# The Tungsten Bronzes and Related Compounds

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## 1 Introduction

In 1824, Wöhler,[1] in passing dry hydrogen over heated acid sodium tungstate, observed the formation of golden yellow crystals of metallic appearance. His was the first account of the formation of a tungsten bronze, a name originating from the metallic lustre characteristic of these compounds.

Tungsten bronzes are well defined non-stoicheiometric compounds of general formula $M_xWO_3$ where M is some other metal, most commonly an alkali, and $x$ is a variable $<1$. The large variety of metal species M which are known to participate in tungsten bronze formation is shown in Table 1; it is probable that the discovery of optimum preparative conditions will enable this list to be extended further.

**Table 1** *Elements known to form tungsten bronzes shown in bold type*

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **H** | | | | | | | | | | | | | | | | | |
| **Li** | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| **Na** | Mg | | | | | | | | | | | **Al** | Si | P | S | Cl | A |
| **K** | **Ca** | Sc | Ti | V | Cr | Mn | Fe | Cr | Ni | **Cu** | **Zn** | Ga | Ge | As | Se | Br | Kr |
| **Rb** | **Sr** | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | **Cd** | **In** | Sn | Sb | Te | I | Xe |
| **Cs** | **Ba** | **La** | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | **Tl** | **Pb** | Bi | Po | At | Rd |
| Fr | Ra | Ac | **Th** | Pa | **U** | | | | | | | | | | | | |
| | | **Ce** | **Pr** | **Nd** | Pm | **Sm** | **Eu** | **Gd** | **Tb** | **Dy** | **Ho** | **Er** | **Tm** | **Yb** | **Lu** | | |

For a considerable time the tungsten bronzes were thought to be unique but in recent years analogous compounds of molybdenum,[2] vanadium,[3] niobium[4] and titanium[5] have been prepared and found to have similar properties. The term 'bronze' is now applied to a ternary metal oxide of general formula $M'_xM''_yO_z$ where (i) $M''$ is a transition metal, (ii) $M''_yO_z$ is its highest binary oxide, (iii) $M'$ is some other metal, (iv) $x$ is a variable falling in the range $0 < x < 1$. Such a compound has the following characteristic properties: (*a*) it possesses high

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[1] F. Wöhler, *Ann. Physik*, 1824, **2**, 350.
[2] A. Wold, W. Kunnmann, R. J. Arnott, and A. Ferretti, *Inorg. Chem.*, 1964, **3**, 545.
[3] R. P. Ozerov, *Russian J. Inorg. Chem.*, 1959, **4**, 476.
[4] D. Ridgley and R. Ward, *J. Amer. Chem. Soc.*, 1955, **77**, 6132.
[5] M. Kestigian and R. Ward, *J. Amer. Chem. Soc.*, 1955, **77**, 6199; S. Andersson and A. D. Wadsley, *Acta Cryst.*, 1962, **15**, 201.

electrical conductivity, either metallic or semi-conducting; (*b*) it is intensely coloured and, in crystalline form, shows metallic lustre; (*c*) it is chemically inert; (*d*) sequences of solid phases occur, through variation of $x$, with definite and sometimes wide ranges of homogeneity.

Although in some ways the bronzes constitute a unique class of non-stoicheiometric compounds they show resemblances to other apparently unrelated types of inorganic system. Thus in the structural principles of their lattice architecture they resemble the silicates and the tungstosilicates, in the wide ranges of homogeneity of successive phases they resemble alloys, and in the typical free-electron behaviour underlying their optical and electrical properties they recall solutions of alkali metals in liquid ammonia. From a thermodynamic standpoint they are most simply regarded as solutions of the Metal $M'$ in a matrix of the host oxide $M''_yO_z$.

In this Review most emphasis will be placed on the sodium tungsten bronzes since not only has this system been studied much more extensively than others but the crystal structures adopted are relatively simple and the sequences of solid phases which occur cover the largest continuous range in the variable $x$.

## 2 Preparative Methods

Three basic methods have been used for the preparation of bronzes.

**A. Vapour-phase Reaction.**—As an example may be given the reaction

$$x\mathrm{Tl(g)} + \mathrm{WO_3(g)} = \mathrm{Tl}_x\mathrm{WO_3(s)}$$

Crystals of the bronze are deposited on a cold finger projecting into the reaction vessel. This method is only suitable where the metal M is appreciably volatile at high temperatures and can be manipulated fairly easily at room temperature (this precludes the use of the alkali metals). Good single crystals of $Tl_xWO_3$ have been made[6] by this procedure.

**B. Electrolytic Reduction.**—Tungsten bronzes can be prepared by an electrolytic reaction in which molten mixtures of tungstate and tungstic oxide are decomposed with platinum or tungsten electrodes. Crystals grow at the cathode and oxygen is liberated at the anode. This is the most successful method for the growth of large single crystals. However, optimum experimental conditions can be very difficult to find and careful control of the melt temperature can be crucial. Molybdenum bronzes have been made by this technique.

**C. Solid-state Reaction.**—This is the most versatile method. The finely ground reagents are heated *in vacuo* and react according to the equation:

$$\frac{x}{2}\,\mathrm{Na_2WO_4} + \frac{3-2x}{3}\,\mathrm{WO_3} + \frac{x}{6}\,\mathrm{W} \xrightarrow{850^\circ} \mathrm{Na}_x\,\mathrm{WO_3}$$

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[6] M. J. Sienko, *J. Amer. Chem. Soc.*, 1959, **81**, 5556.

