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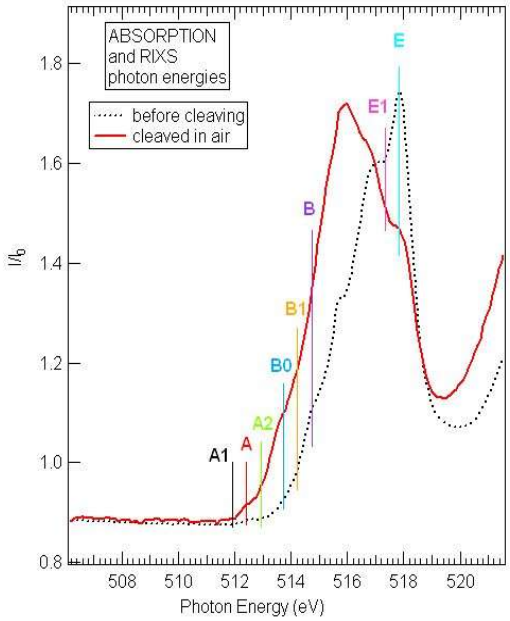
d-localization and anisotropy in $BaVS_3$: Polarization-dependent RIXS at the V L-edge

X-ray absorption spectroscopy (XAS) and room and low temperature (RT/LT) resonant inelastic X-ray scattering (RIXS) measurements were performed on $BaVS_3$ single crystals at the vanadium L_3 edge.

XAS was measured using the drain current on a sample mounted as-received and on a sample cleaved in air. A very marked change was observed in the shape of the V L-edge spectrum as a result of cleaving though an O K signal was still observed. XAS measurements on an in-situ cleaved sample are pending to confirm the validity of the XAS spectrum we used to select excitation energies. Note that the all-photon RIXS experiment is much less sensitive to surface contamination compared to a drain current XAS measurement.

RIXS spectra were taken on a sample mounted in the AXES chamber with the **c**-axis in the horizontal plane and parallel to the sample holder.

Eight energies in the vicinity of the V L_3 absorption edge were measured, for the vertical (V) and horizontal (H) polarizations of incident photons (s and p polarization relative to the sample respectively). The energy calibration was set using the V L_3 absorption spectrum as measured by XAS (see Fig 1).



point	E(eV)
A1	511.94
A	512.44
A2	512.94
B0	513.75
B	514.25
B1	514.75
E1	517.36
E	517.86

Figure 1 : $BaVS_3$ V L_3 absorption edge. The energies measured in RIXS are indicated by colored lines and indicated in the table.

Figure 2 shows the X-ray emission spectra taken at room temperature (RT) with vertical (V, p-polarization, **E** ⊥**c**) and horizontal polarization (H, s-polarization: the sample normal is turned 10° with respect to the incident beam, **E** and **c** are in the horizontal plane).

The spectra are plotted on an energy-loss scale. Two large structures and one shoulder are observed to the low energy side of the elastic peak. At the photon energy of 513.75 eV (B0 spectrum), their energy positions relative to the elastic peak are –1.9 eV, –4.9 eV and – 6.7 eV.

Large low-energy-loss structures are present in all the spectra and disperse on an energy-loss scale as from 512.44 eV (A). It is difficult to say if they disperse from A1 to A as well. There is a slight polarization dependence of these structures in spectra B0 and B.

The structure closer to the elastic peak is clearly observed in the B0 spectrum. Similar structure is less marked in spectra B1 and B. In all the spectra, it has approximately the same intensity as in the case of s-polarization.

