Temperature-dependent electronic structure of $EuNi_2P_2$ revealed by angle-resolved photoemission spectroscopy

H. Anzai[1], K. Ichiki[1], E. F. Schwier[2], H. Iwasawa[2], K. Shimada[2], H. Namatame[2], M. Taniguchi[2], A. Mitsuda[3], H. Wada[3], and K. Mimura[1,2]

[1] Graduate School of Engineering, Osaka Prefecture University, Sakai 599-8531, Japan
[2] Hiroshima Synchrotron Radiation Center, Hiroshima University, Higashi-Hiroshima 739-0046, Japan
[3] Graduate School of Science, Kyushu University, Fukuoka, 819-0395 Japan

E-mail: anzai@ms.osakafu-u.ac.jp

Abstract. We studied the electronic structure of $EuNi_2P_2$, which exhibits both heavy-fermion and mixed-valence behaviors, using angle-resolved photoemission spectroscopy. Multiple Ni $3d$ bands were observed near the Fermi energy, and one of them forms a hole-like Fermi surface around the X point of the Brillouin zone. We also found that the spectral weight of the Ni $3d$ states is rapidly enhanced with decreasing temperature, which is consistent with the temperature dependence of the mean valence of Eu ions. Our results thus demonstrate hybridization between the Ni $3d$ and Eu $4f$ electrons in $EuNi_2P_2$.

1. Introduction

In rare-earth compounds, the hybridization effect between conduction and localized-f electrons (c-f hybridization) leads to the formation of a strongly renormalized quasiparticle, and it is the major contributor to the possible mechanisms for the heavy-fermion state. As the c-f hybridization strength increases, the ground state of rare-earth systems is indeed changed from the magnetic ordered state with localized f moments (RKKY interaction) to the nonmagnetic heavy-fermion state with itinerant f electrons (Kondo effect) and finally to the mixed-valence state [1]. In this respect, $EuNi_2P_2$ provides a unique opportunity to understand the c-f hybridization effect. First, the coefficient of the electronic specific heat is large, $\gamma \sim 100$ mJ / (K^2·mol), and $EuNi_2P_2$ is known as the first heavy-fermion compound among Eu-based materials [2]. Second, the mean valence of Eu ions deduced from the Mössbauer isomer shift varies from 2.25 at 300 K to 2.50 at 1 K, which indicates that the $4f^7$ and $4f^6$ electron configurations are mixed in the ground state [3]. Such a large variation in the mean Eu valence is ideal for the study of the temperature dependence of the c-f hybridization effect.

Angle-resolved photoemission spectroscopy (ARPES) is a direct probe to measure the electronic excitation as functions of energy and momentum. A previous ARPES study of $EuNi_2P_2$ reported that the electronic structure near the Fermi level (E_F) consists of multiple bands and orbitals [4]. Furthermore, an energy gap due to c-f hybridization between the Ni $3d$

and Eu $4f$ states was observed at $|\omega| \sim 0.6$ eV. These results indicate that multiband electronic structure and the hybridization effect are key to the physics of the heavy-fermion behavior. However, the orbital characters of the bands remain unclear.

In this paper, we report ARPES studies of the electronic structure in $EuNi_2P_2$ by using linearly polarized incident synchrotron radiation. We observe three dispersive bands along the Γ-X direction and identify their possible orbital characters. Quantifying the spectral weight of the Ni $3d$ states, we also show that the spectral evolution with temperature is derived from a hybridization effect between the Ni $3d$ and Eu $4f$ states.

2. Experimental

Single crystals of $EuNi_2P_2$ with $ThCr_2Si_2$ type tetragonal structure were synthesized by the Sn-flux method [5]. The ARPES experiments were performed at BL-1 of the Hiroshima Synchrotron Radiation Center, where two polarization geometries (s and p polarization) are achieved by rotating the ARPES chamber around linearly polarized radiation [6]. All the data were taken with 70 eV photons under s polarization. The total energy resolution was set to 25 meV. The samples were cleaved *in situ* and kept under an ultrahigh vacuum (pressure below 5×10^{-11} Torr) at $T = 15$ K during the measurements.

