption maxima. The position of the A band of β,β′-dipyridyl is only slightly changed by salt formation.

The unique band of γ-phenylpyridine is in its ion strongly shifted to longer wave lengths. A similar shift of somewhat smaller extent occurs in the spectrum of γ,γ′-dipyridyl.

The spectra of the unsymmetric dipyridyls and their salts show additive properties with regard to the spectra of the symmetric compounds; this is particularly true of the α,β-isomer, whose absorption spectrum, as shown in Fig. 15, is almost identical with the spectrum obtained by the superposition of two moieties of the symmetric compounds α,α′- and β,β′-dipyridyl. This additivity may have no physical significance but may be of value in the determination of unknown structures as shown in the case of the probable β,γ-dipyridyl.[8]

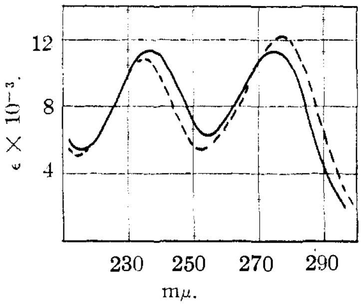

Fig. 15.— —α,β-dipyridyl; – – –, α,α′ + β,β′-dipyridyl.

The absorption spectra of the three phenanthrolines finally show a qualitative similarity with the spectra of the dipyridyls. The spectra of the three isomers, however, are not very different at least in regard to their two principal absorption bands.

The long wave band system, especially pronounced in the salts of para phenanthroline, bears some resemblance to the long wave absorption of phenanthrene.[20]

Acknowledgment.—The author is especially indebted to Prof. H. Stammreich for the permission to carry out the spectral measurements in the Laboratory of the Physical Institute of the Universidade de São Paulo, and for his valuable suggestions and criticisms.

(20) E. Clar, *Ber.*, **65**, 1411 (1932).

SÃO PAULO, BRAZIL RECEIVED NOVEMBER 13, 1950

[CONTRIBUTION FROM THE UNIVERSITY OF MISSOURI SCHOOL OF MINES AND METALLURGY, DEPARTMENT OF METALLURGY]

The System Sodium Tungsten Bronze–Lithium Tungsten Bronze–Tungsten(VI) Oxide[1]

BY M. E. STRAUMANIS AND G. F. DOCTOR

The ternary system sodium tungsten bronze (containing 6.6% by weight tungsten(VI) oxide)–lithium tungsten bronze (with 42.6% tungsten(VI) oxide)–tungsten(VI) oxide has been investigated by measuring the lattice parameters of the phases and by observing the appearance of new lines on the X-ray films. All bronze samples were heated at 850° *in vacuo* and quenched in air. It was found: the sodium bronze dissolves the lithium bronze up to 65% under lattice contraction; there is a large region of the homogeneous cubic ternary solid solution in the sodium bronze corner, one two-phase region in the lithium bronze corner (both phases being cubic), one multiphase region adjacent to the first two regions, containing also tetragonal bronzes, and one small homogeneous region in the tungsten(VI) oxide corner. The cubic ternary sodium lithium bronze–tungsten(VI) oxide solid solution has the structure and the properties of the cubic sodium or lithium bronzes. The crystals of the solution represent simultaneously a cationic (Na^+, Li^+, vacant sites) and anionic (WO_3^-, WO_3) substitutional solid solution. The distribution is at random. The samples of the ternary solid solution have a good electrical conductivity (sp. resistance between 0.1 and 0.6 ohm). The resistance increased considerably when the limits of the homogeneous phase were exceeded. If the composition of the heated samples is known, the crystalline phases present and the lattice parameters of the phases can be read from the diagrams.

Introduction

Sodium tungsten bronze[2a,b] and lithium tungsten bronze[3] can absorb appreciable amounts of tungsten(VI) oxide at elevated temperatures and, as it will be shown in the present paper, the sodium bronze can dissolve also some amounts of the lithium bronze. The intention of the present paper is, therefore, to determine the phases formed, their regions of stability and their limits in the ternary system sodium tungsten bronze–lithium tungsten bronze–tungsten(VI) oxide.

Although the bronzes and solid solutions have metallic properties,[2b,3] they are not bronzes, alloys or intermetallic compounds. Nevertheless, the term bronze will be used throughout the paper because of its brevity.

