

Since the product is not 100% *cis*-2-butene, the ring cleavage into two olefins does not occur without some disturbance of the geometrical features of the *cis*-oriented methyl groups. On the other hand the distribution of the 2-butenes differs from the equilibrium composition (literature values, 43 to 47% *cis*-2-butene near 417°). It appears that if a biradical exists momentarily as an intermediate, it decomposes before the original geom-

etry is completely converted to the equilibrium distribution.

Acknowledgment.—The authors wish to thank the Esso Education Foundation for the grant to the Department of Chemistry which provided the gas chromatograph used in this work. They also wish to thank Mr. Carl Whiteman, Jr., for making the infrared measurements and the least squares calculations.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY, ITHACA, NEW YORK]

Studies in Non-Stoichiometry. Electrical Conductivity and Carrier Mobility in Lithium Tungsten Bronzes¹

BY M. J. SIENKO AND THU BA NGUYEN TRUONG

RECEIVED MARCH 25, 1961

Single crystal resistivity measurements, X-ray spacings and densities are reported for three lithium tungsten bronzes: $\text{Li}_{.394}\text{WO}_3$, $\text{Li}_{.377}\text{WO}_3$, and $\text{Li}_{.365}\text{WO}_3$. In the range -150 to 90° , conduction is metallic, in contradiction to previous reports. The electron mobility increases with lithium content and decreases with temperature. Arguments are given for believing there should be a transition from localization of electrons to delocalization at approximately $\text{Li}_{.25}\text{WO}_3$. Reexamination of previously reported magnetic results suggest a maximum in the effective mass of the carriers at $\text{M}_{.30}\text{WO}_3$. The change in effective mass and mobility is attributed mainly to the effect of cationic point charge defects on the $5d$ conduction band.

The non-stoichiometric alkali metal tungsten bronzes, M_xWO_3 ($0 < x < 1$), also written $x\text{MW}^{\text{VO}}\text{O}_3$ ($(1-x)\text{W}^{\text{VI}}\text{O}_3$), can be considered to be derived from a host WO_3 lattice doped with alkali metal M. The sodium tungsten bronzes, for which the data are most extensive, are metallic—they have a positive thermal coefficient of resistivity,² a small temperature-independent paramagnetism³ and a negative Hall coefficient⁴ that corresponds to one free carrier per sodium atom. A possible model⁵ for the tungsten bronzes is one in which metal M is viewed as an interstitial donor in a WO_3 lattice, with the donated electrons being accepted into the $5d_x$ conduction band levels of the WO_3 host. On this basis there should be little difference between sodium tungsten bronze and lithium tungsten bronze, inasmuch as both have perovskite-type structures and both alkali atoms have nearly the same ionization energy. If, as seems reasonable, a deep lithium trap is excluded, then the semiconductivity reported⁶ for Li_xWO_3 would have to be attributed to contact resistances or to grain boundary effects. Furthermore, the finding in Li_xWO_3 of small, temperature-independent paramagnetic moments,⁷ nearly constant with varying lithium content, strongly suggests a metallic origin of the susceptibility and hence of the conductivity. To this end, we have undertaken in this work the preparation of single crystals of

Li_xWO_3 and the measurement of their electrical resistivities as a function of temperature. By using a potential probe method, we avoid the interpretation complications inherent with contact resistances and measurements on powders.

Preparation.—Crystals of Li_xWO_3 were prepared by electrodeposition from fused mixtures of Li_2CO_3 and WO_3 . The electrolysis cell consisted of a nest of three porcelain crucibles with a Pt or W cathode in the center crucible and a Pt anode in the outer. Slits cut on opposite sides of the two inner crucibles served to increase the effective electrode separation. The best crystals were obtained (on the cathode) under the following conditions: molar ratio $\text{Li}_2\text{CO}_3/\text{WO}_3$, 1/1.75; temperature, 780–850°; cathode current density, 0.35 amp./cm.²; time of electrolysis, 20–25 hr. Under these conditions, with argon flow through the furnace and with electrode geometry arranged so as to minimize migration of the anode-product oxygen into the cathode compartment, well-shaped, blue-black crystals 3 to 4 mm. long and 1.5 to 2 mm. wide usually could be obtained.

