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Electrical and Magnetic Properties of Potassium Tungsten Bronze and Rubidium Tungsten Bronze[1]

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Single crystal conductivities have been measured for $K_{0.40}WO_3$ and $Rb_{0.32}WO_3$ in the range 150 to 370°K. Carrier mobilities, which are somewhat higher than in the Li and Na tungsten bronzes, closely follow a $T \sinh^2 (\theta/2T)$ dependence. Calculations on the basis of the theory of Howarth and Sondheimer strongly support the assumption that the thermal part of the carrier mobility in the tungsten bronzes is primarily determined by polar scattering from optical mode lattice vibrations. Magnetic susceptibilities also have been measured at room temperature for $Rb_{0.26}WO_3$ and $K_{0.23-0.45}WO_3$. Results are as predicted by the Pauli–Peierls theory for quasi-free electrons.

The tungsten bronzes, M_xWO_3 ($0 < x < 1$), which have metallic properties[2] over a wide range of composition, hold considerable promise as model systems for examining theories of metallic binding. In particular, the course of a density-of-states function characteristic of a conducting d-band seems directly accessible experimentally as a function of varying electron concentration. However, except for the cubic sodium and lithium tungsten bronzes, for which considerable data exist[3] on structure, conductivity, magnetic susceptibility, thermal e.m.f., and Hall voltage, observations on the other alkali tungsten bronzes are fragmentary, qualitative, and occasionally contradictory. In anticipation of shortly having band calculations for the tungsten bronzes, we have undertaken this investigation of potassium and of rubidium tungsten bronzes to provide parameters for typical non-cubic bronzes.

Potassium tungsten bronzes first were prepared by Laurent[4] by reduction of K_2WO_4–WO_3 mixtures with hydrogen. Subsequent preparation methods included reduction of K_2WO_4–WO_3 with tin,[5] electrolysis of fused K_2WO_4,[6] reduction of K_2WO_4–WO_3 with WO_2,[7] and reduction of K_2WO_4–WO_3 with elemental tungsten.[8] Schaefer[9] was first to prepare a defined rubidium tungsten bronze by reduction of Rb_2CO_3–H_2WO_4 mixtures with methane and hydrogen. The potassium bronzes, K_xWO_3, have been found to be tetragonal in the range[8,10] $0.40 < x < 0.57$, with $a = 12.285$ Å. and $c = 3.833$ Å. at $x = 0.48$, expanding to $a = 12.317$ Å. and $c = 3.841$ Å. at $x = 0.57$. In the range $0.27 < x < 0.31$ they are hexagonal,[11] with $a = 7.40$ Å. and $c = 7.56$ Å. at $x = 0.27$, contracting to $a = 7.37$ Å. and $c = 7.54$ Å. at $x = 0.31$. In the range $0.27 < x < 0.29$, the rubidium tungsten bronzes Rb_xWO_3 are isomorphous with the hexagonal potassium bronzes. Magnéli's detailed structural studies[11] on $Rb_{0.29}WO_3$ indicate six formula units of Rb_xWO_3 per unit cell, $a = 7.38$ Å. and $c = 7.56$ Å., with the WO_6 octahedra connected by common corners to form a regular network of 3- and 6-membered rings arranged in layers normal to the hexagonal axis.

Conductivity data presently available on K_xWO_3 and Rb_xWO_3 are limited to room temperature measurements on pressed powder samples. Straumanis and co-workers report[12] a specific resistivity of 1.3×10^{-2} ohm cm. for $K_{0.54}WO_3$ increasing with lowered K content to about 5×10^{-2} ohm cm. for $K_{0.46}WO_3$. Magnéli[11] reports 5×10^{-2} ohm cm. for $K_{0.27-0.31}WO_3$ and 3×10^{-2} ohm cm. for $Rb_{0.27-0.29}WO_3$. These values represent upper limits, as usually is true for powder studies, but they seem orders of magnitude too high to be consistent with the obvious metallic appearance of the materials. Furthermore, resistivities of this order would require considerable modification in the total ionization model applicable to Na_xWO_3 and Li_xWO_3.[13] A major effort in this research was to prepare single crystals of K_xWO_3 and Rb_xWO_3 so that bulk resistivities could be determined without grain contact effects such as probably are present in the above work.

