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PARTIAL MOLAR VOLUMES OF HYDROGEN AND
DEUTERIUM IN NIOBIUM AND VANADIUM

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Partial molar volumes of hydrogen and
deuterium in niobium and vanadium

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INTRODUCTION

The group V B transition metals, vanadium, niobium and tantalum, are expanded by the addition of hydrogen in solid solution. Theoretical understanding of this dilation is not well developed, in part because the hydrogen state in a metal lattice is not easily characterized. However, predictions of isotope dependence in the lattice expansion induced by hydrogen and deuterium have been made by Flynn and Stoneham [1] and Wipf [2]. A small isotope effect in the lattice dilation produced by hydrogen and deuterium in tantalum has been measured by Pfeiffer and Peisl [3].

The partial molar volume of hydrogen $\bar{V}_H$ is a macroscopic measure of the solute induced lattice expansion. A thermodynamic definition of $\bar{V}_H$ is

$$\bar{V}_H = \left(\frac{\partial V}{\partial n_H} \right)_{T,P,n_j} \quad (1)$$

where V is the system volume and n_H is the number of moles of hydrogen added at constant temperature (T), pressure (P) and moles of other substances (n_j). For a uniform, macroscopic distribution of hydrogen in solid solution, the x-ray and geometrically determined volume increases are the same [4]. Hence, experimental determinations of the partial molar volumes of hydrogen have frequently been made by x-ray lattice parameter measurements as a function of hydrogen concentration. Several studies [2,5-8] have shown that up to

the solubility limit at room temperature the lattice expansion is proportional to the hydrogen concentration in niobium and vanadium.

X-ray diffraction cannot easily "see" extremely local lattice dilations. Lattice constant measurements reflect only the average hydrogen induced lattice expansion. The magnitude and extent of the local strain field surrounding the hydrogen atom in solid solution is a subject of some controversy [9-14]. Hydrogen occupies tetrahedral voids in niobium and vanadium at room temperature [15-17]. These voids have a structure that leads to the expectation of a tetragonal local distortion of the solid. However, it should be emphasized that the measured partial molar volume of hydrogen is a macroscopic property of the lattice. Random orientation of the hydrogen produced strain fields may be expected. Hence, the form of the local crystal deformation is of minimal importance in the measurement of $\bar{V}_H$.

X-ray diffraction lattice constant measurements do not give $\bar{V}_H$ in niobium or vanadium with a high degree of precision. Lattice constant changes are on the order of $0.002 \text{ \AA}$ per atomic percent hydrogen. Hydrogen solubilities at room temperature are about 3 at% and allow a maximum dilation of about $0.006 \text{ \AA}$. The partial molar volume of hydrogen is proportional to the lattice dilation and errors in $\bar{V}_H$ are proportional to errors in the lattice dilation.

Lattice constants can usually be measured reproducibly to 0.001 Å, and consequently the error in $\bar{V}$ would be about 16 relative percent.

This paper presents a new experimental technique to measure the partial molar volumes of hydrogen and deuterium in niobium and vanadium. The experiment exploits another thermodynamic definition of $\bar{V}_H$.

$$\bar{V}_H = \left(\frac{\partial \mu_H}{\partial P} \right)_{T, n_H, n_j} \quad (2)$$

Here μ_H is the chemical potential. If hydrostatic pressure is applied and maintained on one end of a hydrogen charged slab of niobium or vanadium, the chemical potential of the hydrogen in the high pressure region (μ_H^2) will be raised relative to the chemical potential in the low pressure region (μ_H^1). Thus hydrogen will move from the high to the low pressure end of the sample until a steady state is achieved. At steady state the following relation holds.

