

Low-Energy Excitations in Resonant Inelastic X-Ray Scattering of α' - NaV_2O_5

In a recent study [1] of resonant inelastic x-ray scattering (RIXS) at the vanadium L edge in α' - NaV_2O_5 , Zhang *et al.* assigned a clear peak at 1.56 eV to excitations across the correlation gap. In this Comment, we assign this peak to local crystal field (CF) excitations of vanadium d^1 ions. We argue that transitions to the upper Hubbard band are much weaker than and obscured by CF excitations. This means that CF interactions govern the size of the observed gap, invalidating the claim of Ref. [1] of having determined the Hubbard parameter U . Finally, the $d_{xy} - d_{xy}^*$ gap of 1.2 eV that we observe in RIXS at the oxygen K edge is provided as an upper value for the correlation gap.

α' - NaV_2O_5 can be described as ladders with quarter-filled V-O-V rungs. The lowest V d_{xy} orbitals of the rung are split into a bonding and antibonding state. On the other hand, there is a correlation-induced gap for inter-rung transitions that is responsible for the insulating behavior of α' - NaV_2O_5 .

Zhang *et al.* seem to assign the 1.56 eV peak to transitions across the correlation gap. However, spectral contributions of local transitions such as CF excitations [2,3] dominate over transitions to bandlike (delocalized) states for resonant V L -edge excitation at threshold. The vanadium atom is excited to one of several $2p^5 d_{xy} d_m$ intermediate states, and upon deexcitation the d_{xy} electron, recombines with the core hole leaving the atom in an excited state with $m \neq xy$. Even the band structure calculation of Ref. [1] shows these as sharp hybridized peaks, but an energy scale is not given. The CF parameter $10Dq$ is large in vanadium oxides (around 3 eV), and in the pyramidal coordination of these pentoxides the octahedral e_g and t_{2g} states are split up. The atomic structure of α' - NaV_2O_5 is very similar to the undoped parent compound V_2O_5 , and the crystal field energies are similar. V K -pre-edge quadrupole transitions to empty V $3d$ states of V_2O_5 [4] show that the $d_{xz,yz}$ levels are 1.5 eV above the d_{xy} level. This transition should be prominent in V L -edge spectra; however, Zhang *et al.* did not include CF states in their model calculation.

RIXS at oxygen K edges has recently been shown to be significant in transition metal oxides [5]. On-rung transitions in α' - NaV_2O_5 are likely to be observed in O K -edge RIXS due to strong hybridization between oxygen and the vanadium atoms in the rungs. Figure 1 shows a resonant O K -emission spectrum excited at 531.7 eV, i.e., at the V $3d$ -hybridized low-energy shoulder of the oxygen O1s-absorption (see inset Fig. 1). We find a RIXS peak, resonating in a narrow excitation energy interval, with an energy loss of about 1.2 eV for the $d_{xy} - d_{xy}^*$ gap. This provides a considerably smaller upper value for the correlation gap than the value that Zhang *et al.* assign to it

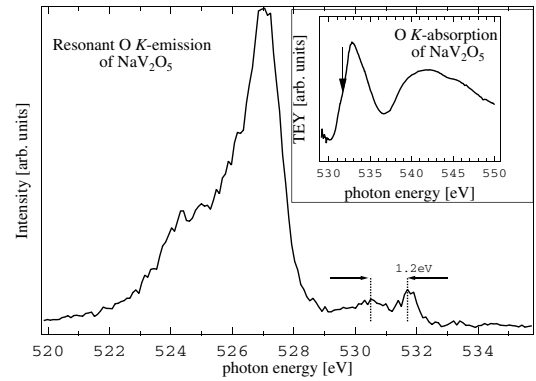


FIG. 1. O K -RIXS of α' - NaV_2O_5 . Inset: Total electron yield (TEY) spectra across the O K edge.

and also shows that the oxygen hybridization of the V d_{xy}^* band should not be neglected.

In conclusion, we emphasize that V L -edge RIXS measures neutral CF excitations and gives no direct information about U or the gap between the lower and upper Hubbard band. The $d_{xy} - d_{xy}^*$ gap on the other hand is accessible through O K -edge RIXS, whereas the correlation gap that involves inter-rung transitions is not a local charge neutral excitation accessible by RIXS.

After submission we have become aware of an independent Comment [6] to Ref. [1] with model calculations that are in good agreement with our experimentally based line of argumentation. We thank D. van der Marel and M. Matsubara for valuable discussions.

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