

Direct evidence of stress-induced site change of H in V observed by the channeling method

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The effect of external stress on the lattice location of H in α -VH_{0.010-0.015} was investigated at room temperature by the channeling method using the reaction ${}^1\text{H}({}^{11}\text{B},\alpha)\alpha\alpha$. A drastic site change of H from *T* sites to the displaced-*T* or 4*T* configuration was observed when a compressive stress of 7 kg/mm² (below the elastic limit) was applied along the $\langle 100 \rangle$ direction. With the release of the stress, the H atoms returned to the *T* sites. The observed stress-induced configuration is believed to be closely connected to the occurrence of an enormous enhancement of diffusivity of H in V under stress.

Recently, Suzuki, Namazue, Koike, and Hayakawa¹ reported that the diffusivity of H in V is enhanced enormously by the application of tensile stress lower than the elastic limit along the $\langle 111 \rangle$ direction, and concluded, with the help of their Huang scattering experiments, that it is a consequence of the stress-induced site change *T* (tetrahedral site) \rightarrow 4*T* (a group of four *T* sites). However, their observation of the "superdiffusion of 4*T* hydrogen" has since been questioned by Metzger² and Schober and Golczewski³ and still remains in dispute. More recently, we observed that the site of H in V was changed by thermal cycling.⁴ In that study, the lattice location of H was determined by the channeling method using the nuclear reaction ${}^1\text{H}({}^{11}\text{B},\alpha)\alpha\alpha$. In the original specimen of α -VH_{0.1}, prepared and measured at 150°C, the lattice location was found to be a *T* site. When the specimen was cooled to room temperature and reheated to 150°C, however, a drastic change in a $\{100\}$ channeling angular profile for H was observed, which indicated a site change from the *T* sites to a displaced-*T* or 4*T* configuration. The measurement of the broadening of the x-ray (200) diffraction line showed that the internal stress was introduced by this thermal cycling, apparently because of precipitation and redissolution of the β phase. Thus we concluded that the observed site change was induced by the internal stress, and the observation should be connected to the occurrence of the superdiffusion of H in V. In this paper we report the direct evidence for the stress-induced site change of H in V obtained by performing channeling experiments under well-controlled external stress.

As in our previous reports, the nuclear reaction ${}^1\text{H}({}^{11}\text{B},\alpha)\alpha\alpha$ was employed for the channeling experiment.⁴⁻⁶ In this method, hydrogen was detected by measuring the α particles by sending a ${}^{11}\text{B}$ beam in the channeling direction. A specimen was cut from a single crystal (99.95%-pure vanadium supplied by Aremco Corporation) into a parallelepiped 2 mm thick, 4 mm wide, and 6 mm long with a wire saw and electropolished. The largest face was a $\{110\}$ plane, and the longest edge was parallel to the $\langle 100 \rangle$ direction. The specimen was annealed at about 1500°C for 75 h in a vacuum of 10^{-10} Torr, and subse-

quently doped with hydrogen from the gas phase up to a concentration of VH_{0.010-0.015}. The specimen was mounted in a specimen holder (to be described later) and set on a three-axis goniometer, with which the crystal orientation could be set to an accuracy of $\pm 0.004^\circ$. The incident ${}^{11}\text{B}^{2+}$ beam (2.02 MeV), having a current of 1.0–1.5 nA, was collimated to have a divergence of less than 0.076° , with a diameter of 1.0 mm. The specimen was maintained at room temperature during the channeling analysis. It was set so that its surface made an angle of 45° with respect to the incident beam. The backscattered ${}^{11}\text{B}$ and the emitted α particles were measured by two solid-state detectors at scattering angles of 150° and 90° . The detector solid angles were 7.8 msr and 1.6 sr, respectively. In front of the detector for α -particle detection 4- μm Mylar foil was placed in order to stop scattered ${}^{11}\text{B}$ particles. In the present experiment, for the $\{100\}$ planar channel configuration, both backscattered ${}^{11}\text{B}$ and emitted α -particle yields were measured as a function of the angle between the incident beam direction and a $\{100\}$ planar channel. In each measurement, the yields were accumulated up to the irradiation dose of 4.5 μC . A more detailed description of the technique was given in our previous papers.⁴⁻⁶

The specimen holder for applying the stress, made of stainless steel, is shown in Fig. 1. A brass plate was used to compensate for a possible difference in thermal expansion between stainless steel and the vanadium specimen. The compressive stress of $\sigma = 7 \text{ kg/mm}^2$, which is lower than the elastic limit, was applied in the $[001]$ direction as described below. A strain gauge was pasted on the rear surface of the specimen and was calibrated by using an Instron-type testing machine. Subsequently, the specimen was set in the specimen holder, and the compressive stress was applied by turning the screw (A in Fig. 1) up to the desired stress level by monitoring the output of the strain gauge. Then, the whole assembly was mounted on the goniometer for the channeling experiment. The specimen holder used for measurement under the stress-free conditions was the same one used in the previous work.^{4,5}