It is assumed that on fusion the Li_2CO_3 – WO_3 mix evolved carbon dioxide with formation of Li_2WO_4 , which then equilibrated with the WO_3 . There seemed to be considerable time lag in this equilibration of the Li_2WO_4 – WO_3 melt. Separate studies of “current *vs.* applied voltage” decomposition curves gave, on extrapolation to zero current, “decomposition potentials” which normally fell in the range 0.9–1.0 volt, but a reproducible decomposition potential was obtainable only after 1 hr. or so of equilibration at the approximate final electrolysis temperature. Such behavior was noted independent of whether the initial charge put in the cell was Li_2CO_3 and WO_3 or, as was used occasionally, Li_2WO_4 and WO_3 . The time lag may be due to poly-anion formation that is slow or to slow clustering of oxytungstate structures

(1) This research was supported by the United States Air Force under Contract No. AF 49(638)-191 and was monitored by the Air Force Office of Scientific Research and Development Command through its Directorate of Solid State Sciences.

(2) B. W. Brown and E. Banks, *Phys. Rev.*, **84**, 609 (1951).

(3) F. Kupka and M. J. Sienko, *J. Chem. Phys.*, **18**, 1296 (1950); P. M. Stubbin and D. P. Mellor, *Proc. Roy. Soc. N. S. Wales*, **82**, 225 (1948).

(4) E. J. Huibregtse, D. B. Barker and G. C. Danielson, *Phys. Rev.*, **84**, 142 (1951).

(5) M. J. Sienko, *J. Am. Chem. Soc.*, **81**, 5556 (1959).

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

(7) L. E. Conroy and M. J. Sienko, *ibid.*, **79**, 4048 (1957).

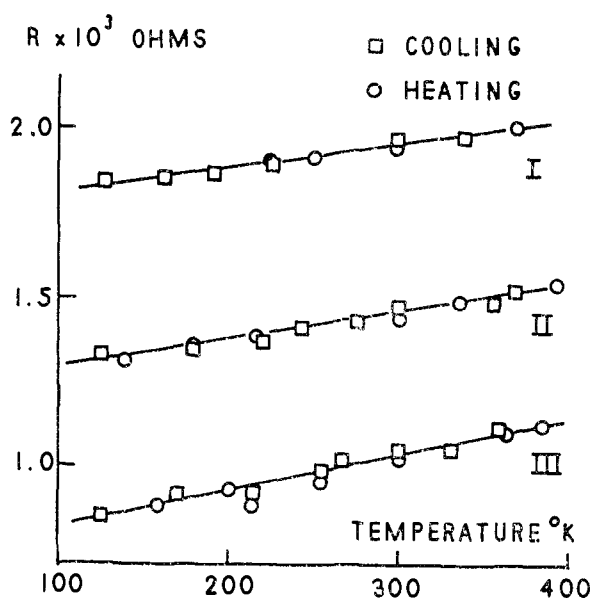


Fig. 1.—Electrical resistance vs. absolute temperature of single crystals of Li_xWO_3 : curve I, $\text{Li}_{.394}\text{WO}_3$; curve II, $\text{Li}_{.377}\text{WO}_3$; curve III, $\text{Li}_{.365}\text{WO}_3$. Probe separations and cross-sectional areas differ in the three cases.

around the Li^+ cations. The electrode processes in these cells are obviously complex and need further study.

Chemical Analysis.—Like the sodium tungsten bronzes, Li_xWO_3 is quite inert to most acidic reagents. Crystals taken off the cathode were cleaned by alternate boiling in water and in 3% Li_2CO_3 to remove Li_2WO_4 and WO_3 , respectively, and then were leached for 24 hr. in 40% HF. For analysis, they were brought into solution by fusion in a $1\text{Na}_2\text{CO}_3:3\text{NaNO}_3$ composition melt. Attempts to dissolve the crystals in a mixture of $(\text{NH}_4)_2\text{SO}_4$ and concentrated H_2SO_4 gave only surface attack with formation of WO_3 as a self-protecting coat.

Analysis for tungsten was as previously described,⁷ using precipitation of tungstic acid plus recovery with cinchonine hydrochloride. Analysis for lithium was by flame photometry, using a Beckman photometer with oxy-hydrogen flame. Standard solutions were made from lithium nitrate with enough sodium nitrate added to match the Na^+ content of the unknown solution obtained from the $\text{Na}_2\text{CO}_3\text{--NaNO}_3$ fusion. The percentage of lithium, determined directly from the flame analysis, agreed with that calculated by subtracting out the WO_3 to within 4% of the lithium content present. The accuracy of the flame analysis is believed to be better than 3% of the lithium content present.