There are a few remarks in the literature concerning the reactivity of lithium bronze with

---

(1) Based on a thesis submitted by G. F. Doctor to the Graduate School of the University of Missouri, School of Mines and Metallurgy in partial fulfillment of the requirements for the Master Degree.

(2) (a) G. Hägg, *Z. physik. Chem.*, **B29**, 192 (1925); (b) M. E. Straumanis, THIS JOURNAL, **71**, 679 (1949).

(3) M. E. Straumanis and S. S. Hsu, *ibid.*, **72**, 4027 (1950).

potassium bronze[4] or of potassium bronze with sodium bronze,[5] but there are no data concerning the lithium–sodium bronzes and the ternary system mentioned above.

In order to investigate this system the three binary systems must be first known. The two binary systems sodium tungsten bronze–tungsten(VI) oxide and lithium tungsten bronze–tungsten(VI) oxide are already described[2b,3]; the third system sodium bronze–lithium bronze will be described in this paper.

Experimental

Preparation.—The materials used as components for the ternary system were a yellow sodium tungsten bronze, containing 6.6% by weight of tungsten(VI) oxide in solid solution,[2b] a dark blue lithium tungsten bronze with 42.6% tungsten(VI) oxide in solid solution[3] and tungsten(VI) oxide of highest purity.

The sodium bronze with 6.6% tungsten(VI) oxide was chosen because this compound was at our disposal and, besides, can be prepared easily. A pure sodium bronze ($NaWO_3$) is difficult to obtain. A lithium bronze of the formula $LiWO_3$ does not exist free from tungsten(VI) oxide in solid solution, containing a minimum of 42.6% oxide.[3] Therefore a lithium bronze of this composition was chosen as one component of the ternary system.

The content of tungsten(VI) oxide in the bronzes was determined by measuring the lattice constants[6] and reading the amount of tungsten(VI) oxide from the diagrams published in the previous paper.[2b,3]

In order to prepare the samples for the binary and ternary systems, the calculated amounts of the bronzes and of the tungstic oxide were weighed, intimately mixed and ground, put into a quartz bulb, evacuated, sealed off and heated to 850° in an electric furnace for one hour. Then all the bulbs were quickly removed from the furnace and air-cooled. Finally, the powder was removed from the bulbs, ground, and used for further examination without any purification.

It was assumed that under the conditions mentioned equilibrium had been reached in all the samples examined. This conclusion was supported by three facts: (1) experiments showed that no change in the lattice spacing was observed if samples at 850° were heated for one half, one, two or three hours; (2) the constants of the samples, as plotted against the concentration of one of the components, usually showed a gradual change without leaps exceeding the error limits, and (3) the patterns of the X-ray pictures were sharp without strange lines, except those of saturated phases.

The samples were examined under the microscope and X-ray powder patterns were made. They served for identification purposes of new phases and for measurement of lattice constants.[6] From these measurements the extent of the solid solution regions and the multiphase regions could be determined or estimated.

The System Sodium Tungsten Bronze–Lithium Tungsten Bronze.—When lithium bronze is added to the sodium bronze and heated at elevated temperatures, the first dissolves in the latter, forming a homogeneous crystalline powder, which has a smaller lattice constant than the original sodium bronze. The results of the measurements obtained with a series of samples of increasing lithium bronze content are summarized in the curve Fig. 1. The figure shows the shrinkage of the lattice spacing of the sodium bronze along a straight line up to 55% lithium bronze, at which point the lattice constant suddenly drops forming a saturated phase with lithium bronze. The lines of this phase were broad and the lattice constants fluctuated (mean value 3.7806 kX. or 3.7882 A.). At the same time the pure lithium bronze phase appeared, showing sharp unshifted lines on the X-ray photographs. The phase had, therefore, an undisturbed lattice; its constant was 3.7145 kX. or 3.7220 Å. which corresponded to that of the pure lithium bronze (3.7143 ± 0.0002 kX.)[3] within the error limits. It follows from the diagram that the sodium bronze dissolved the lithium bronze up to 65% by weight at 850°. The lithium bronze does not dissolve the sodium bronze.

