

Stress-induced site change of H in V observed by channeling experiments

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The lattice location of H in α -VH_{0.1} was determined at 150 °C with the channeling method using the nuclear reaction ${}^1\text{H}({}^{11}\text{B}, \alpha)\alpha\alpha$. A drastic change from *T* sites for the H to a displaced-*T* or 4*T* configuration was observed when internal stress was introduced by thermal cycling, i.e., by precipitation and redissolution of the β phase. As the internal stress estimated by x-ray diffraction was comparable to the external stress which induces enormous diffusion enhancement (superdiffusion), it is suggested that the observed stress-induced site change underlies the occurrence of superdiffusion of H in V.

Recently, Suzuki, Namazue, Koike, and Hayakawa¹ reported that the diffusivity of H in V is enhanced enormously by application of tensile stress along the $\langle 111 \rangle$ direction, and concluded with the help of their Huang scattering experiments that it is a consequence of stress-induced site change *T* (tetrahedral site) \rightarrow 4*T* (a group of four *T* sites). However, their observation of "superdiffusion of 4*T* hydrogen" has since been questioned by Metzger² and Schober and Golczewski,³ and still remains in dispute. The purpose of this Rapid Communication is to report on our first results of channeling experiments on H in V, especially on stress-induced site changes which, we believe, are closely related to the observation of Suzuki *et al.*¹

The lattice location of hydrogen was determined by utilizing the nuclear reaction ${}^1\text{H}({}^{11}\text{B}, \alpha)\alpha\alpha$, measuring the total yield of particles. Because of the lower sensitivity of this reaction for hydrogen detection in comparison with a more familiar $\text{D}({}^3\text{He}, p){}^4\text{He}$ reaction, the hydrogen concentration in specimens must be reasonably high. In the present experiment, the concentration was chosen to be VH_{0.1}. Specimens were cut from a single crystal (99.95% pure vanadium supplied by Aremco Corporation) into disks of 1.5 mm thick, and chemically polished. In order to introduce hydrogen up to the concentration of VH_{0.1} without ever forming β precipitates before observation, hydrogen was electrolytically charged into one-half of the disk (serving as a reservoir) up to the average concentration of VH_{0.2}, and was subsequently diffused into the remaining half (serving as a specimen) by heating the crystal on a target holder up to 150 °C, the temperature well above the α -(α + β) phase boundary (~ 110 °C) for the composition VH_{0.1}. To ensure homogeneous distribution of hydrogen, channeling experiments were performed at 150 °C after holding the specimen at this temperature for 24 h.

The collimation of the incident ${}^{11}\text{B}^{2+}$ beam (2.02 MeV) was better than 0.057° for the $\{111\}$ planar channel, and 0.076° in other cases. The crystal orientation was set to within $\pm 0.004^\circ$. The ${}^{11}\text{B}^{2+}$ beam was 1.0 mm in diameter, with the intensity of about 1 nA. Both α particles and backscattered ${}^{11}\text{B}$ were measured as a function of angle between the direction of the beam and axial or planar channels. For each measurement, the irradiation dose was accumulated to 2.25 μC . More details of the experiment were described in our previous paper on H in Ta.⁴