Attempts to determine lithium as lithium sulfate, following the method of Rammelsberg or the method of Brown and Reedy,⁸ gave a considerably higher lithium content than the more reliable flame photometric method described above. The high values of the lithium analysis by the Li_2SO_4 method may be due to special interference on sulfate precipitation by tungstate. It might well

(8) F. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1937, pp. 282, 285.

explain why Straumanis and Hsu,⁶ who did not use cinchonine mop-up on the tungsten (and therefore probably had a low WO_3 analysis) and who did use the Li_2SO_4 method on the lithium (and therefore probably had a high Li), report their bronzes richer in lithium than corresponding materials prepared in this investigation.

The single crystals for which resistivity measurements are reported below were taken from preparations that analyzed to $\text{Li}_{.394 \pm .01}\text{WO}_3$, $\text{Li}_{.377 \pm .01}\text{WO}_3$, $\text{Li}_{.365 \pm .01}\text{WO}_3$. These correspond, respectively, to starting ratios of $\text{Li}_2\text{CO}_3:\text{WO}_3$ of 1:1.5, 1:1.75 and 1:2.

X-Ray Analysis.—X-Ray diffraction photographs were taken of the powders produced by grinding up well-shaped crystals taken from the above samples. Radiation was $\text{CuK}\alpha$; the camera diameter was 114.60 mm. Excellent photographs were obtained showing diffraction lines corresponding to a simple cubic structure. The observed lattice constants are given in Table I, along with the calculated X-ray densities and the densities as determined by the usual pycnometric, water-immersion method. Quoted error limits are maximum deviations for three independent determinations.

TABLE I

X-RAY AND DENSITY DATA FOR LITHIUM TUNGSTEN BRONZES

Substance	Lattice constant (Å.)	X-Ray density (g./cc.)	Obsd. density (g./cc.)
$\text{Li}_{.394}\text{WO}_3$	3.715 ± 0.002	7.597	7.543 ± 0.040
$\text{Li}_{.377}\text{WO}_3$	$3.718 \pm .003$	7.576	$7.542 \pm .020$
$\text{Li}_{.365}\text{WO}_3$	$3.723 \pm .005$	7.542	$7.541 \pm .026$

Electrical Resistivity Measurements.—The crystals, selected for regularity of surface, were pressure-clamped between the ends of two 2.5 mm. copper rods, which served to carry current through the crystal. Potential sensing probes of brass were spring-loaded against one side of the crystal through spacing holes in a Lucite plate, which fitted rigidly over the porcelain tube holding the copper rods. One of the copper rods doubled back on itself so the whole assembly could be inserted into a protection tube for evacuation and for insertion into a furnace or a low temperature cryostat. The I_r drop between the sensing probes was measured with a type K-2 Leeds and Northrup potentiometer, the current I through the crystal being monitored by measurement of the I_r drop across a standard resistance r_s in series with the copper rods and the crystal. To insure absence of thermally generated e.m.f.'s, the current through the crystal was periodically reversed but without effect.

Temperature control was provided by Dry Ice, liquid nitrogen or a cylindrical electric furnace. Temperature measurement was with a copper-constantan thermocouple, constructed of 3 mil wire, one junction of which was placed adjacent to the crystal in the protection tube.

Probe separation, which could be adjusted from 0.7 mm. to 2.0 mm., and the crystal cross-section were measured with a low-power microscope calibrated with a stage micrometer.

As shown by the three typical curves of Fig. 1, the electrical resistance was observed to increase linearly with increasing temperature. Curve I

was for a crystal taken from $\text{Li}_{.394}\text{WO}_3$; curve II, $\text{Li}_{.377}\text{WO}_3$; and Curve III, $\text{Li}_{.365}\text{WO}_3$. For a given crystal, the resistance-temperature curve was easily reproducible within 2% on repeated cycles of heating and cooling between *ca.* -140 and 100° . (Measurements below -140° were impossible because of appearance of large contact resistance between the copper leads and the crystal; measurements above 100° were excluded because of the likelihood of distorting the Lucite plate and hence the probe separation.) Observed resistivities, as calculated from the appropriate probe separations and cross-sectional areas, are summarized in Table II. Other single crystals taken from the same preparations showed the same specific resistivities within 10% and the same thermal coefficient of resistivity within 0.4%.

