論文内容の要旨

論文題目: High Energy Spectroscopic Study of Transition-Metal Compounds with Electron-Hole Interaction

(電子・ホール相互作用を持つ遷移金属化合物の高エネルギー分光による研究)

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The idea of an excitonic insulator state was first theoretically proposed to be realized in semiconductors having very small band gaps or in semimetals with very small band overlap [1]. A very low carrier concentration results in weakly screened Coulomb interaction between a valence band hole and a conduction band electron leading to an electron-hole bound state or an exciton. If the exciton binding energy exceeds the magnitude of the band gap, then the semiconducting or semimetallic ground state becomes unstable against the formation and condensation of excitons and excitonic insulator transition occurs with charge- or spin- density-waves ordering. Surprisingly, real materials evidently manifesting this excitonic insulator phase is not found to date. One promising candidate is Tm(Se,Te) which shows anomalous resistivity behavior [2] and, more remarkably, a sign of superfluidity of excitons in the intermediate pressure region at low temperature [3]. 1T-$TiSe_2$ is another candidate for the excitonic insulator state which is recently discussed by angle-resolved photoemission spectroscopy (ARPES) measurement and subsequent calculations [4, 5].

In this thesis, ternary layered tantalum chalcogenide $Ta_2(Ni_{1-x}Co_x)Se_5$ and one of the parent materials of the recently discovered FeAs-based superconductor $BaFe_2As_2$ are studied by using x-ray photoemission spectroscopy (XPS), ARPES, and x-ray absorption spectroscopy (XAS) and discussed in the perspective of excitonic insulator.

Ta_2NiSe_5 has a quasi-one-dimensional layered structure with semiconductive ground state [6]. It undergoes a structural phase transition around 330 K though no density-wave order is found. Ni 2p core-level photoemission and x-ray absorption spectra show that the Ni 3d subshell is partially occupied and the Ni 3d states are strongly hybridized with the Se 4p states shown in Fig. 1. The ARPES result shows a distinctively flat dispersion of the valence band as seen in Fig. 2 which is strikingly similar to the experimental ARPES spectra of 1T-$TiSe_2$ and its theoretically reproduced spectra assuming BCS-like excitonic insulator phase transition [4, 5]. Therefore, Ta_2NiSe_5 is proposed to be another promising candidate for excitonic insulator. The existence of a fair amount of holes in Ni 3d-Se 4p and consequently the existence of electrons in the Ta 5d state revealed by XPS

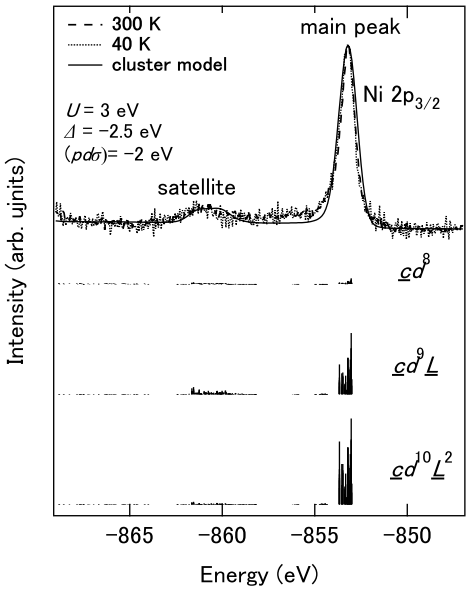

Figure 1: Ni $2p_{3/2}$ core-level spectra of Ta_2NiSe_5 at 300 K (dashed curve) and at 40 K (dotted curve). Experimental Ni $2p$ spectra along with the broadened calculated spectrum (solid curve) obtained from the $NiSe_4$ cluster calculation are shown in the upper panel. In the lower panel, the calculated line spectrum is decomposed into $\underline{c}d^8$, $\underline{c}d^9\underline{L}$, and $\underline{c}d^{10}\underline{L}^2$ components.

and XAS together with the cluster-model calculation would be compatible with the semiconductive transport properties under this excitonic pairing picture. Detailed temperature-dependent ARPES measurements revealed that the top valence band shifts to higher binding energy and its bandwidth increases by decreasing temperature. The latter observation is explained by the shortening of the Ni and Ta atoms distance, thus showing the coupling of excitonic pairing and lattice distortion. No CDW transition is expected because of its direct band gap. Though the flat feature of the valence band weakens as the system is heated toward the structural phase transition temperature, exciton fluctuations remain finite similarily observed in the $1T$-$TiSe_2$ ARPES experiment [4]. From the marked peak-width narrowing below the structural transition temperature, the excitonic insulator (exciton condensate) phase transition seems to occur at the same temperature.

