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## Magnetic Susceptibility of the Lithium Tungsten Bronzes

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RECEIVED FEBRUARY 9, 1952

Lithium tungsten bronzes, differing in lithium concentration, have been prepared and their magnetic moments determined by the Gouy method. The molar susceptibilities are very low and actually become diamagnetic as the concentration of lithium in the bronze is reduced. The results are consistent with magnetic susceptibilities calculated for an electron gas model. The molar susceptibility of  $WO_3$  determined in this work is lower than that previously reported.

The term tungsten bronze is applied to the non-stoichiometric compounds of general formula  $M_xWO_3$  ( $M$  is an alkali metal,  $x$  is less than unity) formed by the reduction of alkali tungstates. Hägg<sup>1</sup> and Straumanis<sup>2</sup> have considered these bronzes to be solutions of tungsten(VI) oxide in the compound  $MWO_3$ . Because of the high conductivity<sup>2</sup> and the low magnetic moments<sup>3,4</sup> observed in these bronzes, it has been suggested<sup>1</sup> that they can more properly be considered as solid solutions of alkali metal in  $WO_3$  and that the properties observed can be explained on the basis of an electron gas model such as is accepted for metals. In this investigation we have prepared a series of lithium tungsten bronzes in which the concentration of lithium in  $WO_3$  is varied over the widest limits possible. The magnetic moments have been measured and compared with those expected for these two models.

## Experimental

**Preparation of Lithium Tungsten Bronzes.**—The most concentrated bronze obtainable (that is, the bronze with the highest Li to  $WO_3$  ratio),  $Li_{0.36}WO_3$ , was prepared by electrolytic reduction of a fused 1:1 molar mixture of lithium tungstate and tungsten(VI) oxide. The electrolysis was carried out in a porcelain crucible with a tungsten cathode and a platinum anode under the following conditions: applied voltage, 6 volts; current, 2 to 4 amperes, temp.  $800 \pm 20^\circ$ ; cathode current density, 0.6 to 0.15 amp. per square millimeter. The bronze was deposited on the cathode as aggregates of blue-black crystals. The unreacted material was leached out with boiling water, followed successively with hot dilute aqueous ammonia, hot concentrated HCl, and again with hot aqueous ammonia. Washing with 40% aqueous hydrofluoric acid and with hot aqua regia ensured the removal of silica and platinum should these be present. The resulting crystals were washed in dilute aqueous ammonia and finally in water. The size of the crystals was approximately inversely proportional to the current density used. The largest crystals obtained were 0.1 mm. on an edge.

The bronzes less concentrated in lithium were prepared, as suggested by Straumanis and Hsu,<sup>3</sup> from the most concentrated bronze. Calculated amounts of  $Li_{0.36}WO_3$  and of pure  $WO_3$  were ground together and heated in evacuated Vycor tubes at  $900^\circ$  for 30 minutes. The products were treated with hydrofluoric acid and washed with water.

**Preparation of Tungsten(VI) Oxide.**—Tungsten(VI) oxide was prepared by igniting tungstic acid at  $750^\circ$  for one hour. The tungstic acid was made from reagent  $Na_2WO_4 \cdot 2H_2O$  by precipitation with concentrated nitric acid. The product was purified of sodium by reprecipitation from aqueous ammonia.

**Preparation of Lithium Tungstate,  $Li_2WO_4$ .**—Reagent grade lithium carbonate (37 g., 0.5 mole) and tungstic acid (116 g., 0.5 mole) were made into a slurry with 150–200 ml.

water. Reaction began immediately and was completed by warming to  $100^\circ$  for 2 hours. The water was evaporated off at  $80^\circ$  and the white powder-cake product dried at  $110^\circ$ .