TABLE II
SPECIFIC RESISTIVITIES OF Li_xWO_3 AT VARIOUS TEMPERATURES

Crystal	Ohm-cm.		
	-150°	$+27^\circ$	$+90^\circ$
$\text{Li}_{.394}\text{WO}_3$	8.37×10^{-6}	8.78×10^{-6}	9.20×10^{-6}
$\text{Li}_{.377}\text{WO}_3$	1.02×10^{-4}	1.26×10^{-4}	1.34×10^{-4}
$\text{Li}_{.365}\text{WO}_3$	1.34×10^{-4}	1.45×10^{-4}	1.48×10^{-4}

Discussion

The finding of a positive thermal coefficient of resistivity in lithium tungsten bronzes is at variance with the results reported by Straumanis and Hsu,⁶ at least in that part of the temperature range where our two investigations overlap. We believe that the Straumanis and Hsu work, based as it is on powders, is complicated by contact resistances between grains of the powder. These contact resistances probably decrease at higher temperatures so that their observed resistivities were not truly representative of the state of the current carriers in the body of the lithium tungsten bronze structure.

A second discrepancy exists in that our X-ray spacings for Li_xWO_3 are somewhat smaller than those reported by Straumanis and Hsu for equal concentrations of lithium. We believe that this discrepancy, also found in a previous investigation,⁷ is traceable to the chemical analysis methods used. As discussed above under "chemical analysis," results based on flame photometer analysis would seem to be the more reliable.

The work of Huibregtse, Barker and Danielson⁴ on the Hall coefficient of the sodium tungsten bronzes clearly indicates that the current carriers in Na_xWO_3 are electrons. It seems reasonable to assume, consistent with the observed positive thermal coefficient of resistivity, that the carriers in Li_xWO_3 are also electrons. If we postulate further there is, as in the case of sodium, one free electron carrier per added alkali atom, then we can estimate a mobility for the electrons from $\sigma = ne\mu$, where σ is the specific conductance, n is the number of free electrons per cc., e is the electronic charge and μ is the carrier mobility in $\text{cm}^2/\text{volt-sec}$. Table III shows the mobilities as so calculated for the three lithium bronzes investigated. This calculation assumes that all the free electrons take part in the conduction process, so that the

TABLE III
ELECTRONIC MOBILITIES IN THE LITHIUM TUNGSTEN BRONZES

Bronze	Electrons n , per cc.	μ , $\text{cm}^2/\text{volt sec.}$		
		-150°	27°	90°
$\text{Li}_{.394}\text{WO}_3$	7.69×10^{21}	9.71	9.26	8.83
$\text{Li}_{.377}\text{WO}_3$	7.34×10^{21}	8.35	6.76	6.35
$\text{Li}_{.365}\text{WO}_3$	7.07×10^{21}	6.60	6.10	5.97

mobility is some kind of average mobility describing the entire assembly of electrons. An alternative calculation would be to count only those electrons at the top of the Fermi distribution in which case calculated mobilities would be considerably higher. The calculation also assumes that the concentration of carriers does not change appreciably with temperature, a condition which would be true for a degenerate electron gas such as is approximated here.

From Table III two trends are evident: the mobility decreases with rising temperature and increases with greater concentration of lithium doping. The decreasing mobility with higher temperature could be taken to indicate that the principal mechanism for scattering the conduction carriers is through the thermal motion of the atoms of the host structure. Such lattice scattering, if it is the dominant process, should lead to a mobility depending on the inverse $3/2$ power of the temperature with dilute doping and on the inverse first power of the temperature with high doping.⁹ Our measurements could not be extended to low enough temperatures to enable us to decide the exact analytic form of the dependence, but, as discussed below, it seems reasonable to believe that the high doping case applies. Separate Hall experiments to determine concentrations independently and to show that carrier concentration does not change appreciably with temperature would be needed before much significance could be attached to the thermal variation of mobility shown by the above data.