$$\mu_H(T, a_H^1, P_1) = \mu_H(T, a_H^2, P_2) \quad (3)$$

Here T is the temperature, P_1 is the pressure in the uncompressed portion of the sample and a_H^1 , a_H^2 are the hydrogen activities in the low and high pressure regions respectively. Equation 3 may be written as

$$\mu_o + RT \ln(C_H^1 \gamma_H^1) + \int_0^{P_1} \bar{V}_H dP = \mu_o + RT \ln(C_H^2 \gamma_H^2) + \int_0^{P_2} \bar{V}_H dP \quad (4)$$

where μ_0 is the reference state chemical potential and C_H^1 and C_H^2 are hydrogen concentrations in the high and low pressure regions respectively. The γ symbols represent the appropriate activity coefficients. Following studies [18] and [19], if hydrogen concentrations are kept low, $\gamma_H^1 = \gamma_H^2$ is a good approximation. Therefore Equation 4 may be expressed as

$$\bar{V}_H = \frac{RT}{P_2 - P_1} \ln\left(\frac{C_H^1}{C_H^2}\right). \quad (5)$$

The partial molar volume can be determined if C_H^1 , C_H^2 , P_1 , P_2 and T are known.

A modification of the above procedure allowed a precise determination of the difference between the partial molar volumes of hydrogen and deuterium ($\bar{V}_H - \bar{V}_D$) in either niobium or vanadium to be made. A single sample was charged with both hydrogen and deuterium. A portion of the sample was compressed causing both hydrogen and deuterium to move from the high to the low pressure portion of the sample until a steady state was reached. Mass spectroscopy was then used to accurately determine the ratio of hydrogen to deuterium in both the high and low pressure portions of the sample. The difference in the partial molar volumes is given by Equation 6.

$$\bar{V}_H - \bar{V}_D = \frac{RT}{P_2 - P_1} \ln\left(\frac{C_H^1/C_D^1}{C_H^2/C_D^2}\right) \quad (6)$$

This differential isotope experiment considerably reduces those errors inherent in direct pressurization experiments. In this experiment the effect of a number of errors was eliminated because they would affect the hydrogen and deuterium concentrations alike. For example, even if the pressure measurements were in error, both hydrogen and deuterium would respond to the same pressure. The differential isotope experiment is capable of measuring differences between partial molar volumes of hydrogen and deuterium as small as one percent. No measurement of the hydrogen or deuterium concentration is necessary either before or after steady state. Mass spectroscopic measurement of the hydrogen to deuterium ratio was of very high precision. Unlike conventional x-ray diffraction lattice parameter studies or linear expansion studies there was little or no disadvantage in using low hydrogen or deuterium concentrations since only the ratio of hydrogen to deuterium concentration was measured, and this can be easily measured even at low concentrations. Finally, the difference in partial molar volumes is measured in the same sample under virtually identical macroscopic stress states for both hydrogen and deuterium.

EXPERIMENTAL PROCEDURE

Sample Preparation

Niobium pellets (Du Pont D-3, Lot DH-715) were arc melted under an argon atmosphere. The resulting finger of niobium was cold rolled into 0.076 cm sheet. The samples were annealed at 10^{-5} Torr at 1000°C for one hour. A technique due to Peterson et al., [20] for reducing the oxygen content was employed. An electron beam melted button of high purity vanadium was cold rolled into 0.064 cm sheet. Samples the same length and width as the niobium blanks were cut from the as rolled sheet. All samples were electropolished and immediately electrolytically charged with hydrogen or deuterium or both hydrogen and deuterium to concentrations well below the H(D) solubility limit at room temperature. Any sample showing more than a 0.005cm variation in thickness was not used in the experiments.

Chemical analysis of the hydrogen charged samples gave 39, 1000 and 700 atomic ppm of N, O and C respectively. Analysis of the hydrogen charged vanadium samples gave 11, 140 and 180 atomic ppm of N, O and C respectively.

Direct Pressure Experiments

The electrolytically charged sample was placed between the hardened steel jaws of a hydraulic press and compressed. Each sample was positioned so that 1.72 cm of it's 2.7 cm length was inside and 0.98 cm was outside these jaws.

