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Fermi surface topology of deuterium-doped vanadium: Compton scattering study

S. Mizusaki[a,b,*], N. Sato[b], Y. Ito[b], M. Itou[c], I. Yamamoto[b], Y. Nagata[a], Y. Sakurai[c], M. Yamaguchi[b]

[a] Department of Electrical Engineering and electronics, Aoyama Gakuin University, Fuchinobe, Chuou-ku, Sagamihara, Kanagawa 252-5258, Japan
[b] Department of Physics, Yokohama National University, Tokiwadai, Hodogaya-ku, Yokohama 240-8501,Japan
[c] Material Science Division, Japan Synchrotron Radiation Research Institute, SPring-8,1-1-1 Kouto, Mikazuki, Sayo, Hyogo 678-5198, Japan

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ABSTRACT

The deuteration-induced effect on the Fermi surface (FS) topology of V was investigated by the synchrotron-based Compton scattering technique with 115 keV X-rays. The three-dimensional occupation number density (OND) of α-$VD_{0.64}$ single crystal and V single crystal was reconstructed by the directional Compton profiles along 13–18 directions. The observed OND shows that the FS topology of α-$VD_{0.64}$.differs from that of V at Γ, N, and H points in the crystal momentum space, which are hole position for V. This indicates that electrons that originate from deuterium modify the upper part of the host metal d bands (3rd and 4th bands) at the Fermi level E_F, and forms the metal–hydrogen bonding states with the lower part of the host metal d band (1st band).

1. Introduction

Understanding the nature of hydrogen in metal or ceramics is a matter of scientific interest as well as technological importance. Information of the electronic structure such as the Fermi surface (FS) topology and the chemical bonding states between hydrogen and the host materials promotes the designing of hydrogen storage materials. The metal hydrogen system has the features of crystallographic instability and many lattice imperfections, which are originated in absorbing a large amount of hydrogen in the lattice. Usually, therefore, it is difficult to observe the electronic structure of hydrogen-rich metal hydrides. However, in a previous work [1], we solved these difficulties and observed the FS topology of $PdH_{0.84}$ by utilizing the synchrotron-based high resolution Compton scattering technique.

Vanadium forms the metal-hydrogen (deuterium) system $VH(D)_x$ ($x \leq 2$). The crystal structure of V is bcc at room temperature. In general, the absorbed H(D) atoms occupy the tetrahedral interstitial sites (T sites) or the octahedral interstitial sites (O sites) [2,3]. $VH(D)_2$ have a fcc structure, where H(D) atoms fully occupy the T sites. The crystal structure changes with increasing the H(D) composition x, showing a H/D isotope effect. At room temperature VH_x ($0.5 < x < 0.7$) has the β phase with the distorted tetragonal lattice structure (bct), on the other hand, VD_x ($0.6 < x < 0.8$) has the α phase with a bcc structure, which is the same as the host metal.

Meanwhile, several authors [4–6] have calculated the electronic structure of VH_x or VD_x and presented almost the same result. The valence states of V consist of three d bands. A part of hydrogen-doped electrons form the chemical bonding states between V (M–H bonding) below the d band states (the 1st band) which is located between −6 and −10 eV below E_F. The rest part of hydrogen-doped electrons occupies the states above E_F of V; as a result, it is shifted upward. These predictions were confirmed by the photoemission experiments such as XPS, UPS and SXES in the aspect of electronic energy [7–9]. However, there has been no direct observation of the electronic structure of those hydrides/deuterides in the aspect of electron momentum [6,10].

In this paper, the FS topology of α-$VD_{0.64}$ and V at room temperature is observed to investigate the effect of deuteration process on the electronic states of V. We combine the preparation of single crystal of $VD_{0.64}$ and the reconstruction method of the occupation number density (OND) $N(\mathbf{k})$ by the synchrotron-based high resolution Compton scattering experiment. $N(\mathbf{k})$ highlights the FS-topology. Presently, the Compton scattering technique is a unique

* Corresponding author at: Department of Electrical Engineering and electronics, Aoyama Gakuin University, Fuchinobe, Chuou-ku, Sagamihara, Kanagawa 252-5258, Japan.
E-mail address: smizusaki@ee.aoyama.ac.jp (S. Mizusaki).