So far as magnetic studies are concerned, there are no available data on Rb_xWO_3 and two fragmentary sets on K_xWO_3. Stubbin and Mellor[14] reported 50×10^{-6} and 30×10^{-6} for the molar susceptibilities at room temperature of $K_{0.63}WO_3$ and $K_{0.57}WO_3$, respectively, with no detectable change over the temperature range 300–457°K. Kupka and Sienko[15] found at 294°K. a molar susceptibility of 100×10^{-6} for $K_{0.63}WO_3$. Both sets of results were interpreted as being consistent with a free-electron model.

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[1] This research was supported by the Air Force Office of Scientific Research under Contract No. AF49(638)-191 and by the Advanced Research Projects Agency.

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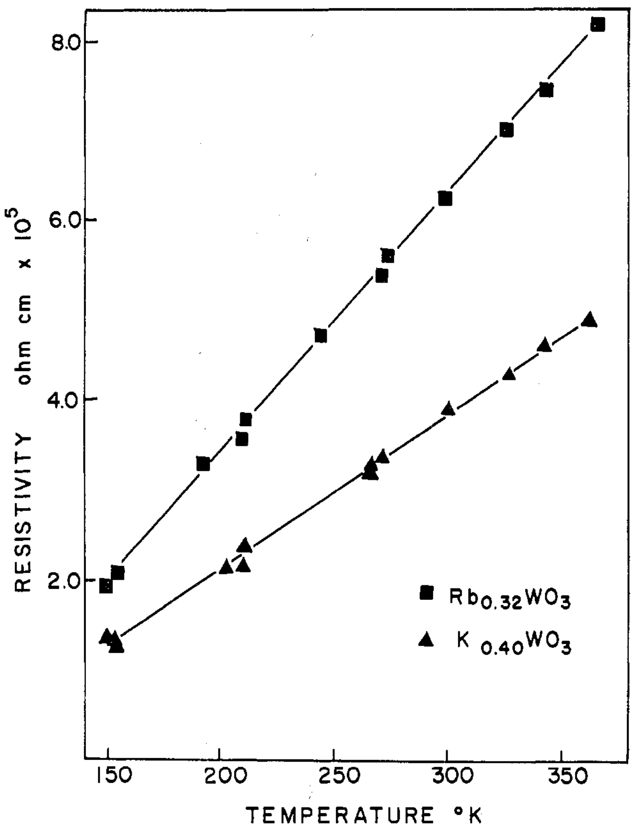

Fig. 1.—Observed resistivity as a function of temperature for typical single crystals of rubidium and potassium tungsten bronzes.

Experimental

Preparation of Materials.—Single crystals of K_xWO_3 were prepared by electrolytic decomposition of melts resulting from fusion of 1:2 molar ratios of K_2CO_3:WO_3 in a Selas crucible inside a porcelain crucible. Tungsten rod (2.5 mm. diameter) in the center unit served as cathode; platinum wire (1.8 mm.) between the walls of the crucibles, as anode. While the cell was heated to 800° in an electric furnace that was continually flushed with argon, electrolysis current was passed through the melt from a 6-volt storage battery for about 5.5 hr. Voltage drop between the electrodes was 1.1 volts; current remained constant at 30 ma. The product, after purification, consisted of rather well formed red crystals, the largest of which were from 8 to 10 mm. long and 1 mm. square.

Useable single crystals of Rb_xWO_3 could not be prepared in the above unit because of impaction in the Selas frit. Large crystalline aggregates were readily made by electrolysis in a Vycor U-cell from which the melt could be poured away from the product, but the individual crystals were poorly formed, probably because of too rapid growth. The best crystals were obtained in a cell consisting simply of a platinum rod cathode centered in a platinum crucible which served as anode. After 3 hr. of electrolysis at 800° under argon, using 18 ma at 1.0 volt, radial clusters of bronze crystals adhering to the cathode could be lifted out of the melt, cooled, and leached successively in H_2O, NH_3, 5% Na_2CO_3, and HF. Remarkably perfect hexagonal prisms were obtained up to 6 mm. long and 2 mm. on hexagonal edge. Because of the possibility of occluding tungstate melt, great care had to be taken to ensure homogeneity of the crystals used for the electrical measurements. Results were considered admissible only if consistent for several probe settings and for different faces of the crystal and if the crystal could be cleaved repeatedly after the measurements were completed without disclosing signs of occlusion.

