ELSEVIER

Journal of Alloys and Compounds 446–447 (2007) 512–515

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

Lattice location of hydrogen in β_1-V_2H (tetragonal)

Tatuya Hayashi [a], Shigetoshi Koike [b], Naota Higami [a], Kazuhiro Hirabayashi [a], Hiroshi Matsuba [a], Kiyoshi Ogiwara [c], Eiichi Yagi [a,c,*]

[a] *The School of Science and Engineering, Waseda University, Shinjuku-ku, Tokyo 169-8555, Japan*
[b] *Department of Physics II, Tokyo University of Science, Shinjuku-ku, Tokyo 162-8601, Japan*
[c] *RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama 351-0198, Japan*

Received 19 September 2006; received in revised form 1 February 2007; accepted 13 February 2007
Available online 16 February 2007

Abstract

In order to investigate the lattice location of hydrogen and its density distribution in a β_1-V_2H crystal with a tetragonal structure, channelling experiment has been performed at room temperature utilizing a nuclear reaction $^1H(^{11}B, \alpha)\alpha\alpha$ with a ^{11}B beam of about 2 MeV. It has been demonstrated that hydrogen occupies an O_z site, and the density distribution of hydrogen is anisotropic; the HWHM of the density distribution is about 0.35 Å in the [1 0 0] direction, while it is less than 0.2 Å in the [0 0 1] direction on the assumption of the Gaussian distribution.

Keywords: V_2H; Nuclear reaction channelling; Lattice location of hydrogen; Density distribution of hydrogen

1. Introduction

On the basis of neutron, electron and X-ray diffraction experiments it had been reported that the crystal structure of a vanadium hydride β_1-V_2H is body-centred monoclinic [1–7], or body-centred tetragonal [8,9], with an ordered arrangement of hydrogen atoms. This monoclinic structure is a pseudo-tetragonal one with an axial ratio of $c_0/a_0 \sim 1.1$ (c_0 and a_0; lattice parameters in the c-direction and the a-direction, respectively) and a slight inclination of the c_0 axis ($\alpha_0 \sim 90.3^\circ$). The β_1-V_2H phase exists below about 450 K, and above about 470 K it transforms to a bcc phase (α-V_2H) with a disordered arrangement of hydrogen atoms at tetrahedral interstitial (T) sites. Later it was found that the β_1-V_2H has two different crystal structures, a body-centered monoclinic one and a body-centered tetragonal one with an axial ratio $c_0/a_0 \sim 1.1$, depending on the condition for crystal growth [10,11]. When tensile stress is applied during transformation from an α- to a β_1-phase, it crystallizes into the tetragonal structure, while without tensile stress it crystallizes into the monoclinic structure. The mechanism of stabilization of the tetragonal structure was theoretically studied [12]. The lattice location of hydrogen in the tetragonal β_1-V_2H has been investigated by the neutron and X-ray diffraction methods [11,13]. By the latter method, the lattice location of hydrogen cannot be directly determined, but it is deduced by taking account of the observed displacement of V atoms from lattice points, which is induced by neighbouring hydrogen. It was indicated that H atoms are located at O_z sites which are octahedral (O) sites between two adjacent V atoms aligned along c_0 axis (z-axis) with separations of c_0. The density distribution of hydrogen around an O_z site was also obtained by the neutron diffraction method [13]. A nuclear reaction channelling method is also useful to locate H(D) in a lattice and to obtain information on their density distribution. This method was applied to β-V_2D (monoclinic) by utilizing a nuclear reaction $D(^3He, p)^4He$ with a ^3He beam [14]. However, for β_1-V_2H no channelling experiment has been performed, because the method with a ^3He beam is ineffective for H detection. For H a method utilizing a reaction $^1H(^{11}B, \alpha)\alpha\alpha$ with a ^{11}B beam has been developed [15]. In the present work, the lattice location and the density distribution of hydrogen have been studied by this channelling method with a ^{11}B beam. The channelling method has the advantage of observing both host metal lattice and hydrogen in the real space.