Figure 1. Position of the sample between the hydraulic press jaws

Figure 1 shows the position of the sample between the press jaws. Great care was taken in positioning the sample between the press jaws. This care was necessary to allow uniform loading of the high pressure portion of the sample. If the sample was not positioned correctly between the press jaws, when slight pressure was applied the press jaws would bind in their housing collar. In such a case the pressure was released and the sample repositioned. Pressure was again applied. This procedure was repeated until the housing collar could be easily slipped up and down on the jaws while the jaws were at full pressure. The sample was brought to pressure by pumping on a hydraulic cylinder. All samples were held at pressure longer than the times listed in Table 1. The rounded ends of the press jaws were designed to reduce unequal loading of the sample. If the ends of the jaws were flat and the vertical axis of the press jaws were not perfectly aligned in the direction of the applied force, cocking of the jaws and consequently unequal loading of the sample would occur. Calculated times to achieve 98% of steady state concentrations of $H(D)$ were about half of the minimum time that the pressure was maintained. Steady state times were estimated by calculating diffusion times for a flat plate of finite thickness but infinite length and width. A relatively impermeable surface oxide layer prevented hydrogen from leaving the samples during the experiment.

Table 1. Minimum time of pressure application

	Hydrogen	Time, seconds	
		Deuterium	Hydrogen+ Deuterium
Nb	2.7×10^5	4.2×10^5	4.4×10^5
V	2.5 "	3.6 "	4.2 "

Initial hydrogen concentrations were kept low enough so that the solubility limit was not exceeded in the low pressure portion of the sample at steady state. Exceeding the hydrogen solubility limit caused hydride to be precipitated, thus removing hydrogen from solid solution. This effectively fixes the hydrogen concentration in the low pressure portion of the sample at the solubility limit. Thus a greater than anticipated amount of hydrogen would be transported from the high and into the low pressure portion of the sample. This sort of behavior would cause an erroneously high value of the partial molar volume to be computed.

The stress in the compressed portion of the sample was not totally hydrostatic. Shear components exist around the periphery of the compressed portion of the sample. Cottrell [21] gives a relation for the pressure in a thin plate in compression as,

$$P = 1.15Y \exp[(2\mu/h)(a-x)], \quad (7)$$

where

Y = Yield stress,
 μ = Static coefficient of friction,
 h = Thickness of the plate,
 a = Half the width of the plate and
 x = Distance from the center of the plate.

The width of the nonhydrostatic region is (a-x). Yield stresses of niobium and vanadium were taken to be 210 MPa and 140 MPa respectively. The coefficient of friction was taken as 0.5. Figure 2 shows the theoretical pressure profile across the width of the niobium and vanadium samples in the high pressure region for a hydrostatic pressure of 1000 MPa.

Nonhydrostatic contributions to the total force on the samples were found by numerically integrating the pressure-area product over the nonhydrostatic region. Such calculations gave small corrections on the hydrostatic pressure of about 5% in most cases. Total force applied to the sample was measured on a Bourdon pressure gauge. This gauge was calibrated to directly show the applied force on the sample. Uncertainty in the applied force was $\pm 2\%$. Dimensions of the high pressure portion of the sample were measured with a vernier caliper and micrometer. Some slight spreading and thinning of the samples was observed at very high trial pressures. Little change in the dimensions of the sample was seen with the range of pressures actually used in the

Figure 2. Theoretical pressure profiles across the width of the high pressure region in the niobium and vanadium samples for a hydrostatic pressure of 1000 MPa

experiment. After pressurization small shallow striations were seen on the surface of the high pressure region of the samples. These striations clearly delineated the region where the press jaws touched the sample and thus allowed the area of the high pressure region to be measured with a vernier caliper. These striations covered the entire surface of the sample between the jaws of the press in all cases. The area of the high pressure region was measured with a precision of $\pm 1\%$.

After the steady state was achieved, the specimen was cut into sections as shown in Figure 3. The shaded pieces in Figure 3 were analyzed for hydrogen content by a vacuum extraction technique. At least five pieces from each of the high and low pressure regions of the sample were analyzed for hydrogen content. Average values were used to find C^1 and C^2 . The average concentrations had an uncertainty of $\pm 2\%$. Sectioning of the samples took less than 5 minutes so back diffusion was insignificant. Sample temperatures were $297 \pm 2\text{K}$.