For the magnetic studies, where powder samples were preferred, K_xWO_3 and Rb_xWO_3 both were made by heating intimately ground mixtures of alkali carbonate, WO_3, and W to about 750° in an evacuated combustion tube for periods of 10 to 24 hr. As with the single crystals, all of the products were purified by successive leaching with boiling water, hot dilute aqueous NH_3, boiling 5% Na_2CO_3, and 48% HF. The Na_2CO_3 was used sparingly because it alone of these reagents appreciably attacks the bronzes. Samples were used for magnetic measurements only if X-ray examination indicated homogeneous bronze composition.

Chemical Analysis.—The bronzes were decomposed by fusion in a 3:1 by weight mixture of $NaNO_3$ and Na_2CO_3. Potassium and rubidium were determined by flame photometry using spectral lines at 767 and 794.8 mμ for K and Rb, respectively. Because the phototube was not so sensitive in the Rb region, the Rb bronzes also were analyzed by a gravimetric technique[16] depending on conversion of Rb_xWO_3 to RbCl by oxidation in an HCl–O_2 stream. A third method of alkali determination was by difference, using tungsten analysis to compute WO_3 which then was subtracted from M_xWO_3. The tungsten method and the HCl method agreed with each other to 3%; they corresponded to the flame photometer method within 10% of the alkali content. The tungsten analysis was performed by H_2WO_4 precipitation with cinchonine scavenging followed by ignition to WO_3.

Density Determination.—Single crystal densities were determined pycnometrically using water as immersion liquid. Results, which are appreciably different from those previously reported,[11] the new ones being closer to the X-ray computed values, are given in Table I along with the X-ray spacings observed. X-Ray powder photographs were taken on ground-up single crystals in a 114.60-mm. camera with CuKα radiation.

Table I

Structure Parameters of K and Rb Bronzes

Composition	Density, g./cc.	Symmetry	a, Å.	c, Å.
$Rb_{0.32}WO_3$	7.16 ± 0.04	Hexagonal	7.386	7.54
$K_{0.40}WO_3$	7.18 ± 0.03	Tetragonal	12.25	3.81

Electrical Measurements.—Well shaped crystals were mounted for potential probe measurement, essentially as previously described,[17] in a soapstone holder with adjustable copper current leads and spring loaded brass probes. Indium inserts between crystal and current leads reduced contact resistance to less than 0.1 ohm. The holder and probe assembly was mounted in a Vycor tube which was evacuated or filled with argon. Temperature variation was produced by an electric furnace or by immersion in a dewar filled with various cryogenic mixtures. Potential difference between the sensing probes was measured with a Leeds and Northrup Type K3 potentiometer. Current through the crystal, periodically reversed to compensate for thermoelectric effects, was monitored by measuring *IR* drop through a standard resistance in series with the crystal. Figure 1 shows observed resistivities as a function of temperature for two specific crystals. Table II gives values averaged over several crystals from the same electrolytic preparation. Because the growth habit favors elongation in the *c*-direction, these values correspond to resistivity parallel to the *c*-axis.

Magnetic Measurements.—Magnetic susceptibilities of the rubidium and potassium bronzes were measured by the Gouy

Table II

Electrical Resistivities of K and Rb Bronzes at 25°

Composition	Resistivity ρ, ohm cm.	Thermal coefficient $1/\rho\ d\rho/dT$
$Rb_{0.32}WO_3$	$(6.32 \pm 0.9) \times 10^{-5}$	4.6×10^{-3}
$K_{0.40}WO_3$	$(3.82 \pm 0.4) \times 10^{-5}$	4.5×10^{-3}

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(16) A. Magnéli, *Arkiv Kemi*, **1**, 273 (1949).

(17) M. J. Sienko and P. F. Weller, *Inorg. Chem.*, **1**, 324 (1962).

method using the electromagnet and procedure previously described.[18] Freshly boiled, doubly distilled water was used as standard. Packing densities of the bronzes for converting measured apparent volume susceptibilities to mass susceptibilities were obtained *via* cathetometric measurement of powder sample dimensions as contained in the precision-bore Pyrex sample tubes. Each sample was measured at three independent packings; each packing, at five separate alignments in the magnetic field. Table III gives the observed susceptibilities for various bronze compositions per gram, χ, and per gram-formula, χ_M, as well as the per cent deviation in the measured values. All measurements were performed at room temperature as monitored in the nitrogen-containing lucite box which isolated the sample from the surroundings. There were no detectable changes in susceptibility as room temperature varied between 24 and 28°.