* Corresponding author at: RIKEN (The Institute of Physical and Chemical Research), Wako, Saitama 351-0198, Japan. Tel.: +81 48 467 9384; fax: +81 48 462 4645.
E-mail address: eyagi@postman.riken.jp (E. Yagi).

0925-8388/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jallcom.2007.02.059

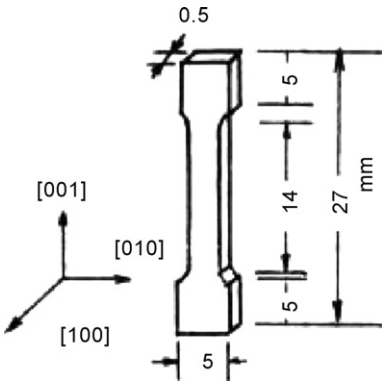

Fig. 1. The dimensions of the β_1-V_2H single crystal.

2. Experimental

A β_1-V_2H single crystal was prepared in the following processes. A vanadium single crystal slice was cut into the form shown in Fig. 1. It was annealed in vacuum of 10^{-10} Torr around 1800 K for 7 days. Hydrogen was doped to this specimen from gas phase up to the concentration corresponding to a composition of V_2H, i. e., [H]/[M] = 0.5 in a hydrogen-to-metal atom ratio, under the tensile stress of 1.0 kg/mm^2 along the [0 0 1] direction. The specimen was kept at 773 K. Hydrogen gas was gradually introduced into a reaction chamber during 30 min up to the amount which is required for an equilibrium state between V_2H and H_2 gas to be achieved at 573 K. The equilibrium H_2 pressure is about 0.6 atm. Then the specimen was cooled to 573 K at a rate of 0.3 K/min and it was kept at 573 K for 10 h to attain an equilibrium state and the homogeneous distribution of hydrogen in the specimen. The specimen was cooled from 573 to 483 K, which is above the $\alpha \rightarrow \beta_1$ transformation temperature, at a rate of about 1.5 K/min, by adjusting hydrogen pressure during cooling so as to keep the composition of V_2H. Thus an α-V_2H single crystal was prepared. In order to grow a single domain of β_1-V_2H the specimen was cooled slowly from 483 K to room temperature at a rate of 0.1 K/min. During whole processes the tensile stress was being applied. It was confirmed by an X-ray Laue method that the specimen crystallized into a tetragonal structure. The concentration of hydrogen was [H]/[M] = 0.5.

Channelling analyses were performed at room temperature for [1 0 0], [1 1 0] and [1 0 1] axial channels, and (1 1 0), (1 0 0) and (0 0 1) planar channels at different spots on the same specimen with a $^{11}B^+$ beam of about 2.02 MeV obtained from an accelerator at RIKEN, utilizing a resonant type of nuclear reaction of $^1H(^{11}B, \alpha)\alpha\alpha$ at about 1.8 MeV as in previous studies on V [16,17]. In this method hydrogen can be detected by measuring the emitted α particles, whose energy ranges from 0 to about 5 MeV. The beam was collimated to give a divergence less than 0.065°. The beam spot was 0.7 mm in diameter and the beam intensity was 1.5–2.0 nA. The specimen was mounted on the specimen holder of the three-axis goniometer. Two solid state Si detectors were set at a scattering angle of 160° to detect ^{11}B ions backscattered by V atoms for observation of the channelling effect and at an angle between 115° and 140° to detect α particles, respectively. In front of the detector for α-particles a 4 μm thick Mylar foil was placed to detect only α particles by eliminating ^{11}B ions which were scattered by host metal atoms V into the direction of the detector. The yield of ^{11}B ions backscattered by V atoms and the yield of the emitted α particles were measured as a function of incident angle ϕ with respect to the channel direction in question, i.e. channelling angular profiles, by tilting the goniometer (angular scan). In an angular scan, to minimize an effect of radiation damage by an analysis beam the measurement was started under an aligned condition, i.e. $\phi = 0°$.

