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High-resolution angle-resolved photoemission study of CeP: Narrow-band formation of 4f electrons

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High-resolution angle-resolved photoemission spectroscopy at low temperature has been performed on the low-carrier Kondo material CeP. It was found that the p-f bonding state with a dominant 4f character exhibits a finite-energy dispersion of about 40 meV along the ΓX direction in the Brillouin zone. This implies that 4f electrons in CeP form a narrow band owing to the strong anisotropic p-f and d-f mixing. [S0163-1829(97)51306-3]

Ce compounds have been intensively studied because of their various intriguing physical properties. The observed anomalous properties are regarded to originate in the nature of Ce 4f electrons in the compounds. However, the character of 4f electrons itself has not been well elucidated and has been interpreted with either of the two extreme models, localized and itinerant ones. The single-impurity Anderson model (SIAM),[1,2] which treats f electrons as localized states, successfully describes the dense Kondo materials with low-Kondo temperature[3,4] (T_k's), while it appears not to work well for intermediate-valence materials with high T_k's.[5–7] Further, recent photoemission studies on various cerium compounds[8,9] reported the existence of a finite-energy dispersion of the ''Kondo-resonance'' peak at the Fermi level (E_F), suggesting a substantial contribution of lattice effect to the electronic structure.

The p-f mixing model,[10] which treats the 4f state as a band, has successfully explained the experimental results of semimetallic Ce monopnictides (CeX; X=N to Bi).[11–17] In this model two different types of carriers strongly interact with the Ce 4f state; one is the holelike state originating in the pnictogen p state located at the Γ point in the Brillouin zone and another is the electronlike state at the X point having the Ce 5d_{t2g} character. The d-f mixing between the Ce 4f doublet (Γ_7) and the Ce 5d_{t2g} states, as well as the p-f mixing (the anisotropic hybridization between the Ce 4f quartet and the pnictogen $p_{3/2}$ states with the same Γ_8 symmetry) together play a significant role in characterizing the observed anomalous properties of Ce monopnictides. Such a strong anisotropic interaction between the Ce 4f state and the pnictogen p as well as the Ce 5d state is expected to give a substantial **k** (wave vector) dependence of the hybridization strength, resulting in the band formation of the Ce 4f states. Angle-resolved photoemission spectroscopy (ARPES) is a unique and powerful experimental technique, providing directly the E (energy) -**k** relation, namely the band structure. In this paper, we report a high-energy resolution (HR) ARPES study on single-crystal CeP and discuss the electronic structure and thereby the validity of the p-f mixing model.

CeP single crystals were grown in a sealed tungsten crucible using a high-frequency induction furnace. High-purity Ce (99.9% pure) and P (99.999% pure) metals with the respective composition ratio were used as starting materials. Obtained single crystals were characterized by the x-ray diffraction as well as the resistivity and transversal magnetic resistance measurements. Measured lattice constant, residual resistivity at 4.2 K, and magnetoresistivity at 0.8 K [$\Delta\varrho/\varrho(0)$ where $\Delta\varrho=\varrho(10\text{ T})$-$\varrho(0)$] were 5.945 Å, 78 $\mu\Omega$ cm, and 2.7, respectively, being almost the same values as those of a single crystal used in the previous de Haas–van Alphen measurement.[17]

Photoemission measurements were carried out with a home-built high-resolution photoemission spectrometer which has a large hemispherical electron energy analyzer (diameter: 300 mm) and a highly bright discharge lamp. The base pressure of the spectrometer was better than 2×10^{-11} Torr. The angular and energy resolutions were set at 2° and 50 meV, respectively, for quick data acquisition because of relatively fast degradation of the sample surface as described below. A clean mirrorlike surface of CeP [100] plane was obtained by *in situ* cleaving at 15 K just before the measurement and kept at the same temperature throughout the experiment. Since we observed degradation of the sample surface as evidenced by increase of background in the spectrum after a few hours after cleaving, we recorded every spectra within one hour. We have measured several samples and confirmed the reproducibility of the ARPES spectra. The Fermi level of the sample was referenced to that of a gold film deposited on the sample substrate and its accuracy was estimated to be better than 5 meV.

