

Inelastic Neutron Scattering Spectra of the Hydrogen Tungsten Bronze $H_{0.4}WO_3$

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Inelastic neutron scattering spectra of metallic $H_{0.4}WO_3$ show only the vibrations that would be expected of a metal hydroxide. The diffusion coefficient of the proton could not be detected from quasi-elastic scattering with the best available neutron spectrometer setting an upper limit to its value of 10^{-7} cm²/sec. Both these results confirm that this material is correctly described as a hydroxide.

Introduction

The hydrogen tungsten bronzes have aroused considerable interest because of the spillover they show when used as supports for platinum catalysts and because of their possible applications as electrochromic materials. Recent measurements on $H_{0.4}WO_3$, however, have led to conflicting descriptions in the literature.

Sienko and Oesterreicher (1) found an excitation at 690 cm⁻¹ in the infrared absorption spectra of various hydrogen tungsten bronzes. This was absent in the spectrum of unreduced WO_3 and was interpreted in terms of a hydrogen atom vibration where the hydrogen moves in and out of a coplanar square of oxygen atoms. Vannice *et al.* (2) were unable to make infrared transmission measurements on their sample of a hydrogen bronze because of the high optical density, but used spin-lattice relaxation measurements to find a proton self-diffusion coefficient with the value 0.7×10^{-5} cm²/sec at room temperature, a value which is of the order of that for water (2.14×10^{-5} cm²/sec). This evidence indicated that the closest analogs of the hydrogen tungsten bronzes were the transition metal interstitial hydrides. More recently, however, neutron diffraction (3)

work has shown that these materials are best described as nonstoichiometric oxide hydroxides and further proton spin relaxation measurements find very much smaller mobilities for the protons (4).

The metallic character of hydrogen tungsten bronze makes optical spectroscopic measurements difficult, as mentioned above, but the system is ideal for investigation with neutrons both in the molecular vibrational region and at very low frequencies where diffusive motions are directly detectable as quasi-elastic scattering.

Experimental

Reported here are studies of $H_{0.4}WO_3$ and WO_3 . The samples were in the form of single crystals with approximate average dimensions $\frac{1}{2} \times \frac{1}{2} \times \frac{1}{2}$ mm. In this form, little water could be adsorbed by the surfaces of the specimens, but as an extra precaution against water scattering the WO_3 sample was roasted in an oxygen atmosphere by being passed slowly through an oxygen coal gas flame. Background counts produced by the silica tubes used to contain the specimens were subtracted from the raw data.

Measurements of the vibrational spectra were made using a beryllium filter spectro-

meter (5) at the ILL Grenoble, and the 6H time of flight spectrometer at AERE Harwell. Diffusion coefficients were investigated using a back-scattering spectrometer at the ILL Grenoble. In the filter spectrometer measurements the sample was held at 80°K, whereas in the others it was held at ambient. The monochromated incident beam in the filter spectrometer was obtained from the 002, 113, and 115 planes of an aluminum crystal.

Results

The vibration spectra corresponding to unnormalized scattering cross sections are shown in Figs. 1 and 2. These represent measured values of I/I_0 corrected for background, empty container counts, and detector efficiencies.

Intensities in $d^2\sigma/d\Omega d\omega$ were obtained from Fig. 1 by correcting for incident beam monitor efficiencies and integrating the area under each peak. No correction for absorption was made as in the energy transfer region above 1000 cm^{-1} such corrections would amount to only 1 to 2%.

Discussion

In the spectral region above 560 cm^{-1} , excitations are observed at 1146, 2340, and 3326 cm^{-1} . The first of these at 1146 cm^{-1} is very similar in energy to that measured by infrared spectroscopy at 1156 cm^{-1} (8) for the transparent material of similar structure to $\text{H}_{0.4}\text{WO}_3$, $\text{In}(\text{OH})_3$ (9). In $\text{In}(\text{OH})_3$ this excitation has been assigned to the W-O-H bending vibration by analogy with a large number of other metallic hydroxides.

The observation of only one W-O-H deformation in the neutron spectrum implies a high symmetry of atomic neighbors, as would be the case if the hydrogen atom occupied the perovskite interstitial site. Neutron diffraction work, however, shows that the hydrogen atoms are displaced from this position toward a neighboring oxygen atom (3). Apparently, our spectrometer has insufficient resolution to detect the effects of this reduction in symmetry upon the vibration spectrum.

