This work covered the range obtained by Magnéli and Jacobs for the lattice parameters in the "c" direction.

On the basis of the crystal structure of hexagonal potassium tungsten bronze, it is apparent that a compound of the formula $K_{0.33}Li_{0.66}WO_3$ could be prepared, if all of the interstices could be filled. However, as indicated in Table III, the maximum total concentration of $x + y$ obtained was 0.51. Since the large holes for potassium could readily contain lithium ions as well, it is possible to prepare samples of the mixed bronze in which the smaller sites are not used at all, *i.e.*, $x = 0.15$ and $y = 0.10$. In such a case, one would not expect the lattice to expand with the addition of lithium. In fact, a contraction might be expected, as found in the cubic lithium bronzes.[11] If the lithium ions are occupying the "triangular" holes, one would expect to observe an expansion of the lattice. This is certainly indicated in the lattice expansion in the "c" direction as shown in Table III.

As the concentration of alkali metal in the hexagonal bronze becomes substantial ($x = 0.35$), the structure tends to stabilize with respect to expansion in the "c" direction as lithium is added (Table III). Apparently, at higher potassium concentrations, the expansion due to increases in the lithium ion concentration tends to reach a maximum in the "a" direction ($a = 7.391$ Å) and "c" direction ($c = 7.570$ Å). This is shown in Figure 2. No phases, other than hexagonal, were discernible in these samples.

Adding lithium to the hexagonal potassium tungsten bronze has permitted the extension of the homogeneity range of the hexagonal phase to increased metal concentrations, up to $x + y = 0.51$. This increase in concentration of carriers should yield a substantially greater conductivity for the material. The catalytic activity of the powders for ortho–parahydrogen conversion[12] and other reactions should also be increased.

Systems which might be expected to show similar behavior would be the rubidium and cesium hexagonal bronzes, the sodium tetragonal bronzes, and possibly the potassium tetragonal bronzes, since there are a substantial number of sites available for the introduction of other ions.

[11] M. E. Straumanis and S. S. Hsu, *J. Am. Chem. Soc.*, **72**, 4027 (1950).

[12] F. T. Jones, Dissertation, Polytechnic Institute of Brooklyn, 1960, unpublished.

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Hexagonal Indium Tungsten Bronze

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The electrical resistivity of single crystals of hexagonal In_xWO_3 ($x = 0.21$–0.27) has been measured both perpendicular to and parallel with the c axis. Nearly isotropic metallic behavior was found. Seebeck voltages were small and negative, while magnetic susceptibility measurements showed isotropic diamagnetism. These results are consistent with covalent t_{2g}–$p\pi$ bonding and the formation of a π^* band.

Introduction

At least three possible mechanisms have been proposed to explain the metallic conductivity in the cubic tungsten bronzes A_xWO_3 (A = alkali metal): (a) direct A–A overlap,[1] (b) direct W–W overlap,[2] and (c) covalent $p\pi$–$d\pi$ interactions[3,4] with the formation of a π^* band. Several difficulties are associated with the first of these models, and the W–W separation in these materials is probably too great for the second. The work of Ferretti, Rogers, and Goodenough[5] provides convincing evidence that the third mechanism, involving the formation of π^* bands *via* t_{2g}–$p\pi$ covalent interactions, is responsible for the observed properties of these materials. If this is the case, the framework of WO_6 octahedra is the most important property-determining feature of the metallic bronzes and the particular bronze structure should be secondary. Therefore, metallic hexagonal bronzes would be expected to exhibit isotropic conductivity even though their crystal structures are highly anisotropic.

Sienko and Morehouse[6] measured resistivities on single crystals of K_xWO_3 and Rb_xWO_3 hexagonal bronzes, but only in the direction parallel with the c axis. Hexagonal $In_{0.11}WO_3$ was prepared earlier in this laboratory[7] as a powder by hydrothermal reaction. A subsequent study revealed that single crystals of the general formula In_xWO_3 could be easily prepared by solid-state techniques and vapor-transport reactions. It was therefore considered a good candidate to test the above ideas.

[1] A. R. Mackintosh, *J. Chem. Phys.*, **38**, 199 (1963).

[2] M. J. Sienko, Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, p 224.

[3] J. B. Goodenough, *Bull. Soc. Chim. France*, **4**, 1200 (1965).

[4] See also the brief statement on p 226 of ref 2, where the possibility of π-molecular orbital formation is mentioned in passing.