The other trend evident from Table III—increasing mobility with increasing lithium content—is more difficult to account for. It apparently is real, especially when one considers that the sodium tungsten bronzes show a similar rise in electron mobility with increasing sodium content. Using the data of Ellerbeck, Sidles and Danielson¹⁰ on carefully chosen crystals of Na_xWO_3 that do not show the previously reported but spurious resistivity minimum, we calculate at room temperature a mobility of $10.5 \text{ cm}^2/\text{volt-sec}$. in $\text{Na}_{.48}\text{WO}_3$ and $25.6 \text{ cm}^2/\text{volt-sec}$. in $\text{Na}_{.88}\text{WO}_3$ —values which effectively extrapolate the lithium-doping experiments to higher electron densities. One possible interpretation is that there is "impurity banding" in the tungsten bronzes. Such an impurity band would widen at higher concentrations of alkali metal and thus lead to a higher mobility of the conduction electrons. The case against impurity banding is the virtual absence of a Knight shift in the nuclear magnetic

(9) See, for example, R. A. Smith "Semiconductors," Cambridge University Press, New York, N. Y., 1959, p. 115.

(10) L. D. Ellerbeck, P. H. Sidles and G. C. Danielson, *Bull. Am. Phys. Soc.*, Series II, 5, 187 (1960).

resonance of either Na^{23} in $\text{Na}_x\text{WO}_3^{11}$ or Li^7 in Li_xWO_3 .¹² If an impurity band were formed, it would certainly use $3s$ (for Na) or $2s$ (for Li) wave functions, thus leading to a finite probability of excess unpaired electrons at the nucleus in a magnetic field and hence to an observable down-field shift of the n.m.r. Another possibility is that the alkali cations introduce point charge defects in the WO_3 structure, and these extra centers of positive charge break up the band structure at low doping but essentially get smoothed out when present in sufficiently high concentrations so have less effect at high doping. In other words, it may be that in these bronzes electrons at low concentrations are essentially "localized" whereas at higher concentrations they become "free" carriers. A third possibility is that ionic scattering may be an important mechanism for relaxation in the conduction process. Since the mobile carriers are only those near the top of the Fermi distribution, it is only the "hot" electrons that need be considered. As we dope WO_3 with increasing alkali metal, we populate the conduction band to higher energies thus effectively making the conduction electrons "hotter" as x in M_xWO_3 increases. Since the ionic scattering cross-section for energetic electrons is less than for the electrons at the bottom of the band, the electron mobility would be greatest for the alkali rich bronzes. The case against this explanation is that, as shown by the Conwell-Weisskopf analysis,¹³ mobility associated with such ionic scattering should increase with the $3/2$ power of the temperature whereas we observe a linear decrease.

Re-examination of presently available data gives most support to the second of the above possibilities—*viz.*, in the tungsten bronze series as alkali metal is added there appears a transition from localization to delocalization of the electrons. We can estimate approximately the concentration at which this may occur by the following analysis: in a medium of dielectric constant D , the maximum in the radial distribution function for a hydrogen-like orbit is given by

$$r = D \frac{m}{m^*} a_0$$

where m is the electronic mass, m^* is its effective mass and a_0 is the first Bohr radius. The dielectric constant of WO_3 can be estimated from the square of the mean refractive index¹⁴ as 6.0. The effective mass of the electrons can be calculated from the observed magnetic susceptibility of M_xWO_3 by using the Pauli-Peierls calculation as given below. In the highly doped materials, where degeneracy is most probable and the assumptions of the Pauli-Peierls calculation are most closely fulfilled, we find an effective mass 2.5 times the electronic mass. Using 0.53\AA . for the Bohr radius, we calculate 1.3\AA . as the most probable radius of a localized electron in WO_3 . Mott has treated the theoretical problem of estimating the concentration at which there will be transition

from the non-metallic to the metallic state.¹⁵ He finds the crossover from the Heitler-London description to one using Bloch functions should occur when the mean distance between atoms is 4.5 times the mean radius of any one of them. Carrying this analysis over to our case we would expect delocalization of the electrons to occur when they are no more than 5.9\AA . apart. For a simple cubic array of such electrons, we would need 1.5×10^{23} electrons in the molar volume of WO_3 (31 cc.), corresponding to $\text{M}_{0.25}\text{WO}_3$. Thus, as x in M_xWO_3 increases from 0 to 1, we expect a transition to delocalization at $\text{Li}_{0.25}\text{WO}_3$ and a drop in activation energy for excitation to the conduction band from some finite value to zero. (The metallic behavior usually observed even for the dilute tungsten bronzes suggests that the activation energy is small compared to kT at room temperature. Measurements of conductivity and the Hall voltage would be extremely informative especially near liquid helium temperatures.)