Figure 1 shows ARPES spectra of CeP measured at 15 K along the ΓX direction in the fcc Brillouin zone using He I [21.2 eV, Fig. 1(a)] and He II [40.8 eV, Fig. 1(b)] resonance lines. The intensity of spectra is normalized at a prominent peak at about 2 eV. The polar angle (θ) measured from the surface normal of the cleaved [100] plane is denoted on each spectrum. We find in Fig. 1 that ARPES spectra excited by two different photons (He I and He II) show remarkably different spectral features; He I spectra have a prominent peak at about 2 eV while He II spectra exhibit two additional peaks comparable to the 2-eV peak at about 0.3 and 3 eV, respectively. In particular, the 0.3-eV peak is remarkably enhanced in He II spectra compared with that of He I spectra. This difference of spectral shape is due to the photon-energy

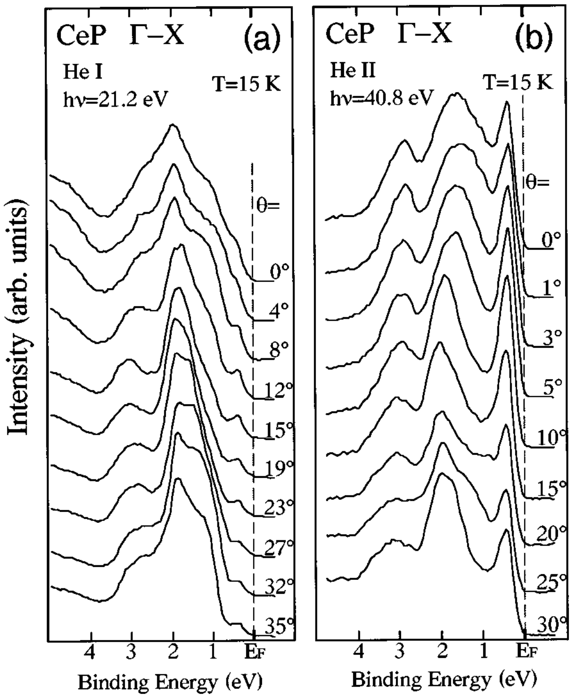

FIG. 1. Angle-resolved photoemission spectra of a CeP [100] single-crystal surface measured along the ΓX direction in the Brillouin zone using the He I (21.2 eV) (a) and He II (40.8 eV) (b) resonance lines at 15 K. Polar angle (θ) referred to the surface normal is indicated on each spectrum.

dependence of the photoionization cross section of atomic orbitals.[18] Since the photoionization cross section of the P 3p orbital is dominant over those of the other two orbitals (Ce 4f and 5d) in the He I photon-energy range, the 2-eV peak is ascribed to the P 3p states. On the other hand, since the photoionization cross section of the Ce 4f orbital drastically increases from the He I photon (21.2 eV) to the He II (40.8 eV) in comparison with other atomic orbitals (P 3p and Ce 5d orbitals), the additional two peaks at 0.3 and 3 eV in He II spectra have a substantial Ce 4f character, especially the 0.3-eV peak which appears to have a dominant Ce 4f character as is clearly seen from the large enhancement rate from the He I to the He II excitation.

It is interesting to compare the present result on CeP with our previous measurements on CeBi.[19] It is found from the comparison of the He I ARPES spectra that the energy bands with binding energies higher than 1 eV exhibit a similar **k** dependence in the two compounds, although the relative intensity of the bands is different between the two. A remarkable difference in the band structure derived from the He I ARPES spectra lies near E_F; in CeBi a prominent dispersive band is observed near E_F around the Γ point (θ~0°) (Ref. 19) while in CeP the spectral intensity near E_F is considerably reduced and, on the contrary, the intensity is rather enhanced in the He II measurement, as shown in Fig. 1. This is explained by the difference in the hybridization strength between the pnictogen p states and the Ce 4f level. The stronger p-f hybridization (mixing) in CeP leads to the increase of Ce 4f character in the bands near E_F. Actually, a small dispersive structure near E_F, which may correspond to the prominent peak in the He I spectrum in CeBi, is observed in the He II spectrum of CeP (shown later).