TABLE III

Composition	χ, susceptibility per g.	χ_M, susceptibility per mole	% deviation
$Rb_{0.26}WO_3$	-5.52×10^{-8}	-1.40×10^{-6}	3
$K_{0.23}WO_3$	-3.62×10^{-8}	-8.71×10^{-6}	6
$K_{0.29}WO_3$	-1.74×10^{-8}	-4.32×10^{-6}	4
$K_{0.30}WO_3$	-1.89×10^{-8}	-4.60×10^{-6}	2
$K_{0.45}WO_3$	9.82×10^{-8}	24.5×10^{-6}	3

Discussion

For both the potassium and the rubidium tungsten bronzes the conductivity is very high, being some three orders of magnitude greater than the values previously reported by Straumanis[12] and Magnéli.[11] Furthermore, at least in the range studied, between 150 and 350°K., behavior is metallic in that resistivity is almost linear with temperature. Assuming that the K and the Rb in M_xWO_3 are completely dissociated into cations and free electrons, the carrier mobility μ can be calculated from $\sigma = ne\mu$, where σ is the observed specific conductivity and n is the number of carriers per cc. As shown in Fig. 2, for $Rb_{0.32}WO_3$, μ decreases from 55.9 cm.²/volt sec. at −120° to 14.3 at 90°; for $K_{0.40}WO_3$, from 66.1 to 18.1 cm.²/volt sec. The curve for $Rb_{0.32}WO_3$ corresponds to a $T^{-1.76}$ dependence at low temperature and a $T^{-1.35}$ dependence at high: for $K_{0.40}WO_3$, to $T^{-1.61}$ and $T^{-1.30}$, respectively. These functions are close to the $T^{-3/2}$ predicted theoretically for lattice scattering.[19]

The carrier mobilities calculated on the assumption of total ionization of Rb and K are of the same order of magnitude as those found for sodium tungsten and lithium tungsten bronzes.[13] The inference is that the same band of delocalized molecular orbitals produced by overlap of 5d (t_{2g}) tungsten orbitals, used to account for the metallic properties of Na and Li W bronzes, also provides the mechanism of electrical transport in the K and Rb W bronzes. The fact that the observed mobilities in the K and Rb bronzes are somewhat higher than those in Li and Na bronzes at the same temperature and alkali content may be a result of anisotropy in the structure of the hexagonal and tetragonal bronzes, the resistivity results given above representing mobilities parallel to the c-axis. Measurements made on a single crystal of $Rb_{0.32}WO_3$, which accidentally grew as a thin plate of large extension in the ab-plane, gave at room temperature a significantly higher resistivity (4×10^{-4} ohm-cm., perpendicular to the c-axis, compared to 6.3×10^{-5} ohm-cm. parallel to c). Nevertheless there is no correlation between increased carrier mobility and decreased spacing between W atoms, as might be naïvely predicted from a 5d overlap model. In fact, with the exception of the sodium case, data summarized in Table IV suggest *decreased* carrier mobility with decreased W–W spacing. However, because it is difficult to attain experimentally full values of the mobility, influences such as defects acting to reduce the true value, mobility comparisons between different substances have to be made with extreme caution. If the comparison indicated by Table IV is supported by independent measurements, then before significance is attached to it, the resistivity measure-