For the tungsten bronzes the highest value of $x$ which can be obtained in this way is *ca.* 0·8. To avoid the need to break down the very stable tungstate lattice an alternative reaction has been used:[7]

$$xBaCl_2 + xWO_2 + WO_3 \xrightarrow[\text{in argon}]{900^\circ} Ba_xWO_3 + xWO_2Cl_2$$

A further extension of the basic method is to make use of high pressures.[8] The reaction is then carried out in a platinum container in a hydraulic press at pressures in the range 60—65 kbars. By this means several hitherto unknown phases in the tungsten and molybdenum systems have recently been prepared, *e.g.*, cubic $K_xWO_3$.

## 3 Crystal Structures

**A. Tungsten Bronzes.**—The structures of the tungsten bronzes and of the related oxides of tungsten were determined by Hägg and Magneli[9] using $X$-ray methods. There are three general features of the crystal structures of the tungsten bronzes which emerge: (i) as the value of $x$ in $M_xWO_3$ decreases so does the symmetry of the structure; (ii) the particular structure adopted is controlled to a considerable degree by the ionic radius of M; (iii) all the structures are based on the linking together of $WO_6$ octahedra by the sharing of corners.

The limiting structure of '$NaWO_3$' is that of perovskite (Figure 1). The unit cell has a tungsten atom at the centre of a cube octahedrally surrounded by six oxygen atoms at the face centres; there are eight 'interstitial' sites at the cube corners occupied by sodium atoms. The structure of $WO_3$ is a distorted version of the $ReO_3$ structure (Figure 2) in which tungsten atoms are slightly off-centre in adjacent unit cells such that the W–W distances are alternately long and short. For $Na_xWO_3$ in the approximate composition range $0{\cdot}30 < x < 0{\cdot}95$ a cubic structure is found which is intermediate between the hypothetical $NaWO_3$ and undistorted $WO_3$ structures and in which a fraction $1 - x$ of sodium atoms

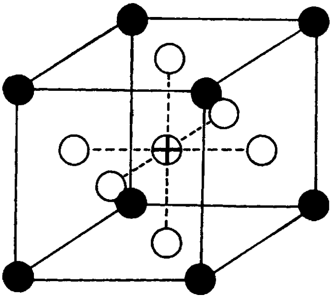

**Figure 1** *Perovskite structure of* $NaWO_3$
●, Na; ⊕, W; ○, O

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[7] L. E. Conroy and T. Yokokowa, *Inorg. Chem.*, 1965, **4**, 994.

[8] T. A. Bither, J. L. Gillson, and H. S. Young, *Inorg. Chem.*, 1966, **5**, 1559.

[9] G. Hägg and A. Magneli, *Rev. Pure Appl. Chem.* (*Australia*), 1954, **4**, 235.

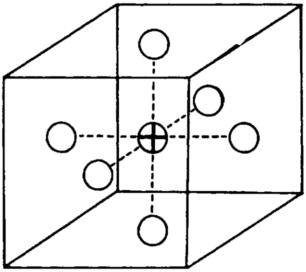

**Figure 2** $ReO_3$ *structure*
⊕, Re; ○, O

are missing from the cube corners of the $NaWO_3$ unit cell. As the sodium content of the bronze decreases the high (cubic) symmetry of the lattice is lowered and the structure passes through two tetragonal phases (I and II) (the nomenclature used here for the tetragonal phases is that of Hägg and Magneli) to the monoclinically distorted phase of pure $WO_3$. At very low sodium contents ($x \leqslant 0{\cdot}05$) an orthorhombic structure may also be observed; an analogous structure is found for pure $WO_3$ in the temperature range 320—720°. At slightly higher $x$ values the tetragonal structure, tetragonal II, is formed. The relationship between these structures in terms of the basic cube is shown in Figure 3.