3. Results and discussion

Fig. 2 shows the angular profiles obtained for ^{11}B ions backscattered by V atoms (^{11}B-angular profiles; ^{11}B-dips) and those for emitted α particles (α-angular profiles). The α-angular profile exhibits a central peak for the [1 0 0] and [1 0 1] channels,

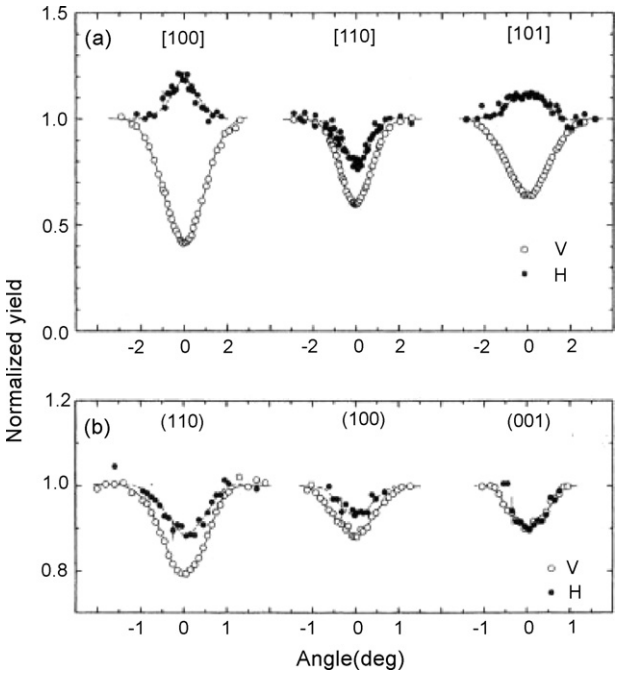

Fig. 2. Channelling angular profiles obtained for ^{11}B ions backscattered by V atoms, and emitted α particles for (a) [1 0 0], [1 1 0] and [1 0 1] axial channels and (b) (1 1 0), (1 0 0) and (0 0 1) planar channels. Solid and broken curves have been drawn only to guide the eye.

while it exhibits a dip for the [1 1 0], (1 1 0), (1 0 0) and (0 0 1) channels. These results suggest that hydrogen is located at a site which is near centres of both [1 0 0] and [1 0 1] channels and shadowed behind the [1 1 0] atomic rows and the (1 1 0), (1 0 0) and (0 0 1) atomic planes. As the hydrogen location T and O sites were examined. Fig. 3 shows two kinds of T sites, T_1 and T_2, and three kinds of O sites, O_x, O_y and O_z, in a tetragonal structure. Their projections on the plane perpendicular to the channel in question are shown in Fig. 4 with their weights (numbers in open squares) and the expected α-angular profiles for them. The T_1 and T_2 sites are not equivalent in a tetragonal structure. If H atoms are located at T_1 or T_2 sites, it is expected that the

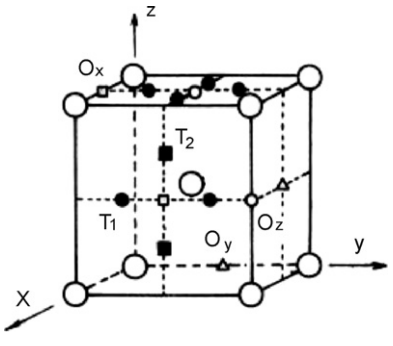

Fig. 3. Two kinds of T sites, T_1 and T_2, and three kinds of O sites, O_x, O_y and O_z, in a body-centred tetragonal crystal. For each type of site only some of equivalent sites are indicated. The coordinates of these sites are as follows: T_1: (1/4, 0, 1/2), (3/4, 0, 1/2), (0, 1/4, 1/2), (0, 3/4, 1/2), (1/2, 1/4, 0), (1/2, 3/4, 0), (1/4, 1/2, 0), (3/4, 1/2, 0); T_2: (1/2, 0, 1/4), (1/2, 0, 3/4), (0, 1/2, 1/4), (0, 1/2, 3/4); O_x: (1/2, 0, 0), (0, 1/2, 1/2); O_y: (0, 1/2, 0), (1/2, 0, 1/2); O_z: (0, 0, 1/2), (1/2, 1/2, 0).