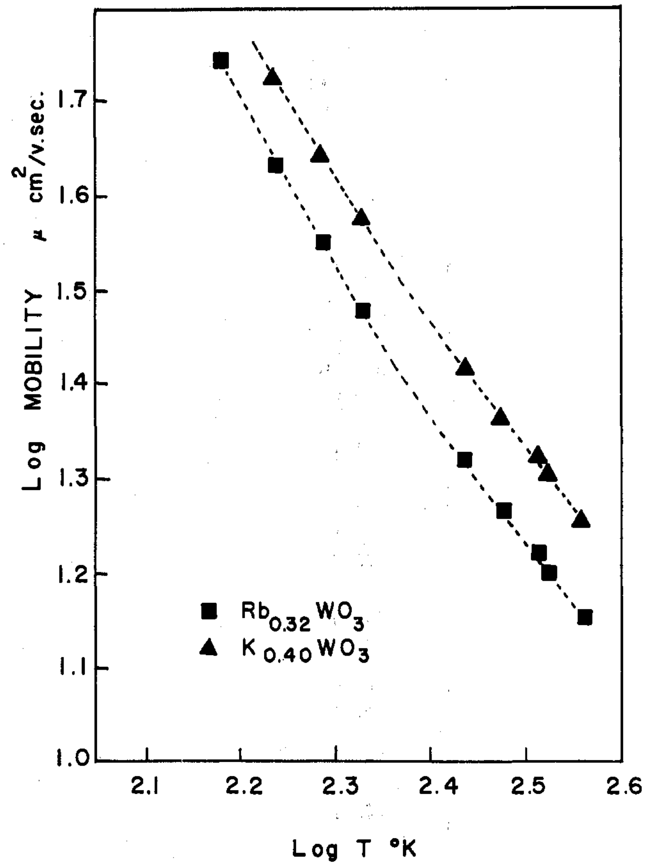

Fig. 2.—Logarithmic plot of carrier mobility *vs.* temperature for single crystals of rubidium and potassium tungsten bronzes.

TABLE IV

Composition	Structure	μ, cm.²/volt sec.	Nearest W–W, Å.	Reference
$Li_{0.37}WO_3$	Cubic	6.1–9.3	3.72	Sienko–Truong[13]
$Na_{0.36}WO_3$	Cubic	4.0	3.81	McNeill–Conroy[20]
$K_{0.40}WO_3$	Tetragonal	23.4 (‖ to c)	3.84 (‖ to c)	This work
$Rb_{0.32}WO_3$	Hexagonal	18.5 (‖ to c)	3.78 (‖ to c)	This work
		3.3 (⊥ to c)	3.70 (⊥ to c)	This work

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ments need to be extended to lower temperature so that the "residual resistivity" can be corrected for. Also, Hall measurements need to be done to give a direct measure of carrier concentration, something which has been done only for the Li and the Na bronzes.

In connection with carrier studies in the γ phase of WO_3, Crowder and Sienko[21] have found that the electrical resistivity and the thermal e.m.f. of *n*-type WO_3 can be explained quantitatively by assuming that the thermally dependent part of the carrier motion is limited primarily by polar scattering from optical mode lattice vibrations. Using three parameters to describe the interaction between the electron and the lattice—*viz.*, an optical mode characteristic temperature of 600°K., a static dielectric constant of approximately 1000, and an optical frequency dielectric constant of 6.2—they were able to compute optical contributions to the resistivity which satisfactorily reproduce not only the dependence of conductivity and thermal e.m.f. on temperature but also the change of these variables as a function of the composition parameter x in Na_xWO_3.

Assuming that the same conduction process is operative in Rb_xWO_3 and K_xWO_3 as in Na_xWO_3—*i.e.*, ignoring anisotropy—it is possible to extend the above calculations to these bronzes. For this purpose, the total resistivity, ρ, is defined as the sum of a residual part, ρ_0, which results from neutral impurity or defect scattering, and a thermal part, ρ_{opt}, which is believed to arise only from optical mode scattering. Acoustical mode scattering, although undoubtedly present, is assumed to contribute a negligible amount. Following the theoretical analysis of Howarth and Sondheimer[22] for electronic conduction in polar semiconductors, the optical part of the resistivity can be written

$$\frac{1}{\rho_{opt}} = ATE_F{}^2 \sinh^2 \frac{\theta}{2T} = \sigma_{opt}$$

where A is a constant, E_F is the Fermi energy, and θ is a characteristic temperature for the crystal. In the case of Na_xWO_3, resistivity measurements[2] have been carried to low enough temperatures that the ρ *vs.* T curve can be extrapolated to $T = 0$. This gives ρ_0, which can be subtracted from $\rho(T = 300°K.)$ to give $\rho_{opt}(T = 300°K.)$, hence permitting calculation of A. For $Na_{0.5}WO_3$, A so found is 1.23×10^{37} in c.g.s. units, or 1.37×10^{25} in practical units. In the case of Rb_xWO_3 and K_xWO_3, the resistivity measurements have not been taken to low enough temperature to permit direct evaluation of ρ_0 by extrapolation. Instead, the observed value of the thermal coefficient of ρ has been used to evaluate ρ_{opt} (and hence A) at room temperature. Once ρ_{opt} is known at a given temperature, it can be used to correct an observed ρ at that temperature to disclose ρ_0. The pertinent equations are