$BaFe_2As_2$ has a layered structure with FeAs square lattice. It is recently discovered to exhibit superconductivity by chemical doping or applying pressure, though $BaFe_2As_2$ itself undergoes a concomitant structural and spin-density-wave (SDW) ordering phase transition at around 140 K [7]. In order to elucidate the nature of this SDW phase transition, temperature-dependent and three-dimensional ARPES measurements were performed. The second derivative and EDC plots around the zone center and around the corner are shown in Figs. 3 and 4. Pseudogap behavior was found at E_F in the paramagnetic state in relation to spin and orbital

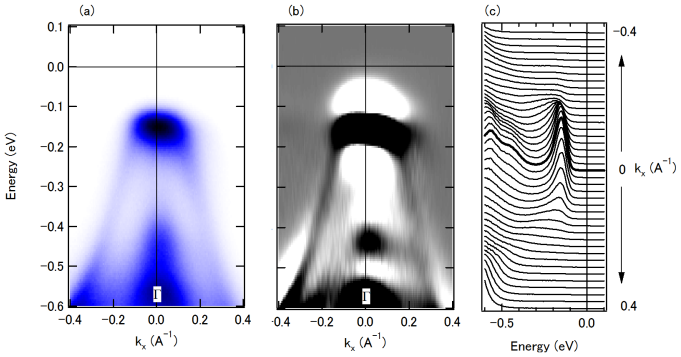

Figure 2: Band dispersion of Ta_2NiSe_5 near the Γ point along the chain direction at 40 K. (a) Intensity, (b) second derivative, and (c) EDC plots.

fluctuations. Crossing the SDW transition temperature, the spectral weight at $\sim$ 50 meV is transferred to the flat broad band at 70 - 100 meV and the near-E_F bands (three hole-like valence bands) at 0 - 30 meV. This coexistence of the Fermi surfaces and the flat broad band at 70 - 100 meV was interpreted within the model of orbital-dependent excitonic coupling accompanied with orbital reconstruction. That is, two hole bands having yz/zx characters and one electron band closer to the Fermi energy are assumed to couple by electron-hole or excitonic interaction. Then a pair of one hole band and one electron band will be gapped and the other hole band remains ungapped. During this process, orbital (yz/zx) reconstruction occurs between the two hole bands inducing the remaining hole band to gain large anisotropy. The k_z dependence of this remaining hole band may explain the observed three-dimensional Fermi surface mapping. This implies that the exciton mechanism would be the origin of the observed commensurate SDW.

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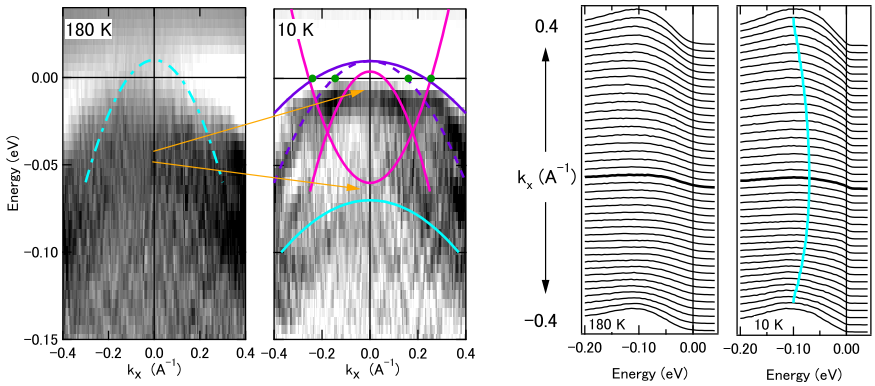

Figure 3: Second derivative plots and EDC plots around the zone center ($k_x = k_y = 0$) at 180 K and 10 K with photon energy 17 eV. The arrows indicate the spectral weight transfer by the SDW transition. The hole band and the folded electron bands crossing the Fermi level unchanged by the SDW transition are schematically shown by red solid curves while blue dot-dashed and solid curves represent bands before and after the excitonic gap effect. The purple solid curve represents the remaining hole band gainining anisotropy and the dashed curve comes from its twinned structure. The green circles indicate the E_F crossing points.

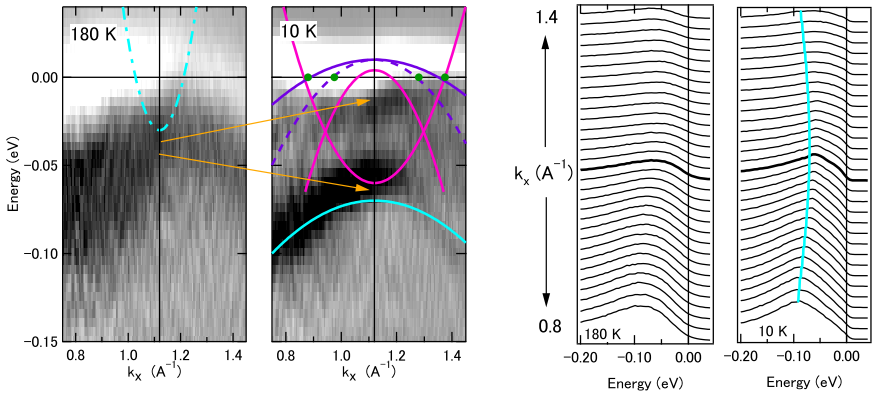

Figure 4: Second derivative plots and EDC plots around the zone corner ($k_x = 1.12$ Å^{-1} and $k_y = 0$) at 180 K and 10 K with photon energy 17 eV. The arrows indicate the spectral weight transfer by the SDW transition. The electron band and the folded hole bands crossing the Fermi level unchanged by the SDW transition are schematically shown by red solid curves, otherwise the colored lines represent the same meanings as those in Fig. 3.