

## Pulsed NMR Study of Proton Mobility in a Hydrogen Tungsten Bronze

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Crystalline hydrogen tungsten bronze  $H_{0.46}WO_3$  was prepared by reduction of  $WO_3$  single crystals. NMR relaxation times  $T_2$ ,  $T_1$ , and  $T_{1\rho}$  were measured for  $80\text{ K} < T < 450\text{ K}$  at 16 MHz and second moments for  $160\text{ K} < T < 450\text{ K}$  at 100 MHz. The relaxation data were analyzed in terms of proton diffusion to give an activation energy of about  $16\text{ kJ mole}^{-1}$  and a correlation time preexponential factor of about 70 nsec for the process.

### Introduction

Hydrogen tungsten bronzes,  $H_xWO_3$ , ( $0 < x < 0.6$ ), are ternary oxide phases formed by the reduction of  $WO_3$  by atomic hydrogen (1, 2). They are classified as "oxide bronzes" because of similar electronic and structural features to those of the alkali metal tungsten bronzes. A recent structural study by Wiseman and Dickens (3) suggests that these compounds are more properly formulated as oxide hydroxides,  $WO_{3-x}(OH)_x$  in which each hydrogen atom participates in a hydroxyl bond and where  $WO_{6-2x}(OH)_{2x}$  octahedrons link together through corner oxygens to form a distorted  $ReO_3$  structure such that a H atom is directed towards an O atom of a neighboring octahedron.

A recent NMR study by Vannice, Boudart and Fripiat (4) of the proton mobility in samples of  $H_xWO_3$  ( $x < 0.35$ ) prepared by the reduction of a  $WO_3/Pt$  mixture in wet hydrogen was interpreted in terms of a very high diffusion coefficient of H in  $H_xWO_3$ , ( $D = 7 \times 10^{-6}\text{ cm}^2\text{ sec}^{-1}$  at 298 K); the proton mobility was appreciable even at the lowest temperature of measurement, 80 K. This result is surprising in the light of a decomposition temperature for  $H_xWO_3$  of 500 K *in vacuo* and the structural evidence for the presence of a normal O-H bond. In the present

work the NMR relaxation times,  $T_2$ ,  $T_1$  and  $T_{1\rho}$  of a pure hydrogen tungsten bronze sample  $H_{0.46}WO_3$  have been measured in the range  $80\text{ K} < T < 450\text{ K}$ ; complementary broad line spectra have also been recorded.

### Experimental Methods

#### Materials

A crystalline sample of  $H_{0.46}WO_3$  was prepared by refluxing  $WO_3$  single crystals (5), with zinc turnings and boiling 2 moles liter<sup>-1</sup> HCl for 3 days. Excess zinc was removed by boiling with concentrated HCl solution. The red sample of bronze was thoroughly washed with water, dried by prolonged vacuum pumping at room temperature and sealed in Pyrex tubes under vacuum. All operations were carried out in an inert atmosphere.

The hydrogen content of the bronze,  $H_xWO_3$ , was determined by thermogravimetric oxidation to  $WO_3$  (uncertainty in  $x$ ,  $\pm 0.02$ ).

A Debye-Scherrer X-ray powder pattern of the sample  $H_{0.46}WO_3$  revealed only the presence of the  $T_A$  phase (1).

A second preparation resulted in the formation of a sample of composition  $H_{0.39}WO_3$  which was characterized by the same methods.

### NMR Studies

*a. Relaxation Time Measurements.* The nuclear spin relaxation times,  $T_2$ ,  $T_1$  and  $T_{1\rho}$  of  $\text{H}_{0.46}\text{WO}_3$  in the temperature range  $80 \text{ K} < T < 450 \text{ K}$  were measured using a Polaron rf pulsed spectrometer operating at 16 MHz. The probe consisted of a cross coiled arrangement. The coils were wound on a PTFE former; the transmitter coil consisted of 4 turns wound in the Helmholtz manner on a 24 mm diameter and the receiver coil of 8 turns wound in a solenoid on a 12 mm diameter. Sample volumes of 1 ml were used.

