Electronic Structure of Transition Metal Oxides Studied by X-ray Fluorescent Spectroscopy

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The new results are presented of the experimental study of ferroelectrics ($KNbO_3$ and $KTaO_3$) by means of X-ray fluorescence spectroscopy. In particular, *Nb* $M_{4.5}$ (5p4f→$3d_{5/2,3/2}$ transition), *Nb* M_3 (4d5s→$3p_{3/2}$ transition), *Ta* N_3 (5d6s→$4p_{,3/2}$ transition) and *O* $K\alpha$ (2p→1s transition) X-ray emission spectra (XES) have been measured over a range of near-threshold excitation energies [1-2] at Beamline 8.0 of the ALS. The emission spectra are explained by the calculations (based on DOS and first-principle band structure calculations taking into account the dipole transition matrix elements). The changes in the spectra occur exactly where we see structure in the absorption spectrum, at the $3d_{5/2,\ 3/2}$, 3d-5p and 3d-4f thresholds. The emission is due to refill of the $3d_{5/2}$ (peaks C and A) and $3d_{3/2}$ (peaks D and B) holes via valence emission. It was suggested [3] that *Nb* $M_{4,5}$ XES only reveals the M_5 ($3d_{5/2}$) features because the M_4 ($3d_{3/2}$) is filled by radiationless transition. Hovewer, we found that the excitation energy dependence of *Nb* $M_{4,5}$ XES is distorted by the spin-orbit splitting of the Nb 3d-levels and hence the band dispersion effects to be blurred. The *Nb* $M_{2,3}$ and *Ta* $N_{2,3}$ XES have not been, to our knowledge, measured before, they were not listed in the Beardeen tables [4]. These spectra lie in a convenient energy region for the synchrotron study to be well separated by selective excitation and can be used for study of d-states distribution in 4d and 5d-transition metal compounds.

Excitation energy dependence of *Ti* $L_{2,3}$ XES of TiO_2 is measured near the *Ti* 2p threshold at E_{exc}=458.2-476.9 eV [5]. It is found that *Ti* $L_{2,3}$ XES of TiO_2 contains the normal X-ray emission (*NXES*), which is insensitive to the excitation energy and similar to the spectrum excited far from the threshold and spectrum of resonance X-ray emission (*RXES*), spectral features of which strongly depend on the excitation energy. We have used a band approach for the discussion of the excitation energy dependence of *Ti* $L_{2,3}$ *RXES* of TiO_2. The *RXES* process is described as convolution of d-states of intermediate and final states under fulfillment of the *k*-conservation rule. The curves of restricted joint density of states (*rJDOS*) are calculated using *FP LMTO* method and found to be in a reasonable agreement with experimental *Ti* $L_{2,3}$ *RXES* of TiO_2 measured at different excitation energies.

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