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by

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EFFECTS OF HYDROSTATIC PRESSURE ON THE CHANGES IN ELASTIC CONSTANTS CAUSED BY HYDROGEN IN VANADIUM AND $Nb_{53}Ta_{47}$*

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Abstract

Hydrogen dissolved in V, Nb or Ta or their solid solutions causes the C' shear modulus to decrease, whereas C_{44} increases. These appear to be entirely different effects, with ΔC' being a result of interstitial relaxation and ΔC_{44} arising from the electronic contribution. The apparent inverse dependence of ΔC', i.e., relaxation strength, on atomic volume of the alloys implies that the positive hydrostatic pressure derivative of C' should decrease with addition of H. This prediction has been tested with duplicate measurements at ANL and at HIG on two different vanadium samples with measurements of C', C_{44} and K (bulk modulus) to 3kb. The results show dC'/dP decreasing significantly by 8% and 6.5%, respectively at HIG and ANL, with no significant changes in dC_{44}/dP or dK/dP. A second experiment on the alloy $Nb_{53}Ta_{47}$, showed dC'/dP decreasing by 10% with addition of 4.4 at. % H, with no changes in dC_{44}/dP or dK/dP.

1. Introduction

Recent studies[1,2,3] have consistently shown that the addition of hydrogen (H), and its isotopes, to the unalloyed Group V metals, V, Nb, and Ta causes relatively large decreases in the elastic shear moduli C' and increases in C_{44} when the H concentration is limited to the interstitial solid-solution range. Figure 1 shows the observed effect in vanadium[1]. At a temperature of 300 K the addition of 1.3 a/o H caused a relative change in C', i.e., ΔC'/C', of -25.2×10^{-3}. On cooling, the gradual precipitation of the hydride beginning at ∿250 K, caused C' to return to a value near but slightly greater than the hydrogen-free value. The relative effects at 300 K on the three metals, V, Nb, and Ta are very close to linear in C' vs. at.% H with (ΔC/C')/at.% H of -19×10^{-3}, -5×10^{-3} and -1×10^{-3}, respectively. Except for the anomalous behavior in the high V alloys, Fig. 2 shows the relatively continuous changes of the H effect in the binary substitutional solid solutions of V-Nb and Nb-Ta.[4]

In view of the relatively large but nearly linear increases in atomic volume on adding Nb to V and the very small increases in atomic volume from Nb to Ta, there is clearly a strong dependence of the ΔC' on atomic volume. This is consistent with the explanation for ΔC' that is based on anelastic relaxation of the proton, rather than on electronic effects, and it is the purpose of the present research to show that the variations in ΔC' are indeed primarily derived from atomic volume differences.

The mechanism for associating the ΔC' relaxation with volume is commonly referred to as the Snoek model originally proposed for the anelastic relaxation due to carbon interstitials in Fe.[5] It is commonly known that carbon as well as the gaseous atoms, N, O and H are retained as interstitial solutes in the b.c.c. transition metals, with a preference for the octahedral sites for C, N and O and tetrahedral sites for H. When either of these two interstitial positions are occupied the lattice is elastically extended in one of the cube, <100> directions by a strain λ_1 and contracts equally along the orthagonal <010> and <001> axes by λ_2 strains. Since the interstitial strains will be equally distributed among the three cube axes, the lattice will show only a macroscopic volume increase, but on the atomic level there will be a tetragonal distortion. When an elastic wave is propagated at a frequency $\omega < 1/\tau$, where τ is the interstitial jump period, with displacements that cause contraction of one of the extended axes and expansion of the other two axes, i.e., a C' shear or a $E_{100} = 1/S_{11}$ extension, there will be a concurrent anelastic relaxation. The relaxation strength is dependent on $\lambda_1 - \lambda_2$ according to the following model equation:

$$\frac{\Delta C'}{C'} = -\frac{2\,C_o(\bar{V}\,C')}{3kT}\,(\lambda_1 - \lambda_2)^2 \qquad (1)$$

where C_o is the relative concentration of interstitial atoms, $\bar{V}$ is the atomic volume and the Boltzman kT term is intended to account for effects of temperature T on the equilibrium distribution of tetragonal axes among the three cube axes.[6]