$$\rho = \rho_0 + \rho_{opt} = \rho_0 + \frac{1}{\sigma_{opt}}$$

$$\frac{d\rho}{dT} = -\frac{1}{\sigma_{opt}{}^2}\frac{d\sigma_{opt}}{dT}$$

$$\sigma_{opt} = \frac{1}{T\dfrac{d\rho}{dT}}\left[\frac{\theta}{T}\frac{\cosh \theta/2T}{\sinh \theta/2T} - 1\right]$$

where θ is taken to have the value 600°K. (On the basis of heat capacity measurements, Vest, Griffel, and Smith[23] reported that the acoustic mode characteristic temperature varied from 454–505°K. in the range $Na_{0.56-0.89}WO_3$ but rose to 589°K. in $Na_{0.73}WO_3$ after annealing. Crowder[24] finds the optical mode characteristic temperature to be somewhat higher and that $\theta = 600°K.$ gives a best fit for the WO_3 and Na_xWO_3 electrical data.)

The Fermi energy, E_F, assumed to be constant in the above differentiation, is calculated as for a degenerate electron gas[25]

$$E_F = \frac{(3\pi^2 n)^{2/3}h^2}{8\pi^2 m}$$

where n is the number of free electrons per cc., h is Planck's constant, and m is the electronic mass. Assuming that n is equal to the number of M atoms per cc. of M_xWO_3 and m is the same as the electronic rest mass, we calculate that the Fermi energy in $K_{0.40}WO_3$ is 2.14×10^{-12} erg (or 1.34 e.v.) and that in $Rb_{0.32}WO_3$, 1.76×10^{-12} erg (or 1.10 e.v.). Under these assumptions, the constant A becomes 1.54×10^{37} (c.g.s. units) in $K_{0.40}WO_3$ and 1.32×10^{37} in $Rb_{0.32}WO_3$.

In the theory of Howarth and Sondheimer, the constant A has the form $(32/3)(a^3Mk/e^2h^3)$, where a is the interionic distance in the polar lattice, M is the reduced mass of the vibrating ions, k is Boltzmann's constant, e is the charge, and h is Planck's constant. A crude estimate of A can be made by equating a to 1.9×10^{-8} cm., the observed W–O distance[26] in WO_3 and the tungsten bronzes, and setting M equal to the oxygen mass. The value of A so estimated, 4.1×10^{36}, is remarkably close to the empirical values quoted above, especially considering that there is probably a high degree of covalence in the WO_3 network which acts to reduce the effective charges.

Table V displays the comparison between the computed and the observed resistivities using the equations

$$\rho\ (\text{ohm cm.}) = 0.69 \times 10^{-5} + \left[1.71 \times 10^{25}TE_F{}^2 \sinh^2 \frac{\theta}{2T}\right]^{-1}$$

$$\rho\ (\text{ohm cm.}) = 1.00 \times 10^{-5} + \left[1.47 \times 10^{25}TE_F{}^2 \sinh^2 \frac{\theta}{2T}\right]^{-1}$$

for $K_{0.40}WO_3$ and $Rb_{0.32}WO_3$, respectively.

As with the lithium tungsten bronzes[27] and the sodium tungsten bronzes[15,28] the magnetic susceptibility of K_xWO_3 and of Rb_xWO_3 is quite low—much lower than would be predicted for locally bound unpaired electrons such as would pertain to M^0 plus WO_3 or M^+ plus W(V). Qualitatively, the low moments

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[21] B. L. Crowder and M. J. Sienko, *J. Chem. Phys.*, in press.

[22] D. Howarth and E. Sondheimer, *Proc. Roy. Soc.* (London), **A219**, 53 (1953).

[23] R. W. Vest, M. Griffel, and J. F. Smith, *J. Chem. Phys.*, **28**, 293 (1958).

[24] B. L. Crowder, private communication.

[25] See, for example, N. Cusack, "The Electrical and Magnetic Properties of Solids," Longmans, Green, and Co., New York, N. Y., 1958, p. 24.

[26] For summary, see R. P. Ozerov, *Usp. Khim.*, **24**, 951 (1955).

[27] L. E. Conroy and M. J. Sienko, *J. Am. Chem. Soc.*, **74**, 3520 (1952).

[28] J. D. Greiner, H. R. Shanks, and D. C. Wallace, *J. Chem. Phys.*, **36**, 772 (1962).

TABLE V

ELECTRICAL RESISTIVITIES (μOHM CM.)

