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Inverse-photoemission spectroscopy of iron-based superconductors $\text{NdFeAsO}_{1-\delta}$ and $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$

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Abstract. Unoccupied electronic structure of iron-based superconductors $\text{NdFeAsO}_{0.7}$ ($T_c=51$ K), BaFe_2As_2 and $\text{Ba}(\text{Fe}_{0.89}\text{Co}_{0.11})_2\text{As}_2$ ($T_c=23$ K) has been investigated by means of inverse-photoemission spectroscopy (IPES). The unoccupied Fe 3d states are observed around 1 eV above the Fermi level for all compounds. The Fe 3p-3d resonant IPES suggests that the unoccupied Fe 3d states of $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ have more localized character compared with those of $\text{NdFeAsO}_{0.7}$. The unoccupied Nd 4f states of $\text{NdFeAsO}_{0.7}$ are located around 5 and 7 eV, and the Ba 5d and Ba 4f states of $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ are located around 5 and 12 eV, respectively.

1. Introduction

The recent discovery of new superconductivity in the Fe-pnictide $\text{LaFeAsO}_{1-x}\text{F}_x$ with the critical temperature of $T_c=26$ K [1] has generated great interest because of its high T_c except for the cuprates. For RFeAsO (R: rare-earth metals), so-called 1111 system, $\text{SmFeAsO}_{1-x}\text{F}_x$ exhibits the highest T_c of 56 K [2], and for AFe_2As_2 (A: alkali and alkali-earth metals), so-called 122 system, the highest T_c of 38 K has been reported in $(\text{Ba}_{1-x}\text{K}_x)\text{Fe}_2\text{As}_2$ [3]. The FeAs-based superconductors are commonly composed of the FeAs layers and electronic structure of the FeAs layer is considered to play an essential role to superconductivity. The tremendous studies by means of angle-resolved photoemission spectroscopy have been carried out, so far, for, for example, $\text{NdFeAsO}_{1-x}\text{F}_x$ [4], BaFe_2As_2 [5] and $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ [6], in order to reveal detailed feature of the Fermi surfaces with the hole pockets around the Γ point and electron pockets around the M point.

In this paper, we report whole feature of unoccupied electronic structure of $\text{NdFeAsO}_{1-\delta}$ and $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ investigated by means of inverse-photoemission spectroscopy (IPES). Experimental information on unoccupied density of states (DOS) is important because it is directly related to the excited states. In addition, theoretical unoccupied DOS derived from the band-structure calculations is known to be often located at the lower energy compared

with experimentally determined DOS [7]. In particular, in this study, by tuning incident electron energy (E_k) to the Fe 3p-3d excitation region, the Fe 3d structure near the Fermi level (E_F) is successfully specified. The IPES results suggest that the unoccupied Fe 3d states of $\text{Ba}(\text{Fe}_{1-x}\text{Co}_x)_2\text{As}_2$ have more localized character compared with those of $\text{NdFeAsO}_{1-\delta}$.

2. Experimental

IPES experiments were carried out at Hiroshima Synchrotron Radiation Center (HSRC) using the self-developed IPES spectrometer equipped with a low-energy electron gun, a non-periodic spherical grating and a one-dimensional photon detector [9]. The total energy resolution was ~ 0.5 eV at $E_k=50$ eV. The energy of the IPES spectra is referred to E_F , determined from the Fermi edge of the IPES spectra of Au film. All experiments were carried out at 26 K [10].

The polycrystals of $\text{NdFeAsO}_{0.7}$ (Nd1111), and single crystals of BaFe_2As_2 (Ba122) and $\text{Ba}(\text{Fe}_{0.89}\text{Co}_{0.11})_2\text{As}_2$ (Co-Ba122) were grown by the high-pressure synthesis method [11] and flux method [12], respectively. The oxygen deficiency for Nd1111 and the Co content for Co-Ba122 presented here are estimated values from the starting materials. The actual T_c -values of the grown samples were 51 K for Nd1111 and 23 K for Co-Ba122. Clean surfaces were *in situ* prepared by fracturing for Nd1111 and cleaving for (Co-)Ba122 at 26 K.