[5] A. Ferretti, D. B. Rogers, and J. B. Goodenough, *J. Phys. Chem. Solids*, **26**, 2007 (1965).

[6] M. J. Sienko and S. M. Morehouse, *Inorg. Chem.*, **2**, 485 (1963).

[7] P. E. Bierstedt, T. A. Bither, and F. J. Darnell, *Solid State Commun.*, **4**, 25 (1966).

Crystallographic Considerations

The cubic A_xWO_3 structure consists of a regular array of WO_6 octahedra, connected at all corners extending in three dimensions. On looking down any cubic axis, strings of octahedra are connected to form regular four-membered rings, resulting in square channels in which A ions can be accommodated. The next two most complicated ways to arrange these strings are to form five- and six-membered rings, which result in the two common modifications of the cubic bronzes, the tetragonal and hexagonal bronzes, respectively. In the former, there are triangular, rectangular, and pentagonal channels along the *c* axis while those of the hexagonal are triangular and hexagonal, as illustrated in Figure 1. In the hexagonal structure, each A ion in a hexagonal channel is surrounded by six WO_6 groups which in turn share two A ions each. This provides a limiting composition of $A_{0.33}WO_3$ if the hexagonal holes are completely full. In the *a* plane the only possibility for W–W interactions not involving oxygen intermediates is across the center of a hexagonal hole. However, this distance is greater than 7 Å, clearly too large for effective overlap of tungsten d orbitals. Along the *c* axis direct interactions are conceivable between W atoms in adjacent layers through edges in the WO_6 octahedra in neighboring chains. If these occur, zigzag overlap of tungsten d orbitals might result in conduction paths along both the *a* and *c* directions. This is unlikely for two reasons: (a) the distance between W atoms in this configuration is about 5.3–5.4 Å, which is probably too large a separation for interactions strong enough to form a set of band states;[5] (b) the octahedra in adjacent chains are skewed about 30° away from the typical perovskite-type linkage in such a way that a t_{2g} orbital from one tungsten atom would meet a corresponding orbital from its neighbor at an angle of 150° instead of 180°. It is concluded, therefore, that the likelihood of strong, direct interactions in this particular structure is very tenuous and could not lead to a nearly isotropic, metallic conductivity.

On the other hand, since the cation t_{2g} orbitals are degenerate in energy for an octahedral site ion and π orbitals are available on the oxygen atoms, three-dimensional π^* bonding is quite possible. These bonds will have extensions in both the *a* and *c* directions of the hexagonal unit cell. While no qualitative bonding scheme can lead to a band model that can predict the precise behavior of transport properties as a function of direction, it is at least possible on the basis of this model to predict metallic conductivity along the principal crystallographic axes of the hexagonal unit cell.

Experimental Section

Mixtures of WO_3, W, and In_2O_3 were weighed out in accordance with the reaction

$$\frac{x}{2}In_2O_3 + \frac{x}{2}W + \left(1 - \frac{x}{2}\right)WO_3 \longrightarrow In_xWO_3$$

Compositions were made up with x varying between 0.01 and 0.4. The powdered, high-purity starting materials were ground together mechanically with an agate mortar and pestle for approximately 1 hr, pressed into pellets, and fired to 800–1000° for 24 hr in evacuated silica tubes. It was also found that firing In metal and WO_3 together would result in comparable products.

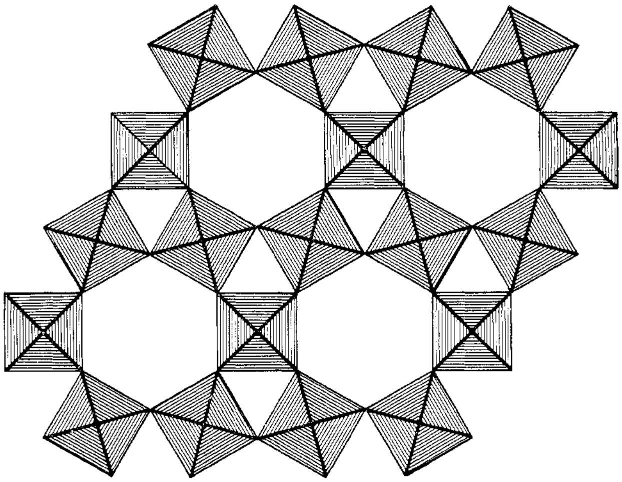

Figure 1.—View down the *c* axis of the hexagonal tungsten bronze structure.