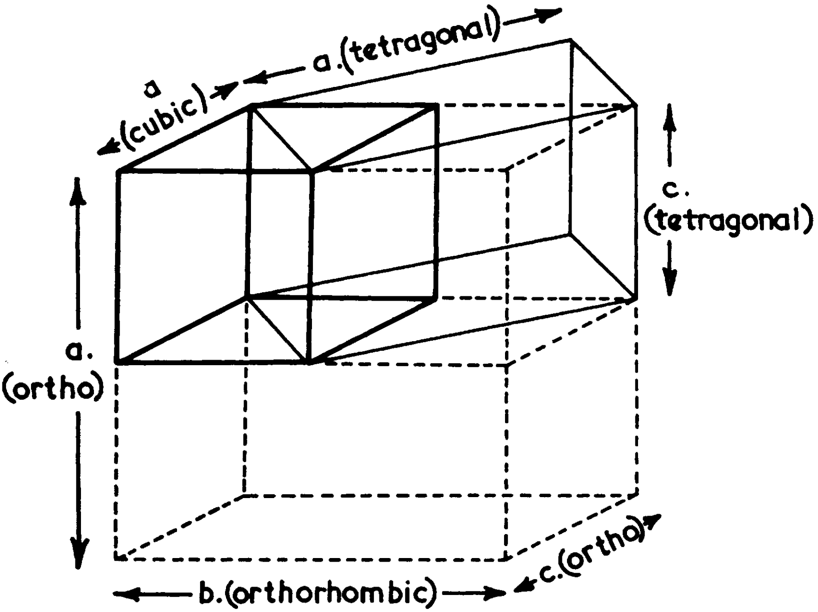

**Figure 3** *Relationship between the cubic, tetragonal II, and orthorhombic phases*

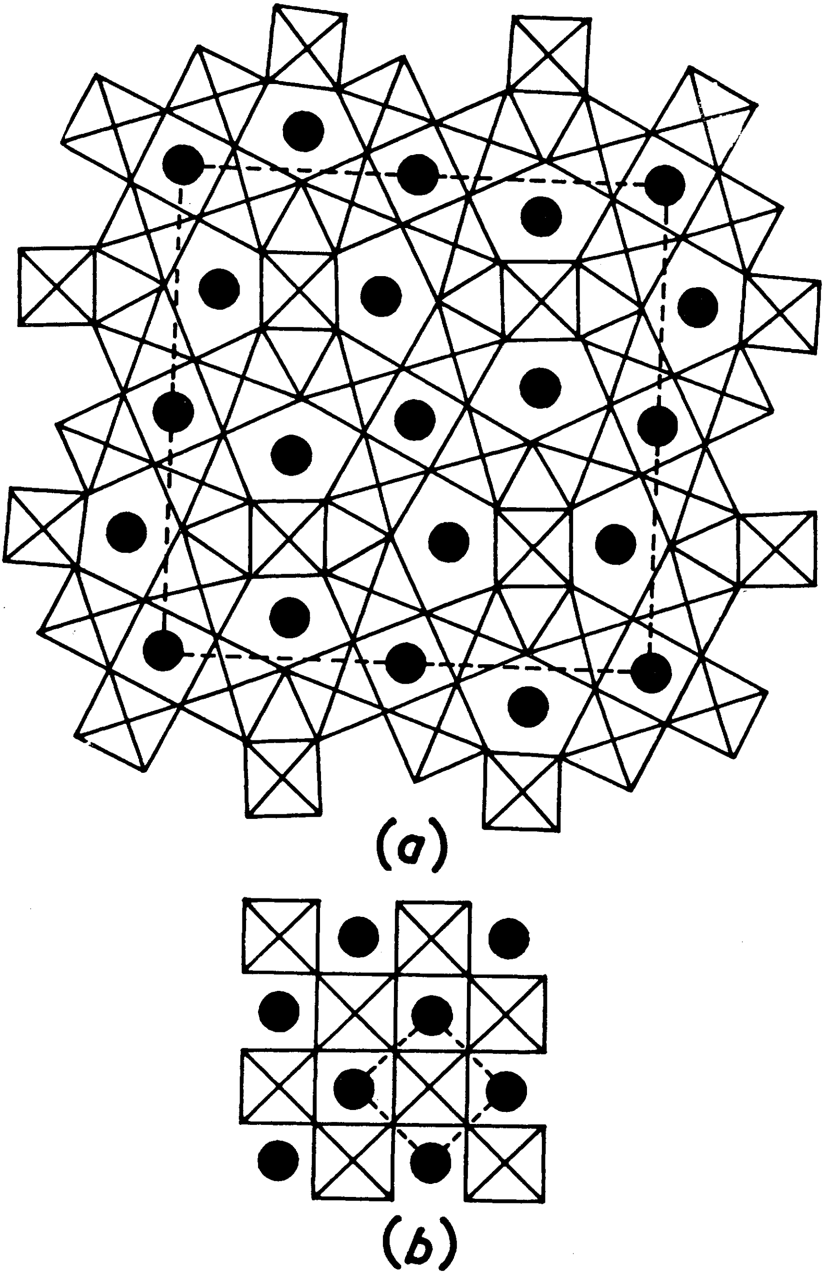

**Figure 4** 001 *Projections of tetragonal I and cubic structures*

☒ ,$WO_6$ octahedra; ●, alkali metal; – – – – , boundary of unit cell

(*a*) *Tetragonal I structure*, (*b*) *Cubic structure*

Above $x = 0{\cdot}1$ the tetragonal I structure occurs. A projection of this complex structure is shown in Figure 4*a*. It can be regarded as being built up of three-, four-, and five-membered rings of $WO_6$ octahedra. In this arrangement each unit cell contains interstitial holes of two types which can be occupied by sodium atoms; four holes per unit cell are each surrounded by eight tungsten ions situated at the corners of a cube, and eight holes per unit cell are each surrounded by ten tungsten ions in the form of a pentagonal prism. For comparative purposes the perovskite structure of $NaWO_3$ is shown in an analogous projection in Figure 4*b*. In this case only four-membered rings are present. The maximum alkali-metal content of the tetragonal I phase would correspond to $x = 0{\cdot}6$ on the assumption that only the larger holes in the lattice can be so occupied. For the sodium tungsten bronzes the observed homogeneity range of this phase is $Na_{0.28}WO_3$—$Na_{0.38}WO_3$. However for the potassium tungsten bronzes it is $K_{0.40}WO_3$—$K_{0.57}WO_3$. The complete set of phase relationships for $Na_xWO_3$ as determined by Ribnick, Post, and Banks[10] is shown in Figure 5.

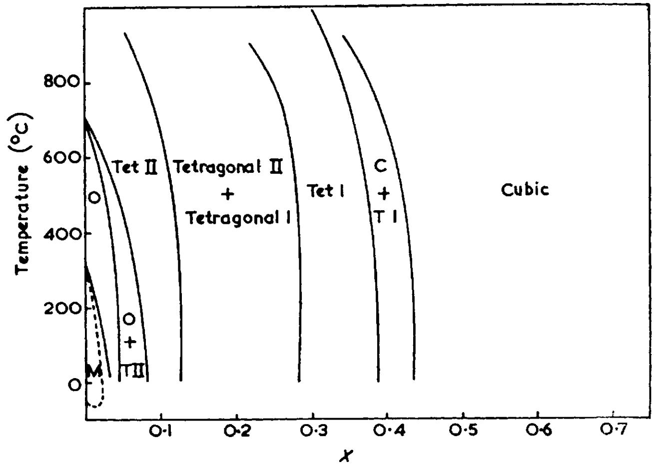

**Figure 5** *Phase diagram for* $Na_xWO_3$

The phase transformations observed in this system resemble those occurring in many alloy systems. They all show a lowering of the transition temperature with increasing solute (*i.e.*, Na) concentration, the appearance of two phases between the regions of homogeneity, and a progression from lower to higher crystal symmetry as the temperature increases.