3. Results and discussion

Figure 1 shows IPES spectra of Nd1111 measured in the Nd 4d-4f excitation region ($E_k=120\sim 138$ eV). We notice that the feature of the spectra strongly depends on E_k and the spectra exhibit prominent resonance above $E_k=122$ eV. In the spectrum at $E_k=120$ eV below the Nd 4d-4f excitation, two broad structures are observed around 2 and 7 eV. With increasing E_k to 122 eV, the structure around 5 eV, a dip region in the spectrum at $E_k=120$ eV, starts to be gradually enhanced and becomes a remarkable peak at $E_k=124$ eV. With further increasing E_k to 126 eV, a new component begins to be observed as a shoulder around 7 eV. The IPES spectra reach maximum in intensity at $E_k=130$ eV, and turn to decrease in intensity at $E_k=134$ and 138 eV. Since only the cross section of the Nd 4f inverse-photoemission resonantly increases in the Nd 4d-4f excitation region, the enhanced structures with the two components around 5 and 7 eV are attributed to the unoccupied Nd 4f states.

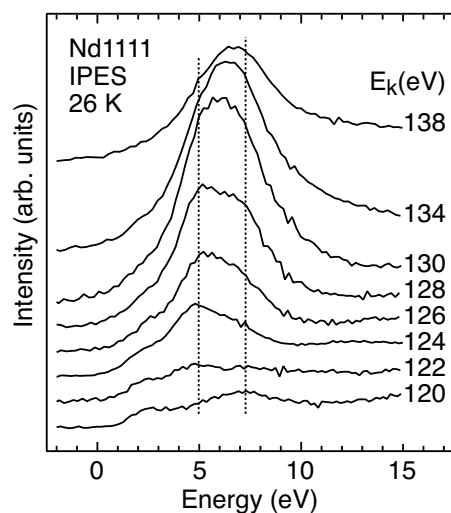


Figure 1. A series of IPES spectra of Nd1111 measured in the Nd 4d-4f excitation region.

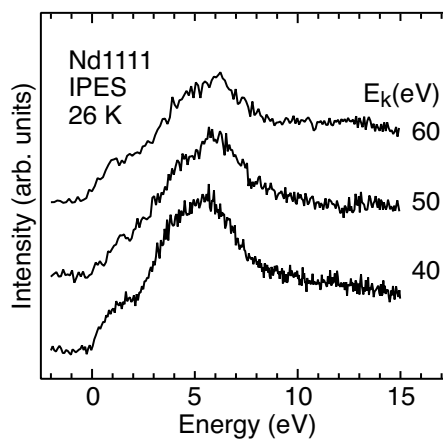


Figure 2. IPES spectra of Nd1111 measured at $E_k=40, 50$ and 60 eV.

Figure 2 shows the IPES spectra of Nd1111 measured at $E_k=40, 50$ and 60 eV. Note that the Fe 3p-3d excitation takes place between $E_k=50$ and 60 eV. In contrast to the Nd 4d-4f resonant IPES results (Fig. 1), the resonance enhancement is not observed between $E_k=50$ and 60 eV and the Fe 3d states can not be specified experimentally. The whole feature of the spectra is essentially unchanged up to $E_k=100$ eV. We find a weak structure near E_F and a broad structure centered at 6 eV in the spectra at $E_k=40$ eV. The higher-lying one is derived from the unoccupied Nd 4f states. According to the band-structure calculation [13], the theoretical Fe 3d DOS of LaFeAsO exists from -5 to 2 eV region across E_F , and have a prominent and narrow peak at 1 eV in the conduction bands. From the comparison, the structure near E_F is attributed to the unoccupied Fe 3d states. Almost no resonance behavior of this structure in the Fe 3p-3d excitation region suggests that the unoccupied Fe 3d states are rather delocalized, in consistent with no satellite structure of the Fe 2p photoemission spectra of LaFeAsO $_{1-x}$ F $_x$ [14].

