Resonant inelastic x-ray scattering in single-crystal superconducting PrFeAsO$_{0.7}$

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Abstract

Resonant inelastic x-ray scattering (RIXS) spectra at the Fe K-edge were measured for a single crystal of the iron oxypnictide superconductor PrFeAsO$_{0.7}$ ($T_c=42$ K). They disclose a weak, broad feature centered around 4.5 eV energy loss, which is slightly resonantly enhanced when the incident energy is tuned in the vicinity of the 4$p$ white line. We tentatively ascribe it to the charge-transfer excitation between As 4$p$ and Fe 3$d$.

Key words: Iron pnictides, Resonant inelastic x-ray scattering

1. Introduction

The recent discovery of high-Tc superconductivity in the iron oxypnictides$^{[1]}$ was shortly followed by the attainment of the highest critical temperature in all non-cuprate materials for the samarium-based system$^{[2]}$. It was rapidly ensued by a plethora of experimental and theoretical works on the electronic properties of this new class of compounds. Interestingly enough, their electronic structure is not fully elucidated yet. It is usually described by one or the other of two theoretical approaches, the first one suggesting an itinerant-electron state$^{[3,4]}$, and the second one underlining on-site correlations$^{[5,6]}$. Seemingly discordant results were obtained experimentally as well, with a somewhat correlated electronic structure$^{[8]}$. This fundamental cleavage highlights the need for more compelling insight about by the Coulomb interaction between the core-hole potential and the valence electrons in the intermediate state. The more delocalized the valence electrons are, the weaker their interaction with the core hole gets. Notwithstanding these difficulties, we here report on an examination of the electronic structure of a single-crystal of superconducting PrFeAsO$_{0.7}$ employing RIXS at the Fe K-edge. We discern a broad feature near 4.5 eV, reminiscent of a ligand-to-metal charge-transfer excitation.

2. Experimental details

The data were taken at the Taiwan beamline BL12XU at SPring-8 with both the horizontal scattering plane and the incident photon polarization ($\epsilon$) parallel to the $ac$ plane. A total energy resolution of 1 eV was achieved using a double-crystal monochromator Si (111) and a 1-m bent Ge (620) crystal analyzer for the incident and scattered beams, respectively. The size of the beam at the sample position was 24 $\mu$m (horizontal) x 37 $\mu$m (vertical). A single crystal of PrFeAsO$_{0.7}$ was grown by a high-pressure synthesis method using a belt-type anvil apparatus$^{[1]}$.

3. Results and discussion

The absorption spectrum measured in the total fluorescence yield mode at the Fe K-edge for incident photon polarization $\epsilon$ both parallel ($\epsilon//ac$) and perpendicular ($\epsilon//c$) to the FeAs planes is shown in Fig. 1. The maximum of the white line, corresponding to transitions to the Fe 4$p$ states making antibonding interactions with As electronic orbitals, is shifted towards...
the high-energy side in the ε//a geometry (7129 eV) compared with ε//c (7121 eV). This is concordant with the fact that, in the former geometry, one probes the Fe orbitals that lie within the FeAs plane and interact most with the As orbitals, hence the shift of the antibonding states towards high energies. For the same reason, the pre-edge, mostly relating to the Fe 3d orbitals, is seen to dwindle and slightly broaden for ε//a compared with ε//c.

The incident-energy (E$_1$) dependence of the RIXS spectrum was measured across the 7110-7130 eV range at the (0,0,6.5) tetragonal reciprocal lattice point. The corresponding scattering angle is approximately 83°, where a relatively reduced elastic scattering can be achieved. Apart from the prominent Kβ$_5$ fluorescence peak that drifts linearly with E$_1$, almost featureless spectra were obtained, at stark contrast with the usual RIXS signal obtained on the cuprates. This flagrant difference may stem from the itinerant nature of the Fe 3d electrons in the iron oxypnictides, resulting in a large bandwidth, and therefore a weak interaction with the core-hole potential in the RIXS intermediate state. Another plausible reason could be that the Kβ$_5$ fluorescence line, because the Fe site is not centrosymmetric, gains intensity from both quadrupolar (3d $\rightarrow$ 1s) and dipolar (4p-3d $\rightarrow$ 1s) transitions, the latter occurring through 4p-3d hybridization. This behavior would be analogous to that in the pre-edge of the K absorption spectra of 3d metals [12]. A stronger intensity would accordingly ensue for the Kβ$_5$ of Fe in the oxypnictides compared with the cuprates where Cu occupies a centrosymmetric site and therefore yields a pure quadrupolar Kβ$_5$ line.

Our main finding is a faint, broad peak centered at ~4.5 eV which undergoes a slight resonant enhancement at constant loss energy when E$_1$ is set to 7124~7125 eV (cf. vertical ticks in Fig. 2). The energy of this feature is reminiscent of the charge transfer from O 2p to Cu 3d in the cuprates, it is therefore tempting to assign it to the charge transfer between As 4p and Fe 3d. According to first-principle calculations of the local densities of states (DOS) of LaFeAsO by Ishibashi et al. [13], the maximum of the As 4p occupied states lies around -3 eV and the Fe 3d unoccupied states show a peak near 1 eV. We suggest therefore to assign the 4.5-eV RIXS feature to the charge transfer between As 4p and Fe 3d. We plan to refine our analysis via further measurements with a higher energy resolution.

4. Summary

We have studied the incident-energy dependence of the RIXS spectrum of the superconductor PrFeAsO$_{0.7}$. The spectra are found to be rather featureless, which could be explained either by the itinerant nature of the Fe 3d electrons, or by the strong intensity of the Kβ$_5$ line that could hide some of the RIXS features, or by both. The only feature which we observed is a broad peak near 4.5-eV energy loss, lying in between the elastic peak and the tail of the Kβ$_5$ fluorescence line. Based on a comparison with DOS calculations, this feature is likely related to the charge transfer excitation between As 4p and Fe 3d.

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