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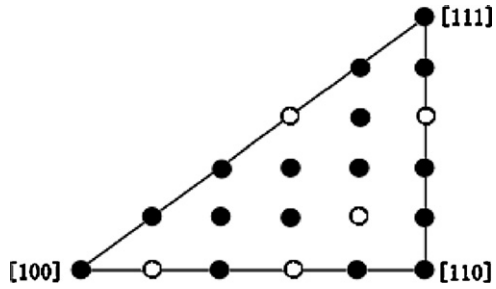

Fig. 1. 18 measurement directions.

method to observe the OND [11–13] and find the FS topology of metal hydrides with absorbing a large amount of hydrogen [1].

The OND is obtained by reducing the electron momentum density (EMD) $\rho(\mathbf{p})$ into the first Brillouin zone by the Lock–Crisp–West (LCW) method [14]. This procedure is described by the following equation,

$$N(\mathbf{k}) = \sum_{\mathbf{G}} \rho(\mathbf{p} + \mathbf{G}), \tag{1}$$

where $\mathbf{k} = \mathbf{p} + \mathbf{G}$ and $\mathbf{G}$'s are reciprocal lattice vectors. The Compton scattering experiment allows to obtain $\rho(\mathbf{p})$ by the reconstruction procedure from the Compton profiles (CPs $J(p_z)$, along different scattering directions. [1,11–13], which is related to the ground-state EMD by

$$J(p_z) = \iint \rho(\mathbf{p}) dp_x dp_y \tag{2}$$

where p_z is the electron momentum along the X-ray scattering vector; $\rho(\mathbf{p})$ is expressed in terms of the electron wave function Ψ_j.

$$\rho(\mathbf{p}) = (2\pi)^{-3} \sum_j \left| \Psi_j(\mathbf{r}) \exp(-i\mathbf{p}\cdot\mathbf{r}) d\ \mathbf{r} \right|^2 \tag{3}$$

where the summation in Eq. (3) extends over all occupied electron states. For the description of the analytical method used in this study we refer the reader to Ref. [1,11–14].

2. Experimental

α-$VD_{0.64}$ single crystal was prepared by reacting deuterium with a single crystal V, which was a cylinder of 5 mm diameter and 5 mm length with 99.9% purity supplied from Furuuchi Co. The sample preparation method was the same as described in the previous paper [1]. The deuterium composition was determined to be $x = 0.64$ by weight increase after the reaction. The sample weight was unchanged after the measurement of Compton profiles under 0.1 MPa helium gas atmosphere. The crystalline direction was confirmed at the accuracy of 0.2° by Laue patterns of V and α-$VD_{0.64}$.

The Compton scattering experiment was carried out at the BL08W beamline of SPring-8 with a high resolution Compton scattering spectrometer. Compton profiles $J(p_z)$ were measured in 13–18 directions at room temperature as shown in Fig. 1. Each Compton peak collects about 2×10^6 counts, yielding a statistical accuracy of 0.07% at the Compton peak. The experimental overall momentum resolution was 0.15 a.u. (1 a.u. = 1.99×10^{-24} kg m s^{-1}). The detailed data analysis and the reconstruct procedure from CPs to OND were described in Ref. [1] also. The effective momentum resolution after the reconstruction procedure was 0.16 a.u. The error of $N(\mathbf{k})$ was determined to be less than 10^{-4} electron/a.u.^{3} from the statistical error of the measured CPs.

3. Results and discussion

CPs of V along the [1 0 0], [1 1 0] and [1 1 1] directions agrees to the previous experimental results [15,19], and furthermore the difference CPs between them accord with the previous calculated results [15,19].

Figs. 2 and 3 summarize the OND $\boldsymbol{N}(\mathbf{k})$ for α-$VD_{0.64}$ and V in (1 1 0) and (1 0 0) planes, respectively. The OND of V in Figs. 2(b) and 3(b) shows that (1) the electrons gather at N and P points, (2) there are deep hole pockets at Γ and H points, and (3) there are shallow holes at N and P points on the top of the high electron density. These facts indicates that the existence of the three kinds of hole structure, which are the octahedral hole surfaces centered at Γ and H points and the distorted ellipsoidal hole surface at N point on the (1 0 0) plane. The hole-depth at the Γ position is larger than that at the other two points. The highest electron density region is located around the holes at N point on the (1 0 0) plane and P point on the (1 1 0) plane.