There is no evidence from the neutron scattering of any vibration at 690 cm^{-1}

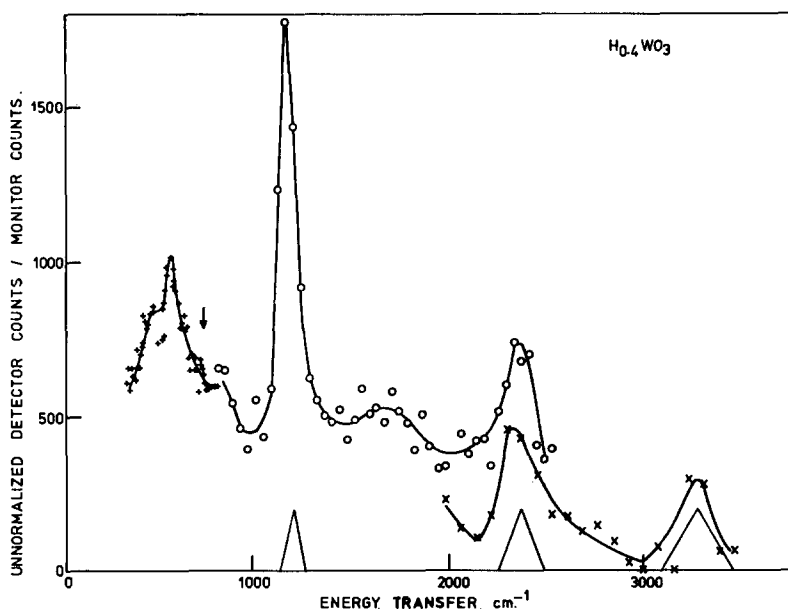


FIG. 1. Beryllium filter spectrum of $\text{H}_{0.4}\text{WO}_3$ at 80°K and scattering angle $\theta = 42^\circ$. +, O, and x represent the use of 111, 311, and 511 planes, respectively, of an aluminum monochromator. Triangles represent the resolution function.

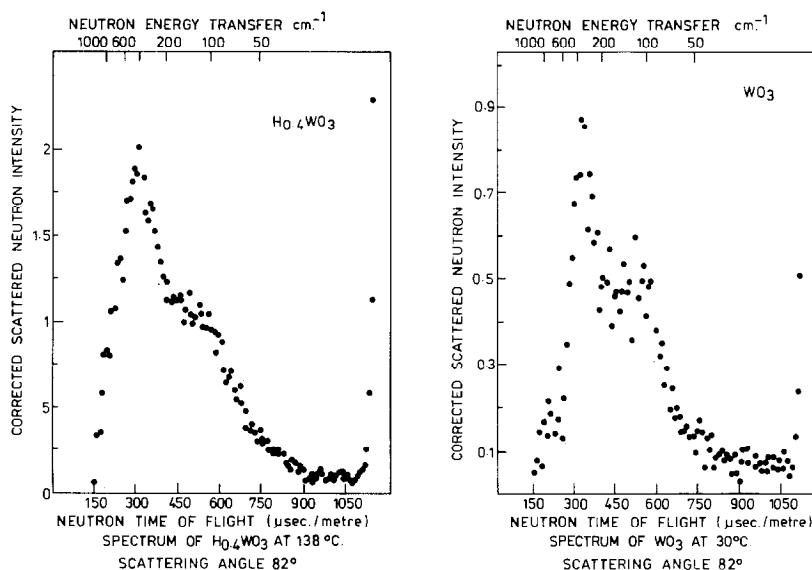


FIG. 2. Neutron time-of-flight spectra of WO_3 and $\text{H}_{0.4}\text{WO}_3$, at scattering angle $\theta = 82^\circ$.

(arrowed in Fig. 1) where previous authors had found a trampoline vibration (1).

The higher energy excitations are most likely to be the $0 \rightarrow 2$ and $0 \rightarrow 3$ transitions of the same oscillator, and an attempt is made below to provide a reasonable theoretical understanding of the experimental intensities.

The scattering law for a process in which a neutron loses n quanta of vibrational energy to a simple harmonic oscillator of frequency ω_0 is proportional to (10)

$$S_n = \exp\left(-\frac{\hbar\mathbf{K}^2}{2M\omega_0} \coth \frac{\hbar\omega_0}{2K_B T}\right) \exp\left(\frac{n\hbar\omega_0}{2K_B T}\right) I_n(y)$$

where M is the mass of the oscillator and $\hbar\mathbf{K}$ is the neutron's momentum change upon scattering; $y = \hbar\mathbf{K}^2/(2M\omega_0) \operatorname{cosech} [\hbar\omega_0/(2K_B T)]$; and $I_n(y)$ is the modified Bessel function of the first kind. In these experiments the detected scattered intensities are proportional to S_n since they are normalized to detected incident fluxes uncorrected for monitor efficiencies.