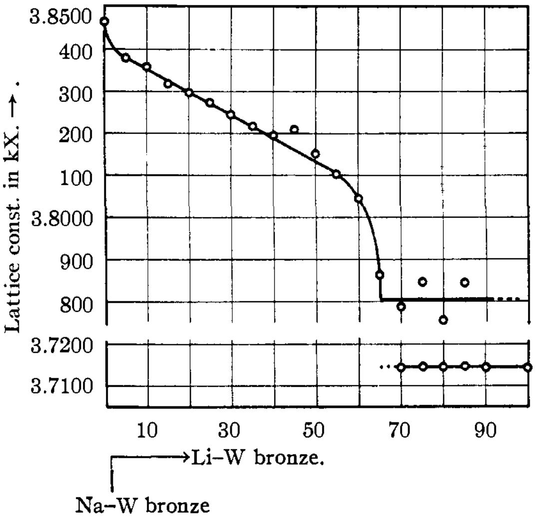

Fig. 1.—The contraction of the lattice of sodium tungsten bronze (with 6.6% WO_3), if lithium tungsten bronze is added. Co radiation was used.

Since both bronzes are cubic and the difference in the lattice constants is only 3.7% the formation of a solid solution up to 65% is quite natural. Further proofs in favor of a solid solution are: (1) The X-ray pattern of the sodium bronze was maintained, although the lattice contracted, even the intensities of the lines remained the same and, (2) the color of the resulting bronze changed gradually from bright yellow over light brown, brownish-red, brown, deep brown, grayish-blue to dark blue with increasing lithium bronze content, all the samples showing a brownish tint, different from that obtained in the solid solution series sodium tungsten bronze–tungsten(VI) oxide.[2]

The objection can be made that the contraction of the lattice of the sodium bronze was caused by the tungstic oxide that was present in the lithium bronze (42.6%). However, Fig. 2 will show that such an objection is unjustified. The upper curve shows the dependence of the lattice constant of the sodium bronze on the concentration of pure tungstic oxide, and the lower curve the dependence on the same amount of tungstic oxide but dissolved in lithium

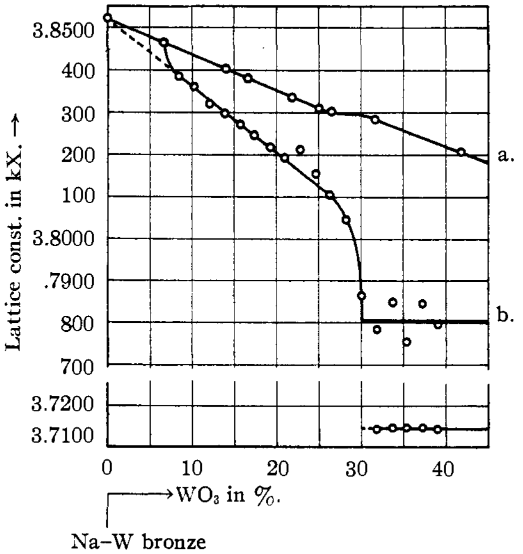

Fig. 2.—Lattice constant of sodium tungsten bronze (100%) *versus* tungsten (VI) oxide (curve a) and *versus* tungsten(VI) oxide dissolved in the lithium bronze (curve b).

---

[4] W. Feit, *Ber.*, **21**, 135 (1888).

[5] G. v. Knorre, *J. prakt. Chem.*, **27**, 65 (1883).

[6] M. E. Straumanis, *J. Appl. Phys.*, **20**, 726 (1949).

bronze. If the contraction of the sodium bronze lattice were due only to the tungstic oxide content, the two curves would coincide. The presence of the curve b shows clearly that the effect of contraction is caused not only by the tungsten(VI) oxide, but also by the lithium ions present. A further support of this is that both series of solid solutions, as represented by the curves a and b, show a difference in color, as mentioned above. Thus in the crystals of the sodium–lithium tungsten bronze cationic sites are filled by sodium cations, lithium cations, or remain empty, corresponding to the amount of dissolved tungstic oxide molecules, which occupies one part of the anionic places.[2a] The remainder of these places is filled by WO_3^-. The powder gives sharp excellent X-ray pictures up to 55% lithium tungsten bronze.

Sections in the Ternary System.—Since the sodium and especially the lithium bronze contain tungsten(VI) oxide, the system just investigated is actually a quasi-binary system with tungsten(VI) oxide as the third component. Therefore, only the study of this ternary system will give a survey over all the possibilities which may occur if sodium bronze, lithium bronze and tungsten(VI) oxide are heated *in vacuo* at 850°.