α-angular profile exhibits a central peak superposed on a dip for the (1 0 0) channel, or a central peak for the (0 0 1) channel, respectively. This expectation is incompatible with the experimental results. Therefore, H atoms are not located at *T* sites. As to the *O* site occupancy, the O_x and O_y sites are shadowed behind the [1 0 0] atomic rows and the [1 0 1] atomic rows, respectively, to exhibit a simple dip in the α-angular profile. This expectation is also incompatible with the experimental results. On the basis of the projections of O_z sites and the expected α-angular profiles (Fig. 4), the most probable site for hydrogen is an O_z site. For the O_z site occupancy, [1 0 1] α-angular profile should consist of two subpeaks around ±0.1°, but these two are not well resolved because of a small separation in peak positions. The O_z site occupancy is the same as the result of the neutron diffraction experiment [13].

In the following section the density distribution of hydrogen will be discussed. It is to be noted that the α-angular profile is completely the same as the ^{11}B-dip for the (0 0 1) channel, whereas it is also a dip but narrower and shallower than the ^{11}B-dip for the (1 0 0) channel. This result indicates that hydrogen at O_z site is completely shadowed behind the (0 0 1) plane, but it is not completely shadowed behind the (1 0 0) plane; the density distribution of hydrogen extends beyond the region shadowed behind the (1 0 0) plane. Therefore, the density distribution of hydrogen projected onto the plane perpendicular to the (0 0 1) channel, i.e. the distribution in the [0 0 1] direction, is narrower than that to the (1 0 0) channel, i.e. the distribution in the [1 0 0] direction.

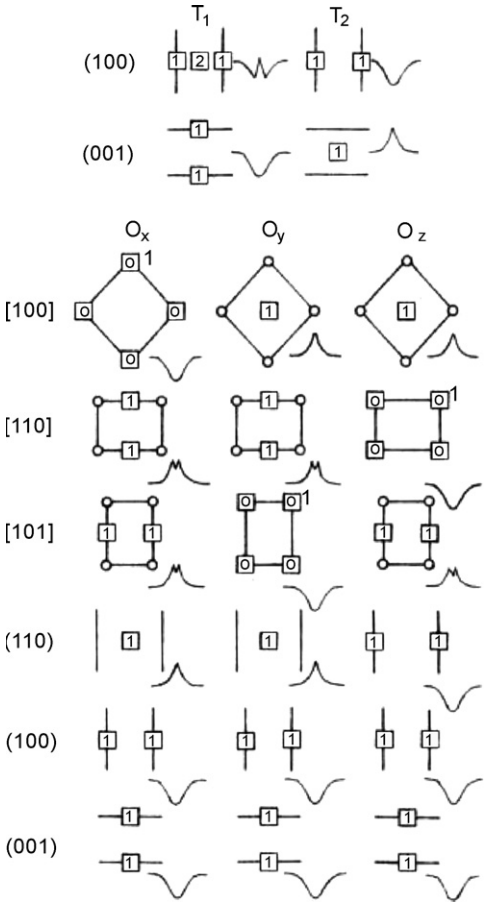

Fig. 4. Projections of T_1, T_2, O_x, O_y and O_z sites onto the plane perpendicular to the channel in question. They are indicated by open squares with weights, together with the expected α-angular profiles. Open circles and lines represent the projection of atomic rows and atomic planes, respectively.

In order to estimate the width of this distribution in the [1 0 0] direction, the (1 0 0) α-angular profile was compared with the calculated results. The width of the (1 0 0) ^{11}B-dip is larger than that calculated for the perfect lattice (the calculated HWHM ∼0.3°, the observed HWHM for a V crystal ∼0.3°; Ref. [16]). For other channels the width of the ^{11}B-dip is also larger. This is considered to be a result of mosaic spread of the β_1-V_2H single crystal specimen. The HWHM of the (1 0 0) ^{11}B-dip was calculated on the basis of the flux distribution of a ^{11}B beam in the channel by assuming a Gaussian distribution for the mosaic spread:

$$p(x) = \frac{1}{\theta(2\pi)^{1/2}} \exp\left(-\frac{x^2}{2\theta^2}\right). \quad (1)$$