3. Results and discussion

Figure 1(b) shows a photoemission intensity plot, $I(k, \omega)$, along the Γ-X direction. To better visualize the band dispersions, we also plot the second derivative of the photoemission intensity with respect to the energy, $\partial^2 I(k, \omega)/\partial \omega^2$, in Fig. 1(c). The horizontal stripe seen at $0.1 < |\omega| < 0.8$ eV is assigned to multiplet splitting of the Eu $4f^6$ final state configurations [4]. Around the Γ point, a weak but observable band (labeled as α) crosses E_F, as demonstrated by the momentum distribution curves (MDCs) in Fig. 1(d). We found that this band forms a hole-like Fermi pocket around the X point, as shown in Fig. 1(a). Two other bands, assigned to
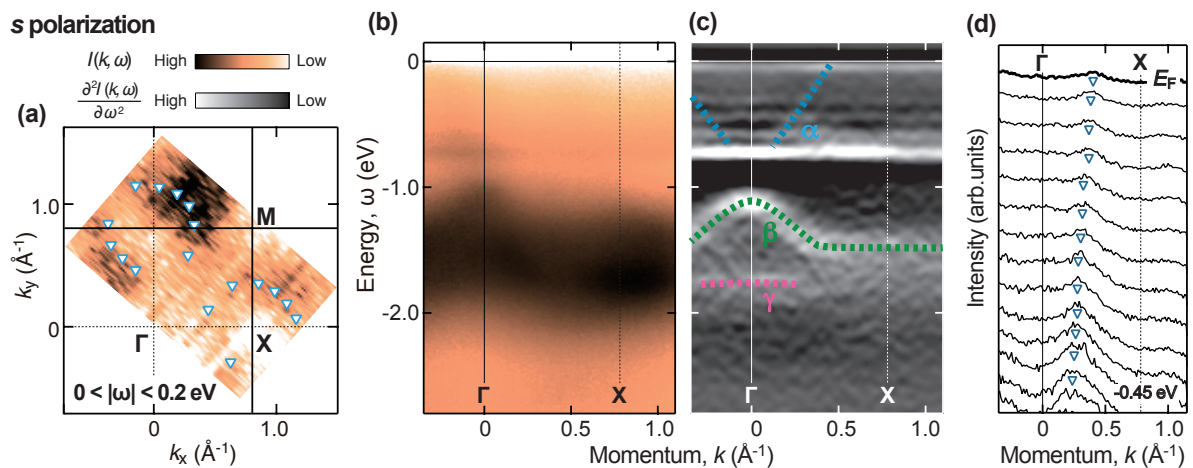

Figure 1. Electronic structure of $EuNi_2P_2$ in the s-polarization geometry. The data were collected at $T = 15$ K with $h\nu = 70$ eV. (a) ARPES intensity map in the Brillouin zone integrated over $0 < |\omega| < 0.2$ eV. Open triangles are Fermi-level crossings determined from the analysis of MDCs. (b) Photoemission intensity plot, $I(k, \omega)$, along Γ-X direction. (c) Second energy derivatives, $\partial^2 I(k, \omega)/\partial \omega^2$, for data in (b). The band dispersions are marked with dashed curves obtained by tracking the peak positions of the MDCs and the local minimum locus of $\partial^2 I(k, \omega)/\partial \omega^2$. (d) MDCs near E_F for data in (b).

β and γ, are determined by tracking the peak positions of the MDCs and the local minimum locus of $\partial^2 I(k,\omega)/\partial\omega^2$. The overall band structure is consistent with previous observations [4].

Polarization-dependent ARPES is a powerful tool for identifying the orbital characters of bands. The photoemission intensity is proportional to the square of the dipole-transition matrix element, $I(k,\omega) \propto |\langle\phi_f^k|\boldsymbol{A}\cdot\boldsymbol{p}|\phi_i^k\rangle|^2$, where ϕ_i^k (ϕ_f^k) is the initial (final) state of the electron wave function, and $\boldsymbol{A}$ and $\boldsymbol{p}$ are the vector potential and momentum operator, respectively. The final state ϕ_f^k can be approximated by a plane-wave state in the mirror plane of the crystal. The overall matrix element and ϕ_f^k should be even. Thus, the initial state ϕ_i^k must have the same symmetry as the dipole operator $\boldsymbol{A}\cdot\boldsymbol{p}$ [7]. In the current experimental geometry (s polarization), $\boldsymbol{A}$ is perpendicular to the mirror plane, so we can selectively observe the odd-symmetry initial state [8].

To determine the orbital characters of the three bands shown in Fig. 1(c), we performed numerical calculations using the density functional theory (DFT) method. The calculated total density of states (DOS) is dominated by the Ni $3d$ states at the energies of $|\omega| > 0.5$ eV, as shown in Fig. 2(a). Considering the spacial symmetry of the $3d$ orbitals, d_{xy} and d_{yz} are odd with respect to the mirror plane, which now lies along the Γ-X direction of the sample. Thus, the β and γ band consist of d_{xy} and/or d_{yz} orbitals. The α band is likely to be hybridized with the Eu $4f$ states, taking into account the large DOS of the Eu $4f$ states near E_F. Further experiments in p-polarization geometry along both the Γ-X and Γ-M directions are necessary to confirm the orbital characters.

