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Experimental determination of the $PdH_{0.84}$ Fermi surface

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Abstract

The three-dimensional electron momentum distribution (3D-EMD) of β-$PdH_{0.84}$ were determined by the Compton scattering technique with 115 keV X-ray synchrotron radiation. The obtained 3D-EMD shows the existence of the neck around the [1 1 1] direction in the Fermi surface, which agrees well with the result of the band structure calculation by the LDA-FLAPW method. This result indicates that the synchrotron-based Compton scattering technique can be used for the Fermiology of metal hydrides.

Keywords: Palladium hydride; Fermi surface; Electron momentum distribution; Compton scattering

1. Introduction

There are many investigations for the effect the hydrogen absorption on the electronic structure of palladium [1–11]. These have indicated that the electrons brought by hydrogen contribute partially to form the metal –hydrogen bonding band below the d-band and partially to raise the Fermi energy from the d-band into the sp-band. Accordingly, hydrogen absorption causes to change in the Fermi surface (FS) geometry of Pd. The band calculation showed the change in the FS from Pd to the stoichiometric PdH, which has a neck around the L point [7,8]. In experiments, meanwhile, the very dilute hydride of PdH_x ($x \prec 0.03$) was examined by means of the de Hass-Von Alphen effect [9]. Positron annihilation in β-$PdH_{0.72}$ was reported by Hasegawa et al. [11]. They reported the Fermi momentum p_F along high symmetrical directions and supported the existence of the neck in the FS. However, it is very difficult to observe the FS of metal hydrides in detail because the above methods are very sensitive to crystalline imperfections.

Recently, FS's have been mapped out from the reconstructed electron momentum distribution (EMD) by the high-resolution synchrotron-based Compton scattering experiment [12–15]. The Compton scattering method has more advantages than other methods for observing the electronic structure of metal hydrides. The Compton scattering is insensitive to lattice imperfections and allows to use an ambient gas to stabilize the hydride. In addition, it is possible to examine a bulk metal hydride because the thickness of the probing depth is more than ∼1 mm. In a previous paper, the high-resolution momentum synchrotron-based Compton scattering method was adopted to measure the electron momenta in β-PdH_x and confirmed the band structure from the viewpoint of electron momentum [16].

In this paper, we reconstruct the three-dimensional electron momentum distribution (3D-EMD) of the β-$PdH_{0.84}$ via directional Compton profiles by the synchrotron-based Compton scattering technique in order to determine the FS geometry.

2. Reconstruction of EMD

In a Compton scattering experiment one measures the Compton profile (CP), $J(p_z)$, which is related to the ground-state EMD $\rho(\mathbf{p})$ by

$$J(p_z) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \rho(\mathbf{p})\mathrm{d}p_x\mathrm{d}p_y \quad (1)$$

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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.

$$\rho(\mathbf{p}) = \left(\frac{2}{\pi}\right)^{-3} \sum | \int \psi(\mathbf{r}) \exp(-i\mathbf{pr}) \mathrm{d}r |^2 \quad (2)$$

The summation in Eq. (2) extends over all occupied states. In principle, the CP possibly contains fingerprints of the FS break in $\rho(\mathbf{p})$ [12]. But, usually, the breaks are not clear because of the double integration $J(p_z)$. Alternatively, $\rho(\mathbf{p})$ was obtained by the direct Fourier method from CPs along different scattering directions: [13–15] We define the reciprocal form factor.

$$B(\mathbf{r}) = \int \rho(\mathbf{p}) \exp(-i\mathbf{pr}) \mathrm{d}\mathbf{p} \quad (3)$$

From Eqs. (1) and (3) we get

$$B(0, 0, z) = \int J(p_z) \exp(-ip_z r) \mathrm{d}p_z. \quad (4)$$

When a set of $J(p_z)$ along different crystalline directions is measured, the value of $B(\mathbf{r})$ can be obtained on the lines in real space which are parallel to p_z. Once $B(\mathbf{r})$ is known, $\rho(\mathbf{p})$ can be obtained by Fourier transformation,

$$\rho(\mathbf{p}) = \left(\frac{2}{\pi}\right)^{-3} \int\int\int B(\mathbf{r}) \exp(i\mathbf{pr}) \mathrm{d}\mathbf{r}. \quad (5)$$

3. Experiment

The single crystal β-$PdH_{0.84}$ was prepared by reacting single crystal Pd (99.99% purity, a cylinder of 5 mm diameter and 5 mm length) with hydrogen gas. The sample preparation was described fully in ref [16]. The hydrogen composition was determined to be $x = 0.84$ from weight increase after the reaction.