The calculation of the flux distribution was made in the same way as described in a previous paper [18]. From the comparison of the calculated results with the experimental one, θ was estimated to be 0.4°, which is of a reasonable order of magnitude as observed in other channelling studies [19]. Then the (1 0 0) α-angular profile for the O_z site occupancy was calculated by also assuming a Gaussian function for a density distribution of hydrogen:

$$q(x) = \frac{1}{u(2\pi)^{1/2}} \exp\left(-\frac{x^2}{2u^2}\right). \quad (2)$$

The observed (1 0 0) α-angular profile is well reproduced for $u = 0.3$ Å as shown in Fig. 5(a). This corresponds to be 0.35 Å as the HWHM of the density distribution of hydrogen in the [1 0 0] direction on the assumption of the Gaussian distribution.

On the other hand the width of the density distribution of hydrogen in the [0 0 1] direction is narrower, because hydrogen is completely shadowed behind the (0 0 1) plane as described above. The vibration amplitude of V atoms is 0.082 Å [20]. The

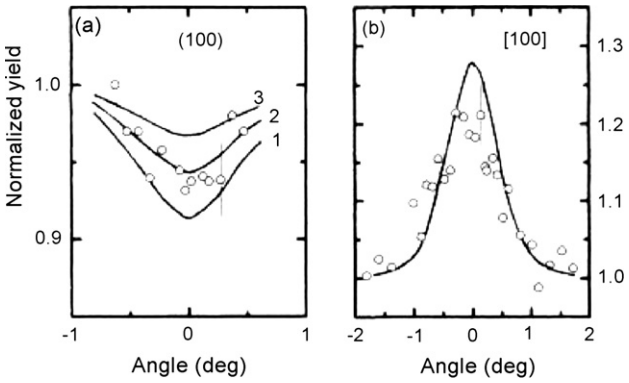

Fig. 5. Comparison of the observed α-angular profiles (open circles) with those calculated (solid curves) with $\theta = 0.4°$ for the mosaic spread and various values of u for the density distribution of hydrogen, for both of which the Gaussian distributions are assumed: (a) (1 0 0) channel, curve 1: $u = 0.2$ Å, curve 2: 0.3 Å, and curve 3: 0.4 Å; (b) [1 0 0] channel, $u = 0.3$ Å.

Table 1
The HWHM of the density distribution of H in β_1-V_2H and D in β-V_2D

	β-V_2D (monoclinic) (Å)				β_1-V_2H (tetragonal) (Å)	
	[0 0 1]	[1 0 0]	([0 0 1]	[1 1 0])	[0 0 1]	[1 0 0]
Neutron diffraction [13]	0.28[a]	0.36[a]			0.4[a]	0.63[a]
Chanelling [14]	0.28		0.84[b]	0.67[b]		
Theory [12,21]	0.09[a]	0.25[a]				0.3[a]
Present results					< 0.2	0.35

[a] These values were estimated from the curves given in Ref. [13].
[b] These values were deduced from the measurements for [0 0 1] and the [1 1 0] channels. Therefore, they do not necessarily mean the HWHM for the [0 0 1] and the [1 1 0] directions, respectively.

magnitude of displacement of V atoms induced by neighbouring hydrogen is about 0.11 Å in the [0 0 1] direction [11]. These values are smaller than the Thomas–Fermi screening distance $a_{TF} = 0.128$ Å for incident ^{11}B ions in V. a_{TF} is a distance of the closest approach of channelling ions to atomic rows or planes, and is considered to be a width of the shadowing region behind an atomic row or plane. Therefore, even if vibration of V atoms is taken into account, the width of the density distribution of hydrogen in the [0 0 1] direction is considered to be less than 0.2 Å, which is smaller than that in the [1 0 0] direction by a factor of about 1.8. The central peaks observed in the [1 0 0] and [1 1 0] α-angular profiles are broader than the peaks expected for the hydrogen occupancy around the centre of the channel, i.e. O_z site, in a perfect lattice. (For example, the HWHM of the peak is about 0.4° for the ⟨1 0 0⟩ channel in a pure V at 423 K, in which H atoms are located at T sites, i.e. around the centre of the channel [16].) However, for example, this [1 0 0] broad peak is well reproduced taking account of the Gaussian distribution with $\theta = 0.4°$ and $u = 0.3$ Å as shown in Fig. 5(b).