**Analysis of the Lithium Tungsten Bronze,  $Li_{0.36}WO_3$ .**—The analysis was complicated by the difficulty of getting the bronze into solution. Fusion with ammonium sulfate-sulfuric acid mixture, which has been reported,<sup>5</sup> did not completely decompose the bronze. The ammonium sulfate-sulfuric acid mixture attacked only the surface. Since repeated fusions were tedious, the method used in this work was fusion with a sodium nitrate-sodium carbonate mixture despite the fact that the fusion introduced sodium ion into the analysis solution.

Lithium was determined with a Beckman model DU spectrophotometer with Beckman flame photometer attachment. The instrument was standardized with a lithium solution containing all the other constituents of the analysis solution in the approximate proportions present in the analysis solution. The 670.8  $m\mu$  line of lithium was used for the measurements, the intensity being measured on the 600–1000  $m\mu$  phototube. The precision was 9.2% in terms of the lithium content of the solution.

Tungsten was determined by precipitation of the tungstic acid-tannin complex in the presence of cinchonine,<sup>6</sup> followed by ignition to  $WO_3$ .

**Magnetic Measurements.**—Magnetic susceptibilities of the bronzes were determined by the Gouy method using a semi-micro balance sensitive to 0.05 mg. Current for the air-cooled electromagnet was supplied by storage batteries and the magnetic field determined from the potential drop across a fixed manganin wire resistance in series with the coils. The field was calibrated with a 30% nickel chloride solution made up from J. T. Baker "Special Low Cobalt"  $NiCl_2 \cdot 6H_2O$ . The field calibration was reproducible to better than 1% over the range 4000–8000 gauss. It was confirmed by determining the proton resonance frequency with a coil containing 0.05  $M$   $MnSO_4$  solution as one component of a regenerative oscillator. In employing the proton resonance technique,<sup>7</sup> the magnetic field was modulated by small coils wound concentrically with the field windings of the electromagnet. The field modulation was of the order of 20 gauss.

Mapping of the magnetic field with the proton resonance coil indicated that the field was homogeneous over a distance of about 5 mm. from the center of the gap perpendicular to and along the magnet axis. For precision, two cross-hair telescopes sighting at right angles to each other were used to align the samples vertically and horizontally. Samples were packed in a precision bore Pyrex tube ( $7.00 \pm 0.01$  mm.). The height of the sample was about 15 cm. and was measured for each packing cathetometrically to  $\pm 0.05$  mm. Pole pieces were tapered with pole faces 4 cm. in diameter. The sample tube and its suspensions were completely enclosed in a lucite box so as to allow for an atmosphere of nitrogen around the sample tube.

The reproducibility of the measurements of the magnetic susceptibilities of the bronzes was limited by the reproducibility of the magnetic field and by the difficulty in reproducing sample alignment. Each sample was measured using at least five independent alignments. Deviations due to packing of the sample were not directly measurable since repacking a sample also necessitated re-aligning it. At least three separate tube packings were used for each sample. Results quoted below represent averages of at least 6 deter-

(1) G. Hägg, *Z. physik. Chem.*, **B29**, 192 (1935).(2) M. E. Straumanis, *This Journal*, **71**, 679 (1949).(3) P. M. Stubbin and D. P. Mellor, *Proc. Roy. Soc. N. S. Wales*, **82**, 225 (1948).(4) E. Kopka and M. J. Sienko, *J. Chem. Phys.*, **18**, 1296 (1950).(5) M. E. Straumanis and S. S. Hsu, *This Journal*, **72**, 4027 (1950).

(6) P. P. Treadwell and W. T. Hall, "Analytical Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 9th ed., 1942, p. 226.

(7) F. Bloch, W. W. Hansen and M. Packard, *Phys. Rev.*, **70**, 474 (1946).

minations for each sample. The accuracy of the results can be judged from check determinations using freshly boiled distilled water and reagent grade sodium chloride. The value of the gram susceptibility of water was found to be  $-0.735 \pm 0.024 \times 10^{-6}$  as compared to the best literature value<sup>8</sup> of  $-0.720 \times 10^{-6}$ . The molar susceptibility of sodium chloride was found to be  $-31.4 \pm 0.5 \times 10^{-6}$  as compared to the value suggested by Klemm<sup>9</sup> of  $-30.2 \times 10^{-6}$ .

