Detection of Superlattice Reflections from Ta₂H by X-Ray Powder Diffraction

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This paper reports the first finding that X-ray powder diffraction can detect superlattice reflections from the metal hydride. A hydrogen-ordered structure of Ta_2H has been studied on powdered specimens by means of a conventional X-ray diffractometer equipped with a monochromator between the sample and the detector. The use of the monochromator gives an excellent signal to background ratio in the diffraction pattern and enables us to observe weak superlattice reflections which have been missed so far. The obtained powder pattern can be indexed consistently with the superstructure reported by neutron diffraction work. Quantitative intensity measurements show that these superlattice reflections come from a systematic metal atom displacement induced by the ordered hydrogen arrangement, and the displacement has been estimated at 6.0×10^{-3} nm.

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I. Introduction

Va transition metals dissolve a large amount of hydrogen in the *bcc* metal matrix and form a nonstoichiometric metal hydride over a wide composition range. Interstitial hydrogen atoms arrange regularly at low temperatures and various ordered structures are formed⁽¹⁾. Such a subject has been dealt with mainly by neutron diffraction, because X-rays cannot see hydrogen. In recent years, it became evident that hydrogen ordering was able to be studied by X-ray diffraction using single crystals of Ta₂H⁽²⁾ and V₂H⁽³⁾; X-rays see a modulation of metal atoms induced by the ordered hydrogen arrangement. In the present paper we report the first finding of superlattice reflections from Ta₂H by X-ray powder diffraction.

Figure 1 shows a superstructure of Ta₂H reported by previous neutron⁽⁴⁾ and electron diffraction studies⁽⁵⁾ and recent single crystal X-ray diffraction work⁽²⁾. Hydrogen atoms are ordered in the specific tetrahedral sites of the metal lattice. The superstructure is described by the orthorhombic space group C222 with lattice parameters $A=a[2(1+\cos\gamma)]^{1/2}=0.4738$, $B=$

Fig. 1 Crystal structure of Ta₂H. The original *bcc* tantalum lattice shown by dotted lines is deformed slightly to monoclinic (*c/a* ~ 1.01 and γ ~ 90.3°).

$c = 0.3398$ and $C = a[2(1 - \cos \gamma)]^{1/2} = 0.4763$ nm, where a and c are the lattice parameters of fundamental lattice and γ the axial angle. The atomic coordinates are

$$(0\ 0\ 0; 1/2\ 1/2\ 0) +$$

4Ta in 4(*k*): $1/4 \ 1/4 \ z$; $1/4 \ 3/4 \ \bar{z}$ with $z=3/4-\Delta$
 2H in 2(*a*): 0 0 0.

It should be noted that tantalum atoms are shifted from the normal positions by an amount Δ due to the hydrogen ordering. The value of Δ has been reported as 0.012 from neutron pow-

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der diffraction on $\text{Ta}_2\text{D}^{(4)}$, and 0.015 and 0.018, respectively, from neutron⁽⁶⁾ and X-ray diffraction⁽²⁾ on single crystals of Ta_2H .

II. Experimental

The specimen was obtained by the reaction of hydrogen gas with metal powder. The preparation method is similar to that in a previous report⁽⁷⁾. To avoid the effect of preferred orientation on the X-ray diffraction intensity, sample powders were prepared under 325 mesh. X-ray diffraction experiments were carried out using a conventional X-ray diffractometer RAD-IIA (Rigaku Corporation) equipped with a bent monochromator of pyrolytic graphite between the sample and the detector. The use of the monochromator gives an excellent signal to background ratio in the diffraction pattern and enables us to detect weak superlattice reflections which have been missed without it. Cu $K\alpha$ radiation was used at the operating condition of 40 kV $\times$ 30 mA.