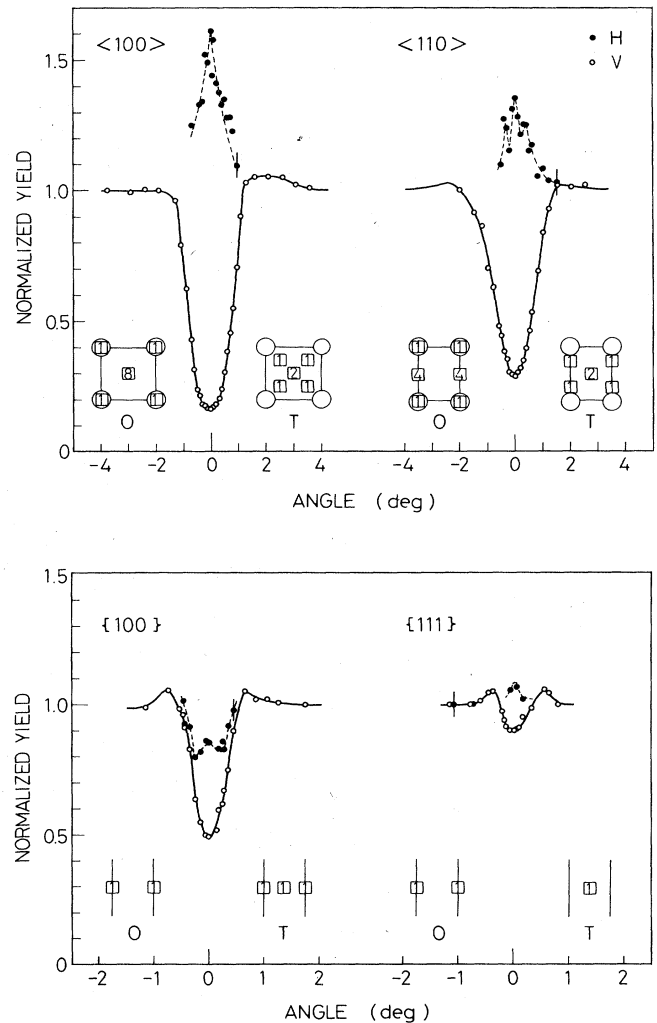


FIG. 1. Angular profiles of α particle and backscattered ${}^{11}\text{B}$ yields across $\langle 100 \rangle$ and $\langle 110 \rangle$ axes, and $\{100\}$ and $\{111\}$ planes in VH_{0.1}. The full curves and the dashed curves have been drawn to guide the eye. These angular scans were made at 150 °C with ${}^{11}\text{B}^{2+}$ beam of 2.02 MeV.

Results of the angular scans are shown in Fig. 1 for two axial channels, $\langle 100 \rangle$ and $\langle 110 \rangle$, and two planar channels, $\{100\}$ and $\{111\}$. The projections of O (octahedral) and T sites on the plane perpendicular to the axis or the plane in question are shown in the insets. The circles and the lines represent the projections of atomic rows and planes, respectively. The squares represent the projected positions of interstitial sites with their relative weights indicated by numbers in the squares. From the results on $\{100\}$ and $\{111\}$ planar channels, it was unambiguously concluded that most H atoms are located on T sites. The results on $\langle 100 \rangle$ and $\langle 110 \rangle$ axial channels are also consistent with this conclusion. [The position of two subsidiary peaks observed in the $\langle 110 \rangle$ axial scan, located at $\pm 0.35^\circ$ from the center, is consistent with the position expected for the T site ($\pm 0.31^\circ$) based on Eq. (1) below.] The T -site occupancy of H in V in the α phase has already been concluded from other experiments, including neutron diffraction,⁵ inelastic neutron scattering,^{6,7} and Huang scattering of x rays.¹ Systematics of site occupancies of hydrogen in bcc metals and its implications have been discussed by Fukai.^{8,9}

After the measurements at 150°C described above, the specimen was cooled to room temperature at the rate of 0.8 K/min and was kept there for 24 h. It was then reheated to 150°C at the rate of 0.35 K/min , and kept there for 24 h before the angular scan for a $\{100\}$ channel was made. The result is shown in Fig. 2. One of the most important findings of the present experiment is that the profile of the α yield is markedly changed by the heat treatment. After the heat treatment, the profile consists of a wide dip with approximately the same width as that of the ^{11}B dip, and two shoulder peaks located at about $\pm 0.25^\circ$. This result indicates that a major proportion of H atoms occupy interstitial sites displaced from normal positions of T sites (see the in-

set). A similar channeling profile was observed by Carstensen for D atoms trapped to N in Ta, and was attributed to the displaced- T configuration.¹⁰ We shall here assume, from symmetry considerations, that the observed profile originates from displaced- T (dis- T) or $4T$ configurations, in both of which the position of maximum density of hydrogen is displaced towards the O site. (The channeling experiment cannot distinguish between dis- T and $4T$ configurations.) The displacement can be estimated from the position of the two small peaks by using the relation

$$E\psi^2 = U(r_l) \quad (1)$$

where ψ is the angle for the peak position, E the incident beam energy, and $U(r_l)$ the continuum potential at the projected interstitial site in the channel. The potential can be calculated by using the Erginsoy formula.¹¹ The displacement from T site, thus deduced, amounts to 0.44 \AA , which, in comparison to the T - O distance of 0.76 \AA , means that the position of maximum density is closer to O sites than T sites.