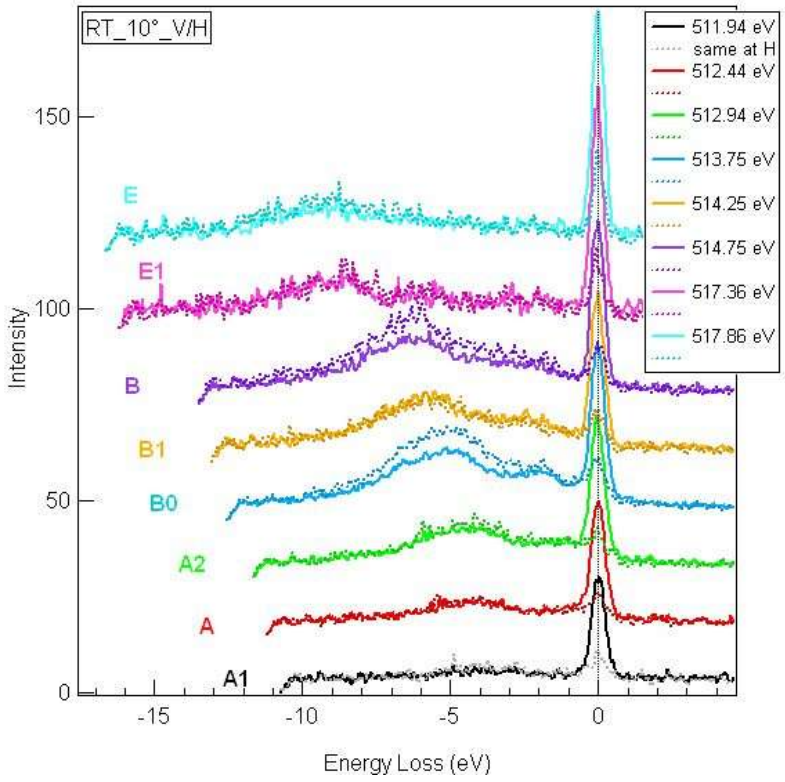


Figure 2 : Room temperature, photon incidence angle 10°, vertical and horizontal polarization RIXS for photon energies indicated in the figure 1.

In the case of H-polarization, turning the incident photon angle shows changes in intensities in large low-energy-loss structure, indicating that it is consists of non-resonant features (x-ray fluorescence) as well as resonant features, appearing when photon energy is tuned to particular values.

Cooling to 25K changes slightly low-energy-loss structures, but destroys their V/H polarization dependence.

According to the LDA-DOS calculations in the orthorhombic phase [1], from 6 eV to 1 eV below the Fermi level, the V 3d orbitals (mixed t_{2g} and e_g) are strongly hybridized with sulfur 3p orbitals. The t_{2g} orbitals are distributed over the valence band from - 6 eV to – 1 eV while the e_g orbitals peak at about – 3.5 eV. Just below the Fermi level, and separated from the sulfur-hybridized part of the valence band, the DOS consist of A_{1g}, E_{g1} and E_{g2} t_{2g} -bands.

In the unoccupied part of the calculated DOS, there are three peaks, one close to E_F, one at about 1.5 eV, and one at 2.3 eV. The first has small e_g + A_{1g} character, and very strong Eg character. The second has increased, e_g and A_{1g} contributions, but E_g vanishes. In the third, e_g dominates. We should note that the DMFT calculations, including correlations, modify considerably the DOS structures close to the Fermi level, pushing E_g states to lower energies and introducing an upper Hubbard band in unoccupied A_{1g} and E_g states.

Assuming the x-ray Raman features observed are directly related to elementary excitations close to the ground state, symmetry considerations would suggest that the observed structure can be interpreted as follows :

1. The peak at – 0.5 e V corresponds to A_{1g}, E_g –> E_g excitations
2. At – 2 e V corresponds to A_{1g}, E_g –> e_g excitations
3. At – 6 e V corresponding to transitions involving well-bound- e_g –> e_g bands

The first excitation is very close to the elastic peak and is seen as a shoulder in our measurements.

The second clearly observed in the B0 spectra corresponds to resonant structure for an energy loss of about 2 eV attributable to excitations from just below the Fermi level to unoccupied states at about 1.3 eV above the Fermi level. More detailed analysis of the results are in progress, particularly concerning their polarization dependence.

[1] Lechermann et al. Arxiv preprint cond-mat/0605539, 2006