論文内容の要旨

Electronic structure of layered transition-metal compounds with t_{2g} orbital degeneracy

（t_{2g} 軌道縮退を持つ層状遷移金属化合物の電子構造）

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Transition-metal compounds with orbital degeneracy of transition-metal *d* orbitals show remarkably rich electric and magnetic properties such as high T_c superconductivity in cuprates, triplet superconductivity in ruthernates, and colossal magnetoresistance in manganites. Geometry of Fermi surfaces and band dispersions are key issues to understand the nature of the superconductivity and the effect of the antiferromagnetism.

We have studied electronic structures of three transition-metal compounds, $Ba(Fe_{1-x}Co_x)_2As_2$ (x = 0.06, 0.14, and 0.24), $FeSe_{1-x}Te_x$ (x = 0.6 and 0.9), and $BiCoO_3$, by using angle-resolved photoemission spectroscopy (ARPES), and x-ray photoemission spectroscopy (XPS), x-ray absorption spectroscopy (XAS), cluster model calculation, and model Hartree-Fock calculation. All three compounds have layered structure with t_{2g} orbital degeneracy and have rich physical properties.

The FeAs-based superconductors commonly have the FeAs layers where Fe atoms are tetrahedrally coordinated by As. $BaFe_2As_2$ shows superconductivity by electron doping with the highest T_c of 25 K in $Ba(Fe_{1-x}Co_x)_2As_2$ although the FeAs plane is highly disordered by the Co doping [1-4]. We have studied evolution of dispersions and Fermi surfaces by Co doping for $Ba(Fe_{1-x}Co_x)_2As_2$ (x = 0.06, 0.14, and 0.24) by ARPES. In optimally-doped case, we found that one of the *yz/zx* hole bands is missing and the renormalization factor of the observed *yz/zx* hole band is strongly enhanced compared to that in the overdoped regimes. In contrast, the x^2-y^2 and $3z^2$-r^2 bands show rigid band energy shift due to the Co doping and their renormalization factors do not depend on the doping level. The fact that the anomalous effect is observed only in the *yz/zx* band suggests

that the band Jahn-Teller type instability due to the orthorhombic distortion is important. In the optimally-doped system, the tetragonal phase with superconductivity and the orthorhombic phase with spin-orbital ordering are competing with each other. When a local and dynamic orthorhombic distortion exists in the tetragonal phase, *yz/zx* orbital degeneracy should be lifted due to a kind of dynamic band Jahn-Teller effect, and, consequently, one of the two hole pockets with *yz/zx* character is expected to disappear. The ARPES results indicate that the electron correlation effect depends on the orbital character and the doping level and that the orbital degeneracy of *yz/zx* bands is deeply related to the superconductivity.

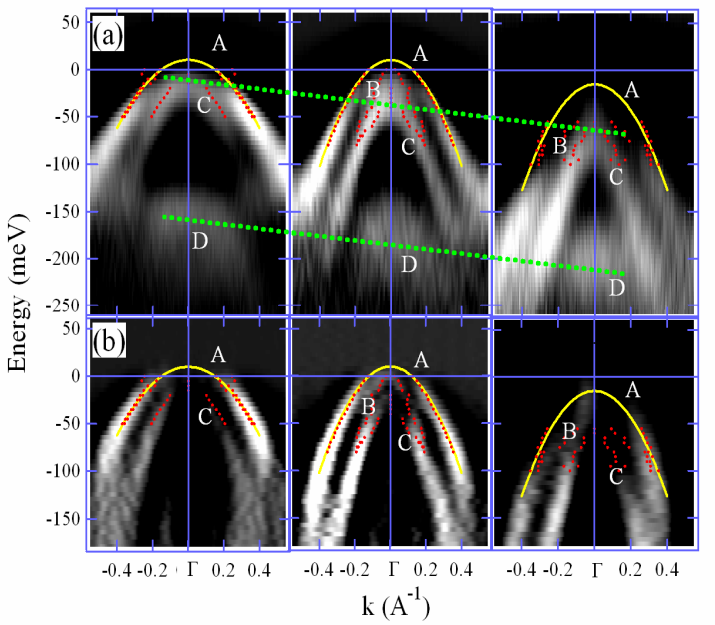

Figure 1: (a) Second derivative plot of EDCs of $Ba(Fe_{1-x}Co_x)_2As_2$ with x = 0.06 (left panel), 0.14 (center panel), and 0.24 (right panel) taken at $h\nu$ = 23 eV. The dots indicate the band locations determined by fitting the momentum distribution curves to Lorentzian functions. The solid parabolic curves roughly show the dispersion of hole band A. The dotted lines roughly show the energy shift of top of hole band C and that of band D. (b) Second derivative plot of MDCs of $Ba(Fe_{1-x}Co_x)_2As_2$ with x = 0.06 (left panel), 0.14 (center panel), and 0.24 (right panel) taken at $h\nu$ = 23 eV. Band A, B, C, and D correspond to *yz/zx*, *yz/zx*, x^2-y^2, and $3z^2$-r^2 characters, respectively.

