Metal-Insulator Transition of Na_xWO_3 Studied by High-Resolution ARPES

S. Raj[1], D. Hashimoto[1], H. Matsui[1], S. Ray[2], D. D. Sarma[2], S. Souma[1], T. Sato[1], S. Oishi[3], W. H. McCarroll[4], M. Greenblatt[5], T. Takahashi[1]

[1] *Department of Physics, Tohoku University, Sendai 980-8578, Japan*
[2] *Solid State & Structural Chemistry Unit, Indian Institute of Science, Bangalore 560012, India*
[3] *Faculty of Engineering, Shinshu University, Nagano 380-8553, Japan*
[4] *Department of Chemistry and Biochemistry, Rider University, NJ 08648, USA*
[5] *Department of Chemistry and Chemical Biology, The State University of New Jersey, NJ 08854, USA*

The properties of tungsten-oxide based materials have created enormous interest in material science for a long time due to its various applications. It is possible to change the color of WO_3 by doping sodium metal, thus forming Na_xWO_3 bronze for all composition of x. Na_xWO_3 bronze exhibits very interesting electronic properties, especially a metal-insulator transition (MIT) as function of x. A high metallic conduction is obtained for higher x-compounds ($x \geq 0.3$), while the system undergoes MIT with decreasing x. In Na_xWO_3, Na atom occupies the central position, while W shares the corner of the cubic quasi-perovskite structure forming WO_6 octahedron. Due to the octahedral crystal field, the W 5d band splits into 5d T_{2g} and e_g bands, and the Fermi level (E_F) lies just below the 5d T_{2g} band in WO_3 and the crystal becomes a band insulator, while in Na_xWO_3 the Na 3s electron goes to the W 5d T_{2g} band and the system becomes metallic for higher values of x ($x \geq 0.3$). For low concentration of x ($x \leq 0.3$) the crystal still shows insulating properties although the origin is now under debate. Hence the study of electronic structure of Na_xWO_3 has much interest from both technological and fundamental perspectives.

We have carried out angle-resolved photoemission (ARPES) measurements for both insulating (x = 0.025) and metallic (x=0.58, 0.65. 0.7 and, 0.8) Na_xWO_3. The band dispersion in insulating sample is studied with the variation of temperature and compared with its metallic counter part. The random distribution of Na^+ ions in WO_3 lattice gives rise to a strong disorder effect, and as a consequence the Anderson localization occurs in the conduction band tail and the system undergoes MIT for low Na concentration (x < 0.3). Due to the localization the soft Coulomb gap arises and the density of state vanishes to zero exactly at E_F. The remnant Fermi surface mapped in insulating phase is found to be replica of real Fermi surface in metallic system. We found rigid band model is not appropriate in metallic Na_xWO_3 and this finding support the linear variation of magnetic susceptibility and specific heat with Na doping. We did not observe any signature of impurity band (level) near E_F region and hence, the possibility of development of *Na* induced impurity band (level), which causes localization at impurity band (level) tail leading to metal-to-insulator transition at low concentration, is ruled out. The spectral evolution of DOS at E_F in metallic region has a good agreement with the prediction for disorder metal and varies as a function of $(E - E_F)^{1/2}$. We observed electron-like FS at Γ(X) point in metallic sample as predicted from band calculation and the FS gradually increases with increase in *Na* concentration in Na_xWO_3 due to W 5d T_{2g} band filling.

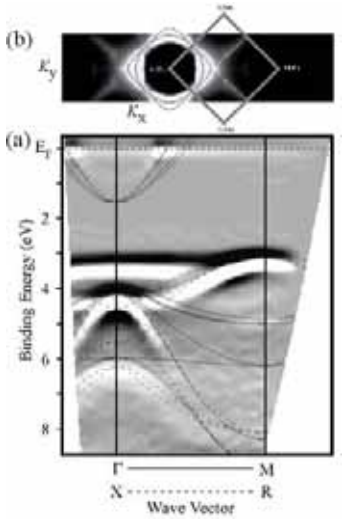

Fig.1 (a) Experimental valence band structure of $Na_{0.8}WO_3$ along with band calculation (b) Two dimensional intensity map of the intensity at E_F with the calculated Fermi surface.