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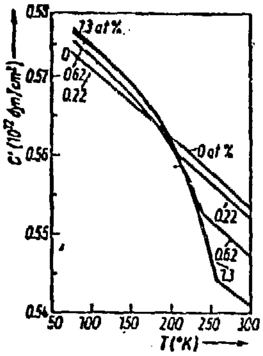

Fig. 1. Effect of increasing hydrogen concentrations on the temperature dependence of C' in a vanadium crystal. (Ref. 1)

There are, then two ways that $\bar{V}$ is related to $\Delta C'$: 1) the absolute value of $\Delta C'$ will increase directly with $\bar{V}$, 2) the inverse effect where $(\lambda_1-\lambda_2)$ increases with decreasing volume. The latter variation has indeed been verified for deuterium in Nb, where the effects of the tetragonal distortion on the diffracted intensities of γ-rays have been shown[7] to increase very significantly under hydrostatic pressures. Thus, hydrostatic pressure should also increase the absolute value of $\Delta C'$ and the measurement of the rate of this increase should be of value in confirming our assumption that the variation of $\Delta C'/C'$ among V, Nb, and Ta and their alloys is primarily due to atomic volume differences.

It should be noted that the assumption of the Snoek model as an explanation for $\Delta C'$ is not generally accepted[2] because of, (a) the absence of a 1/T dependence for $\Delta C'/C'$, (b) the absence of tetragonal-distortion evidence in diffuse scattering of x-rays or neutrons[8] at atmospheric pressure and (c) the absence of an internal friction peak in Nb or Ta when the oxygen and carbon impurities are removed by ultra-high-vacuum annealing.[9] None of these arguments are, however, without qualification in regard to either accuracy of the model or accuracy of measurement. Since the $(\lambda_1-\lambda_2)$ values for H in these b.c.c. metals are nearly an order of magnitude smaller than those for O, N, or C, the techniques that have been used for direct detection are perhaps lacking in the necessary resolution.

2. Experimental Procedure

The technique used here to detect the changes in $\Delta C'$ with atomic volume is to measure the hydrostatic pressure derivative of C', dC'/dP, in two different vanadium crystals and a crystal of random substitutional binary alloy $Nb_{53}Ta_{47}$. As illustrated in the schematic plot of Fig. 3, an increase in $\Delta C'$ with increasing pressure, P, necessarily requires a decrease in dC'/dP with increasing H. In anticipation that the changes in dC'/dP, especially in V, will be small, because of the limited terminal solubility of H at room temperatures, it was necessary to be reasonably certain that the possible errors in measuring changes in ultrasonic velocities with pressure did not bias the significance of the conclusions. Since the largest errors are associated with the changes in transducer resonance frequency and changes in impedance of the transducer-sample coupling cement with pressure, the experiments on vanadium were carried out at two different laboratories, with different equipment and samples. The measurements at the Hawaii Institute of Geophysics (HIG) were carried out with a pulse-superposition apparatus, as described by Katahara et al.[10] The measurements at Argonne National Laboratory (ANL) were carried out with a phase comparison system. In both cases the wave frequencies were in the range of 20-60 MHz, with careful adjustments to match the transducer resonance frequency changes with pressure.

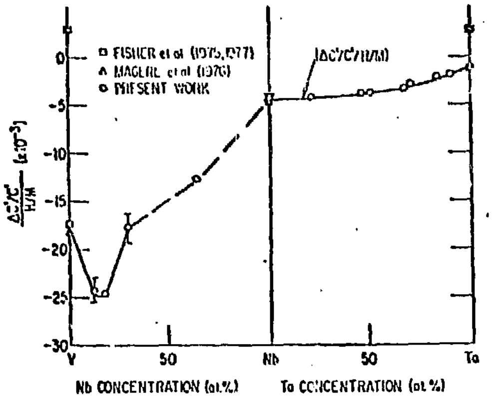

Fig. 2. Relative change in C' for H/M = .01 in V-Nb and Nb-Ta solid solutions.

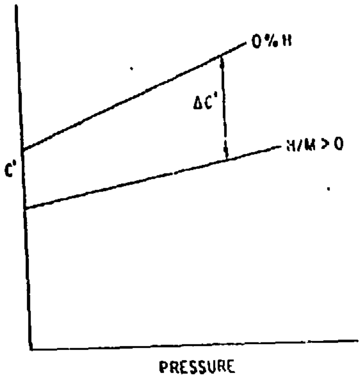

Fig. 3. Schematic example showing decrease in dC'/dP with H if $\Delta C'$ increases with pressure.