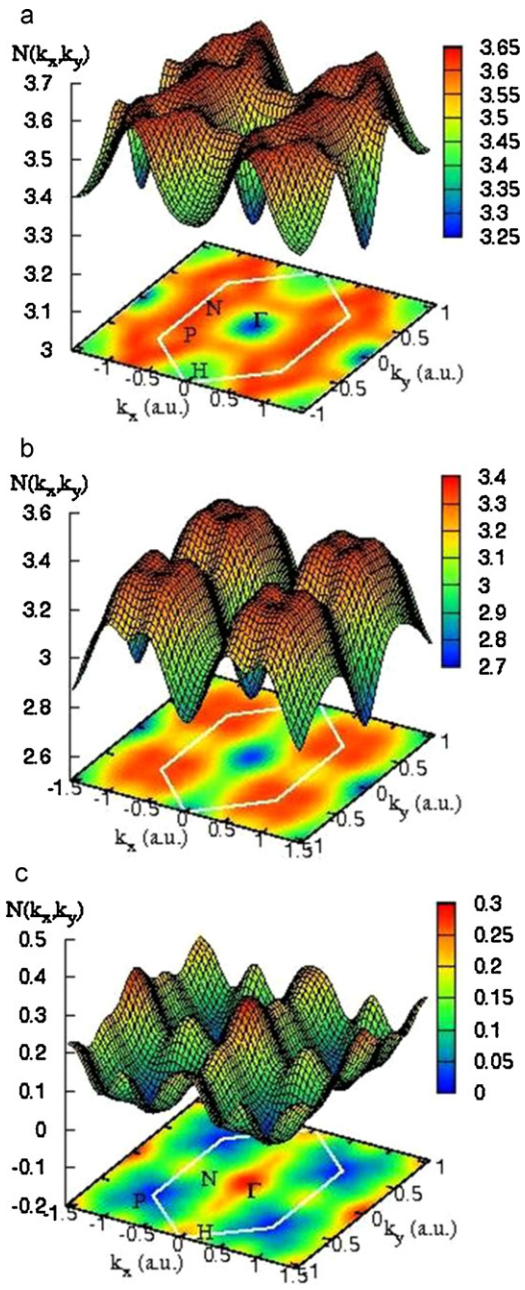

Fig. 2. Occupation number density of (a) $VD_{0.64}$, (b) V, and (c) difference between $VD_{0.64}$ and V, respectively for (1 1 0) plane at room temperature.

Many band calculations [15–22] show that (1) the FS of V is composed of the 3rd and the 4th bands, and (2) the hole pockets exist at Γ and N points and lies along the Γ–H direction, and (3) the FS of V has a jungle gym structure. On the other hand, the FS topology of V has been experimentally investigated by the de Hass-van Alphen effect (dHvA), magnetothermal oscillations (MTO) [16], the

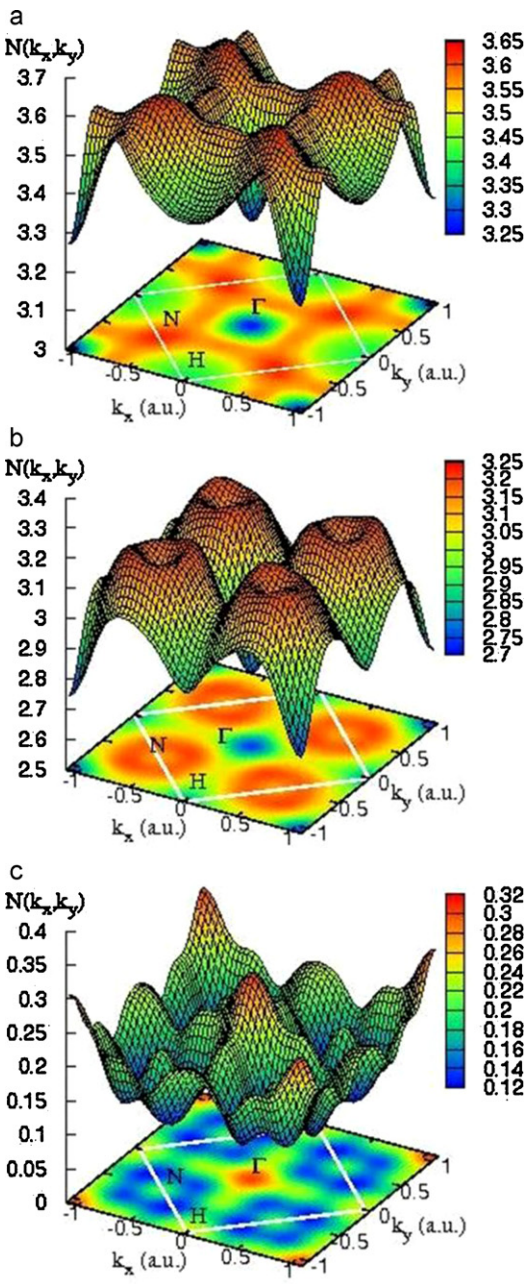

Fig. 3. Occupation number density of (a) $VD_{0.64}$, (b) V, and (c) difference between $VD_{0.64}$ and V, respectively for (1 0 0) plane at room temperature.