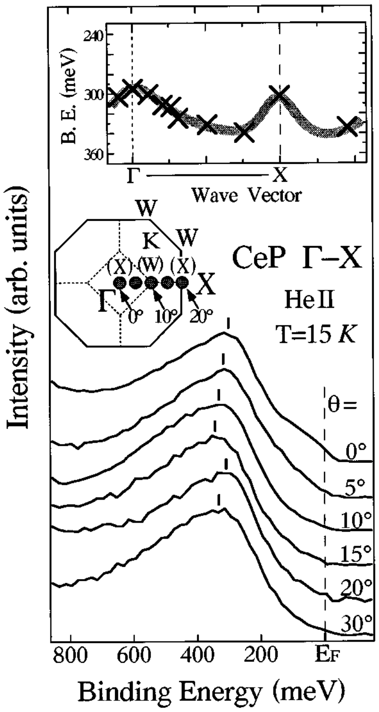

FIG. 2. High-resolution angle-resolved photoemission spectra near E_F of CeP [100] single-crystal surface measured using He II photons (40.8 eV). One of the insets shows the fcc Brillouin zone of CeP projected onto the [100] plane, together with some representative ARPES measurement points. The upper inset shows the measured energy position (binding energy) of the p-f bonding peak at about 300 meV as a function of the wave vector along the ΓX direction.

The two peaks observed at 0.3 and 3 eV in the He II spectra are ascribed to the p-f bonding and antibonding states, respectively, produced through the many-body correlation effect.[20–22] In order to observe a possible dispersive feature of the bonding peak at 0.3 eV, we measured the He II spectra near E_F with a higher energy resolution (50 meV) and show them in Fig. 2. One of the insets to Fig. 2 shows the fcc Brillouin zone projected onto the [100] plane, together with some ARPES measurement points. Since it is established that the electronic states along the high-symmetry lines in the Brillouin zone make a dominant contribution to an ARPES spectrum because of the lifetime broadening and the large density of states on the high-symmetry lines,[23] the normal emission (θ=0°) spectrum reflects the electronic structure mainly at both Γ and X points while the ARPES spectrum at θ=20° corresponds to the X point as shown in the inset. In Fig. 2, we clearly find a small but definite energy dispersion of the bonding peak from the Γ(X) point (θ=0°) to the X point (θ=20°). Another inset to Fig. 2 shows the measured binding energy of the bonding peak as a function of the wave vector along the ΓX direction. The peak of bonding states is located at about 290 meV at the Γ(X) point, starts to move away from E_F to the high binding energy with increasing polar angle (θ), turns around at θ=15°, and moves back to the low binding energy till θ=20°. The magnitude of total energy dispersion is about 40 meV. We find that the observed energy dispersion matches the crystal periodicity, as is evident by the symmetric behavior both at the $\Gamma(X)$ point ($\theta=0°$) and the X point ($\theta=20°$). This indicates that the observed energy dispersion is of an intrinsic bulk origin. Considering the strong Ce $4f$ character of the band, it is inferred that Ce $4f$ electrons in CeP form a narrow band having the energy dispersion of about 40 meV. The observed energy dispersion shows a good accordance with the prediction by the p-f mixing model.[10] The p-f mixing model explains that the finite-energy dispersion of Ce $4f$ electrons is produced through the anisotropic p-f mixing around the Γ point and the interatomic d-f mixing at the X point. Actually, a small shoulder near E_F in the ARPES spectrum of $\theta=0°$ may represent the hole pocket, as has been suggested in the ARPES study on CeBi.[19] A quantitative comparison of the energy dispersion of the Ce $4f$ band between the present ARPES results and the band calculation based on the p-f mixing model would give a deeper insight into the hybridization strength between the Ce $4f$ states and the P $3p$ and Ce $5d$ states. However, at the present stage, the calculation[10] treats the many-body effect as one effective f level and approximates the self-energy using a mean field. A more realistic band calculation based on the p-f mixing model including two f levels is necessary to be compared with the present ARPES results.

In conclusion, we have performed a high-resolution angle-resolved photoemission spectroscopy (HR-ARPES) on single crystal CeP. The He I (21.2 eV) spectrum shows a prominent peak at 2 eV while the He II (40.8 eV) spectrum exhibits two additional peaks comparable to the 2-eV peak at 0.3 and 3 eV. By considering the photoionization cross section of each atomic orbital, the 2-eV peak is assigned to the P $3p$ states while the 0.3- and 3-eV peaks are ascribed to the p-f bonding and antibonding states, respectively, with a dominant Ce $4f$ character. HR-ARPES measurements near E_F showed that the bonding peak has a small but definite (about 40 meV) energy dispersion matching well the crystal periodicity. This suggests that Ce $4f$ electrons in CeP form a narrow band through the anisotropic p-f and d-f many-body interaction.

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