The sample temperature was controlled to within  $\pm \frac{1}{2}$  K by means of a proportional temperature controller. The sample temperature after an equilibration period of 0.5 hr was measured by a thermocouple which fitted into an indentation in the sample container.  $T_2$ , the spin-spin relaxation time, was determined from the free induction decay following a  $90^\circ$  pulse.  $T_1$ , the spin-lattice relaxation time, was measured using a  $90^\circ$ - $\tau$ - $90^\circ$  pulse sequence.  $T_{1\rho}$ , the spin-lattice relaxation time in the rotating frame was measured using the method of Hartmann and Hahn (6); a  $90^\circ$  pulse was immediately followed by a second pulse of variable duration  $\tau$  whose rf phase was shifted  $90^\circ$  from that of the first pulse. The  $B_1$  field strength was determined from the length of a  $90^\circ$  pulse.

The signal was usually observed  $\sim 15 \mu\text{sec}$  after the end of the pulse. The room temperature signal to noise ratio of the free induction decay after a  $90^\circ$  pulse for  $\text{H}_{0.46}\text{WO}$  was  $\sim 6:1$ .

*b. Broad Line Measurements.* A Jeol 100 MHz high resolution spectrometer, fitted with a broad line attachment, was used to measure the derivative absorption of  $\text{H}_{0.46}\text{WO}_3$  at 160 K and corresponding spectra for  $\text{H}_{0.39}\text{WO}_3$  over the range  $160 \text{ K} < T < 450 \text{ K}$ . Temperatures were maintained constant to within  $\pm 1$  K during each measurement and the normal precautions to avoid modulation and saturation effects were taken (7).

### Results

The relaxation times  $T_2$ ,  $T_1$  and  $T_{1\rho}$  for  $\text{H}_{0.46}\text{WO}_3$  are plotted in Figs. 1 and 2 as  $\log_{10} T_2$  and  $\log_{10}(T_1$  and  $T_{1\rho})$  versus  $1/T$ , respectively. The variation with temperature of the peak to peak separation of the derivative absorption of  $\text{H}_{0.39}\text{WO}_3$  is shown in Fig. 3. Second moments of the low temperature spectra (160 K) were

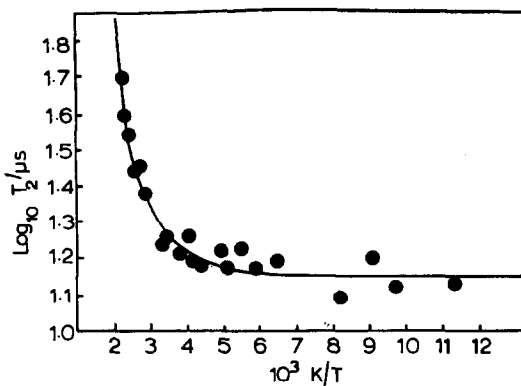


FIG. 1.  $\log_{10} T_2$  versus  $1/T$  for hydrogen tungsten bronze.

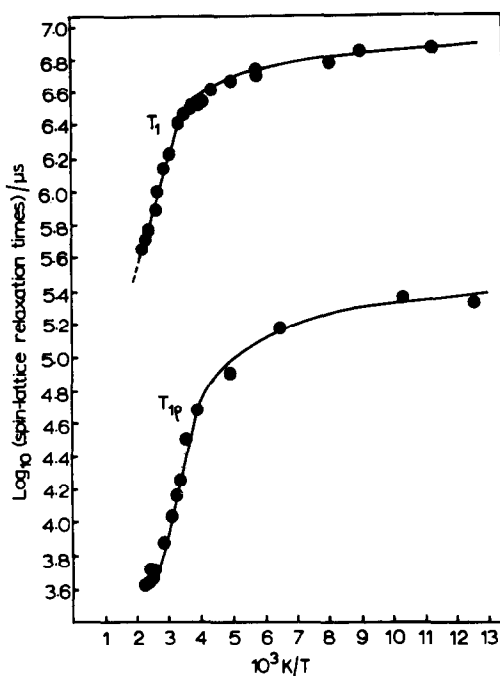


FIG. 2.  $\log_{10}$  (spin-lattice relaxation times) versus  $1/T$  for  $\text{H}_{0.46}\text{WO}_3$ .