The magnetic data, which are the only ones available at low concentrations, support the idea there is a change in band character around $\text{M}_{0.25}\text{WO}_3$. Table IV shows the volume susceptibilities of various tungsten bronzes along with the effective masses deduced by means of the Pauli-Peierls equation.

TABLE IV
MAGNETIC PROPERTIES OF THE ALKALI TUNGSTEN BRONZES

Composition	$\chi_M \times 10^6$	Electron concn.	$\kappa_e^- \times 10^6$	m^*
$\text{Li}_{0.05}\text{WO}_3$	-15	9.69×10^{20}	0.19	1.2
$\text{Li}_{0.10}\text{WO}_3$	-14	1.94×10^{21}	.23	1.1
$\text{Li}_{0.20}\text{WO}_3$	- 5.3	3.89×10^{21}	.51	1.7
$\text{Li}_{0.30}\text{WO}_3$	+ 8.8	5.84×10^{21}	.97	2.6
$\text{Li}_{0.36}\text{WO}_3$	+10.0	7.00×10^{21}	1.0	2.5
$\text{Na}_{0.48}\text{WO}_3$	+ 3.2	7.75×10^{21}	0.80	2.0
$\text{Na}_{0.78}\text{WO}_3$	+14.6	1.37×10^{22}	1.2	2.4

The data for the lithium bronzes are taken directly from the work of Conroy and Sienko⁷; the data for the sodium bronzes are taken from the work of Kupka and Sienko³ except that a correction has been made for the concentration, which in the original paper was based on an X-ray *vs.* composition curve¹⁶ that has since been revised.¹⁷ The column headed χ_M shows the observed magnetic moments per gram-formula-weight of bronze. The electron concentrations have been calculated from the observed X-ray spacings assuming each alkali metal atom is totally ionized to give a free electron. The column headed κ_e^- represents calculated values of the electronic magnetic moment per cc. of bronze. The numbers were obtained by subtracting from the observed magnetic moment χ_M , a diamagnetic correction for the WO_3 host lattice (-21.0×10^{-6} from the work of Conroy and Sienko⁷), a diamagnetic correction for Li^+ (-0.7×10^{-6}) or Na^+ (-6.1×10^{-6}) from the work of Brindley and Hoare¹⁸ and dividing by the molar volume of the bronze as calculated from the observed X-ray spacings. Effective masses were obtained from the

(11) R. G. Barnes, R. A. Hultsch and W. H. Jones, Jr., *Bull. Am. Phys. Soc.*, Series II, **4**, 166 (1959).

(12) R. G. Barnes and W. H. Jones, to be published.

(13) E. M. Conwell and V. F. Weisskopf, *Phys. Rev.*, **77**, 388 (1950).

(14) S. Sawada and G. C. Danielson, *ibid.*, **113**, 1011 (1959).

(15) N. F. Mott, *Nuovo Cimento*, **7**, 312 (1958).

(16) M. E. Straumanis, *J. Am. Chem. Soc.*, **71**, 679 (1949).

(17) B. W. Brown and E. Banks, *ibid.*, **76**, 963 (1954).

(18) G. W. Brindley and F. E. Hoare, *Trans. Faraday Soc.*, **33**, 268 (1937); *Proc. Phys. Soc. (London)*, **49**, 619 (1937).

Pauli-Peierls equation¹⁹

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

where m^* is the effective mass, μ_0 is the Bohr magneton, n is the electron density, m is the electron mass and h is the Planck constant. Without the subtractive term in the parentheses, the magnetic susceptibility is the Pauli susceptibility arising from the unpaired electrons at the top of the Fermi distribution. The subtractive term with $m = m^*$ is the Landau diamagnetism which amounts to one-third of the Pauli moment. Introduction of m^* after Peierls corrects for departure from a perfectly free electron gas.

Except for the value for $\text{Na}_{.78}\text{WO}_3$, the effective masses show a rise to a maximum at $\text{M}_{.30}\text{WO}_3$ and then a fall-off. (It might be noted here that we have restricted ourselves to cubic bronzes only, so problems of anisotropy have been avoided.) The existence of this maximum in m^* suggests that there is a perturbation of the band structure which diminishes as x in M_xWO_3 exceeds 0.3. The decay in m^* at large x is consistent with the increasing mobility of the electrons in the alkali-richer bronzes. The source of the initial rise in m^* is not clear. It may only be an apparent effect coming from the assumption that all the electrons are free. As discussed above, there might be localization of the electrons in the dilute bronzes which would reduce the number of free carriers. However, in $\text{Ag}_{0.01}\text{WO}_3$ ²⁰ where trapping would be more likely because of the higher ionization potential of silver, the conductivity data seem to imply complete freeing of the carriers at room temperature and above.