One of the steady state hydrogen charged vanadium samples was sectioned longitudinally in the high pressure region. Nonhydrostatic areas near the interface and end of the high pressure region were cut off. The resulting lateral concentration profile is shown in Figure 4. The validity of Equation 7 is well-demonstrated. In the central

Figure 3. Sectioning of a direct pressure experiment sample

Figure 4. Steady state, lateral hydrogen concentration profile across the high pressure region of a vanadium sample

portion of the sample there was a uniform, constant and low hydrogen concentration due to the high hydrostatic pressure in that region of the sample. Higher concentrations of hydrogen were seen at the edges of the sample showing the lower nonhydrostatic stress state there. A typical steady state hydrogen concentration profile along the length of a niobium sample is shown in Figure 5. As expected, high hydrogen concentrations were seen in the low pressure portion of the sample and low concentrations in the high pressure region. A transition region is seen between the high and low concentration plateaus in the sample. The stress state is complex in this region and therefore, sections of this region were not used to determine the steady state hydrogen concentrations. Only sections of the sample from the constant concentration areas were used to determine C^1 and C^2 , i.e., the shaded pieces in Figure 3.

Differential Isotope Experiments

In this modification of the method, individual samples were charged with both hydrogen and deuterium. The sample was positioned in the press as in the single solute experiments and brought to pressure. After the steady state was achieved the sample was removed from the press. The nonhydrostatic regions were trimmed off and discarded. This left the high hydrostatic pressure region and the low pressure regions intact but separated from one another.

Figure 5. Steady state, longitudinal hydrogen concentration profile in a niobium sample

Hydrogen and deuterium were evolved from each of these regions by vacuum extraction and mass spectroscopic analysis of the gas gave the ratio of hydrogen to deuterium in the high hydrostatic and in the low pressure regions of the sample. The concentrations of H_2 , D_2 and HD were all measured on each sample. The relative concentrations of these gas species in a given sample showed they were an equilibrated mixture as evolved in the extraction system. Precision of the mass spectroscopic hydrogen to deuterium ratio was ± 0.002 or better. The mass spectroscopy analysis was performed by Gerald Flesch.

RESULTS

Direct Pressure Measurements

The partial molar volumes of hydrogen and deuterium are given in Table 2 with the standard deviation of each mean value. Comparison of these values with those of Table 3 shows that for niobium the lattice parameter method and the direct pressure measurement give essentially the same values. In vanadium the agreement is worse but the lattice parameter data for vanadium are rather sparse.

Table 2. Partial molar volumes of H and D in Nb and V from pressurization experiments

	$\bar{V}_H$ cm ³ /mol H	$\bar{V}_D$ cm ³ /mol D
Nb	1.78±0.09	1.77±0.12
V	1.82±0.06	1.90±0.08

No strong dependence of the partial molar volumes of hydrogen and deuterium on hydrostatic pressure or initial H(D) concentration was found. Figures 6-9 show plots of the partial molar volume versus hydrostatic pressure and initial H(D) concentration. Scatter in the vanadium data is less than in niobium results. However, the range of pressures and concentrations used is smaller in vanadium.

Table 3. Partial molar volumes of hydrogen in niobium and vanadium from lattice dilation studies

	$\bar{V}$ cm ³ /mol H(D)	Solute	Reference
Nb	1.7±0.2	H	[6]
	1.88±0.06	H,D	[3]
	1.8±0.6	H	[7]
	1.82±0.03	H,D	[13]
	1.6±0.1	H	[16]
	1.5	H	[8]
V	1.7±0.2	H	[5]
	1.58±0.08	H,D	[13]
	1.4	D	[22]

Figure 6. Partial molar volumes of hydrogen and deuterium in niobium versus hydrostatic pressure

Figure 7. Partial molar volumes of hydrogen and deuterium in vanadium versus hydrostatic pressure