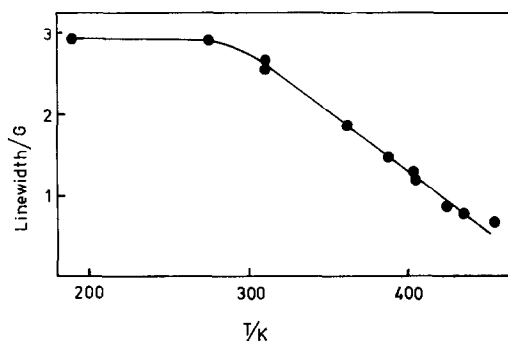


FIG. 3. Line width versus temperature for  $\text{H}_{0.46}\text{WO}_3$ .

calculated graphically as  $H_{0.46}WO_3$ ,  $1.8 G^2$  and  $H_{0.39}WO_3$ ,  $1.6 G^2$  ( $1 G^2 = 715 \times 10^6 Hz^2$ ).

## Discussion

### The Linewidth and $T_2$ Data

Figures 1 and 3 show that at temperatures below 240 K both the line width and  $T_2$  have approximately constant values; above 240 K the line width narrows and  $T_2$  increases indicating the onset of protonic motion.

The line width data in the narrowing region have been analyzed using the expression

$$1/\tau_c = 2 \frac{(2 \log_e 2)^{1/2} \delta\omega}{\tan [\pi(\delta\omega/\delta\omega_0)^2/2]}, \quad (1)$$

where  $\delta\omega$  is the line width expressed as a frequency,  $\delta\omega_0$  is the line width before the narrowing and  $\tau_c$  is the correlation time for the motion (8). From this analysis  $\tau_c$  values are obtained as a function of temperature and these are plotted in Fig. 4(a) as  $\log_{10} \tau_c$  against  $1/T$ . The observed linear relationship of these quantities indicates that the  $\tau_c$  values obey the Arrhenius equation

$$\tau_c = \tau_c^0 e^{E/RT}. \quad (2)$$

Assuming Eq. 2 values of  $E = 19.3 (\pm 1.1)$  kJ mole $^{-1}$  and  $\tau_c^0 = 47 (\pm 14)$  nsec were obtained from the best fit straight line of  $\log_{10} \tau_c$  against  $1/T$ .

A calculation of the rigid lattice second moment for  $H_{0.46}WO_3$  made on the assumption that the hydrogen atoms occupy randomly an appropriate fraction of the possible sites determined for the cubic phase (3) (but excluding simultaneous occupancy of adjacent sites), gave a value of  $1.58 G^2$ . This value is comparable with that measured at low temperatures for the tetragonal  $T_A$  phase,  $1.8 G^2$ , but for which detailed hydrogen atom positions are unknown.

### Spin-Lattice Relaxation Times

At temperatures greater than 250 K,  $T_1$  and  $T_{1\rho}$  decrease linearly in the  $\log_{10}(T_1$  or  $T_{1\rho})$  versus  $1/T$  plot, Fig. 2. At the highest temperatures at which measurements were possible it is seen that  $T_{1\rho}$  approaches a minimum value. This behavior is consistent with a motion of the protons associated with a single correlation time  $\tau_c$  which obeys the Arrhenius equation (2).

### $T_1$ Data

A minimum value in  $T_1$  could not be reached in the available temperature range (80–450 K).

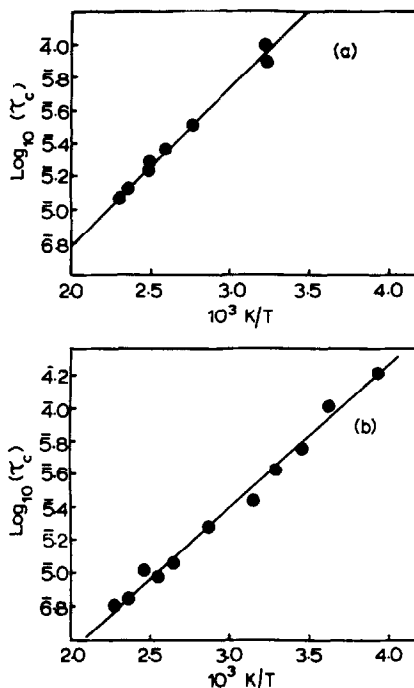


FIG. 4.  $\log_{10} \tau_c$  versus  $1/T$  for  $\tau_c$  values derived from (a) line width data for  $H_{0.39}WO_3$ , (b)  $T_{1\rho}$  data for  $H_{0.46}WO_3$ .