The calibration of the magnet with nickel chloride was carried out at  $26.0 \pm 0.2^\circ$ . No special effort was made to thermostat the samples of bronzes since Stubbin and Mellor have reported<sup>8</sup> that within the limits of experimental error the magnetic susceptibility of the sodium tungsten bronzes and of the potassium tungsten bronzes is independent of the temperature over the range from 292 to 485 Å.

In order to rule out the possibility of traces of ferromagnetic impurities, the measurements reported here have been checked at three different field strengths ranging from 4000 to 8000 gauss. The susceptibility was found to be independent of field strength.

**Lattice Constants.**—Lattice constants for the bronzes were determined from X-ray powder diffraction photographs taken with copper radiation.

### Results

The magnetic susceptibilities of the lithium tungsten bronzes and of pure tungsten(VI) oxide prepared in this investigation are presented in Table I with the lattice constants.

TABLE I  
EXPERIMENTAL MAGNETIC SUSCEPTIBILITIES OF LITHIUM TUNGSTEN BRONZES

Composition $x$ in $\text{Li}_x\text{WO}_3$	Gram suscept. $\chi \times 10^6$	Molar suscept. $\chi_M \times 10^6$	No. of Detn.	Av. devn., %	Lat. const. Å.
0.36	0.043	10.0	9	3.2	3.718
.30	.038	8.8	6	4.2	3.718
.20	— .023	— 5.3	9	11.0	3.720
.10	— .059	— 14	8	3.4	3.722
.050	— .064	— 15	9	4.5	3.723
.010	— .070	— 16	9	19.7	<div style="border: 1px solid black; padding: 2px; display: inline-block;">           a = 7.28            b = 7.48            c = 3.82         </div>
.0050	— .089	— 21	7	4.7	
.0010	— .096	— 22	13	5.9	
.00050	— .10	— 24	8	16.1	↓
.00010	— .083	— 19	8	8.3	
Pure $\text{WO}_3$	— .091	— 21	14	16.7	

In this table the composition of the bronzes is given in terms of  $x$  in the conventional formula  $\text{Li}_x\text{WO}_3$ , i.e., the number of gram atoms of lithium per mole of  $\text{WO}_3$ . The molar susceptibility,  $\chi_M$ , is calculated from the gram susceptibility,  $\chi$ , by multiplying by the gram-formula-weight calculated for the conventional formula. Because of the small forces measured in these experiments, the number of independent susceptibility determinations on each bronze and the average deviation from the mean are also included in the table in columns 4 and 5, respectively. The lattice constants in column 6 indicate a simple cubic structure for the five most concentrated bronzes. The X-ray diffraction patterns for the more dilute bronzes are identical within the limits of error to the pattern found for pure  $\text{WO}_3$ .

TABLE II  
COMPARISON OF EXPERIMENTAL AND CALCULATED MOLAR SUSCEPTIBILITIES OF LITHIUM TUNGSTEN BRONZES

Composition $x$ in $\text{Li}_x\text{WO}_3$	Molar susceptibility, $\chi_M \times 10^6$		
	Experimental	Calcd. for W(V)	Calcd. for electron gas
0.36	10.0	321	— 8.2
.30	8.8	264	— 8.4
.20	— 5.3	170	— 10.5
.10	— 14	74	— 12.7
.050	— 15	27	— 14.5

(8) P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1943, p. 28.

(9) W. Klemm, *Z. anorg. allgem. Chem.*, **244**, 391 (1940).

In Table II the experimentally determined molar susceptibilities of the cubic bronzes are compared with susceptibilities expected for the two models.