A recent theoretical calculation¹² has shown that, as the vanadium lattice is elongated along one of its cube axis (z axis), the most stable self-trapped configuration changes continuously: $T \rightarrow \text{dis-}T \rightarrow 4T \rightarrow O_z$. The wave function of a H atom, originally localized on one of the four T sites around an O_z site, is gradually displaced towards the O_z site (dis- T), and after going through a resonant state of these four dis- T configurations ($4T$), finally attains a single maximum localized around the O_z site. Conversely, it is expected that the presence of tensile stress, either external or internal, may induce transition from T to dis- T or $4T$ configurations.

In the present experiment, precipitation of the β phase on

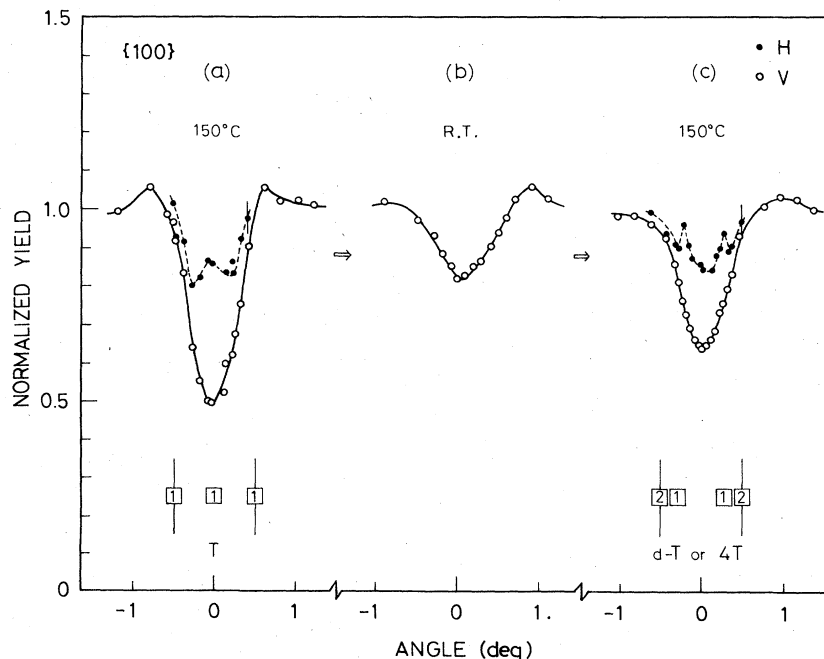


FIG. 2. A change of $\{100\}$ angular profiles of α particle and backscattered ^{11}B yields in (a) the virgin α state (150°C), (b) the β -precipitated state (room temperature), and (c) the β -redissolved α state (150°C). The full curves and the dashed curves have been drawn to guide the eye. The incident energy of $^{11}\text{B}^{2+}$ beam is 2.02 MeV .

cooling to room temperature is expected to produce internal stress. (Since the terminal solubility of H in V is about $H/V = 0.018$ at room temperature, most of the H atoms precipitate into the β phase, and get redissolved in the course of heating to 150°C .) The effect of internal stress is evident in Fig. 2. The depth of the ^{11}B dip, which recovers to only 75% of its original value after reheating, clearly shows that the internal strain in the β -redissolved state is appreciably larger than in the virgin α state.

In order to estimate the magnitude of the internal stress introduced by precipitation of the β phase, the x-ray diffraction was measured on a single-crystal specimen subjected to the same thermal cycling process as in the channeling experiment. The width of the (200) diffraction line of $\text{VH}_{0.1}$, measured at 150°C by using the $\text{Cu-K}\alpha_1$ radiation monochromatized by a LiF crystal, was found to increase on repeated thermal cycling. In the virgin α state, the half-width at half maximum (HWHM) was 0.0158° , which increased to 0.0180° in the β -redissolved α state. Thus, the rms angular broadening caused by precipitation amounts to 0.0086° , giving the rms strain of 2.6×10^{-4} , and the internal stress of $\frac{1}{4}$ to $\frac{1}{3}$ of the elastic limit.

We conclude from these observations that the configura-

tion of H in V is extremely sensitive to the presence of stress. The transition $T \rightarrow$ displaced- T or $4T$ takes place at stress levels much lower than the yield stress. As the internal stress in the β -redissolved α phase is just comparable to the values of external stress at which the superdiffusion sets in,¹ we may further conclude that the stress-induced configuration presently observed is responsible for the occurrence of superdiffusion. We believe that the present observation, though preliminary, should help to eradicate certain confusion over superdiffusion of $4T$ hydrogen, thus promoting more serious investigation of its physics.

More detailed investigation of site changes by channeling under external stress is now planned and will be reported in the near future.

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