A further crystal structure which is found with other alkali-metal tungsten bronzes is the one of hexagonal symmetry shown in Figure 6. Here the $WO_6$ octahedra are formed into a six-membered ring. The maximum alkali-metal

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[10] A. S. Ribnick, B. Post, and E. Banks, 'Advances in Chemistry', Series No. 39, Amer. Chem. Soc., 1963.

content is 0·3 and K, Rb, and Cs all form tungsten bronzes with $x$ values close to this. The relationship between the nature of M and the range of structures adopted in $M_xWO_3$ is summarised in Figure 7 (for the alkali-metal tungsten bronzes).

The radii of the inscribed spheres of the cavities available for occupation by M in the foregoing structures are: cubic, 0·96 Å, tetragonal I, 0·96 and 1·29 Å, hexagonal, 1·63 Å. As can be seen from Figure 7 the smaller cations, $Li^+$ (0·60 Å)

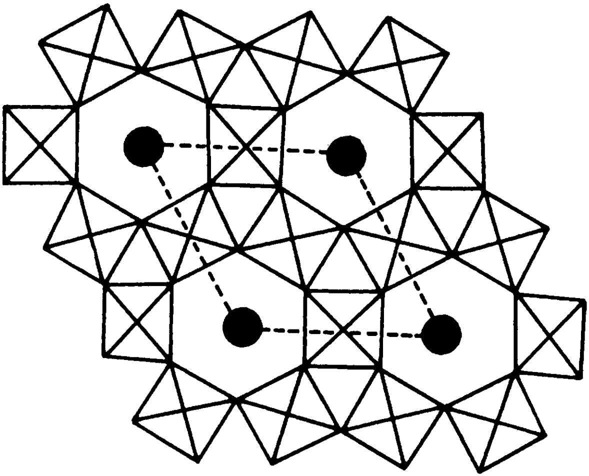

**Figure 6** *Hexagonal structure of the tungsten bronzes* (001 *projection*)

☒, $WO_6$ octahedra; ●, alkali metal; ----, boundary of unit cell

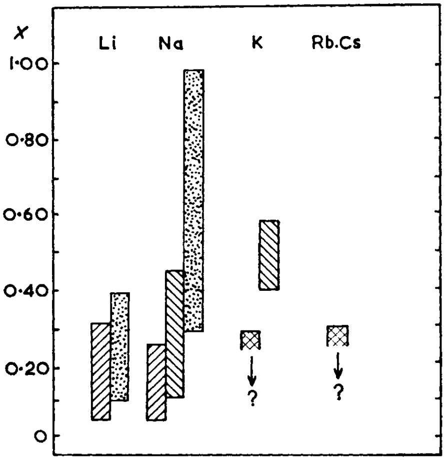

**Figure 7** *Relationship between crystal structure and composition for the alkali-metal tungsten bronzes*

░, cubic; ▧, tetr. I; ▨, tetr. II; ▩, hexagonal and $Na^+$ (0·95 Å), tend to adopt the cubic structure whereas $K^+$ (1·33 Å), $Rb^+$ (1·48 Å), and $Cs^+$ (1·69 Å) form hexagonal bronzes. Although there is no reason to suppose that the crystal structures described here are not valid it should be stressed that the conventional *X*-ray methods employed are insensitive to the actual sodium and oxygen atom positions since the scattering process is dominated by the much heavier tungsten atoms. However, a neutron diffraction study[11] of $Na_{0.75}WO_3$ revealed that the sodium atoms were indeed at the lattice sites assumed for the cubic structure (Figure 1) and moreover formed an ordered (rather than random) sub-lattice.

**B. Other Bronzes.**—The bronzes formed by elements other than tungsten have more complex structures and only some of their more general features are outlined here. Those of molybdenum[12] reflect the greater complexity found generally in the chemistry of oxy-compounds of molybdenum relative to that of tungsten. The potassium molybdenum bronzes consist of $MoO_6$ units forming infinite sheets held together by potassium ions. Wide ranges of homogeneity do not occur and two compounds of definite composition are known, $K_{0.33}MoO_3$* which is red, and $K_{0.28}MoO_3$ which is blue. A sodium molybdenum bronze $Na_{0.9}Mo_6O_{17}$ exists and has a distorted perovskite structure. The alkali-metal vanadium bronzes, $M_xV_2O_5$ and $M_{1+x}VO_3$ differ from those of tungsten in that the nature of M appears to have no effect on the structure adopted. In $M_xV_2O_5$ the alkali-metal atoms reside in tunnels in the $V_2O_5$ matrix and in $M_{1+x}VO_3$ between layers in the $VO_3$ structure. These and related structures have been reviewed in detail recently by Wadsley.[13] Recently a number of bronzes of previously unknown structures have been prepared by the high-pressure technique.[8] Some typical examples are $Na_{0.95}MoO_3$-cubic, perovskite; $K_{0.9}MoO_3$-cubic, perovskite, $K_{0.5}MoO_3$, tetragonal I (isostructural with $K_{0.5}WO_3$). A hexagonal sodium tungsten bronze has also been prepared.