Under the compressive stress applied in the $[001]$ direction, an angular scan was made for a (001) planar channel

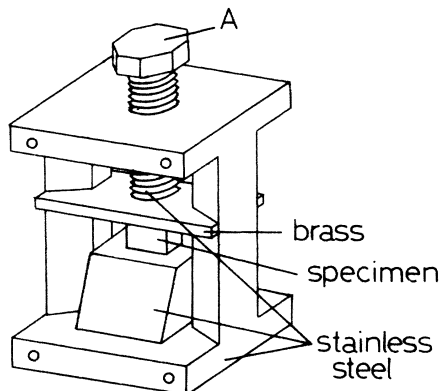


FIG. 1. A specimen holder for applying the compressive stress.

(perpendicular to the direction of the applied stress) and a (010) planar channel (parallel to the direction of the applied stress). Angular profiles thus obtained on the specimen of $VH_{0.010}$ are shown in Figs. 2(a) and 2(b), and the result obtained after releasing the stress is shown in Fig. 2(c). Results of additional measurements on other specimens, under the conditions corresponding to Figs. 2(a), 2(b), and 2(c), are shown in Figs. 2(d) for $VH_{0.014}$, 2(e) for $VH_{0.015}$,

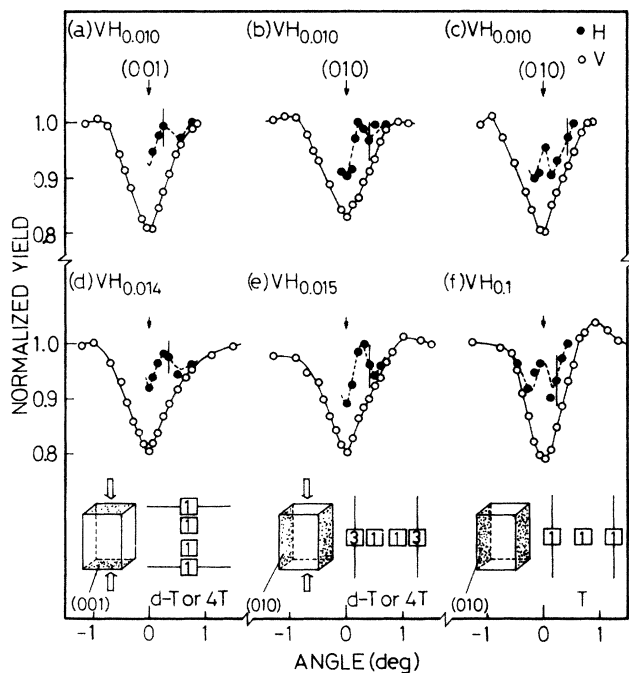


FIG. 2. (001) and (010) channeling angular profiles of backscattered ^{11}B and α -particle yields under the [001] compressive stress $\sigma = 7 \text{ kg/mm}^2$ [(a), (b), (d), and (e)] or after releasing the stress [(c)] in $VH_{0.010}$, $VH_{0.014}$, and $VH_{0.015}$ (room temperature). (010) angular profiles in $VH_{0.1}$ at 150°C under $\sigma = 0$ is shown in (f). The full curves and the dashed curves have been drawn to guide the eye. The insets indicate the projections of T sites and displaced- T ($d-T$) or $4T$ configuration onto the plane perpendicular to the (001) or (010) planar channel. The lines represent the projections of atomic planes, and the squares represent the projected positions of interstitial sites with their relative weights indicated by numbers in the squares.

and 2(f) for $VH_{0.1}$, respectively. The angular profile in Fig. 2(f) is the one obtained on α - $VH_{0.1}$ prepared at 150°C as described in our previous report.⁴

The results shown in Fig. 2 clearly indicate that the hydrogen location under the uniaxial compressive stress of 7 kg/mm^2 is distinctly different from that in the stress-free state. The angular profile shown in Fig. 2(c), which coincides with that in Fig. 2(f), indicates that the hydrogen location returns to the T sites after the stress is released. Under $\sigma = 7 \text{ kg/mm}^2$, the (001) and (010) α -angular scans give similar profiles consisting of a wide dip with approximately the same width as that of the ^{11}B dip and a subsidiary peak located at about 0.25° , the (001) dip being shallower than the (010) dip. They are very similar to the α -angular profile obtained after thermal cycling in our previous experiment on H in $VH_{0.1}$.⁴ The present result indicates that, under the external stress, a major proportion of H atoms occupy interstitial sites displaced from the normal position of T sites.