### Discussion

The models chosen for the calculation are (I) that proposed by Straumanis and Hsu<sup>5</sup> in which the bronze is considered a solution of  $\text{WO}_3$  in the hypothetical compound  $\text{LiWO}_3$  and (II) that proposed by Kupka and Sienko<sup>4</sup> in which the bronze is considered a solution of Li in  $\text{WO}_3$ . The essential difference in these models lies in the fact that in model I the electron from the lithium is considered to be strongly associated with the tungsten to give a tungsten(V) ion, whereas in model II the electron from the lithium is part of the free electron gas that is weakly associated with the whole lattice. The latter model is similar to that used in the Pauli-Bloch treatment of metals.

In calculating the magnetic susceptibilities expected for the bronzes by either model, we have assumed that the contribution of the  $\text{WO}_3$  to the susceptibility can be calculated from the molar susceptibility of tungsten(VI) oxide,  $\chi_{\text{WO}_3}$ . Tilk and Klemm have reported<sup>10</sup> a value of  $-14.0 \times 10^{-6}$  for  $\chi_{\text{WO}_3}$ . We have preferred to use  $-21 \times 10^{-6}$  for the molar susceptibility of tungsten(VI) oxide because this is the value determined on the pure  $\text{WO}_3$  from which the bronzes were prepared and because the new value is actually in better agreement with the values found by Tilk and Klemm for W(VI) ion in  $\text{Na}_2\text{WO}_4$  and in  $\text{K}_2\text{WO}_4$ .

For calculation of the magnetic susceptibility according to model I we have assumed that the bronze  $\text{Li}_x\text{WO}_3$  can be written as  $(\text{LiWO}_3)_x(\text{WO}_3)_{1-x}$  so that the molar susceptibility of the bronze can be written

$$\chi_M = x\chi_{\text{LiWO}_3} + (1-x)\chi_{\text{WO}_3}$$

where  $\chi_{\text{LiWO}_3}$  is the molar susceptibility of the compound  $\text{LiWO}_3$  and  $\chi_{\text{WO}_3}$  is the molar susceptibility of  $\text{WO}_3$ . Since the compound  $\text{LiWO}_3$  is hypothetical and has not been prepared we have assumed that its molar susceptibility can be calculated from

$$\chi_{\text{LiWO}_3} = \chi_{\text{Li}^+} + \chi_{\text{W}^{+5}} + 3\chi_{\text{O}^-}$$

For the diamagnetic increments we have used  $-0.7 \times 10^{-6}$  for  $\text{Li}^+$ ,  $-16.7 \times 10^{-6}$  for  $\text{O}^-$ , and  $-19 \times 10^{-6}$  for  $\text{W}^{+5}$  after Klemm.<sup>11</sup> The major contribution to the molar susceptibility comes from the magnetic moment of the W(V) ion. The magnetic moment of the "free ion" is 1.55 Bohr magnetons assuming Russell-Saunders coupling of the orbital and spin moments of the unpaired electron. If the orbital moment is assumed to be quenched, the "spin only" moment is the usual 1.73 Bohr magnetons. Since the "spin only" calculations do not agree as well with the magnetic susceptibilities of many of the salts of heavy transition metals as do the "free ion" calculations, we have assumed that the W(V) ion has a moment of 1.55 Bohr magnetons. The susceptibility corresponding to this moment is calculated to be  $1000 \times 10^{-6}$  at  $26^\circ$ . The "spin only" susceptibility would be about 20% higher. It might be noted that, since the

(10) W. Tilk and W. Klemm, *ibid.*, **240**, 362 (1939).

(11) W. Klemm, *ibid.*, **246**, 347 (1941).

W(V) ion has only one unpaired electron in the 5d orbit, the above calculation is valid even if  $d^2sp^3$  bonding is set up with the surrounding oxygen atoms.