III. Results and Discussion

Figure 2 shows an X-ray diffraction pattern of Ta_2H . Measurements were carried out by

step scans of 0.1° intervals for 10 s. In the vicinities of the positions where the superlattice reflections appear, data were accumulated for 1000 s at each angle. The indexing is based on the orthorhombic superlattice cell of Fig. 1, where unmixed and mixed indices refer to the fundamental and superlattice reflections, respectively. Note that many superlattice reflections except reflections of $L=0$ are clearly observed. Integrated intensities I_o were evaluated from accumulated peak intensities during continuous $\theta-2\theta$ scans minus background ones. Then I_o was compared with the calculation I_c including Δ as an adjustable parameter. The intensity is expressed as $I = k|F|^2 Lp$, where k is a scale factor, j the multiplicity factor, F the structure factor and Lp the Lorentz-polarization factor. The structure factors are written as $F = 2f_H \pm 4(i)f_{Ta} \cos 2\pi L\Delta$ and $F = 2f_H \pm 4(i)f_{Ta} \sin 2\pi L\Delta$ for the fundamental and superlattice reflections, respectively, where $\pm$ and i depend on the indices hkl . Debye parameters of $B_{Ta} = 3 \times 10^{-3}$ and $B_H = 1 \times 10^{-2} \text{ nm}^2$ were used according to the previous report⁽²⁾. The value of Δ was so determined as to minimize the R -factor only for the superlattice reflections. Figure 3 shows a variation of R -factor with Δ , where the minimum is obtained

Fig. 2 X-ray powder diffraction pattern of Ta_2H .

Fig. 3 Variation of R -factor with Δ . R -factor is defined as $\Sigma|I_o - I_c|/\Sigma I_o$.

Table 1 Comparison between I_o and I_c with $\Delta = 0.0127$.

HKL	hkl	I_o	I_c
001		0.40	0.53
110		0.00	0.00
002, 200, 111	110	100.00	100.00
201		0.16	0.17
112		0.73	0.74
020, 202	200	18.57	17.32
021 }		0.44	0.34
003 }			
310		0.00	0.00
113, 311, 220, 022	211	35.26	34.51
221 }		0.39	0.35
203 }			

HKL and hkl represent indices based on the superlattice and the original bcc metal lattice, respectively.

when $\Delta = 0.0127$. Comparison between I_o and I_c with $\Delta = 0.0127$ is listed in Table 1, and the agreement between I_o and I_c is satisfactory.

The metal atom displacement in Ta₂H was first pointed out by Petrunin *et al.*⁽⁴⁾ on the basis of neutron powder diffraction on Ta₂D. From the analysis of intensity data, they reported $\Delta = 0.012$. Later, one of the present authors reported $\Delta = 0.018$ from X-ray diffraction of single crystal Ta₂H⁽²⁾. Recent neutron diffraction work⁽⁶⁾ on a single crystal of Ta₂H gives $\Delta = 0.015$. The present result $\Delta = 0.0127$, or $\Delta \cdot C = 6.0 \times 10^{-3}$ nm, agrees rather with the neutron diffraction data of powdered Ta₂D ($\Delta = 0.012$) and Ta₂H single crystal ($\Delta = 0.015$).

Fig. 4 Composition dependence of the displacement in the Ta-H system.

Composition dependence of the displacement was studied with samples TaH_{0.48}–TaH_{0.52}. The result is shown in Fig. 4, where it is seen that the displacement decreases on both sides of the stoichiometric composition. According to the structure model⁽⁸⁾ in the nonstoichiometric compositions Ta₂H_{1+x}, the hydrogen positions in Fig. 1 are partly occupied when $x < 0$ and the excess hydrogen atoms fill the empty interstitial sites (0 0 1/2, 1/2 1/2 1/2) when $x > 0$. It is natural, therefore, that the displacement decreases with deviating composition from the stoichiometry.

In conclusion, the present work demonstrates that X-ray powder diffraction can be a useful tool to study the hydrogen ordering in metal hydrides. It should also be emphasized that hydrides are usually obtained in a powdered form and that the X-ray machine is far readily available in comparison with the neutron machine.

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