論文の内容の要旨

論文題目　Spectroscopic studies of the electronic structures of 122-type superconductors and ferromagnetic semiconductors
(122 型超伝導体および強磁性半導体の電子構造の分光研究)

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Iron-based superconductors (FeSCs) which exhibit the highest transition temperature (T_c) of ~ 55 K have been extensively studied since their discovery in 2008. In spite of the fact that all the FeSCs share the iron-pnictide/chalcogenide planes like the CuO_2 planes in the cuprates, the T_c's and the superconducting gap structures differ between materials and dopants. In particular, superconductors with line nodes in the superconducting gap have attracted much attention. Nodal superconductivity in FeSCs is unconventional in that the presence of line nodes is determined not only by the symmetry of the order parameter but also by sign change of the *s*-wave order parameter under the C_4 point-group symmetry.

$BaFe_2(As_{1-x}P_x)_2$ (Ba122P), an isovalently-substituted FeSC, exhibits evidence for quasiparticle excitations well below T_c from various experimental probes including penetration depths, nuclear magnetic resonance, and thermal conductivity. Since the discovery, the identification of the nodal superconducting gap structure has been the central focus of FeSC research. However, a consensus has not been reached because of mutually

inconsistent experimental results. To gain further insight into the nodal superconductivity in the P-doped 122 compounds and consequently to solve the dispute on Ba122P, we have performed angle-resolved photoemission spectroscopy study of the three-dimensional gap structure of $SrFe_2(As_{1-x}P_x)_2$ (Sr122P) in Chap. 3. Reflecting the smaller atomic radius of Sr than Ba, Sr122P has a more three-dimensional electronic structure along the k_z direction. We observed that, while the three hole Fermi surfaces (FSs) show orbital-dependent superconducting gaps, the electron FSs show almost isotropic and k_z-independent superconducting gaps. We propose that the SC gap of the outer hole FS is reduced or changes the sign around the Z-X line. We also found that the spectral weight of the coherence peak is the largest for the inner hole FS.

Chapter 4 is devoted to time- and angle-resolved photoemission spectroscopy (TrARPES) of the parent compound $BaFe_2As_2$. $BaFe_2As_2$ exhibits stripe-type spin-density- wave (SDW) antiferromagnetic (AFM) order at the Ne'el temperature (T_N) of 138 K. Below T_N, the band structure of the paramagnetic state is folded by the ordering vector (π/a, π/a, 2π/c). Our motivation is to optically excite the AFM ordered state by a pump pulse at a low temperature and to search for an ultrafast phase transition to the paramagnetic states and subsequent relaxation back to the SDW state. For this purpose, we have employed a new TrARPES apparatus that utilizes the rare-gas higher harmonic generation with photon energy $h\nu$ in the extreme ultraviolet regime. We observed electronic modifications from the folded band structure within ~ 1 ps after the pump pulse, which we interpret as the melting of SDW.

The latter half of the thesis is devoted to soft x-ray spectroscopic studies of a new diluted magnetic semiconductor (DMS) which has the same crystal structure as the Ba122-type FeSC. DMSs have attracted much attention as a candidate for future spintronics devices after the discovery of ferromagnetism in Mn-doped GaAs (GaMnAs). However, the limited chemical solubility of the magnetic element Mn and the uncontrollability of the carrier density independently of the magnetic element concentration are major obstacles to systematic material design.

The newly-found DMS $Ba_{1-x}K_x(Zn_{1-y}Mn_y)_2As_2$, which has the same crystal structure as the FeSC $BaFe_2As_2$, circumvents these problems and realizes the ferromagnetic transition temperature as high as 230 K and, therefore, understanding its basic electronic structure

has been highly desired. In the latter half of this thesis, I have studied the electronic properties by soft x-ray spectroscopies.

In Chap. 5, I show by x-ray absorption and resonance photoemission spectroscopy that the doped Mn has the valence of 2+ and that the Mn *3d* partial density of states has great similarity to that of GaMnAs. Ferromagnetic correlation between *S*=5/2 local magnetic moments mediated by hole carriers is therefore considered to create ferromagnetism. In Chap. 6, I present soft x-ray angle-resolved photoemission spectroscopy (ARPES) of $Ba_{1-x}K_x(Zn_{1-y}Mn_y)_2As_2$ single crystals. Due to the longer probing depth of soft x rays than vacuum-ultraviolet light, we have successfully observed bulk band dispersions. Also, by tuning the photon energy to the Mn L_3 edge, we selectively enhance Mn *3d*-related electronic states, and found that the Mn *3d* impurity band is formed below the Fermi level as in GaMnAs. On the other hand, the metallic transport may predominantly occur in the host valence band, rather than in the impurity band as in GaMnAs.

In Chap. 7, I present x-ray magnetic circular dichroism (XMCD) and resonant inelastic x-ray scattering (RIXS) studies using Mn $L_{2,3}$ edge. XMCD directly reveals the spin and orbital magnetic moments by the application of spectral sum rules. RIXS reveals electronic excitations of the Mn impurity. We observed ferromagnetic XMCD signals with the spin moment of $0.45\mu_B$/Mn and the nearly quenched orbital moment of 0.05 μ_B/Mn. However, the line shape is typical of the high-spin configurations of d^5. These results indicate the presence of competing antiferromagnetic and ferromagnetic interactions between Mn local spins. RIXS spectra show broad peaks from 6 eV to 1 eV in energy loss which originate from *d-d* orbital excitations from the ground states. From the comparison with the RIXS spectra of GaMnAs, we conclude that both the pure $3d^5$ and charge-transferred $3d^5\underline{L}$ electron configurations constitute the ground state of Mn in $Ba_{1-x}K_x(Zn_{1-y}Mn_y)_2As_2$.

Our studies have thus explicitly demonstrated that the $ThCr_2Si_2$-type crystal structure with chemical flexibility is an ideal stage both for high-temperature superconductivity and for carrier-induced ferromagnetism.