positron annihilation [17,18] and the Compton scattering [18–22]. These reveals that V has the closed hole pocket at Γ and N points and the jungle-gym structure extends along the Γ–H direction. Accordingly, those band structure calculations agree satisfactorily to the experimental results [15,23,24]. Moreover, Wakoh and Yamashita [15,19] has calculated for V the contribution to the total momentum density even from the filled 1st band which is very anisotropic, and that from the 2nd band is also anisotropic because of the dε and dγ character of the wave functions. In addition, that from the 3rd band reflects the strong anisotropy in the topology of FS. These features of the calculated results agree well to that of the present experimental results.

Figs. 2a and 3a show the feature of the $N(\mathbf{k})$ for α-$VD_{0.64}$ as follows: In (1 1 0) plane, OND at P and N points are high although P point shows a hollow character. The low-density states are located at Γ and H points. Especially, the OND at Γ point has the lowest density. The $N(\mathbf{k})$ at (1 0 0) plane shows a similar feature to that of (1 1 0) plane. The low-density points correspond to the hole pockets. Therefore, α-$VD_{0.64}$ has hole pockets at Γ, H, and P points: (1) the hole at H point is a shallow pocket with large radius, (2) the hole at Γ point is a deep pocket with narrow radius, and (3) the hole at P point is a shallow and narrow pocket. Then, the deuterium-doped electrons seem to gather at N points.

The comparison of OND between α-$VD_{0.64}$ and V reveals that the hole pocket at N point in V vanished in α-$VD_{0.64}$ and the structure of $N(\mathbf{k})$ is different from each other, particularly around Γ point. This means that the absorbtion of hydrogen/deuteride modifies the anisotropic character of electronic structure around E_F of the host metal. In detail, the comparison of Fig. 2(a) for α-$VD_{0.64}$ and Fig. 2(b) shows that (1) the OND at N point become high density, (2) the high density connects that at both P points and (3) the hole structure lying along Γ–H directions in V is separated into two hole pockets at Γ and H points in α-$VD_{0.64}$, respectively. Furthermore, Fig. 3 shows that the hole radius and depth at P point for $N(\mathbf{k})$ of α-$VD_{0.64}$ are smaller and deeper than that of V. On the other hand, the hole-radius of α-$VD_{0.64}$ at H point becomes lager than that of V.

The difference in $N(\mathbf{k})$ between α-$VD_{0.64}$ and V, denoted by $dN(\mathbf{k})$, makes clearer the facts mentioned above. The values of $dN(k)$ are large at Γ, N, and H points, but small at P point. Especially, the high value region of $dN(\mathbf{k})$ exist only along the Γ–H direction and at Γ point with the anisotropic character. These results show that deuterium-doped electrons gather around Γ, N and H points and that the absorption of hydrogen/deuteride changes the electronic structure of mother metals.

The experimental result for α-$VD_{0.64}$ can be explained using the results of the band calculation studies for V and V hydrides [6,10]. The present results means that the hydrogen/deuterium electrons occupy the hole states in both 3rd and 4th bands and modify their band shapes, at the same time, E_F move upward. The present interpretation is yielded by the following reasons. In this electron donation, the hydrogen/deuterium electrons occupy the hole pockets in the 3rd band and some H electrons occupy the 4th band of V. The strong anisotropic structure of 3rd band is largely changed by the donated H electrons in E_F. As results, the 3rd and 4th bands shape is modified. However, the calculated electronic structure of α-VH by Eriksson and co-workers [6] suggests that the modification of electronic states by doping hydrogen electrons is composed of the formation of M–H bonding states (1st band) with a significant variation from the 1st band states of V and the occupation of the empty states at E_F (3rd and 4th bands) by forming the s–d hybridization states. Unfortunately, the present results could not directly establish the formation of M–H bonding states; however, the ultraviolet photoemission spectroscopy (UPS) measurement [9] observed the M–H bonding states in V 3d lower band states.

In summary, the FS topology of mother metal changes its structure by doping the hydride/deuteride electrons. The experimental results show that a disappearance of hole pockets for V by absorbing the deuterium. The doped deuterium electrons occupy the empty states around E_F which corresponds to the hole pockets and modify the electronic states around E_F.

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