Lattice location and density distribution of hydrogen in $\beta_1$-V$_2$H

E. Yagi,*1,*2 T. Hayashi,*2 T. Yoshida,*2 S. Koike,*1 N. Higami,*2 K. Hirabayashi,*2 A. Takebayashi,*2 H. Matsuba,*2 and K. Ogiwara*1

On the atomic state of hydrogen in V$_2$H, it has been reported that hydrogen atoms are distributed randomly at tetrahedral ($T$) sites in the $\alpha$-phase with a bcc crystal structure at high temperatures above about 470 K, whereas in the low-temperature $\beta_1$-phase below about 450 K, they occupy specific octahedral ($O$) sites with an ordered arrangement. The $\beta_1$-V$_2$H has two different crystal structures, a body-centred tetragonal (bct) structure, and a body-centred monoclinic one (bmc) with slight inclination of the $c$-axis ($a_0 \approx 90.3-91^\circ$) (a pseudo-tetragonal structure), both of which have an axial ratio between $a$- and $c$-axes $c/a_0 \approx 4.1$, depending on the condition for crystal growth. When tensile stress is applied along the [001] axis during transformation from the $\alpha$ to $\beta_1$-phases, the V$_2$H crystallizes into the bct structure, while without tensile stress it crystallizes into the bmc structure. The $O$ sites are octahedral ($O$) sites between two adjacent V atoms aligned along the $c$-axis (z-axis) (Fig.1). The change of hydrogen site from $T$ to $O$ sites implies that the $O$-site occupancy is stabilized by elongation of the $c$-axis, which, conversely, has been induced by forces exerted by hydrogen atoms on neighbouring V atoms. The mechanism of occurrence of the bct structure and the $O$-site occupancy in the $\beta_1$-phase was theoretically studied for the uniform elongation of the $c$-axis under the condition of constant volume, and it was proposed that the elongation of the c-axis is effective for the $O$-site occupancy. Therefore, to examine this effectiveness, in the present study, the site occupancy of hydrogen in both tetragonal $\beta_1$-V$_2$H and monoclinic $\beta_1$-V$_2$H is to be investigated in detail.

Another fundamental problem on hydrogen is the density distribution of hydrogen around its occupation site. This problem is related to the extent of wave function of hydrogen. Experimental values hitherto reported by a neutron diffraction method for the tetragonal $\beta_1$-V$_2$H are larger than the theoretically calculated values and, therefore, there has been a large discrepancy between them. In order to clarify the site occupancy and the spatial density distribution of hydrogen, the channelling method is very useful. In the present study, the channelling method utilizing a nuclear reaction $^1$H($^1$B, $^1$H)$\alpha\alpha$ with a $^1$B beam of an energy of about 2 MeV, which had been developed to locate hydrogen dissolved in Ta and V, is applied.

The lattice location of hydrogen and its density distribution in the tetragonal $\beta_1$-V$_2$H single crystal prepared under tensile stress and the monoclinic $\beta_1$-V$_2$H single crystal prepared without tensile stress have been studied at room temperature. In these crystals, H atoms are located at octahedral ($O$) sites with different distributions over $O_0$, $O_1$, and $O_2$ sites. In the tetragonal $\beta_1$-V$_2$H, about 80% of the H atoms are located at $O_1$ sites, about 10% of them at $O_2$ sites and about 10% of them at $O_3$ sites. In the monoclinic $\beta_1$-V$_2$H, about 65% of the H atoms are located at $O_1$ sites, about 20% of them at $O_2$ sites and about 15% of them at $O_3$ sites. These results support the theoretical prediction that hydrogen preferentially occupies $O_1$ sites under tensile stress along the z-axis (c-axis).

In both crystals, the HWHM of the density distribution of hydrogen is about 0.35 Å in the [100] direction, whereas it is less than 0.13 Å in the [001] direction on the assumption of the Gaussian distribution. The HWHM in the [110] direction has been measured only in the tetragonal crystal to be about 0.35 Å. These values are much smaller than those hitherto obtained by the neutron diffraction method, and close to the values theoretically calculated for the ground state (~0.28 Å for the [100] direction and ~0.093 Å for the [001] direction).

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References