Figure 3 shows the IPES spectra of Ba122 measured at $E_k=40, 50$ and 60 eV. The IPES spectra show a weak structure near E_F , a broad structure around 5 eV and a remarkable peak around 12 eV. In comparison with the IPES spectra of Nd1111 in Fig. 2, the remarkable peak is related to the Ba ion. The feature of the spectra of Co-Ba122 is similar to that of Ba122. It should be noticed that the structure near E_F is enhanced between $E_k=50$ and 60 eV, in contrast to the IPES results of Nd1111. This enhancement experimentally indicates that this structure is attributed to the unoccupied Fe 3d states and suggests the unoccupied Fe 3d states of Ba122 have a relatively localized character compared with those of Nd1111. Since the Fe 3d states of the FeAs layer is expected to be almost unchanged between Nd1111 and Ba122, the IPES results of Ba122 also support the assignment of the weak structure near E_F of the Nd1111 to the unoccupied Fe 3d states. Regarding the other structure, with the aid of the band-structure calculations [15], the broad structure around 5 eV, the most clearly observed at $E_k=40$ eV, is assigned to the unoccupied Ba 5d states and the remarkable peak around 12 eV to the unoccupied Ba 4f states.

Finally, the IPES spectra of Nd1111, Ba122 and Co-Ba122 measured at $E_k=60$ eV are compared in Fig. 4. The Fe 3d structures are observed near E_F for all compounds. Even taking into account the Nd 4f contribution to the spectra around 6 eV, the intensity of the Fe 3d structure of Nd1111 is smaller than those of (Co-)Ba122. The Fe 3d structure of Nd1111

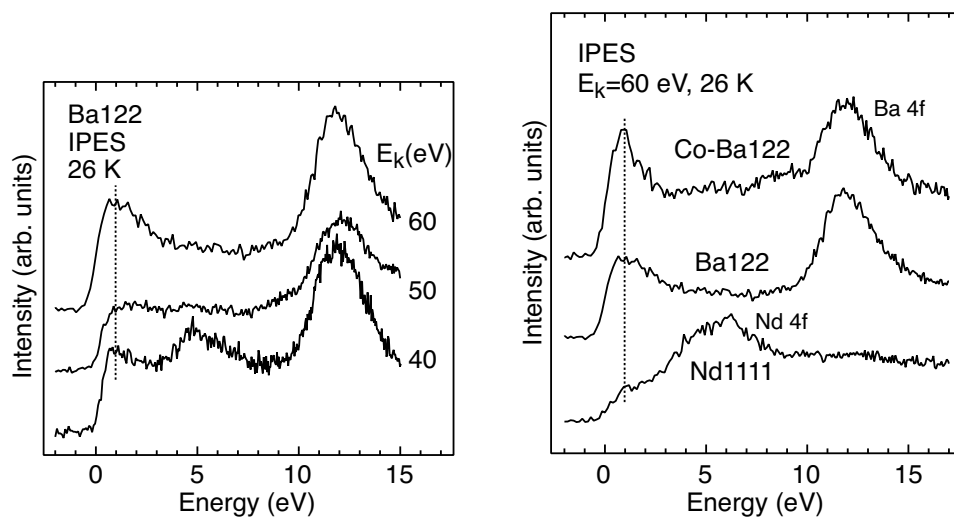


Figure 3. IPES spectra of Ba122 measured at $E_k=40, 50$ and 60 eV.

Figure 4. Comparisons of IPES spectra of Nd1111, Ba122 and Co-Ba122 measured at $E_k=60$ eV.

exhibits almost no resonance in the Fe 3p-3d excitation region, while those of (Co-)Ba122 exhibit clear resonance. The experimental results suggest that the unoccupied Fe 3d states of (Co-)Ba122 are relatively localized compared with those of Nd1111. This increase of the localized character of the Fe 3d states from 1111 to 122 system qualitatively correspond to the recent indications by Miyake *et al.*; the electron correlation becomes strong in order from 1111 (LaFePO and LaFeAsO) to 11 (FeSe and FeTe) through 122 (BaFe₂As₂) systems and, in this order, the compounds progressively lose covalent character of the chemical bonding between Fe and the pnictogen/chalcogen elements and gain stronger ionic character [16]. The IPES results are also qualitatively consistent with the smaller Fe moment of $\sim 0.63 \mu_B$ for La1111 [17] than that of $\sim 0.87 \mu_B$ for Ba122 [18, 19].

4. Summary

The unoccupied electronic structures of Nd1111 and (Co-)Ba122 have been investigated by means of IPES. The unoccupied Fe 3d states are located around ~ 1 eV for all compounds and are relatively localized for (Co-)Ba122 compared with Nd1111. The unoccupied Nd 4f states of Nd1111 locate around 5 and 7 eV, and the Ba 5d and Ba 4f states of (Co-)Ba122 around 5 and 12 eV, respectively.

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