The Compton profiles were measured at the BL08W beamline of SPring-8, Japan Synchrotron Radiation Research Institute. The energy of the incident X-ray was 115 keV and the scattering angle was 165°. The sample was placed under helium gas atmosphere at room temperature to stabilize the hydride sample. Compton profiles were measured along 12 scattering vector directions. The count at the Compton peak was about 2×10^5. The overall experimental momentum resolution was 0.15 a.u. (1 a.u. = 1.99×10^{-24} kg ms^{-1}). The data analysis from raw data to the CP was described in ref. [16]. The 3D-EMD was reconstructed from the obtained CPs by the direct Fourier method, which was developed by Tanaka et al. [13]. The effective total momentum resolution after the reconstruction is 0.16 a.u.

4. Calculation

The band structure of the stoichiometric PdH was calculated by the full potential linearized augmented plane wave method within the local density approximation (LDA-FLAPW) method [17]. Although hydrogen atoms are randomly located on the octahedral sites in the FCC crystal structure of β-$PdH_{0.84}$, the electronic structure was calculated for the stoichiometric NaCl structure in which hydrogen atoms were ordered. The calculated results of the band structure reported in ref. [16], showed good agreement with other calculated results [7,8]. The CPs were calculated along the same directions as the experimental ones when they were convoluted with the experimental overall momentum resolution of 0.15 a.u. Then, the 3D-EMD was reconstructed from the calculated CPs by the same method as used in the experiment.

5. Results and discussion

Fig. 1 shows the contour maps of the experimental EMD and the calculated one on the [1 1 0] plane. In outline, the experimental electron momentum was distributed in the spherical symmetry. This means that most valence electrons have an isotropic momentum. The experimental EMD agrees well with the calculated one in the momentum region over 1.0 a.u.

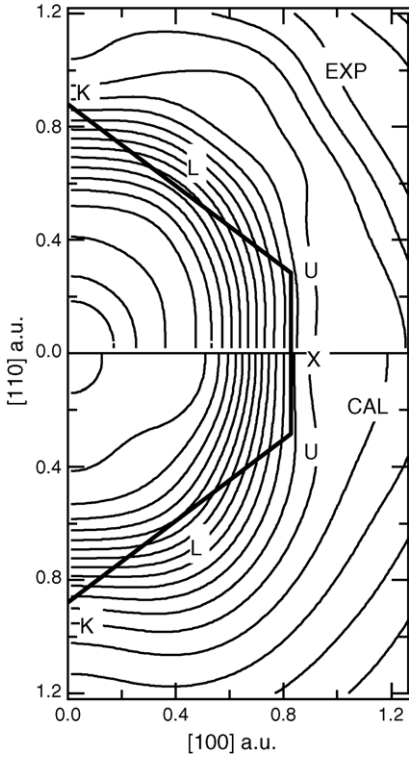

Fig. 1. The electron momentum distribution of β-$PdH_{0.84}$ on the [1 1 0] plane. The upper part is reconstructed from the experimental CPs and the lower one is reconstructed from the calculated CPs. The solid line is the first Brillouin zone boundary. The line separation is 0.03 electron/a.u.^{3}.

Especially, the experimental momentum distribution was deformed around the L [1 1 0] direction and the calculated result showed the same tendency. This indicates that the neck exists along the L direction. The slight discrepancy between the experiment and the calculation in the momentum region under 1.0 a.u. was caused by the Fourier transformation in the reconstruction process of the experimental result.

The inflection point on the EMD inside of the first Brillouin zone(BZ) corresponds to the Fermi momentum p_F [12]. As a result, the p_F equals 0.65 a.u. in the [1 0 0] direction, while the first BZ boundary p_{BZ} in this direction is 0.828 a.u. Similarly, the p_F of the [1 1 0] direction is 0.65 a.u. while p_{BZ} is 0.89 a.u. But the inflection point of EMD exceeds the first BZ boundary in the [1 1 1] direction ($p_{BZ} = 0.716$ a.u.). That is, the Fermi surface makes contact with the neighboring zone, having necks along the [1 1 1] direction. Accordingly, the Fermi surface of β-$PdH_{0.84}$ is geometrically quite similar to that of Ag metal. It is reasonable because PdH has a hypothetical electron configuration of $4d^{10}5s^1$ like Ag.

6. Summary

The 3-dimensional electron momentum distribution of β-$PdH_{0.84}$ was obtained from the synchrotron-based Compton scattering measurements. The experiment confirmed the existence of the neck on the FS of the β-$PdH_{0.84}$ around the [1 1 1] direction like Ag metal [18]. The Compton scattering method is useful to study the Fermiology of metal hydrides.

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