A recent theoretical calculation⁷ has shown that as the vanadium lattice is elongated along one of its cube axes (z axis), the most stable self-trapped configuration changes continuously, $T \rightarrow$ displaced- $T \rightarrow 4T \rightarrow O_z$ (octahedral site). The wave function of a H atom, originally localized on one of the four T sites around the O_z sites (1 T configuration), is gradually displaced towards the O_z sites (displaced- T) and after going through a resonant state of these four displaced- T configurations (4 T), finally attains a single maximum localized around the O_z site.

In Fig. 3 tetrahedral sites and the displaced- T or $4T$ configuration in a bcc lattice and their projections onto the planes perpendicular to the (001) and (010) planar channels are shown. T_1 , T_2 , and T_3 represent three kinds of T site, the tetragonal axes of which are parallel to the x , y , and z axes, respectively [Fig. 3(a)]. It is easy to show that the angular profiles observed under stress are incompatible with T -site occupancy. If we assume that only T_3 sites are occupied under stress, we would expect a single peak for a (001) α -angular scan and a single dip for a (010) α -angular scan [Fig. 3(b)]. If, on the contrary, we assume T_1 - and T_2 -site occupancy, we would expect a single dip in a (001) profile and a dip superposed with a central peak in a (010) profile [Fig. 3(c)]. None of these expectations are realized experimentally.

The only possible explanation is in terms of the

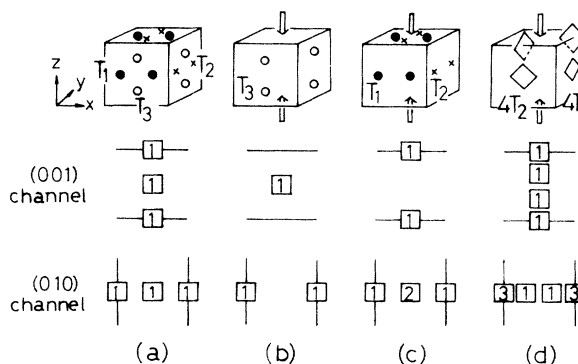


FIG. 3. Tetrahedral sites [(a), (b), and (c)], displaced- T or $4T$ configuration [(d)] and their projections onto the plane perpendicular to (001) or (010) planar channel, without stress [(a)] and under the [001] compressive stress [(b), (c), and (d)].

displaced- T or the $4T$ configuration. Among the three types of $4T$ configuration those having the tetragonal axis along the x and y directions [shown as $4T_1$ and $4T_2$ in Fig. 3(d)] are believed to be energetically favored when the compressive stress is applied along the z direction. In the case of the (001) channel, half of such displaced T -sites are shadowed by (001) planes, and the remaining half are at off-center positions in the (001) channel, while in the (010) case three-fourths are shadowed by (010) planes and the one-fourth is at off-center positions in the (010) channel [Fig. 3(d)]. Thus, it is expected that both (001) and (010) α -angular profiles should consist of a dip and two subsidiary peaks superposed on it, and that the (001) dip should be shallower than the (010) dip. The observed angular profiles are in good agreement with these expectations. We conclude, therefore, that under external stress H atoms occupy the displaced- T or $4T$ configuration in which the position of the maximum hydrogen density is displaced towards the O sites (octahedral sites). (From the present result it is difficult to make a distinction between the displaced- T and $4T$ configurations.) The amount of displacement can be estimated from the position of a subsidiary peak by using the relation

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

where ψ is the angle for the subsidiary peak ($\sim 0.25^\circ$), E the incident beam energy, and $U(r_i)$ the continuum potential at the projected interstitial site in the channel. The potential can be calculated by using the Erginsoy formula.⁸ The displacement from a T site, thus obtained, amounts to 0.44 Å which, in comparison with the T - O distance of 0.76 Å, means that the position of maximum density is closer to the O sites than to the T sites.

Summarizing, we can definitely conclude that the config-

uration of H in V is extremely sensitive to the presence of stress; the transition $T \rightarrow$ displaced T or $4T$ can be induced by applying compressive stress lower than the elastic limit, and the transition can be reversed by releasing the stress. The fact that the structure in the channeling profile, observed in the presence of internal stress, was very sharp and similar to what was observed under external stress indicates that the stress-induced configuration is a well-defined one. It appears as if we were observing a phase transition between two well-defined states. In fact, we suggest here that some cooperative effect could be involved in the transition. The energy of interaction of an individual H atom with the external stress, which amounts to only $\sim 10^{-3}$ eV (estimated from Fig. 2 of Ref. 7), is far too small to cause a site change which requires an energy of at least 0.01 eV.⁹

The present observation appears thus far to corroborate the proposition of Suzuki *et al.*¹ that the "superdiffusion" is caused by a stress-induced site change $T \rightarrow 4T$. It is our belief, however, that a more detailed investigation on the stress-induced transition should be performed before any definitive discussions can be made on the mechanism of superdiffusion.

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