In this temperature range,  $\omega_0 \tau_c \gg 1$ ,  $T_1 \propto \tau_c$  and therefore the plot of  $\log_{10} T_1$  against  $1/T$  (Fig. 2) yields the value of  $E$  in Eq. (2). The best fit straight line of  $\log_{10} T_1$  versus  $1/T$  gives  $E = 14.0 (\pm 0.5)$  kJ mole $^{-1}$ . This value is in reasonable agreement with that found from the line narrowing and suggests that the same molecular motion is responsible for both phenomena.

### $T_{1\rho}$ Data

The dependence of  $T_{1\rho}$  on correlation time for a diffusion process is given by the following expression resulting from Jones's analysis for  $T_{1\rho}$  (9) and Torrey's theory of spin-lattice relaxation by translational diffusion (10–12):

$$T_{1\rho}^{-1} = K \left[ \frac{3}{2} y_1 G(k, 2y_1) + \frac{5}{2} y_0 G(k, y_0) + y_0 G(k, 2y_0) \right] \quad (3)$$

where  $K = \text{constant}$ ,  $y_1 = \frac{1}{2} \omega_1 \tau_c$ ,  $y_0 = \frac{1}{2} \omega_0 \tau_c$  (in this work  $\omega_1 = 165$  kHz and  $\omega_0 = 100$  MHz),  $G(k, y)$  is a function which Torrey has tabulated against  $y$  for both bcc and fcc lattices. In the

region of the  $T_{1\rho}$  minimum and at lower temperatures, Eq. (3) simplifies to

$$T_{1\rho}^{-1} = K \frac{3}{2} y_1 G(k, 2y_1). \quad (4)$$

Using the numerical values of  $G(k, y)$  tabulated by Torrey for a bcc lattice,  $\tau_c$  values were obtained as a function of temperature. These are plotted in Fig. 4(b) as  $\log_{10} \tau_c$  versus  $1/T$ . Assuming Eq. 2 the best fit straight line is obtained when  $E = 16.4 (\pm 0.7)$  kJ mole<sup>-1</sup> and  $\tau_c^0 = 69 (\pm 16)$  nsec. The value obtained for  $E$  is again in agreement with the values obtained from the line narrowing and  $T_1$  data. The  $\tau_c$  values derived from the  $T_{1\rho}$  data for  $H_{0.46}WO_3$  agree to within a factor of 2 with those obtained from the line width data for  $H_{0.39}WO_3$ .

#### The Low Temperature $T_1$ and $T_{1\rho}$ Data

Below 200 K both  $T_1$  and  $T_{1\rho}$  have nearly constant values (8 sec and 230 msec, respectively, at the lowest temperatures of measurement). These limiting values are probably caused by a relaxation mechanism independent of molecular motion and based on spin diffusion to paramagnetic impurities (13). An alternative mechanism based on the interaction of the nuclei with  $s$  electrons of the conduction band is unlikely to be important because Knight shifts have not been found for the isoelectronic alkali metal tungsten bronzes (14).

#### Conclusion

At the lowest temperatures of measurement (80 K) the hydrogen atoms in  $H_xWO_3$  are rigidly held at their lattice sites and only at temperatures greater than 250 K does proton mobility significantly affect the NMR parameters. A single relaxation process can account for the line narrowing, increase in  $T_2$  and decrease in  $T_1$  (and  $T_{1\rho}$ ) observed in the temperature range 250 K  $< T < 450$  K. From an analysis of these phenomena in terms of a correlation time  $\tau_c$  of the form  $\tau_c = \tau_c^0 e^{E/RT}$ , derived values of  $E$

TABLE I

Compound	$E$ /(kJ mole <sup>-1</sup> )	$\tau_c^0$ /(nsec)	Technique
$H_{0.46}WO_3$	14.0	—	$T_1$
$H_{0.46}WO_3$	16.4	69.0	$T_{1\rho}$
$H_{0.39}WO_3$	19.3	47.0	Broad line

and  $\tau_c^0$  are summarized in Table I. The behavior of the NMR parameters observed here is completely at variance with that found by Vannice, Boudart, and Fripiat (4) who concluded that the protons in  $H_xWO_3$  were mobile at  $T < 80$  K. We presume that the disagreement is due primarily to the use of samples prepared differently and probably of different chemical constitution.

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