Lattice location and density distribution of hydrogen in β_1-V_2H†

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On the atomistic state of hydrogen in V_2H, it has been reported that hydrogen atoms are distributed randomly at tetrahedral (T) sites in the α-phase with a bcc crystal structure at high temperatures above about 470 K, whereas in the low-temperature β_1-phase below about 450 K, they occupy specific octahedral (O_z) sites with an ordered arrangement.[1] The β_1-V_2H has two different crystal structures, a body-centred tetragonal (bct) structure, and a body-centred monoclinic one (bcm) with slight inclination of the c-axis ($\alpha_0 \approx 90.3\text{-}91^\circ$) (a pseudo-tetragonal structure),[1] both of which have an axial ratio between a-and c-axes $c_0/a_0 \approx 1.1$, depending on the condition for crystal growth.[1] When tensile stress is applied along the [001] axis during transformation from the α to β_1-phases, the V_2H crystallizes into the bct structure, while without tensile stress it crystallizes into the bcm structure. The O_z 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_z sites implies that the O_z-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_z-site occupancy in the β_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_z-site occupancy.[2] Therefore, to examine this effectiveness, in the present study, the site occupancy of hydrogen in both tetragonal β_1-V_2H and monoclinic β_1-V_2H 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 β_1-V_2H are larger than the theoretically calculated values and, therefore, there has been a large discrepancy between them.[3,4]

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 $^1H(^{11}B, \alpha)\alpha\alpha$ with a ^{11}B beam of an energy of about 2 MeV, which had been developed to locate hydrogen dissolved in Ta and V,[5,6] is applied.

The lattice location of hydrogen and its density distribution in the tetragonal β_1-V_2H single crystal prepared under tensile stress and the monoclinic β_1-$V_2H_{1.1}$ single crystal prepared without tensile stress have been studied at room temperature. The following results have been obtained. In these crystals, H atoms are located at octahedral (O) sites with different distributions over O_x, O_y, and O_z sites. In the tetragonal β_1-V_2H, about 80% of the H atoms are located at O_z sites, about 10% of them at O_y sites and about 10% of them at O_x sites. In the monoclinic β_1-$V_2H_{1.1}$, about 65% of the H atoms are located at O_z sites, about 20% of them at O_y sites and about 15% of them at O_x sites. These results support the theoretical prediction that hydrogen preferentially occupies O_z 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).

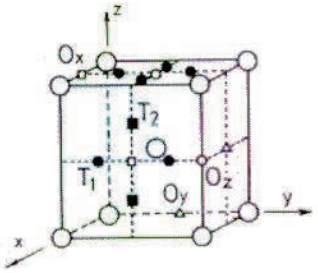

Fig.1. Two kinds of T sites, T_1 and T_2, and three kinds of O sites, O_x. O_y and O_z, in the bct structure. For each type of site, only some of equivalent sites are indicated.

References

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