As shown in Fig. 6, the sections A-a, C-c, b-c, E-E, D-D, 33-39-45-50-61, and 32-40-59-60 were made through the system. On the basis of these sections and the 3 binary systems investigated, the ternary diagram Fig. 6 was derived.

The figures on the drawing represent the numbers of the samples whose composition can be read from the three coordinates. The diagram is based on the measurement of lattice constants and on the appearance of new lines on the X-ray patterns. If the lines were sharp, the lattice constants were determined with a precision of ±0.0005 kX. As the amount of the other two components added to one of the bronzes was increased the lines became broader and film background darker. All samples which had the composition in the vicinity of phase limits showed X-ray patterns with broad lines. In these cases the precision of the measurements was ±0.001 kX. or even less. The phase boundaries could be determined, some points excepted, only with a precision of ± 3%.

The section A-a sodium bronze–lithium bronze 50% and tungsten(VI) oxide 50% is shown on the Fig. 3. The shorter section 45-49-51-52 is placed on the same drawing. The long curve shows that the sodium bronze dissolves both the lithium bronze and tungsten(VI) oxide up to the composition of 32.5% (between point 34 and 35, slight bend in the curve) forming a ternary solid solution. If the amount of the two latter was increased a second phase appeared as shown by the lower curve, belonging to the lithium bronze in which some tungsten(VI) oxide was dissolved (increasing lattice constant with increasing amount of tungstic oxide). The limit between the solid solution and the two phase region in the section 45-49-51-52 lies approximately in the same place. This limit continues up to 65% lithium bronze of the sodium–lithium bronze quasi binary system (Fig. 6 and Fig. 1).

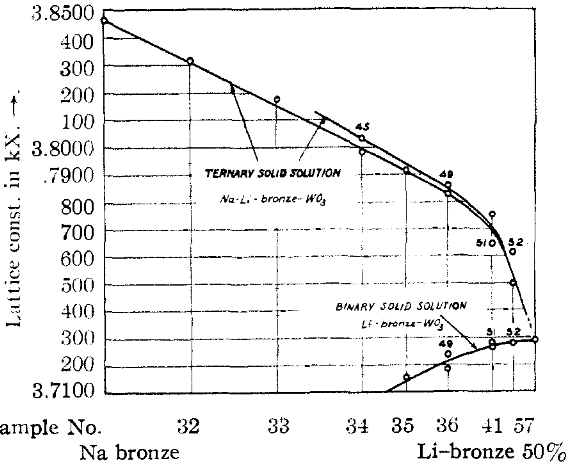

Fig. 3.—Lattice constant *versus* numbered points on sections A-a and 45-49-51-52 of the ternary diagram. The figures represent the samples. For the compositions, see Fig. 6 and Table I.

The section b-38-39-c (Fig. 6) is shown in Fig. 4. The lattice constants for the points b and c are taken from the binary diagrams and they fit well on the curve. All films of this section were very clear with no strange lines. Therefore, only one homogeneous phase was present. With this section the existence of the ternary solid solution was established.

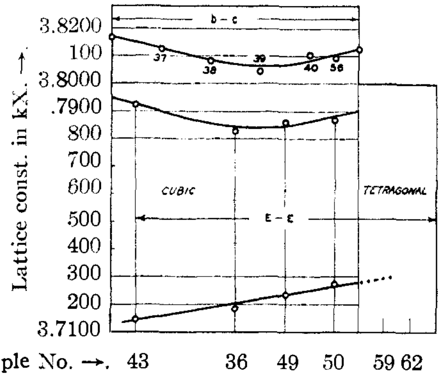

Fig. 4.—Lattice constant *versus* numbered points on section b-c and E-E of the ternary diagram. All phases are cubic. For composition of samples, see Fig. 6 and Table I.

The quasi-binary system sodium–lithium bronze already showed that the lithium bronze did not dissolve the sodium bronze. A two phase region, therefore, must be expected in the lithium bronze corner. The section C-c confirms this fully (see Fig. 5). The two phase region ceases between point 44 and 45 (Fig. 6), the limit of the homogeneous ternary solid solution. The lattice constant of the lithium bronze (lower curve) rises slowly from 3.7143 kX. to 3.7147 kX. (the lines were very sharp). The change of lattice constant (upper curve) for the sodium–lithium bronze solid solution is also a straight line but rises faster. No distinct bend could be detected at the point where the lithium bronze lines disappeared on the films.

