Photoemission Study of Rh$_{17}$S$_{15}$ Superconductor

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We have investigated the electronic structures of Rh$_{17}$S$_{15}$ by using soft x-ray photoemission spectroscopy and first principle band structure calculation. While S 2p core level spectra are explained by symmetric components, Rh 3d core level exhibits asymmetric line shape, suggesting dominant a Rh 4p character at the states near the Fermi level. The binding energy of Rh 4p in Rh$_{17}$S$_{15}$ is similar to the one in Rh metal, and this observation implies metallic Rh-Rh bonding. Experimental valence band spectra are found very similar to the calculated one, indicating that one particle approximation is a good starting point to understand the electronic properties of Rh$_{17}$S$_{15}$. Good correspondence between the experiment and the calculation suggest that Rh 4d character at the states near the Fermi level is essential for the correlated superconductivity in Rh$_{17}$S$_{15}$. However, a small deviation between the experiment and the calculation as well as a finite mass enhancement are found, indicating some corrections on the treatment of electron-phonon coupling and/or electron correlations are necessary.

KEYWORDS: correlated superconductor, soft x-ray photoemission spectroscopy, electronic structures

1. Introduction

Rh$_{17}$S$_{15}$ belongs to the cubic space group $Pm3m$ with a lattice constant of 0.99093 nm and contains 64 atoms [four rhodium sites (1b, 3d, 6e and 24m), and three sulfur sites (12i, 12j and 6f)] in the unit cell, as shown in Fig. 1. While the superconductivity in Rh$_{17}$S$_{15}$ has been reported earlier,$^1$ the recent work by Naren et al. classifies Rh$_{17}$S$_{15}$ as a correlated superconductor by performing a systematic study on various physical properties. There are several interesting superconducting properties to mention.$^2$ For example, the temperature dependence of upper critical field estimates $H_{c2}$ at $T = 0$ K to be 23.5 T, which significantly exceeds the Pauli limit (9.99 T). The result of temperature dependence of the heat capacity indicates the strongly-coupled superconductivity by the fact that $\Delta C/\gamma T_c$ is approximately 2
and the value is larger than 1.43 (BCS theoretical value). Moreover, normal state properties are worth mentioning as well. Sommerfeld constant takes a relatively large value ($\gamma \equiv 104.8$ mJ/mol K$^2$) while temperature (T) dependence of resistivity shows T square dependence from 6 K to 30 K. Temperature dependence of magnetic susceptibility increases as temperature is lowered. The result of Hall resistivity as a function of magnetic field at several temperatures reveals that the sign of Hall coefficient changes at 50-60 K. The experimental result of NMR finds that $1/(T_1T)$ does not stay constant, showing that the Korringa relation is not well-satisfied. Despite these anomalous properties in Rh$_{17}$S$_{15}$, the information on its basic electronic structures is currently lacking. To understand the origin of the anomalous properties, the electronic structures of Rh$_{17}$S$_{15}$ are encouraged to be investigated, preferentially with a direct probe.

In this paper, we report the electronic structures Rh$_{17}$S$_{15}$ studied by soft x-ray photoemission spectroscopy and the band structure calculation. We present the core level and the valence band spectra as well as the calculated partial densities of states and discuss the possible implications.

2. Experimental

The single crystalline samples of Rh$_{17}$S$_{15}$ were grown by mineralization whose detail is published elsewhere. Soft x-ray photoemission spectroscopy (SXPES) was performed at BL25SU, SPring-8, using a SCIENTA SES-200 spectrometer with total energy resolution of 100 meV.

Fig. 1. Crystal structure of Rh$_{17}$S$_{15}$. There are four rhodium sites (1b, 3d, 6e, 24m) and three sulfur sites (12i, 12j, 6f).
and 300 meV for photon energies of 500 eV and 1100 eV, respectively. Clean surfaces for the PES measurement were obtained by in situ fracturing of the crystals under the ultrahigh vacuum better than $3.0 \times 10^{-8}$ Pa. PES measurements as well as the surface preparation were done at 20K. The binding energies of the spectra were calibrated in reference to the Fermi edge of gold thin film evaporated near the sample. For comparison, we carry out a band structure calculation using the full-potential augmented plane wave method (FLAPW) with the local density approximation (LDA). The calculation followed the formalism proposed by Gunnarsson and Lundqvist,\textsuperscript{5)} and the densities of states were calculated with the program package codes KANSAI-04 and TSPACE on the scalar relativistic scheme with the spin-orbit interaction included as a second variational procedure. For crystallographic parameters, we employed the values experimentally determined.

3. Results and discussion

S 2p core level SXPES spectra of Rh$_{17}$S$_{15}$ measured with 500 eV and 1100 eV photon energies (filled circles), together with the results of peak fitting (lines), are shown in Fig. 2, respectively. Five distinct peaks are observed in both spectra. It is also noted that the intensity of the lowest binding energy shoulder increase as the photon energy is decreased. Because the S 2p core level should be observed as a doublet due to the spin-orbit splitting with the energy separation of $\sim$1.2 eV, the observation of five structures suggests that the S 2p core level spectra consist of several components. In order to resolve possible components, we have performed peak fitting analyses and find that the experimental spectra can be well-reproduced by three doublets with symmetric spectral shapes. In a metal where the Fermi edge is well-defined, the excitation of core electrons induces particle-hole pair excitations near the Fermi level ($E_F$). This phenomena decreases the kinetic energy of photoelectron and gives rise to a
Fig. 3. Experimental Rh 3d spectrum taken with the photons of 1100 eV. The binding energy of 3d_{5/2} is similar to the one reported for pure metal.