Single crystals could be obtained by heating pellets of the reaction mixture at 1000° in evacuated silica tubes for several days. The crystals developed on the sides of the pellets. Crystal formation could be greatly enhanced by the addition of 0.5 atm of Cl_2 before heating, and in this case, the finely divided powder was used rather than pellets. Crystals as large as 3–4 mm on an edge could be grown by chemical transport down the temperature gradient normally present from the center to the outside of a furnace at 1000°. This reaction presumably utilizes the indium halides and the tungsten oxyhalides, many of which are volatile at these temperatures. WO_3 itself can also be transported with Cl_2 down a temperature gradient.[8] In practice, the crystals that developed in the powder charge were often larger and of better quality than those transported. Electrical measurements on crystals produced by chlorine transport were compared with those of the smaller crystals of the same composition obtained simply by heating the pellets. No dependence on the method of preparation was found. For this reason, the possibility that the larger crystals contained a trace amount of chlorine impurity was not pursued. The brilliant blue-black crystals possessed habits that were triangular, diamond-shaped, or hexagonal prisms or tablets. The crystals were oriented for electrical measurements by single-crystal X-ray diffraction. Density measurements were used to specify the composition of the single crystals.

Electrical resistivities were measured in a nitrogen atmosphere on small rectangular crystals or rectangular bars cut from the larger crystals. The crystals were cut so as to facilitate measurements in a particular direction, either parallel with or perpendicular to the *c* axis. Four probes were attached with low-melting indium alloy solder for all of the low-temperature measurements. For measurements above room temperature, platinum-tipped tungsten probes under spring tension in an all-quartz sample holder were utilized. To monitor possible decomposition with rising temperature, readings were checked by cooling samples back to lower temperatures to confirm previous measurements. In all, 11 single crystals were measured, some in the parallel and some in the perpendicular direction to the *c* axis. Compositions of these crystals varied between $x = 0.21$ and $x = 0.27$.

Crystallographic Results and Discussion

At very low values of x (0.01–0.05), a tetragonal phase was formed almost exclusively with lattice constants *a*

[8] W. Kleber, M. Hähnert, and R. Muller, *Z. Anorg. Allgem. Chem.*, **346**, 113 (1966).

$= 5.233$ and $c = 3.863$ Å. Gado[9] has pointed out that WO_3, which is monoclinic at room temperature, commonly becomes tetragonal when combined with small amounts of metal ions. The hexagonal phase started to form at $x \sim 0.05$. With increasing values of x, the tetragonal phase gradually decreased in concentration relative to the hexagonal until at $x \sim 0.2$, single-phase, blue-black hexagonal products results. At $x \geq 0.35$, unreacted In_2O_3 was also present.

Lattice constants were derived from a least-squares refinement of slow-scan diffractometer data on the powders. Table I lists these crystallographic constants for $In_{0.2}WO_3$ and $In_{0.3}WO_3$.

TABLE I

Formula	a, Å	c, Å	V, Å^3
$In_{0.2}WO_3$	7.3882 ± 0.0005	7.5041 ± 0.0008	354.7
$In_{0.3}WO_3$	7.3840 ± 0.0001	7.5088 ± 0.0002	354.6

The environment of the A ion in a hexagonal hole is unusual in that there are 12 oxygen nearest neighbors and 6 others only about 20% further away than these first 12. This gives a coordination of 18, not counting A–A contacts along the channels. These considerations were pointed out by Isupov, *et al.*,[10] who concluded that a suitable A ion must be large, be highly distorted, and possess only a small charge. These conclusions imply a highly polarizable A ion. In an attempt to correlate the adoption of the hexagonal A_xWO_3 structure with the metal ion A, several factors were considered. Ionic radius is an unsuitable parameter, since it strongly depends on coordination and no radii are known for 18-coordination. However, we have observed a correlation between ionization potential and suitable A ions. This may be related to the polarizability requirement, since the polarizability of a low-valent ion should be proportional to the tendency of the corresponding atom to donate its outer electron(s). A convenient measure of this tendency is the first ionization potential. These potentials are tabulated in Table II for all elements which have first ionization potentials below an arbitrary limiting value of 6.10 ev. Interestingly, most of these elements form hexagonal tungsten bronzes including Cs,[11] Rb,[11] K,[11] Ba,[7] Li,[12] Sr,[7] Ca,[7] and Tl.[7] One exception is Na which usually forms a cubic[13] or tetragonal[14] bronze type. Later work,[15] however, indicates the formation of a hexagonal bronze under high pressure. The three rare earth atoms La, Pr, and Eu have been reported only in the cubic form.[16,17] Since the evidence points to the rare earth ions in the trivalent state in the rare earth bronzes, it is perhaps not unexpected that they would be exceptions to a correlation based on first ionization potentials. Only two elements in the list do not appear to form bronzes. These are Al and Ga whose sizes are probably too small for the much larger (~2 Å) hexagonal holes. It should be noted that some elements whose large lower-valent ions would be expected to fulfill the size criterion easily do not form hexagonal bronzes. In these cases, as for Ag, Cd, Hg, Au, and Pb, the first ionization potential is considerably greater than 6.1 ev. It appears therefore that there is a definite empirical correlation between the first ionization potential of a metal A and the occurrence of the hexagonal bronze phase A_xWO_3.