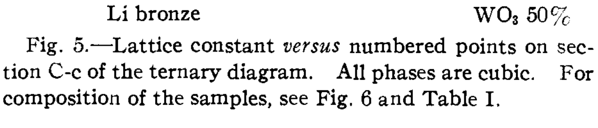

Fig. 5.—Lattice constant *versus* numbered points on section C-c of the ternary diagram. All phases are cubic. For composition of the samples, see Fig. 6 and Table I.

The section E-E (Fig. 6) is made through the heterogeneous region where the two phases are cubic, and continues into the tetragonal heterogeneous region. This section is parallel to the section b-c and is shown by the two lower curves on the same Fig. 4. The lithium bronze lines (lowest curve) began to disappear between point 50 and 59; on the film of sample 59 the lines of a new phase, probably tetragonal, could be distinguished. The lattice constant of the lithium bronze increased because of the increasing content of tungsten(VI) oxide.

The discontinuities which appeared on the curves of the

Fig. 4 are not associated with phase changes (no strange lines were recorded on the films). Similar bends not connected with the appearance or disappearance of phases were previously observed on the lattice spacing-concentration curves in ternary systems.[7]

Discussion

The Ternary Diagram.—The ternary diagram, Fig. 6, was composed on the basis of the binary diagrams and the ternary sections described.

The figures on the drawing represent the numbers of the samples whose composition can be read from the three coördinates. The real composition of all samples in terms of pure $NaWO_3$ (without WO_3), hypothetical $LiWO_3$ and WO_3 is given in Table I.

TABLE I

COMPOSITION OF THE SAMPLES REPRESENTED BY NUMBERED POINTS IN THE FIGURES IN TERMS OF PURE $NaWO_3$, HYPOTHETICAL $LiWO_3$ AND TOTAL AMOUNT OF WO_3 IN % BY WEIGHT.

Point	$NaWO_3$	$LiWO_3$	WO_3	Point	$NaWO_3$	$LiWO_3$	WO_3
a	...	28.7	71.3	43	18.68	34.45	46.87
b	46.7	28.7	24.6	44	28.02	22.97	49.01
c	46.7	...	53.3	45	37.38	11.48	51.14
d	32.69	37.31	30.00	46	4.67	51.65	43.68
e	43.00	...	57.00	49	18.68	17.22	64.10
f	...	32.00	68.00	50	18.68	11.48	69.84
32	74.76	5.74	19.50	51	9.34	20.10	70.56
33	56.06	11.48	32.46	52	4.67	22.97	72.36
34	37.38	17.22	45.40	53	14.01	8.61	77.38
35	28.02	20.10	51.88	56	46.70	2.87	50.43
36	18.68	22.97	58.35	57	4.67	27.28	68.05
37	46.70	22.97	30.33	58	28.02	2.87	69.11
38	46.70	17.22	36.08	59	18.68	5.74	75.58
39	46.70	11.48	41.82	60	9.34	5.74	84.92
40	46.70	5.74	47.56	61	4.67	11.48	83.85
41	9.34	25.81	64.85	62	18.68	2.87	78.45
42	9.34	45.90	44.76	63	23.35	1.43	75.22

The limits of the phases are determined with a precision of ±3%. The diagram shows that a ternary solid solution exists in quite a large region in the sodium bronze corner, and to a much lesser extent in the tungsten(VI) oxide corner, the phases being cubic (TSS) and triclinic, respectively, (Tr). There is a two phase region in the lithium bronze corner (TSS + BSS) since this bronze does not dissolve in the sodium bronze. The cubic ternary and binary solid solution phases passed over into tetragonal phases[8,2b] (which might be in solid solution) as the tungsten(VI) oxide content was increased. Due to complications resulting from the patterns of the samples in the tungsten(VI) oxide corner being so rich in lines (Points 58 to 63, Fig. 6) no attempt was made to determine the phase relations for this area.