## 4 Electrical Properties[14]

Considerable interest has been aroused by the unusual electrical conductivities of the bronzes. Single crystals of alkali-metal tungsten bronzes with $x > 0{\cdot}25$ exhibit metallic conductivity, that is, the specific resistance is very low and increases (linearly) with temperature. Room-temperature resistivities and their thermal coefficients are shown in Table 2. The observed constancy of the thermal coefficient of resistance suggests a common origin for the charge-carrier scatter-

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[11] M. Atoji and R. E. Rundle, *J. Chem. Phys.*, 1960, **32**, 627.

[12] J. Graham and A. D. Wadsley, *Acta Cryst.*, 1966, **20**, 93; N. C. Stephenson, *ibid.*, p. 59; N. C. Stephenson and A. D. Wadsley, *ibid.*, 1965, **19**, 241.

[13] A. D. Wadsley, 'Non-Stoichiometric Compounds', ed. L. Mandelcorn, Academic Press, New York, 1964.

[14] H. R. Shanks, P. H. Sidles, and G. C. Danielson, 'Advances in Chemistry' Series, No. 39, Amer. Chem. Soc., 1963.

**Note added in proof:*

The analytical composition of the red potassium bronze is that due to G. H. Bouchard, J. Perlstein, and M. J. Sienko, *Inorg. Chem.*, 1967, **6**, 1682 and differs slightly from that given in ref. 2.

**Table 2** *Resistivity* ($\rho$) *and temperature coefficient of resistivity at 25° for some tungsten bronzes*

| *Compound* | $\rho$(*ohm-cm.*) | $\frac{1}{\rho}\frac{d\rho}{dT}$ | *Free electron concentration per mole* |
|---|---|---|---|
| $Tl_{0.20}WO_3$ | $6{\cdot}0 \times 10^{-3}$ | $2{\cdot}3 \times 10^{-3}$ | 0·20 |
| $Ba_{0.12}WO_3$ | $1{\cdot}5 \times 10^{-4}$ | $8{\cdot}0 \times 10^{-4}$ | 0·24 |
| $Tm_{0.1}WO_3$ | $5{\cdot}0 \times 10^{-4}$ | — | 0·30 |
| $Rb_{0.32}WO_3$ | $6{\cdot}3 \times 10^{-5}$ | $4.7 \times 10^{-3}$ | 0·32 |
| $Li_{0.38}WO_3$ | $1{\cdot}26 \times 10^{-4}$ | $1{\cdot}1 \times 10^{-3}$ | 0·38 |
| $K_{0.40}WO_3$ | $3{\cdot}82 \times 10^{-5}$ | $4{\cdot}5 \times 10^{-3}$ | 0·40 |
| $Na_{0.49}WO_3$ | $1{\cdot}05 \times 10^{-4}$ | $1{\cdot}4 \times 10^{-3}$ | 0·49 |
| $Na_{0.33}Ba_{0.10}WO_3$ | $2{\cdot}4 \times 10^{-4}$ | $1{\cdot}1 \times 10^{-3}$ | 0·53 |
| $ReO_3$ | $6{\cdot}7 \times 10^{-6}$ | — | 1·00 |

ing process which might most reasonably be associated with the lattice vibrations of the common $WO_3$ matrix. That the charge carriers are free electrons is confirmed by measurement of (*a*) the Hall effect (an e.m.f. generated in a sample when a magnetic field is applied at right angles to the direction of a current passing through it); (*b*) the Seebeck effect (an e.m.f. generated when a temperature gradient is applied across the sample). Detailed consideration of these effects reveals that there is one free electron per metal atom in the host lattice and that the carrier mobility is comparable with that of free electrons in the conduction band of a typical metal. A plot of conductivity against alkali-metal content, $x$, over the full cubic range of the alkali-metal tungsten bronzes extrapolates to zero conductivity at $x = 0{\cdot}25$. This suggests that a different mechanism of conduction is operative below $x = 0{\cdot}25$. For a single crystal of a sodium tungsten bronze of composition $Na_{0.025}WO_3$ semiconductor-type behaviour has been established;[15] that is resistivity *decreases* with increasing temperature according to a relationship $\log \rho \propto 1/T$. Similar behaviour was also found for $Li_{0.097}WO_3$. In both cases an activation energy for the conduction process of *ca.* 0·02 ev was recorded. Conductivity measurements on homogeneous crystals are sparse for other types of bronze but Sienko and Sohn[16] showed that $Na_{0.33}V_2O_5$ behaved as a semiconductor in the range 77—500°K. Cubic niobium[4] and titanium[5] bronzes appear to be metallic conductors. The potassium molybdenum bronzes[2] are interesting in that the blue $K_{0.28}MoO_3$ is metallic at room temperature whereas the red $K_{0.33}MoO_3$ is a semiconductor. At lower temperatures the blue bronze undergoes a metallic–semiconductor transition.