The density distribution of hydrogen in β_1-V_2H has been theoretically calculated [12,21] and also measured by the neutron diffraction method [13]. Its anisotropy has been observed for both H and D. In Table 1 the HWHM's of the density distribution in the [1 0 0] and [0 0 1] directions obtained for H in β_1-V_2H and D in β-V_2D are summarized. The neutron diffraction experiments indicated that the density distribution deviates from the Gaussian type and has a tail spreading over surrounding T sites [13]. From the present experiments a detail form of the density distribution function cannot be obtained. However, the magnitudes of the HWHM are smaller than those obtained from the neutron diffraction experiments. They are rather near the results of theoretical calculation. The anisotropy in the density distribution is qualitatively consistent with the results by the neutron diffraction [13].

In summary, hydrogen is located at an O_z site and its density distribution is anisotropic; the HWHM of the density distribution is about 0.35 Å in the [1 0 0] direction, while it is less than 0.2 Å in the [0 0 1] direction on the assumption of the Gaussian distribution.

Acknowledgements

The authors thank Professor K. Asahi, Dr. Y. Yano and Dr. Y. Kobayashi at RIKEN for their support in various phases during this research. This research was financially supported in part by Special Coordination Funds of Ministry of Education, Culture, Sports, Science and Technology, the Japanese Government.

References

[1] J. Wanagel, S.L. Sass, B.W. Batterman, Phys. Stat. Sol. (a) 10 (1972) 49.
[2] S. Takano, T. Suzuki, Acta Metall. 22 (1974) 265.
[3] M. Cambini, R. Serneels, R. Gervers, Phys. Stat. Sol. (a) 21 (1974) K57.
[4] H. Asano, Y. Abe, M. Hirabayashi, J. Phys. Soc. Jpn. 41 (1976) 974.
[5] M.P. Cassidy, B.C. Muddle, T.E. Scott, C.M. Wayman, J.S. Boweles, Acta Metall. 25 (1977) 829.
[6] S. Koike, T. Suzuki, Acta Metall. 29 (1981) 553.
[7] S.C. Moss, in: P. Jena, C.B. Satterthwaite (Eds.), Electronic Structure and Properties of Hydrogen in Metals, Plenum, New York, 1983, p. 153.
[8] A.J. Maeland, J. Phys. Chem. 68 (1964) 2197.
[9] J.J. Reilly, R.H. Wiswall Jr., Inorg. Chem. 9 (1970) 1678.
[10] Y. Noda, T. Kajitani, M. Hirabayashi, S. Sato, Acta Cryst. C41 (1985) 1566.
[11] Y. Noda, K. Matsumoto, S. Koike, T. Suzuki, S. Sato, Acta Cryst. B42 (1986) 529.
[12] H. Sugimoto, J. Phys. Soc. Jpn. 53 (1984) 2592.
[13] T. Kajitani, M. Hirabayashi, Phys. Chem. N.F. 145 (1985) 281.
[14] S. Yamaguchi, K. Takahiro, S. Nagata, Y. Fujino, H. Naramoto, K. Ozawa, J. Alloys Compd. 231 (1995) 132.
[15] E. Yagi, T. Kobayashi, S. Nakamura, Y. Fukai, K. Watanabe, J. Phys. Soc. Jpn. 52 (1983) 3441.
[16] E. Yagi, T. Kobayashi, S. Nakamura, Y. Fukai, K. Watanabe, Phys. Rev. B 31 (1985) 1640.
[17] E. Yagi, T. Kobayashi, S. Nakamura, F. Kano, K. Watanabe, Y. Fukai, S. Koike, Phys. Rev. B 33 (1986) 5121.
[18] E. Yagi, S. Koike, T. Matsumoto, T. Urai, K. Ogiwara, Phys. Rev. B 66 (2002) 024206.
[19] H.D. Carstanjen, R. Sizmann, Phys. Lett. 40A (1972) 93.
[20] D.S. Gemmel, Rev. Mod. Phys. 46 (1974) 129.
[21] Y. Fukai, Jpn. J. Appl. Phys. 22 (1983) 207.