(19) See, for example, A. H. Wilson, "The Theory of Metals," 2nd Ed., Cambridge University Press, Cambridge, 1954, p. 155.

(20) M. J. Sienko and B. R. Mazumder, *J. Am. Chem. Soc.*, **82**, 3508 (1960).

Alternatively, the initial rise in m^* might be attributable to the fact that at low values of x in M_xWO_3 , the concentration of M^+ ions introduced may not seriously perturb a $5d_e$ band, if the latter indeed is the principal conducting band. As more M^+ is introduced into the lattice, the concentration of scattering centers increases, each M^+ appreciably lowering the energy of the eight tungsten neighbors that comprise the unit cell. States are thus effectively removed from the band, since banding can occur only with approximately equal energy states. On the other hand, when sufficiently high concentrations of M^+ have been added, a major portion of the tungsten atoms may be so perturbed and hence their states could mix to give band formation. The higher the concentration of M^+ , the more valid is the approximation of a regularly periodic potential.

In summary, the model that begins to develop for the tungsten bronzes is a $5d_e$ conduction band with local traps arising from tungsten atoms that have M^+ ions in their vicinity. There should be a finite excitation energy from these traps, but a fairly high mobility and low effective mass for any electrons that have been ejected from the traps. As the concentration of M^+ increases, the number of trapping centers increases, leading to reduced mobility and higher effective mass. Eventually the traps begin to overlap, the activation energy vanishes and metallic conduction sets in. From there on, increasing the concentration of M^+ reduces the aperiodicity in the band and leads to increasing mobility and decreasing effective mass. A major test of these ideas would come from experiments at lower temperatures.

Acknowledgments.—We acknowledge with thanks the stimulating discussions we have had with Professors Raymond Bowers and James Krumhansl of the Cornell Physics Department.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS]

Nitrite Substitution in Chloroamineplatinum(IV) Complexes

BY HERBERT R. ELLISON,¹ FRED BASOLO AND RALPH G. PEARSON

RECEIVED OCTOBER 31, 1960

A kinetic study was made of the nitrite substitution reaction in several chloroamineplatinum(IV) complexes. In the absence of platinum(II) the reaction was found to involve an induction period of from 1 to 2 hr. and variable dependence upon platinum(IV) concentration. With the addition of platinum(II) the induction period disappeared and the reaction was found to obey the rate law $R = k[\text{Pt(IV)}][\text{Pt(II)}][\text{NO}_2^-]$ and to be roughly the same as the rate of chloride exchange. All of these observations are explained on the basis of a slow reduction of platinum(IV) to platinum(II) by nitrite ion and then a second two electron oxidation-reduction reaction involving a bridged intermediate. *trans*-[Pt(tetrameen)₂Cl₂]²⁺ reacts with nitrite ion only to be reduced to [Pt(tetrameen)₂]²⁺ and no substitution occurs.

Much of the information concerning reaction mechanisms of hexacoordinated complexes has been gained from kinetic studies with the many complexes of cobalt(III).³ Preliminary investigations by Wilks⁴ of the reaction between *trans*-

[Pt(en)₂Cl₂]²⁺ and nitrite ion indicated that the reaction proceeded by the direct replacement of one chloride ion to yield [Pt(en)₂NO₂Cl]²⁺. Recently, Musket⁵ observed that the reaction was much more complex than it previously had been believed to be.⁶ For example, Musket found that the reaction has an induction period lasting from 1 to 3 hr. and that the reaction is catalyzed by the

(1) Department of Chemistry, Wheaton College, Norton, Massachusetts.

(2) Symbols of ligands are en = $\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2$ and tetrameen = $\text{NH}_2\text{C}(\text{CH}_3)_2\text{C}(\text{CH}_3)_2\text{NH}_2$.

(3) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, Ch. 3.

(4) P. H. Wilks, Masters Thesis, Northwestern University (1957).

(5) S. F. Musket, Masters Thesis, Northwestern University (1960).

(6) F. Basolo, A. F. Messing, P. H. Wilks, R. G. Pearson and R. G. Wilkins, *J. Inorg. Nuclear Chem.*, **8**, 203 (1958).