At the temperature of measurement, 80°K , $\hbar\omega_0/K_B T \gg 1$ so that the hyperbolic functions may be replaced by their asymptotic values, and $I_n(y)$ by $(1/n!)(y/2)^n$. Hence,

$$S = \exp\left(\frac{-\hbar\mathbf{K}^2}{2M\omega_0}\right) \frac{1}{n!} \left(\frac{\hbar\mathbf{K}^2}{2M\omega_0}\right)^n$$

Now the proton in $\text{H}_{0.4}\text{WO}_3$ differs from an ideal simple harmonic oscillator because of its interactions with the vibrations of other atoms in the lattice, and to take account of this the above expression can be modified by replacing the exponential term with a Debye-Waller factor obtained from neutron diffraction measurements. Only a measurement of an isotropic factor measured at 300°K is available in the literature, but assuming that this does not change between 300 and 80°K (because of the high frequencies of the contributing vibrations), then reasonable agreement is obtained between the calculated and experimental intensities.

One further probable contribution to the intensity near 3300 cm^{-1} is the oxygen-hydrogen stretching vibration fundamental whose intensity normalized to the intensity of the deformation vibration fundamental is given by

$$\frac{1}{2} \exp(-2W_v + 2W_\delta) \frac{\hbar\mathbf{K}^2/(2M_v)}{\hbar\mathbf{K}^2/(2M_\delta)}$$

where $\exp(-2W_v)$ and $\exp(-2W_\delta)$ are Debye-Waller factors at the momentum

transfers of the stretching and deformation vibrations, respectively.

In conclusion, the relative values for these predicted intensities are $\omega_{0\delta}:\omega_{1\delta}:\omega_{2\delta} + \omega_{0\nu} = 1:0.48:0.27 + 0.04 = 1:0.48:0.31$. This compares with the measured values of $1:0.32:0.22$, although the scattering in the region of the second harmonic is not sufficiently well defined for any great significance to be attached to its intensity ratio. (An estimate of the error of this intensity is $\pm 25\%$.) Further analysis would not be possible without accurate values of the temperature and \mathbf{K} -dependent Debye-Waller factors.

One conclusion from this calculation is that there is a need for either higher instrumental resolution or lower momentum transfers before it will be possible to resolve the second harmonic of the W-O-H deformation vibration from the stretching vibration fundamental using inelastic neutron scattering. This conclusion is obviously capable of generalization to other molecular solids.

The frequency ratio of $\omega_{1\delta}:\omega_{2\delta}$ is $1:2.04$, so it can be concluded that there is no evidence of any anharmonicity in the vibration.

In the low-frequency region of the beryllium filter spectrum a peak at 540.5 and a shoulder at 435 cm^{-1} are seen. The most likely origin of these excitations is the density of states of the oxide lattice activated to scatter neutrons by the protons. In confirmation of this, the time of flight spectra of WO_3 and $\text{H}_{0.4}\text{WO}_3$ (Fig. 2) both have broad peaks in their intensity at about 500 cm^{-1} so that the frequency distributions of the oxygen atoms and the protons to which the two spectra, respectively, are related must be strongly coupled.

The elastic scattering from the bronze was examined using the back-scattering spectrometer IN10 in an attempt to observe diffusion. No broadening of the elastic scattering was seen even at 0.97 \AA^{-1} so that the diffusion coefficient must be less than $10^{-7}\text{ cm}^2/\text{sec}$. This limit is lower by 2 orders

of magnitude than the first value determined by proton spin-lattice relaxation, and so again a conventional hydroxide picture is confirmed in accord with the diffraction and relaxation data obtained by Dickens and co-workers (3, 4).

Conclusion

The inelastic scattering in this paper shows:

- (a) that there is no hydrogen vibration occurring at 690 cm^{-1} in our material; and
- (b) that the description, of our material as a hydroxide, based upon previous workers' analysis of neutron diffraction data, is consistent with our vibration frequencies having similar values to those of the M-O-H bending vibrations in similar hydroxides.

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