## 5 Magnetic Properties

**A. Magnetic Susceptibility.**—The magnetic susceptibilities of single crystals of the cubic sodium tungsten bronzes have been measured[17] and weak temperature-

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[15] W. McNeill and L. E. Conroy, *J. Chem. Phys.*, 1962, **36,** 87.
[16] M. J. Sienko and J. B. Sohn, *J. Chem. Phys.*, 1966, **44,** 1369.
[17] J. D. Grêiner, H. R. Shanks, and D. C. Wallace, *J. Chem. Phys.*, 1962, **36,** 772.

independent paramagnetism found, such as occurs for example in sodium metal itself. Measurements on powder samples of other alkali-metal tungsten bronzes in the metallic range reveal similar behaviour. The band theory of metals predicts that if the charge carriers are treated as quasi-free electrons the electronic contribution to the magnetic susceptibility per unit volume will be

$$\chi_e = \frac{4\boldsymbol{m}^*\mu_0^{\,2}}{\boldsymbol{h}^2}(3\pi^2 n)^{\frac{1}{3}}\left(1 - \frac{\boldsymbol{m}_0^{\,2}}{3\boldsymbol{m}^{*2}}\right) \tag{1}$$

where $\boldsymbol{m}_0$ = electron rest mass, $\boldsymbol{m}^*$ = effective mass, $\mu_0$ = Bohr magneton, $n$ = carrier density, $\boldsymbol{h}$ = Planck's constant and $\chi_e$ = electronic susceptibility per unit volume. A reasonable fit to the data of Greiner, Shanks, and Wallace for the sodium tungsten bronzes can be obtained if $\boldsymbol{m}^*$ is taken as $1{\cdot}6\boldsymbol{m}_0$, and the closeness of the effective mass to the electronic mass substantiates the general correctness of the band model for these compounds. However, the variation of $\chi_e$ with the Na content as predicted by the use of (1) is of the form $\chi_e \propto x^{\frac{1}{3}}$; this is not in good agreement with the measured variation which suggests a relation of the form $\chi_e \propto x$. The significance of this result will be emphasised later in the discussion of the electronic structures of these compounds. For the semiconductor $Na_{0.33}V_2O_5$ a susceptibility an order of magnitude greater was reported by Sienko and Sohn.[16] In contrast to the behaviour of the metallic sodium tungsten bronzes the temperature-dependence in this case was that of a typical paramagnetic material possessing localised unpaired electrons, *i.e.*, $\chi_e$ $1 \propto /T$.

**B. Nuclear Magnetic Resonance.**—In many metals a large chemical shift of the n.m.r. signal to lower magnetic fields is observed relative to the signal of the same nucleus in some non-metallic environment. This is known as the 'Knight' shift and the magnitude of the effect is directly proportional to the electron density of the conduction electrons at the nucleus. Electrons in *s* type orbitals or bands can contribute to the shift whereas those in *p* or *d* orbitals cannot. Studies[18] on the alkali-metal tungsten bronzes reveal *very small* or *zero* Knight shifts for both the alkali metal and tungsten nuclei. The *s* orbitals of the alkali metal cannot therefore participate in the conduction band whereas the 5*d* (but not 6*s*) orbitals of the tungsten may do so. The line-widths of the alkali-metal resonances in the tungsten bronzes are *ca.* 1 OE. Calculations of the line-width due to nuclear dipolar interactions (van Vleck) are in fair agreement with this value. Lithium and sodium vanadium bronzes again show the absence of a Knight shift for the alkali-metal nucleus. In the case of $Li_xV_2O_5$ a significant line narrowing was found[19] between 77°K and room temperature for the Li resonance suggesting the onset of some diffusional motion of the lithium ions

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[18] R. G. Barnes, R. A. Hultsch, and W. H. Jones, *Bull. Amer. Phys. Soc.*, 1959, **4**, 166; A. Narath and D. C. Wallace, *Phys. Rev.*, 1962, **127**, 724; W. H. Jones, E. A. Garbaty, and R. G. Barnes, *J. Chem. Phys.*, 1962, **36**, 494; A. T. Fromhold and A. Narath, *Phys. Rev.*, 1964, **136**, *A*, 487.

[19] J. Gendell, R. M. Cotts, and M. J. Sienko, *J. Chem. Phys.*, 1962, **37**, 220.

through the lattice. There was no evidence for a similar motion of the larger sodium ions in the corresponding sodium vanadium bronze.

**C. Electron Spin Resonance.**—The conduction electrons in a metal do not usually give rise to a well-defined e.s.r. signal since the short spin–spin relaxation time causes a massive broadening of the absorption region. No e.s.r. signal has been reported for the sodium tungsten bronzes. However, well-resolved signals have been found for the semiconducting $M_xV_2O_5$[19] and $M_xMoO_3$[20] bronzes. The $g$ value of 1·96 reported for both $Li_xV_2O_5$ and $Na_xV_2O_5$ ($x = ca.$ 0·33) is consistent with the $g$ values found for $V^{4+}$ centres in other vanadium compounds and the measured intensities indicate the presence of one $V^{4+}$ for each alkali-metal atom in the bronze. This evidence is consistent with the electrical conductivity and magnetic susceptibility data presented previously for these compounds. The $g$ value found for the red potassium molybdenum bronze ($g = 1{\cdot}97$) agrees with that found for oxygen-deficient $MoO_3$ and may be identified with the presence of $Mo^{5+}$ centres. Again a localised set of electron states is suggested for this semiconducting material in which an electron transfer has occurred:

$$M^0 + Mo^{6+} \rightarrow M^+ + Mo^{5+}$$

## 6 Spectra

The intense colours exhibited by the bronzes are one of their most characteristic features. For the sodium tungsten bronzes the sequence shown in Figure 8 is observed.