TABLE II[a]

Element	First ionization potential, ev
Cs	3.87
Rb	4.159
K	4.318
Na	5.12
Ba	5.19
Li	5.363
La	5.6
Eu	5.64
Sr	5.667
In	5.76
Pr	5.8
Al	5.96
Ga	5.97
Ca	6.07
Tl	6.09

[a] "Handbook of Chemistry and Physics," 46th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1965–1966, p 61.

Electrical and Magnetic Results

The results of the resistivity measurements from 4.2 to 300°K are shown in Figures 2 and 3 for five samples cut from an $In_{0.21}WO_3$ crystal and two samples cut from an $In_{0.27}WO_3$ crystal. Because it appeared that the resistivity was decreasing slightly near 300°K for the $In_{0.21}WO_3$ samples, measurements were extended to 800°K for two specimens of $In_{0.28}WO_3$. Two other crystals cut from the same crystal were used for low-temperature measurements. These are all illustrated in Figure 4. Seebeck measurements in the parallel and perpendicular directions were made on $In_{0.21}WO_3$ at 45°. The parallel value was -28 μv/deg and the perpendicular value was -18 μv/deg.

Summarized briefly, the low resistivities generally increase monotonically with increasing temperature, are fairly insensitive to composition between $x = 0.21$ and $x = 0.27$, and show slight differences in the directions parallel with and perpendicular to the c axis. The resistivities measured parallel with the c axis show a broad maximum at about 215°K and then start increasing again at ~400°K. The Seebeck voltages are small and negative and are also slightly different for the two crystallographic directions.

Examination of the polycrystalline products for the Meissner effect showed that some samples were superconducting, with very low T_c (<2°K). In general, however, most samples were not superconducting above 1.5°K. This contrasts to the previously reported[7] 2.8°K T_c for $In_{0.11}WO_3$. It should be noted,

(9) P. Gado and A. Magnéli, *Mater. Res. Bull.*, **1**, 33 (1966).

(10) V. A. Isupov, A. I. Agranovskaya, and M. F. Bryzhina, *Soviet Phys. Cryst.*, **8**, 81 (1963).

(11) A. Magnéli, *Acta Chem. Scand.*, **7**, 315 (1953).

(12) T. E. Gier, *et al.*, this laboratory, submitted for publication.

(13) G. Hagg, *Nature*, **135**, 874 (1935).

(14) A. Magnéli and B. Blomberg, *Acta Chem. Scand.*, **5**, 372 (1951).

(15) T. A. Bither, J. L. Gillson, and H. S. Young, *Inorg. Chem.*, **5**, 1559 (1966).

(16) W. Ostertag, *ibid.*, **5**, 1758 (1966).

(17) B. Broyde, *ibid.*, **6**, 1588 (1967).

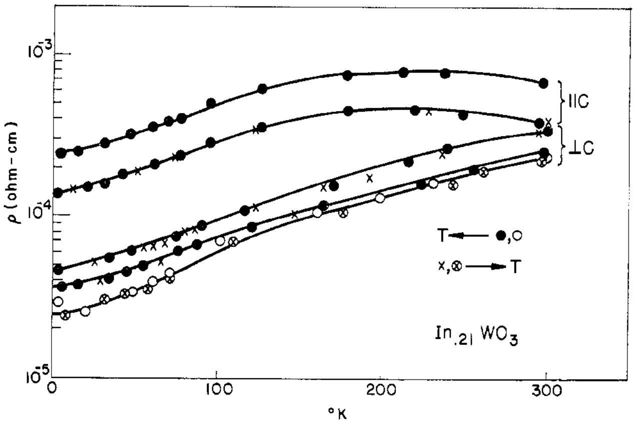

Figure 2.—Resistivity of five samples of $In_{0.21}WO_3$ from 4.2 to 300°K.