Figure 8. Partial molar volumes of hydrogen and deuterium in niobium versus initial H(D) concentration

Figure 9. Partial molar volumes of hydrogen and deuterium in vanadium versus initial H(D) concentration

Standard deviations in the partial molar volumes from these direct pressure measurements are large enough so that no difference between $\bar{V}_H$ and $\bar{V}_D$ could be conclusively shown. The difference between $\bar{V}_H$ and $\bar{V}_D$ could hardly be more than about 13 percent in either niobium or vanadium. Such a small difference in the partial molar volumes would hardly be enough to account for the large differences that have been reported in the activation energies for diffusion. Measurements of lattice constant changes by x-ray methods have little chance of observing differences between $\bar{V}_H$ and $\bar{V}_D$ as small as 10 percent. At 300 K the solubilities of hydrogen in vanadium and niobium are 2.5 and 3.8 atomic percent respectively [23,24]. The solubilities of deuterium and hydrogen in niobium are about equal [25]. Studies suggest greater solubility of deuterium than hydrogen in vanadium [26,27]. However, the higher solubility of deuterium may be due to trapping at interstitial impurities. Maximum lattice parameter increases then, should be only on the order of 0.006 Å. Since two sets of measurements must be made to find the difference in the partial molar volumes, twice the individual measurement error is introduced in evaluating the isotope effect.

Differential Isotope Effects

The experimental method using mass spectroscopy to evaluate the difference between $\bar{V}_H$ and $\bar{V}_D$ has the advantage

of materially decreasing or entirely eliminating many of the sources of error encountered in making two direct pressure measurements. Unlike x-ray lattice constant or linear expansion studies, no measurement of the absolute hydrogen or deuterium concentration is necessary. Only the ratio of hydrogen to deuterium needs to be measured. Unfortunately, this method does not give quantitative, individual determinations of $\bar{V}_H$ or $\bar{V}_D$. Only the difference between $\bar{V}_H$ and $\bar{V}_D$ may be found quantitatively, but this difference may be determined with a precision as small as one percent of the partial molar volume.

The difference in the partial molar volumes of hydrogen and deuterium in niobium and vanadium are given in Table 4 along with the associated standard deviations of the mean. Average values of the difference of the partial molar volumes

Table 4. Difference between the partial molar volumes of H and D in Nb and V from mass spectroscopy experiments

	$\bar{V}_H - \bar{V}_D$ cm ³ /mol H(D)	$\frac{\bar{V}_H - \bar{V}_D}{(\bar{V}_H)_{ave}} \times 100\%$
Nb	+0.18±0.02	+10.0±1.1
V	-0.11±0.01	-6.0±0.6

in percent are also given.

Small isotope effects are seen for hydrogen and deuterium in both vanadium and niobium. In niobium the partial molar volume for hydrogen is 10% greater than for deuterium. In vanadium deuterium has a 6% larger partial molar volume than hydrogen. No variation in $\bar{V}_H - \bar{V}_D$ was seen in the data presented in Table 5 with pressure or initial hydrogen concentration.

These results showing an isotope effect in the partial molar volume and one that has a different sign in vanadium than in niobium are quite interesting and unexpected. Many theoretical discussions of hydrogen induced lattice expansion consider the vibrating H(D) atom as a quantized harmonic oscillator. In such a model the amplitude of vibration of the hydrogen is supposed to be larger than that of deuterium. This larger amplitude is often used to predict a larger partial molar volume for hydrogen. Such simple models seem to lack good predictive powers.