	$K_{0.40}WO_3$		$Rb_{0.32}WO_3$	
T, °K.	Computed	Obsd.	Computed	Obsd.
0	6.9	...	10.0	...
50	6.9	...	10.0	...
100	8.2	...	12.2	...
150	13.4	12.8	21.1	20.6
200	21.0	21.4	34.1	34.8
250	29.4	29.6	48.6	49.2
300	37.9	38.2	63.0	64.0
350	46.1	46.8	77.0	78.4
400	54.7	...	91.7	...

TABLE VI

MAGNETIC PARAMETERS OF K AND Rb TUNGSTEN BRONZES

Composition	$\chi_{\text{dia}} \times 10^6$ correction	$\kappa_{e^-} \times 10^6$ exptl.	$n \times 10^{-21}$, e^-/cc.	$\kappa_{e^-} \times 10^6$ theor.	m^*/m_0
$Rb_{0.26}WO_3$	−18.7	0.49	4.4	0.24	1.6
$K_{0.23}WO_3$	−16.3	.21	3.8	.23	0.9
$K_{0.29}WO_3$	−17.2	.35	4.7	.25	1.2
$K_{0.30}WO_3$	−17.4	.35	4.9	.25	1.2
$K_{0.45}WO_3$	−17.6	1.3	7.8	.29	2.9

can be explained by having a delocalized spin system as would exist in a conduction band. In such a case, the magnetic susceptibility can be computed from the quasi-free-electron model following the procedure of Sienko and Truong.[13] Table VI summarizes the parameters involved in the computation, assuming diamagnetic contributions[29] of -14.6×10^{-6} per mole of K^+, -22.0×10^{-6} per mole of Rb^+, and -13.0×10^{-6} per mole of WO_3. (The correction for WO_3 was determined by actual measurement on the Fisher "purified tungstic anhydride" from which the bronzes were prepared. As also found by Greiner, Shanks, and Wallace,[28] this material is less diamagnetic than the -21.0×10^{-6} value reported by Conroy and Sienko. The latter was based on measurements made on WO_3 samples which were carefully purified by multiple reprecipitation techniques.)

As given in the table, κ_{e^-} experimental is the observed magnetic susceptibility per unit volume attributable to the electrons. It is computed by subtracting the appropriate diamagnetic corrections for M^+ and WO_3 from the observed susceptibility and dividing the difference by the molar volume of the bronze. The values given for κ_{e^-} theoretical are computed from the Pauli–Peierls equation[30]

$$\kappa_{e^-} = \frac{4m^*\mu_0^2}{h^2}(3\pi^2 n)^{1/3}\left(1 - \frac{m_0^2}{3m^{*2}}\right)$$

using the assumption that the conduction electrons are completely free—that is, that the effective mass of the electrons, m^*, is equal to the electronic rest mass, m_0. To reconcile the observed electronic susceptibility with the theoretical, it is necessary to assume that the effective mass of the carriers is greater than the rest mass by the amounts shown in the last column of Table VI. Except for the last entry, for $K_{0.45}WO_3$, the effective masses for the K and Rb tungsten bronzes closely approximate the values characteristic of the Li and Na tungsten bronzes, in spite of the anisotropic character of the former. The unusually high effective mass in $K_{0.45}WO_3$ agrees with the higher susceptibility of $K_{0.53}WO_3$ previously reported by Kupka and Sienko. The break in Table VI between the last and the next-to-last lines coincides with the division between tetragonal and hexagonal structures.

The need for further single crystal work to examine any anisotropy in both the conductivity and the magnetic susceptibility is clearly evident. However, the general model for tungsten bronzes in which M interstitials are assumed to have donated electrons to a conduction band of the host WO_3 seems to be substantially supported by the above work.

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CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT,
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Oxidation of Thin Single Crystals of Copper[1]

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Single crystal films of copper of 700–800 Å. thickness have been prepared in two states: (a) showing many wide stacking faults and few dislocations, and (b) showing no stacking faults and a high density of dislocations. On treatment with oxygen gas at 0.9 μ and 525° cuprous oxide crystals appear with two epitaxial relations to the copper. On the type (a) copper film the oxide particles show some tendency to nucleate along the stacking faults. On both types the oxide growth has a 20-min. incubation period followed by the sudden appearance of oxide grains of 0.5 μ diameter which increase in size by twofold in the following 20 min.

Chemical reactions involving a solid phase as one of the reactants are probably as old as chemistry itself, but only quite recently have the techniques been developed which allow the detailed study of the influence of the physical state of the solid on its chemical behavior. With the techniques of electron microscopy and electron

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