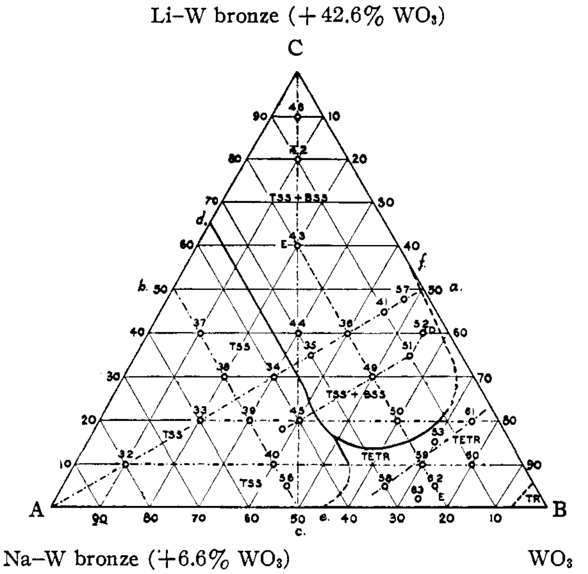

Fig. 6.—Ternary diagram Na–W bronze (+6.6% WO_3)–Li–W bronze (+42.6% WO_3)–WO_3. The figures represent the samples, prepared at approximately 850° and quenched in air. TSS, ternary solid solution, cubic (Na–Li bronze + WO_3); BSS, binary solid solution, cubic (Li bronze + WO_3); TETR., tetragonal phases; TR., triclinic phase; broken lines, estimated limits.

The triclinic (or pseudomonoclinic)[9] tungstic oxide dissolves some sodium and lithium bronze. In the case of sodium bronze the lines of this oxide were distinctly observed at the concentration of 96.4% of the oxide[2b] and in the case of lithium bronze at 99%.[3] Thus the solubility limit was estimated as beginning with 94 or 96% tungstic oxide (TR, Fig. 6). The existence of a solid solution was indicated by the intense dark olive and finally greenish color which was produced when a bronze was present in the amount of several per cent. to fractions of one per cent. in the tungsten(VI) oxide. The X-ray patterns were sharp and showed a slight displacement of the last lines as compared with the pattern of pure tungsten(VI) oxide.

The change of the lattice constants with concentration in ternary systems proceeds in a different manner from that in binary systems. This is clearly pointed out by an inspection of sections. For example in the section A-a (Fig. 3) the new not saturated lithium phase appeared (between points 34 and 35) with hardly noticeable change in the slope of the ternary solid solution curve. The same is true concerning the curves of the section C-c (Fig. 5). This can be understood as follows: The straight line (Fig. 3, section A-a) shows that up to the concentrations of the components represented by point 34 (Fig. 3 and 6) a homogeneous solid solution is formed; its composition can be expressed by the formula

$$(\mathrm{Na, Li})(\mathrm{WO_3})_x \qquad (1)$$

If then the amount of Li bronze and tungsten(VI) oxide was increased, both could not be absorbed by (1) in equal amounts. The ternary solid solution dissolved more tungsten(VI) oxide than Li bronze. As a consequence the new Li bronze phase appeared. This process may be expressed by the equation (2), where $m > n$

$$(\mathrm{Na, Li})(\mathrm{WO_3})_x + (m + n)\mathrm{Li}(\mathrm{WO_3})_y + (m + n)\mathrm{WO_3} \rightleftarrows$$
$$\underset{\text{ternary S.S.}}{[\mathrm{Na}, (\mathrm{Li} + n\mathrm{Li})](\mathrm{WO_3})_{x+ny+m}} + \underset{\text{binary S.S.}}{m\mathrm{Li}(\mathrm{WO_3})_{y+n}} \qquad (2)$$

---

[7] M. Straumanis and W. Stahl, *Z. physik. Chem.*, **194**, 129 (1944). **193**, 97 (1943); **193**, 191 (1943).

[8] A. Magnéli, *Arkiv för Kemi*, **1**, 269 (1949).

[9] A. Magnéli, *Acta Chem. Scand.*, **3**, 88 (1949).

The ternary and binary phases are in equilibrium. Thus, beginning half-way between the points 34 and 35 (Fig. 6) the compositions of the two phases changed along two separate lines so that the ternary solution became more rich in tungsten(VI) oxide than the binary lithium solid solution which does not dissolve the sodium bronze. As a consequence there was only a slight bend on the upper curve of Fig. 3 between points 34 and 35 because the decreasing concentration of lithium bronze in the ternary solid solution was compensated for by the addition of tungsten(VI) oxide, both of which contract the lattice of the sodium bronze (see Fig. 2). On the other hand, the minor part of tungsten(VI) oxide which dissolved in the lithium bronze (eq. 2) caused the expansion of its lattice.[3]

The section C-c (Fig. 5) shows a rising lattice constant for the ternary solid solution phase. This is due to the lithium ions, which have a strong contracting effect (Fig. 1), being gradually replaced by sodium ions. The expansion of the lattice occurs even in the presence of tungsten(VI) oxide, which was added together with the sodium bronze in equal amounts. However, only one part of the oxide dissolved in the ternary solution, the rest dissolved in the cubic lithium bronze, increasing its lattice constant.