The significance of the observed isotope effect was sufficient to justify a rigorous search for other experimental causes for the observed isotope ratios. Any kinetic process involving hydrogen and deuterium can show effects due to the mass difference. The mass spectroscopy measurements were carefully checked to eliminate fractionation during sampling and analysis of the gas. One other source

Table 5. Hydrostatic pressure, initial solute concentrations and difference in the partial molar volumes of H and D from the mass spectroscopic experiment

	P MPa	Initial H Concentration, H/M	Initial D Concentration, D/M	$\frac{\bar{V}_H - \bar{V}_D}{(\bar{V})_{ave}} \times 100\%$
Nb	510	1.14	0.70	11.5
	360	0.56	1.34	7.6
	510	0.32	0.34	8.8
	740	0.58	0.69	12.0
V	640	1.09	0.56	-4.7
	550	1.02	0.62	-6.2
	640	0.71	0.29	-4.9
	690	0.33	0.42	-7.1
	640	0.68	0.35	-8.3
	620	0.55	0.28	-4.8

of kinetic interference in this experiment is the slow change in the hydraulic pressure during an experiment. This pressure fell slowly over a period of time due to small leaks in the hydraulic cylinder packing. Periodically, the pressure was restored by pumping to the original value. The possibility was examined that this variation in pressure could account for an observed difference in the H/D ratio between the high and low pressure portions of the sample.

Hydrogen diffuses faster than deuterium in niobium and vanadium [28]. This difference in diffusion coefficients leads to different times to reach the steady state for hydrogen and deuterium in the same sample. Upon compression of the sample, hydrogen should move more rapidly from the high to the low pressure region than deuterium. Consider the pressurized sample to be initially at steady state. A drop in pressure causes hydrogen and deuterium to move from the high to the low pressure portion of the sample. If it is assumed that most of the change in concentration between the high and low pressure portions of the sample is due to hydrogen, i.e., C_D^1/C_D^2 is essentially unchanged, then the error in $\bar{V}_H - \bar{V}_D$ is approximated by the change in C_H^1/C_H^2 . For the largest drop in pressure allowed during a run, the difference in the concentration of hydrogen in each portion of the sample was calculated and the change in $\bar{V}_H - \bar{V}_D$ was only about two relative percent. This is only

twice as large as the uncertainty introduced by the mass spectroscopy instrumentation. This maximum effect is only one third of the observed value of $\bar{V}_H - \bar{V}_D$ for vanadium and one fifth of the value for niobium.

To experimentally test these calculations, the change in concentration of hydrogen and deuterium due to a fall in pressure on several vanadium samples was measured. After the steady state was reached, the pressure on the sample was allowed to fall by four percent over a period of 24 hours. The sample was then removed from the press. The high and low pressure regions were each cut in half so that in each region a portion of the sample bordering the interface and one bordering the far end of the sample was obtained. The ratio of hydrogen to deuterium in each of these four sections was measured, thus giving this ratio along the length of the sample.

Any difference between the ratios of hydrogen to deuterium from the same region was less than the precision of the mass spectroscopy. Therefore, the error introduced in $\bar{V}_H - \bar{V}_D$ due to the change in pressure was less than one percent. The value of the error in $\bar{V}_H - \bar{V}_D$ introduced by the pressure variation probably was smaller than the calculated one because the calculation assumed that hydrogen moved instantaneously and deuterium not at all. In reality, although hydrogen moves faster, there is not that much

difference. The difference in concentration ratios between the high and low pressure regions gave a value of $(\bar{V}_H - \bar{V}_D)/(\bar{V}_H)_{ave}$ of -6.2%, which is the mean value for vanadium. The ratio of the diffusion coefficients of H to D is about the same in both vanadium and niobium. Errors of a similar small magnitude due to pressure changes can be expected in niobium.

DISCUSSION

As a first approximation the change in volume of metals upon the addition of hydrogen may be viewed as an attempt of the hydrogen and host metal atoms to minimize their potential energy [29-31]. The derivative of the hydrogen potential energy with respect to atom position gives the force exerted on the hydrogen, and consequently, on the metal atoms. If the force constants between the metal atoms and the hydrogen isotopes were known, $\bar{V}$ could be determined [32]. Unfortunately, accurate expressions for these quantities in vanadium and niobium are not known. Further, it is not easy to measure extremely local hydrogen induced strain fields. Hence, the actual forces and the associated lattice atom displacements are not well-known. In light of the preceding discussion it is remarkable that many metals have similar values of $\bar{V}_H$. Table 6 gives experimentally determined partial molar volumes of hydrogen in various alloys. No marked dependence of $\bar{V}_H$ is seen on crystal structure or on electronic structure in these metals.