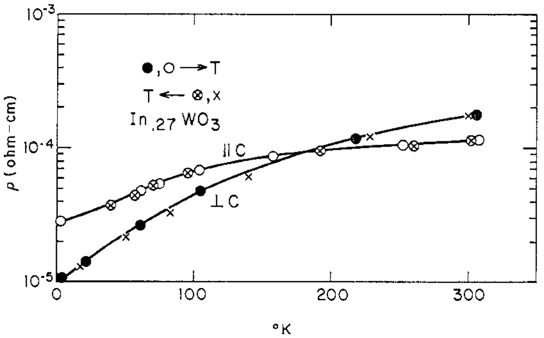

Figure 3.—Resistivity of two samples of $In_{0.27}WO_3$ from 4.2 to 300°K.

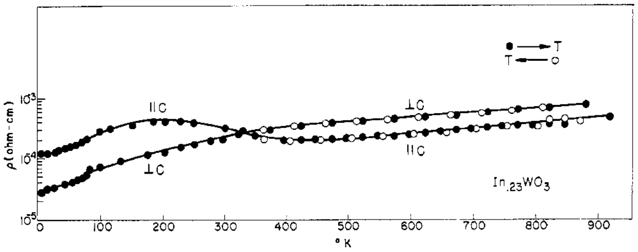

Figure 4.—Resistivity of four samples of $In_{0.23}WO_3$. Two of the samples were measured from 4.2 to 300°K. The other two were measured from 300 to 900°K.

however, that the reported samples had been cleaned in acid to remove unreacted starting materials. Remeika, *et al.*,[18] have shown that acid washing can raise the T_c considerably. When some of our samples were soaked in HF overnight, the T_c did go up to about 3.8°K. Thus, it appears that the In_xWO_3 bronzes are similar to the alkali metal hexagonal bronzes in this respect.

The Faraday method was used to measure the magnetic susceptibility at 78 and 297°K for both a polycrystalline sample and a single crystal from the same preparation of $In_{0.21}WO_3$. The measurements on the single crystal were made with the field parallel with the plane of the plate and provided a value for the susceptibility perpendicular to the symmetry axis, $\chi_{\perp}$. The polycrystalline data provided an average susceptibility, $\bar{\chi}$. This allows $\chi_{\parallel}$ to be calculated, since $\bar{\chi} = (2\chi_{\perp} + \chi_{\parallel})/3$. The results indicate essentially isotropic, temperature-independent weak diamagnetism of approximately -5×10^{-8} emu/g, consistent with the nearly isotropic metallic conductivity. Apparently the diamagnetic contributions of the In and WO_3 more than compensate for the weak Pauli paramagnetism of the metallic conduction electrons.

Discussion

The general insensitivity of the resistivities to composition over the narrow range studied is not unexpected since changing x from 0.21 to 0.27 does little more than change the number of carriers from 0.21 to 0.27 (per WO_3 unit) in a nominally sixfold degenerate π^* band. This assumes that there is one electron per A ion donated to the conduction band, which seems consistent with the requirement that the A ion be large and polarizable.

In general, the results are consistent with Goodenough's model[3] of a small number of electrons in a nearly empty π^* band. Because the crystal structure is so anisotropic, it is not surprising that the conductivity curves for the a and c directions do not coincide exactly. The details of the π^* band structure are undoubtedly somewhat different in these two directions, which would manifest itself in different carrier mobilities.

Conclusions

Although the conductivity and Seebeck measurements on single crystals of the hexagonal indium tungsten bronze show some differences in the a and c directions, they can be considered nearly isotropic for most purposes. The same is true for the weak diamagnetic susceptibility observed. This behavior cannot be offered as a conclusive proof of any particular model because of the very qualitative nature of the considerations discussed. Nonetheless, it is consistent with the presence of a π^* conduction band formed by mixing cation t_{2g} with anion pπ wave functions.

Acknowledgments.—The assistance of J. F. Weiher, who performed the magnetic measurements, is gratefully acknowledged as is the X-ray work of K. R. Babcock, who aligned the single crystals for electrical measurements, and P. Bierstedt, who examined the samples for the Meissner effect. The comments of T. A. Bither are also appreciated, as are those of D. B. Rogers, who critically reviewed the manuscript.

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(18) J. M. Remeika, T. H. Geballe, B. T. Matthias, A. S. Cooper, G. W. Hull, and E. M. Kelly, *Phys. Letters*, **24A**, 565 (1967).