It is somewhat more difficult to explain the change of the lattice constants of the section b-c (Fig. 4) which goes through the homogeneous region of the ternary solid solution. The concentration of the sodium bronze in all samples of the section is the same and in order to explain the minimum it must be assumed that the contracting ability of the lithium bronze and tungsten(VI) oxide is the largest when both are present in the sodium bronze in approximately equal amounts. Such a minimum in dimensions of the lattice constants could be established also in the section E-E.

In order to check the correctness of the diagram (Fig. 6) a space model was built, where the lattice constants were plotted *versus* concentration, using the triangular coördinates (Fig. 6) as a basis for the model. Of course, only the regions of the diagram where the reaction products were cubic could be rendered in this way. There were no points of serious diagreement in the model since the lattice constants of the nine intersections checked, agreed well, although the constants were obtained by different workers, at different time and even in different countries. The largest difference was on the intersection between point 34 and 35, because a lattice constant of 3.7992 kX. followed from the section C-c but 3.7942 kX. from the section A-a, thus, the difference being 0.13%.

Properties of the Sodium–Lithium–Tungsten Bronzes

Structure and Chemical Properties.—It is of significance to check only the properties of the homogeneous cubic ternary solid solution as shown in Fig. 6. The general formula of the samples of those solutions is

$$(\text{Na, Li, v.s.})\,(\text{W}^{\text{V}}\text{O}_3,\ \text{W}^{\text{VI}}\text{O}_3) \qquad (3)$$

The Na^+, Li^+ and vacant sites (v.s.) together occupy the space of one g-cation and the WO_3^- and WO_3 that one of the one g-anion in the crystals. The number of cationic vacant sites is determined by the amount of WO_3 dissolved in the solution. The crystals represent therefore simultaneously cationic and anionic substitutional solid solutions. No superlattice lines were observed on the films. The distribution of the cationic constituents throughout their positions and that one of the anionic constituents in their positions must, therefore, be at random.

It is very probable that the positions of the atoms of the solid solution were the same as already described in the case of the sodium or lithium bronzes,[3] because the sequence of the intensities of the Debye–Scherrer lines of the different solid solutions regardless of their composition was the same (only visual comparisons were made).

The resistance of this ternary solid solution against attack by acids and bases was remarkable. Even boiling concentrated hydrochloric, hydrofluoric, nitric or sulfuric acids, did not attack the powders. They were decomposed slowly into yellow tungstic acid by aqua regia or by a mixture of nitric and hydrofluoric acids. Boiling concentrated acid oxidized the solid solutions only in the presence of ammonium sulfate. Strong bases, even when concentrated and hot, did not dissolve the sodium–lithium bronzes; but they dissolved quickly if some sodium peroxide was added to the basic solution. If fused with a mixture of potassium nitrate and carbonate, solid solutions of the bronzes were decomposed quickly. Thus the chemical behavior of these solutions resembles closely that of the pure sodium or lithium bronzes.[2b,3]

Physical Properties.—The cubic solid solutions were obtained in the form of fine crystalline powders, giving very good X-ray powder patterns. The color of the binary samples has already been partly described. The powders of the cubic ternary solid solutions turned more and more violet blue and deep blue when the Li or WO_3 content of the samples was increased.

All the samples showed good electrical conductivity. The measurements were made at room temperature and under pressure. The pressure was increased until the resistance no longer decreased. The measurements were made with samples of compositions along the straight lines A-C, A-a and b-c (see Fig. 6). It was found that the specific resistance ρ within the region of the ternary solid solution was comparatively low: between 0.1 and 0.6 ohm. It increased with increasing WO_3 content, particularly when the limits of the phase were exceeded.

Acknowledgment.—We wish to thank Dr. Curtis L. Wilson, Dean of the School of Mines and Metallurgy, and Dr. A. W. Schlechten, Chairman of the Metallurgy Department, for their aid in acquiring the necessary equipment with which to carry out the present investigation. We thank Mr. J. S. Winston very much for correcting the English of the paper.

ROLLA, MISSOURI RECEIVED JUNE 30, 1950