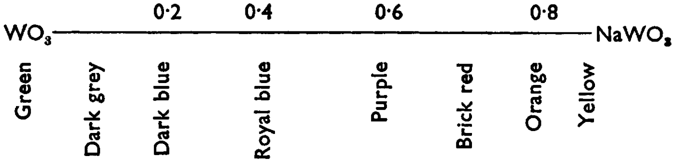

**Figure 8**

Quantitative measurements of the absorption spectra of these compounds are practically impossible to obtain, however, on account of the extremely high extinction coefficients involved. Reflectance spectra of pellets of the sodium tungsten bronzes were recorded by Brown and Banks[21] in which more than 95% of the incident light was absorbed. A single, structureless and very broad absorption band was found in the range 3000–12000 Å the maximum of which moved to lower wavelengths with increasing sodium content. There is a likelihood that the formation of a superficial $WO_3$ layer[22] may interfere with the intrinsic bronze spectra recorded by this method and detailed conclusions concerning the electronic structures of these compounds cannot be drawn from the measurements.

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[20] P. G. Dickens and D. J. Neild, *Trans. Faraday Soc.* (in the press).
[21] B. W. Brown and E. Banks, *J. Amer. Chem. Soc.*, 1954, **76**, 963.
[22] Personal communication from Dr. D. W. Lynch, Iowa State University.

## 7 Electronic Structures of the Sodium Tungsten Bronzes

Straumanis[23] regarded the tungsten bronzes as solutions of $W^{VI}O_3$ in $NaW^{V}O_3$, *i.e.*, as compounds containing W in two valency states. Such a formulation implying as it does isolated spin states is incompatible with the observed small temperature-independent paramagnetism of the cubic alkali-metal tungsten bronzes. Moreover, the electrical transport data demand the presence of nearly free electrons as current carriers. There is now little doubt that the tungsten bronzes are best considered as solutions of M in a $WO_3$ matrix in which the alkali metal is ionised and the nearly free electrons are located in a delocalised conduction band. There is controversy, however, about which atomic orbitals are the constituents of the conduction band. There are two distinct viewpoints here, one theory (Mackintosh,[24] Fuchs[25]) considers the conduction band to be composed of overlapping alkali-metal orbitals, the other (Sienko,[26] Goodenough[27]) supposes that it is mainly the tungsten orbitals which are involved. To examine the consequences of these two approaches it is convenient to consider a possible energy-level diagram for cubic $Na_xWO_3$. Suppose that the atomic arrangement is as shown in Figure 1 (cubic, perovskite). Each oxygen atom can form *sp* hybrids directed towards neighbouring tungsten atoms. The central tungsten atom with 6*s*, 6*p*, and 5*d* ($e_g$) orbitals can combine with the 6$\sigma$-type orbitals of the oxygen atoms directed towards it, in a way exactly comparable with the $\sigma$-bond formation encountered in an octahedral metal complex. If the whole lattice rather than an individual unit cell is considered, the discrete energy levels of the $\sigma$ and $\sigma^*$ molecular orbitals so formed broaden into bands (Figure 9). In the Sienko model the tungsten 5*d* ($t_{2g}$) orbitals combine to form a $\sigma^+$ band while the remaining oxygen *p* orbitals remain as discrete non-bonding levels ($p\pi$ in Figure 9). In the Goodenough refinement of this model half the oxygen *p* orbitals (of $\pi$ symmetry) mix with the W,5*d* ($t_{2g}$) orbitals to convert the previously non-bonding W,$t_{2g}$ orbitals into a bonding and antibonding combination. In both schemes the conduction band is made up predominantly of W,5*d* ($t_{2g}$) orbitals. In the Sienko–Goodenough model electrons are donated from the sodium atoms into the conduction band. That a conduction based on metal *d* orbitals is feasible is supported by the observation[27] that $ReO_3$, which is isoelectronic with $NaWO_3$ and isostructural with cubic $WO_3$, has high metallic conductivity. The model accounts very well for the absence of a Knight shift from the n.m.r. spectra since *d* orbitals have nodes at the parent nuclei and provide very small electron densities at the alkali-metal positions.

In the alternative theory of Mackintosh the energy band formed by the overlap of sodium atomic orbitals is assumed to lie *below* that formed by the tungsten 5*d* ($t_{2g}$) orbitals. The conduction band which is the lowest incomplete energy band is accordingly assumed to be constructed from sodium atomic orbitals

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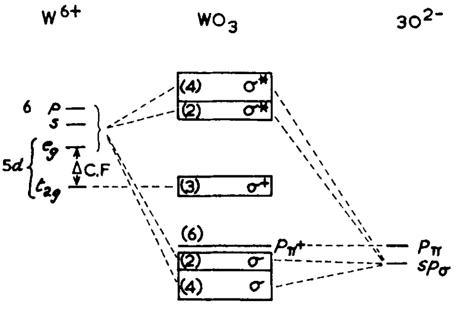
[23] M. E. Straumanis, *J. Amer. Chem. Soc.*, 1949, **71**, 679.

[24] A. R. Mackintosh, *J. Chem. Phys.*, 1963, **38**, 1991.

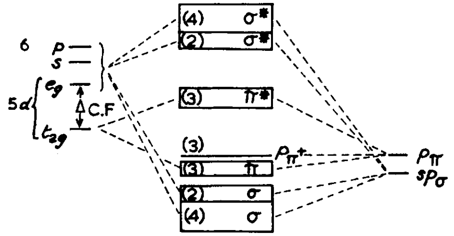
[25] R. Fuchs, *J. Chem. Phys.*, 1965, **42**, 3781.

[26] M. J. Sienko, 'Advances in Chemistry' Series, No. 39, Amer. Chem. Soc., 1963.

[27] J. B. Goodenough, *Bull. Soc. chim. France*, 1965, 1200; A. Ferretti, D. B. Rogers, and J. B. Goodenough, *J. Phys. and Chem. Solids*, 1965, **26**, 2007.