Both vanadium samples were made by electron beam zone melting, but at different locations. Hydrogenation and degassing of the crystals were carried out at ANL by Westlake, as described in Ref. 1. The measurements at ANL also included a crystal of $Nb_{53}Ta_{47}$, random substitutional alloy.

3. Results

The results are given in Table 1. The probable errors given for the results of the phase comparison method V#2 reflect the scatter in the results for several repeated pressure runs, with a variation in bonding agents using V9 Dow resin and Nonaq stopchuck grease. A greater precision was obtained in the pulse superposition data, V#1.

Although there are differences in the absolute values of dC'/dP in vanadium determined at HIG and ANL, the changes in dC'/dP with addition of H are in good agreement, i.e., 8% decrease at HIG vs. 6.5% decrease at ANL, for 1 a/o increase in H. For the alloy the decrease in dC'/dP is 2% per a/o H. In contrast, no significant effects of H were found for dC_{44}/dP or dK/dP.

Table 1. Hydrostatic pressure derivatives at 300 K of C', C_{44} and K with and without H.

	dC'/dP	dC_{44}/dP	dK/dP
V#1 (HIG)	1.042 ± .006	0.185 ± .003	4.26 ± 0.03
V#1 + 2.04 H	0.87 ± .01	0.188 ± .005	4.28 ± 0.04
V#2 (ANL)	0.94 ± .01	0.09 ± .03	5.21 ± 0.13
V#2 + 2.15 H	0.81 ± .03	0.09 ± .03	5.05 ± 0.15
$Nb_{53}Ta_{47}$	0.94 ± .01	0.60 ± .01	4.49 ± 0.13
$Nb_{53}Ta_{47}$ + 4.39 H	0.85 ± .01	0.61 ± .01	4.23 ± 0.6

4. Evaluation of $(\lambda_1-\lambda_2)$ Changes with Volume

Our specific objective is to determine the change in $(\lambda_1-\lambda_2)$ for vanadium with the volume decrease caused by hydrostatic pressure and to compare the results with the observed effects of volume changes caused by alloying in the Nb-V and Nb-Ta binary solid solutions. To calculate $(\lambda_1-\lambda_2)$ from Eq. 1 we need to evaluate the changes in $\Delta C'/C'$ and in the product $(\bar{V}\,C')$ with hydrostatic pressure. The results are given in Table 2, from which it is deduced that

$$\frac{d(\lambda_1-\lambda_2)}{dP} \approx 0.2 \times 10^{-3}/\text{kbar} . \qquad (2)$$

From the bulk modulus, K, for vanadium

$$\frac{\Delta\bar{V}/\bar{V}}{dP} = -0.637 \times 10^{-3}/\text{kbar} \qquad (3)$$

and thus

$$\frac{\Delta(\lambda_1-\lambda_2)}{\Delta\bar{V}/\bar{V}} = -0.3 . \qquad (4)$$

Since the changes in atomic volume, $\bar{V}$, with composition are well established for V → Nb,

$$\frac{\bar{V}_{Nb} - \bar{V}_{V}}{\bar{V}_{V}} = 0.277 \qquad (5)$$

we can predict from Eq. (4) that

$$\Delta(\lambda_1-\lambda_2)_{V \rightarrow Nb} \approx -0.08 \qquad (6)$$

or that $(\lambda_1-\lambda_2)$ at P = 0 for Nb should be 0.03. This is to be compared with the value of 0.05 obtained[1] from $\Delta C'/C'$ at P = 0. This remarkably good agreement suggests that the gradual changes in $\Delta C'/C'$ with composition, given in Fig. 2 are primarily the result of the volume changes and the Snoek relation given in Eq. 1.

Table 2. Calculation of $(\lambda_1-\lambda_2)$ at P = 0 and P = 3 kb from Equation (1).

$$(\lambda_1 - \lambda_2) = (\Delta C'/C')/(\bar{V}\,C') \cdot \frac{3}{2}\,KT^{\;1/2}$$

	$\frac{\Delta C'}{C'}$/at.%H	$\bar{V}\,C'$ (10^{-12} ergs)	$\lambda_1 - \lambda_2$
P = 0	21.0×10^{-3}	9.89	0.1149
P = 3 kb	21.33×10^{-3}	9.92	0.1156
Change in %	1.44	0.3	0.6

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