Vibrational motion of the hydrogen atom is largely responsible for isotope effects in the partial molar volume of hydrogen. Both hydrogen and deuterium have similar electronic structures. Therefore, the forces on and displacements of surrounding lattice atoms due to stationary isotopes would be nearly equal. A model based on static

Table 6. Partial molar volumes of hydrogen in various alloys

Alloy	$\bar{V}_H, \text{cm}^3/\text{mol H}$	Lattice	Reference
Er	2.09	Hcp	[33]
Tm	2.08	Hcp	"
Lu	1.57	Hcp	"
Y	1.59	Hcp	"
V	1.82	Bcc	This Study
Nb	1.78	Bcc	"
Ta	1.57	Bcc	[3]
α -Fe	2.0	Bcc	[34]
Pd	1.4	Fcc	[35]
(Pd-6%Pt)	1.4	Fcc	"
(Pd-12%Pt)	2.4	Fcc	"

atoms is unrealistic since it ignores the important oscillatory motions of the interstitial atoms.

Hydrogen has extremely high vibrational frequencies in niobium and vanadium. If it is assumed that hydrogen and deuterium act as simple harmonic oscillators, quantum theory predicts a larger amplitude of oscillation for the isotope of smaller mass. Neutron studies tend to show larger root-mean-square displacements of hydrogen atoms than deuterium atoms from their equilibrium positions in the metal lattice [36]. This larger displacement is often used to predict a larger partial molar volume for the lighter isotope. Such speculation may account for the isotope effect observed in niobium, but is unable to account for the isotope effect in vanadium.

Inelastic neutron scattering studies of hydrogen and deuterium in vanadium, niobium and palladium show considerable broadening of the hydrogen local mode peaks [37]. The width of these peaks depends, at least in part, on anharmonic lattice vibrations. Thermal expansion is a well known consequence of anharmonic atom vibrations. Anharmonic atom motion means the hydrogen vibrations are not symmetrical about their equilibrium point. Such vibrations can cause multiphonon creation or absorption processes and coupling between local and band modes [38]. In addition, degeneracy of local mode orthogonal hydrogen vibra-

tional components may be lifted by such oscillations. In general, neutron studies do not have sufficient precision to isolate these phenomena from one another. However, even relatively small effects could account for the isotope effect in vanadium. The ratio of hydrogen to metal atom mass is larger in vanadium than in niobium. Therefore, coupling of local and band modes would be greater in vanadium than in niobium.

CONCLUSIONS

Lattice dilation studies in Table 3 and direct pressure experiments gave comparable values for the partial molar volumes of hydrogen and deuterium in niobium and vanadium. Small isotope effects in the partial molar volume of hydrogen were measured in both metals by the differential isotope method. Hydrogen had a larger partial molar volume than deuterium in niobium, but the reverse was true in vanadium.

The direct pressurization method gave values of the partial molar volume of hydrogen about as well as the best available x-ray diffraction lattice parameter studies. The differential isotope method employed in determining isotope effects in the partial molar volumes had significantly better precision than could be achieved with x-ray diffraction lattice parameter measurements or linear expansion studies. The major advantages of the differential isotope method are exceptional precision and great simplicity. Differences as small as one percent of the partial molar volume can be determined. This is almost an order of magnitude gain in precision over x-ray diffraction lattice parameter measurements.

The isotope effect measured in niobium can be represented as being due to the larger amplitude of vibration of the hydrogen atom than the deuterium atom in the metal lattice. Since hydrogen has a larger mean

displacement from the equilibrium position than does deuterium, the average force hydrogen exerts on the metal atoms is greater than the force deuterium exerts. The isotope effect in vanadium is likely a result of anharmonic effects in the lattice and local vibrational modes.

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