Sienko model



Goodenough model

Figure 9 *Energy diagram for* $WO_3$

The σ and π bands consist of bonding orbitals, the $p\pi^+$ energy level and $\sigma^+$ band are non-bonding, and the $\sigma^*$ and $\pi^*$ are antibonding. ( ) signifies the orbital degeneracy per molecule

alone. Clearly these cannot be sodium 3*s* orbitals in view of the Knight-shift evidence and it is postulated that the band arises from the overlap of 3*p* orbitals which can achieve good mutual overlap but at the same time are better able than are the 3*s* to avoid the filled $WO_3$ orbitals. The Na–Na distance in the bronze (3·78 Å) is only a little larger than in sodium metal (3·72 Å). This model can explain the increasing symmetry of the bronze lattice with increasing sodium content since the cubic structure provides maximum mutual overlap of the sodium 3*p* orbitals. It also provides an explanation of the changeover from metallic conductivity to semiconductivity at low $x$ values, since for some composition in the region of $x = ca.\ 0{\cdot}25$ there would be insufficient sodium atoms present for the formation of infinite linkages through the crystal and the band structure would break down in favour of isolated levels. Neither of these features is adequately explained by the Sienko–Goodenough model. However, it appears that the measured spin–lattice relaxation time of the Na nucleus is too long to be compatible with a picture of the conduction band based on sodium atoms; in addition there is also no very good *a priori* ground for believing that the Na,3*s* orbitals should not contribute to such a conduction band.

Both the foregoing theories assume a uniform distribution of alkali-metal atoms throughout the bronze lattice and the normal type of conduction band of an ideal metal in which the Fermi level will rise with increasing alkali-metal concentration. Fuchs has pointed out that such a picture cannot give a quantitative account of the observed magnetic susceptibility and electronic specific heat data which suggest a Fermi level virtually independent of $x$. It is to overcome this difficulty that Fuchs has suggested a model for the sodium tungsten bronzes in which the sodium atoms occur in clusters and for which the *local* conduction electron density (based on Na orbitals) is independent of $x$. The metal–semiconductor transition is explained, in the same spirit as in the Mackintosh theory, as being the critical concentration at which sodium atoms cannot connect throughout the lattice. The magnetic susceptibilities can be accounted for as well as the observation that the spin–lattice relaxation time of the $^{23}$Na nucleus is independent of $x$, since in both cases the local electron density for the clusters is independent of the overall composition. Direct experimental evidence for the existence of clusters is so far lacking, however.

A weakness of the Mackintosh–Fuchs approach is that it is applicable specifically only to the alkali-metal tungsten bronzes whereas the common electronic behaviour of tungsten bronzes containing other metals as M and also that of the lower oxides of tungsten themselves suggests that a more general conduction mechanism is operative involving the parent $WO_3$ lattice. In this respect the Sienko–Goodenough theory appears to be more versatile and applicable to other highly conducting transition-metal oxides (*e.g.*, $CrO_2$) as well as to the bronzes. In any event further measurements, possibly in Mössbauer studies, which could define more precisely the electron density at the tungsten nuclei in the bronzes are needed to distinguish between the rival theories.

## 8 Other Properties

The tungsten bronzes are insoluble in water and very resistant towards acids. Niobium and titanium bronzes behave similarly. The tungsten bronzes are readily oxidised to tungstates in the presence of alkalis:

$$4NaWO_3 + 4OH^+ + O_2 = 4WO_4^{2-} + 2H_2O$$

They are capable of reducing ammoniacal silver nitrate to silver and this reaction may be employed for their quantitative analysis. Other strong electron acceptors such as $I_2$ (or $WO_3$) can degrade the bronzes $Na_xWO_3$ in a controllable manner[23] to compounds closer in composition to $WO_3$. Electron donors such as molecular hydrogen, at high temperatures, cause the formation of compounds closer in composition to $NaWO_3$.[28] The chemical inertness of the tungsten bronzes may be associated with the high energy of activation for diffusion of the alkali metal in the oxide matrix (51·8 kcal./mole for Na in $Na_{0.78}WO_3$).[29] The vanadium bronzes are far more active chemically, being attacked by mineral acids as well as alkalis. The molybdenum compounds are dissolved by aqua regia.

In contrast to the general chemical inertness of the alkali-metal tungsten

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[28] M. S. Whittingham, D.Phil. Thesis, Oxford, 1967.

[29] J. F. Smith and G. C. Danielson, *J. Chem. Phys.*, 1954, **22**, 266.

bronzes, the 'hydrogen bronzes'[30] $H_xWO_3$ prepared by the wet reduction of tungstic acid are extremely reactive. They are slowly attacked by air and rapidly and quantitatively oxidised by hot dichromate solution. These compounds, which are deep blue, have been shown by both[30] *X*-ray and neutron diffraction methods to be structurally related to the sodium tungsten bronzes.

The tungsten and vanadium bronzes have been investigated as heterogeneous catalysts in relation to their special electronic properties. Although they are generally poor catalysts a marked change in activity was observed[31] for the alkali-metal tungsten bronzes on passing through the semiconductor–metallic conductor transition, the activity pattern being largely independent of the nature of the alkali metal.

[30] O. Glemser and C. Naumann, *Z. anorg. Chem.*, 1951, **265**, 288; P. G. Dickens and R. J. Hurditch, *Nature*, 1967, **215**, 1266.

[31] P. G. Dickens and M. S. Whittingham, *Trans. Faraday Soc.*, 1965, **61**, 1226.