The temperature dependence of the energy distribution curves (EDCs) at the Γ point is shown in Fig. 2(b). Two peaks corresponding to the β and γ bands are observed around $|\omega| \sim 1.2$ and 1.7 eV, respectively. The peak intensity of the β band increases strongly with decreasing temperature. On the other hand, the γ band is less sensitive to changes in temperature. The valence or hole-occupation number can be deduced from the photoemission spectral weight [9, 10]. In this study, we quantified the Ni $3d$ spectral weight of the β and γ bands by integrating the intensity of the EDCs over an energy window of $0.9 < |\omega| < 2.5$ eV
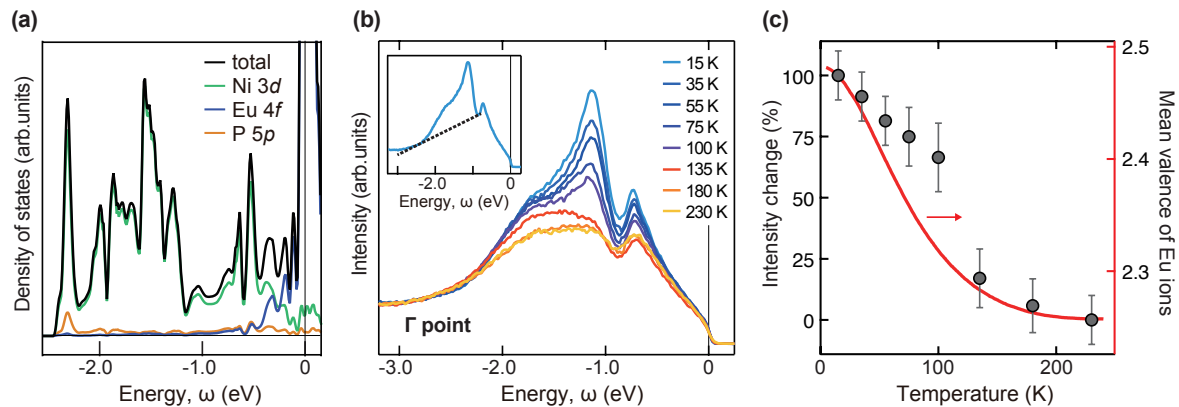

Figure 2. (a) Calculated DOS of $EuNi_2P_2$, where green, blue, and orange curves correspond to the Ni $3d$, Eu $4f$, and P $5p$ partial DOS, respectively. (b) Temperature dependence of EDCs at Γ point taken from the data in Fig. 1(b). Inset shows the EDC at 15 K and a linear background (dashed line). The spectral weight is obtained by integrating the intensities over an energy range of $0.9 < |\omega| < 2.5$ eV after the linear background is subtracted. (c) Evolution of the intensity change (black circles, left axis) and mean valence of Eu ions (red curve, right axis) reported in Ref. 3. The intensity change is normalized to 100% by dividing the difference between the maximum and minimum spectral intensities.

after subtracting the linear background; a typical example is shown in the inset of Fig. 2(b). The difference between the maximum and minimum intensities is normalized to 100% and plotted as a function of temperature in Fig. 2(c) together with the mean Eu valence [3]. Note that the normalized intensity reflects mainly the temperature evolution of the β band, because the background-subtracted intensity of the γ band is approximately constant over a wide temperature range. The intensity change shown in Fig. 2(c) increases with decreasing temperature and is comparable to the temperature variation of the mean Eu valence. This similarity indicates that the Ni $3d$ electron occupation is associated with the mixed-valence state between the $4f^7$ and $4f^6$ configurations of the Eu ions. Therefore, the hybridization between the Ni $3d$ and Eu $4f$ states plays an important role in the heavy-fermion behavior of EuNi$_2$P$_2$. Similar conclusions were reported from resent studies of ARPES, x-ray magnetic circular dichroism, and optical conductivity [4, 11, 12].

The substantial increase of the Ni $3d$ spectral weight around 120 K is likely related to the thermal evolution of the Kondo effect, as proposed from tunneling spectroscopy measurements [13]. Hiranaka *et al.* has suggested that the heavy fermion state in this system is based on the Kondo effect [14]. The characteristic Kondo temperature is estimated as T_K = 75-80 K, which is below the leading-edge midpoint of the intensity change in Fig. 2(c). This deviation implies a fluctuating precursor of the long-range Kondo effect that develops fully at lower temperature.

4. Conclusions

In conclusion, we have studied the electronic structure of EuNi$_2$P$_2$ using ARPES. There is one band intersecting the Fermi level, which forms a hole-like pocket surrounding the X point. The spectral weight of the Ni $3d_{xy}$ and/or $3d_{yz}$ band increases significantly with decreasing temperature. On the basis of a comparison with the DFT calculation and the temperature variation of the mean Eu valence, we suggest that this behavior can be attributed to electron transfer between the Ni $3d$ and Eu $4f$ states. Our results indicate that the c-f hybridization effect makes an essential contribution to the heavy-fermion behavior of EuNi$_2$P$_2$.

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6. References

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