

Resonant Photoemission Study of TiF_3

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Transition Metal(TM) compounds have been subjects of many studies because of their interesting properties such as metal-nonmetal transition, ferro(antiferro)magnetism and superconductivity. With the vigorous studies of many prominent physicists, various properties of TM compounds were understood as the result of the TM $3d$ -anion $2p$ (or $3p$, ...) hybridization.

J.Zaanen *et al.* suggested the charge transfer(CT) model to explain this TM-ligand hybridization. They used hybridization parameter T explicitly to recognize the anion $2p \rightarrow$ TM $3d$ charge transfer energy Δ . In this CT model, neglecting the lattice effects one treats the $3d$ states of a single TM site as a degenerate impurity orbital having Coulomb interaction energy U and hybridized by T to the anion p -band. With successful applications to spectroscopic data for late TM(*eg.* Co, Ni, Cu) halides and oxides like CuCl_2 , NiO, CuO, this framework has been widely accepted. Recently, this model was also used to explain the electron structure of early TM(*eg.* Sc, Ti, V) compounds. However there have been relatively fewer studies on the early TM compounds. In this work we performed the resonant photoemission spectroscopy(RPES) of TiF_3 because its nearly octahedral symmetry makes the analysis quite simple. The distances between Ti atom and neighboring 6 F atoms are all the same and the angle between its symmetry axes is $90 \pm 0.1^\circ$.

The RPES was performed at the 2B1 VUV beam line on the Pohang Light Source(PLS) using ultra-high vacuum chamber equipped with hemispherical multichannel electron analyzer. All of the RPES spectra are normalized by dividing counts by mesh current due to the incident photon flux and the binding energies are referred to the intense core peak instead of the Fermi edge because TiF_3 is insulator. And the total energy resolution($\Delta E/E$) was about $1/4000$. The sample was evaporated on a metal surface to minimize the charging effect. We used a commercial powder sample of Johnson & Matthey Co for evaporation.

We can find the CT type satellite(s_1) which is acquired by diagonalizing a simple Hamiltonian [*H.-J. Kim, Thesis*] in the RPES spectra at the $\text{Ti}2p$ absorption edge(Fig.1). The hybridization of TM($\text{Ti}3d$) and ligand(F) valence states results in the inter-atomic configuration interaction(CI). The effect of the CI shows up as the satellite structure of $\text{Ti}2p$ core-level photoemission spectrum in the $\text{Ti}2p$ -RPES and even in the normal photoemission spectrum. In this spectra, we can find another structure(e_g) located at 2-3 eV higher binding energies than $\text{Ti}3p$ and $\text{Ti}3d$ core peaks, which is remarkably enhanced in the on-resonance spectra. This structure is understood as having the e_g final state. As TiF_3 has octahedral symmetry, $\text{Ti}3d$ electron states are split into the t_{2g} state(ground state) and the e_g state with the energy difference $10Dq$. Most of the $3d$ electrons are in the t_{2g} state after normal photoemission, but after the RPES, they can be in the e_g state as well as the t_{2g} by the intermediate process. So the final e_g state peak is shifted to the higher binding energy by about $10Dq$. We can modify the CT model Hamiltonian to include this crystal field splitting. We can also confirm the existence of the final e_g state from the X-ray absorption spectrum numerical calculation. We performed RPES at the $\text{Ti}3p$ and the $\text{F}1s$ absorption edges too. At the $\text{Ti}3p$ absorption edge, $\text{Ti}3d$ peak shift similar to the $\text{Ti}2p$ absorption edge was observed, and at the $\text{F}1s$ absorption edge we can not find any enhancement of core-level peaks.

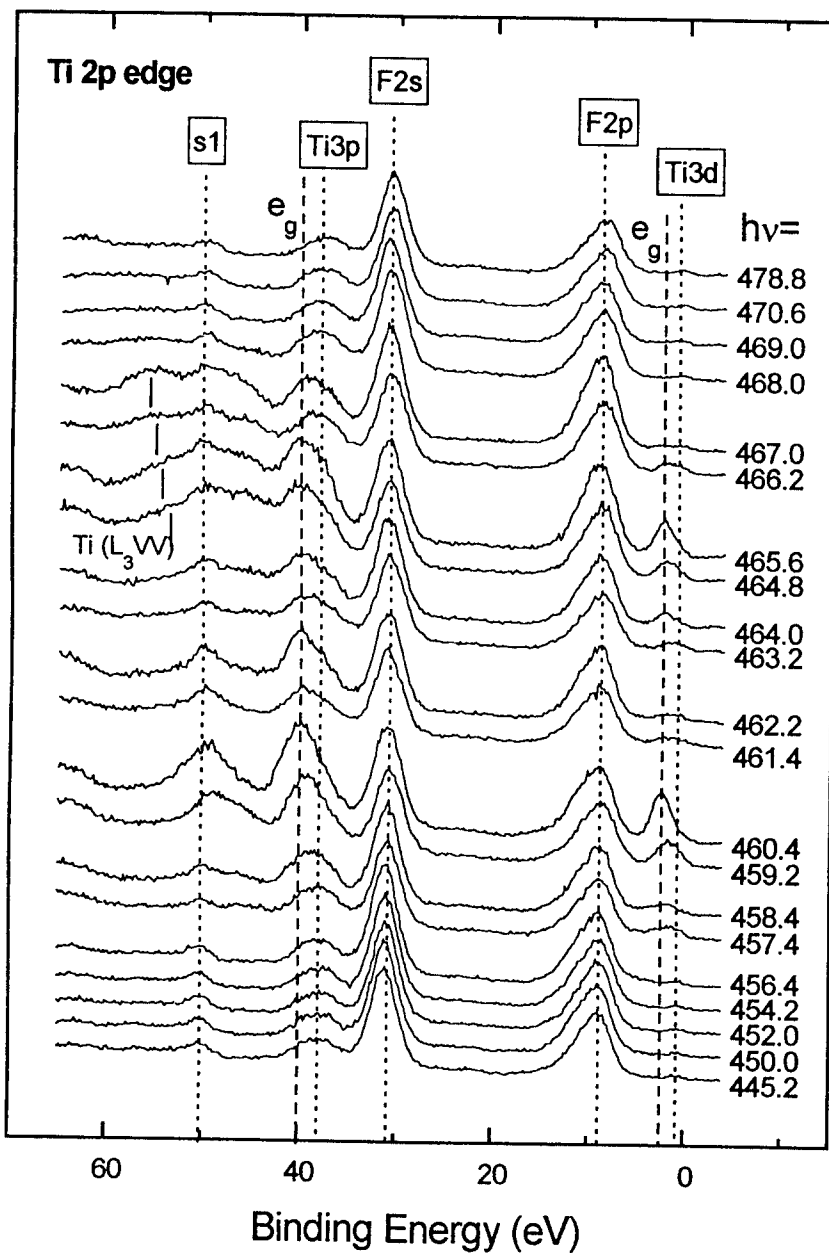


Fig.1 Experimental RPES spectra of TiF_3 at the $\text{Ti} 2p$ absorption edge.