tail-like feature (asymmetric line shape) in the higher binding-energy side of the main peak. Since the asymmetry of a core level is proportional to the states near $E_F$ contributed from the atomic site where core excitation occurs, a core level PES spectra provide information on the partial densities of states at $E_F$. In the present study, the symmetric spectral shape of S 2p suggests that the S electrons have a negligible contribution to the states at $E_F$. As for the photon-energy dependent spectral weight, we find that while the spectral wight ratio of comp. 1 to comp. 2 is not dependent on photon energy, that of comp. 3 to comp. 2 increases as the photon energy is decreased. Since the inelastic mean free path for $h\nu = 500$ eV is shorter than that for $h\nu = 1100$ eV, the observation suggests that the comp. 1 and the comp.2 are bulk derived features and the comp.3 is a surface-related. Furthermore, the area ratio comp.1: comp.2 is nearly 2:3 $\sim$ 12:(12+6), and this can be consistently explained by the occupancy of three crystallographic sites of sulfur (12i, 12j, 6f). This suggests that the two of the three chemical sites (either 12i or 12j and 6f) are similar.

Fig. 3 shows the Rh 3d core-level SXPES spectrum of Rh$_{17}$S$_{15}$ measured with the photons of 1100 eV. It shows a doublet structure due to the spin-orbit coupling. The peak energy is estimated to be 307.3 eV for 3d_{5/2} and 311.9 eV for 3d_{3/2}. It is clear that the peak has a tail on the higher binding-energy side, and the spectral asymmetry is qualitatively different from that of S core levels. The asymmetric peak indicates that Rh electrons contribute to the Fermi level significantly. Comparing the binding energy of Rh 3d_{5/2} of Rh$_{17}$S$_{15}$ with that of Rh metal spectrum, they take nearly the same value (about 307.3 eV). This suggests that the most of Rh-Rh bonding is metallic.

In Fig. 4, we show valence band SXPES spectra measured with photons of 500 eV and 1100 eV, along with a calculated spectrum. The calculated spectrum is obtained by summing the calculated partial densities of states taking photoionization cross sections into account.
and subsequently carrying out the energy-dependent Lorentzian broadening and the Gaussian broadening (FWHM of 0.3 eV). The valence band SXPES spectra have a prominent peak around 2 eV with several fine structures and a broad structure around 7 eV. Overall spectral shape is similar for both 500 and 1100 eV, but the fine structures are more clearly seen in the 500 eV spectrum due to the better energy resolution. It is noticed that the experimental spectrum is very similar to the calculated spectrum, except that the valley structure seen in the calculation is not as evident in the experiment. The overall agreement suggests that one particle approximation is a good starting point to understand the electronic properties of Rh$_{17}$S$_{15}$.

According to the band calculation, the structures in the binding-energy range of 5 - 8 eV is derived from S 3p orbitals strongly hybridized with Rh 4d ones while the states between $E_F$ and the binding energy of 5 eV correspond to Rh 4d orbitals. This indicates that the states near $E_F$ has a dominant Rh 4d character, being consistent with the line-shape analyses discussed above. On the other hand, the small deviation between the calculation and the experiment implies that the influence of electron-electron interaction and/or electron correlations are not fully included in the calculations. Note that, utilizing the higher photon energy (namely bulk sensitive measurement) strongly reduces the possibility of observing surface-related electronic structures as the origin of the deviation. In connection with the small deviation, the Sommerfeld coefficient deduced from specific heat ($\gamma_{\text{heat}} = 104.8$ mJ/ mol K$^2$) is larger than that obtained from the present band calculations ($\gamma_{\text{calc}} = 41.9$ mJ/ mol K$^2$), which gives rise to $\gamma_{\text{heat}}/\gamma_{\text{calc}}$ of approximately 2.5. The $\gamma_{\text{heat}}/\gamma_{\text{calc}}$ value of Rh$_{17}$S$_{15}$ is slightly larger than that reported for borocarbide superconductors (1.5-2.0) in which electron-phonon coupling has been thought to play an important role.$^8$ However, the mass enhancement is not as large as that deduced for LiV$_2$O$_4$,$^9$ which is known as a $d$-electron the heavy-fermion-like material. On the other hand, recent NMR study reports the existence of the electron correlations in Rh$_{17}$S$_{15}$ from the decrease of the isotropic part of the Knight shift with decreasing temperature. Therefore, some corrections on the treatment of electron-phonon coupling and/or electron correlations seem to be necessary for the better description of electronic structures, and this issue is open for future investigations.

4. Conclusion

We have performed first SXPES studies on Rh$_{17}$S$_{15}$ to elucidate the underlying electronic structures. Core level analysis and valence band spectra compared with a band structure calculation consistently indicate that the states near $E_F$ has a dominant Rh 4d character. Moreover, the experimental valence spectra are reasonably described by LDA, indicating that
Fig. 4. Experimental spectra of valence band obtained with photons of 500 eV and 1100 eV and the result of band structure calculations. The agreement between the experimental spectrum and the calculations is fair.

one particle approximation is a good starting point to understand the electronic properties of Rh$_{17}$S$_{15}$. This suggests that Rh 4$d$ character at the states near the Fermi level is essential for the correlated superconductivity in Rh$_{17}$S$_{15}$. However, we also find a small deviation between the experiment and the calculation as well as a finite mass enhancement ($\gamma_{\text{heat}}/\gamma_{\text{calc}} \sim 2.5$), which imply some corrections on the treatment of electron-phonon coupling and/or electron correlations are necessary.

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