In calculating  $\chi_{LiWO}$ , we have neglected to make any correction for exchange demagnetization such as seems to occur in magnetically concentrated solids (e.g., CuO). Since the exchange integral decreases very rapidly with increasing dipole separation, we have assumed that even in the most concentrated bronze,  $Li_{0.36}WO_3$ , the magnetic ions would be far enough apart to make the exchange integral negligible. This assumption becomes better for the more dilute bronzes. However, as can be seen from Table II, even in the most dilute of the cubic bronzes,  $Li_{0.050}WO_3$ , the experimental susceptibility does not agree with that calculated assuming the bronze to contain  $W^{+5}$  ions. These  $W^{+5}$  ions represent of necessity an idealization of the true state of affairs. It is simply for convenience in calculating that we have identified the ionic charge with the admittedly artificial oxidation state. For Model I we have assumed that the electrons from the lithium atoms are firmly bound to  $W^{+6}$  ions and that the resultant  $W^{+5}$  ions have a definite magnetic moment. If, however, the electrons are weakly bound, then the overlapping of their wave functions may be sufficient to lead to a large exchange demagnetization. In the limit of no binding, we are led to the free electron of Model II.

For calculation of the magnetic susceptibility according to model II we have assumed that the lithium atoms are completely dissociated into lithium ions and electrons and that these electrons can be treated as a "free electron gas." The molar susceptibility of the bronze  $Li_xWO_3$  can be calculated from

$$\chi_M = x\chi_{Li^+} + x\chi_{e^-} + \chi_{WO_3}$$

where  $\chi_{e^-}$  is the molar magnetic susceptibility calculated according to the Pauli-Bloch equation for an electron gas. The Pauli-Bloch equation for the volume susceptibility of an electron gas is given<sup>12</sup> as

$$K = 2.20 \times 10^{-10}(N/V)^{2/3} - 1.03 \times 10^7(V/N)T^2$$

where  $N$  is the Avogadro number and  $V$  is the vol-

ume available to one mole of electrons. The temperature dependent term is negligible compared to the temperature independent term except for very dilute systems. We have limited our calculations of the magnetic susceptibility to the five most concentrated bronzes. These are cubic. With a change of symmetry from cubic to tetragonal there is good reason to expect that the electrons cannot be considered as essentially free—an important assumption in the Pauli-Bloch treatment. Thus, we do not extend our comparison into the concentration region where the temperature dependent term may be important.

As can be seen from Table II, the experimental values of the magnetic susceptibility of the lithium tungsten bronzes are in very good agreement with values calculated from the electron gas model. The agreement is more surprising considering that even slight binding of the electrons to any positive center in the lattice introduces an appreciable paramagnetic correction. The slight paramagnetism observed for the two most concentrated bronzes suggests that there actually is a weak coupling of the electrons to the lattice. For this reason, we have assumed that the Landau correction for the diamagnetism of free electrons<sup>13</sup> is not applicable.

The presence of essentially free electrons in these bronzes is not inconsistent with their chemical inertness. Presumably the situation is analogous to that obtaining in many noble metals of high conductivity and low magnetic susceptibility.

The lattice constant for the most concentrated bronze was calculated from X-ray photographs as  $3.718 \pm 0.008$  ångström units. With this accuracy it is not possible to compare the lattice constant closely with the more precise values given by Straumanis and Hsu<sup>5</sup> for their lithium tungsten bronzes. Their most concentrated bronze was reported to have a lattice constant of 3.7218 Å. and a composition corresponding to  $Li_{0.56}WO_3$ . The similarity in lattice constants suggests that these bronzes are in fact identical. Repeated attempts in this work to prepare a bronze more concentrated in lithium than  $Li_{0.36}WO_3$ , both by electrolytic and other methods of reduction, consistently failed.

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(12) See D. M. Yost and H. Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1946, pp. 141-142, for simplified derivation and references to the original papers.

(13) L. Landau, *Z. Physik*, **64**, 629 (1930).