As for $FeSe_{1-x}Te_x$, it is reported that the superconducting region spreads and the spin density wave (SDW) phase shrinks in the phase diagram of $FeSe_{1-x}Te_x$ after the annealing treatment [5]. We have studied electronic structure of high quality single crystals for $FeSe_{1-x}Te_x$ (x = 0.6 and 0.9) before and after the annealing treatment in order to investigate the impact of annealing on the band structure by ARPES. We identified orbital character of Fe 3*d* bands on the basis of the LDA calculation as shown

in Fig. 2. In the as-grown sample, band γ which is x^2-y^2 orbital of FeTe, is smoothly connected to the band at M point and the energy position of the x^2-y^2 band at M point is lower than that of the annealed one. In the annealed one, band β which is *yz/zx* orbital is smoothly connected to the band at M point, and the band at M point can be assigned to the *yz/zx* band for FeSe. We found that the coexistence of the FeSe bands and the FeTe bands around Γ point is characteristic for Fe(Se,Te) and is expected to affect the superconducting properties. We found that ARPES results of the annealed $FeSe_{0.1}Te_{0.9}$ are different from those of the as-grown $FeSe_{0.1}Te_{0.9}$. Firstly, ARPES spectra are much sharper in the annealed sample that in the as-grown one. Secondly, the *yz/zx* bands clearly cross E_F in the annealed sample while they just touch E_F in the as-grown one. This result is important for superconductivity because the annealed $FeSe_{0.1}Te_{0.9}$ appears superconductivity below ~ 12 K.

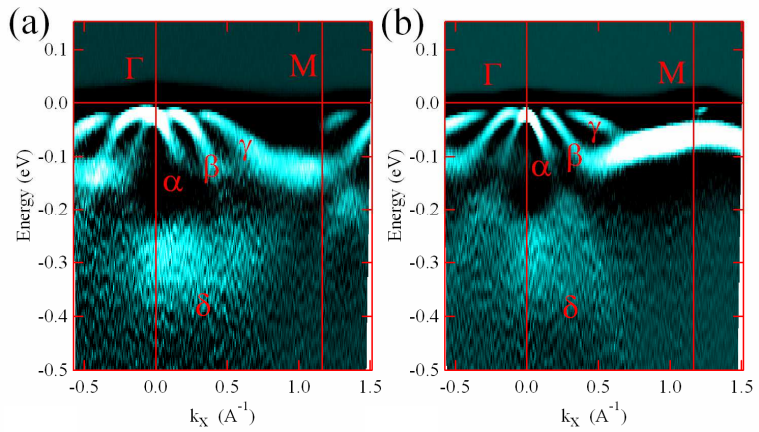

Fig 2: ARPES results for $FeSe_{0.4}Te_{0.6}$ taken at $h\nu$ = 17 eV. (a) Second derivative plot of EDCs for as-grown sample. (b) Second derivative plot of EDCs for annealed sample. Band α, β, γ, and δ correspond to x^2-y^2 orbital of FeSe, *yz/zx* orbital, x^2-y^2 orbital of FeTe, and $3z^2$-r^2 characters, respectively.

In order to clarify the microscopic mechanism, we studied electronic structure of $BiCoO_3$, which has d^6 configuration of Co^{3+} and C-type antiferromagnetic order, by using XAS and XPS and unrestricted Hartree-Fock calculation on a multiband *d-p* model, which does not have self-interaction effect. $BiCoO_3$ has small 10Dq and high-spin Co^{3+} values. We found C-type is the most stable due to transfer integral from oxygen ion to oxygen. Results of Hartree-Fock calculation indicate that Co-O-O-Co superexchange pathway is more important than the direct path of Co-O-Co along the *c*-axis as shown in Fig. 3.

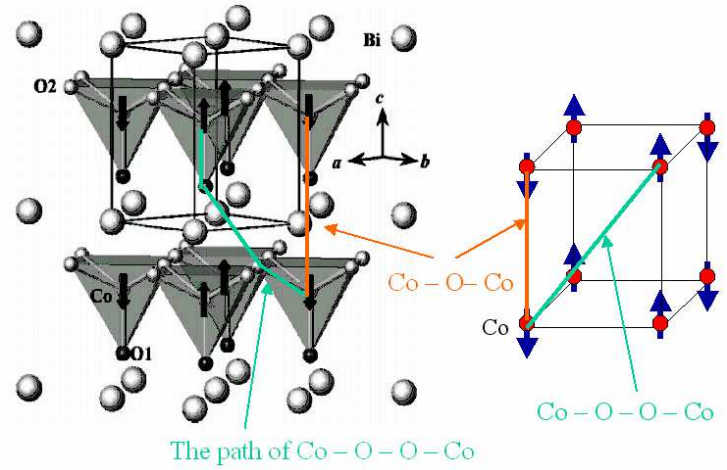

Fig 3: Schematic model of long range superexchange pathway (Co-O-O-Co) for $BiCoO_3$ with C-type antiferromagnetic order [6].

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