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Supporting information for article:

Vanadium *K*-edge XANES in vanadium-bearing model compounds: a full multiple scattering study

Federico Benzi, Gabriele Giuli, Stefano Della Longa and Eleonora Paris

V K-edge XANES in V-bearing model compounds: a Full Multiple Scattering study. Supplementary information

F. Benzi, G. Giuli, S. della Longa and E. Paris

1 Calculation details for palenzonaite

From the crystallographic data the atomic cluster is built, centered around a V atom. Since the FMS theory does not allow partial occupation of the sites we simplified the palenzonaite structure in $Ca_3Mn_2(VO_4)_3$, *i.e.* by filling all of the dodecahedral sites with Ca, all of the Octahedral sites with Mn and all of the tetrahedral sites with V. We checked the convergence of the theoretical calculations with the size of the cluster, and with *lmax*, which is the angular momentum cutoff for the spherical harmonics expansion in the calculation of the FMS equation. First, we performed XANES simulations increasing the cluster size by including further V coordination shells (Fig. 1). We started by calculating a theoretical spectrum using only 5 scatterers (the central V and the 4 oxygen atoms in the tetrahedron, (Fig. 1 lower spectrum). Further coordination shells are then added to the starting cluster. For example, in the second spectrum (19 atoms) we added a Ca and Mn shell. At around 51 atoms all of the features are roughly reproduced, but only after including 90 atoms in the cluster we reached convergence. Then we performed similar calculations by fixing the number of scatterers to 90 and varying the value of *lmax* (Fig. 2). Increasing too much this number can cause drastic performance reduction of the calculation.

As a general behaviour the value of *lmax* follows the rule of "the higher the better", but it is possible to find a good compromise between the accuracy and the speed of the calculation. As it can be seen in Fig. 2 the calculation differs significantly between $lmax = 2$ and $lmax = 3$ (the relative peak intensities and peak positions are significantly different). On the other hand calculations performed at $lmax = 3$ and $lmax = 4$ show similar relative peak intensities and position, so we decided to use $lmax = 3$ as the standard value for the fit.

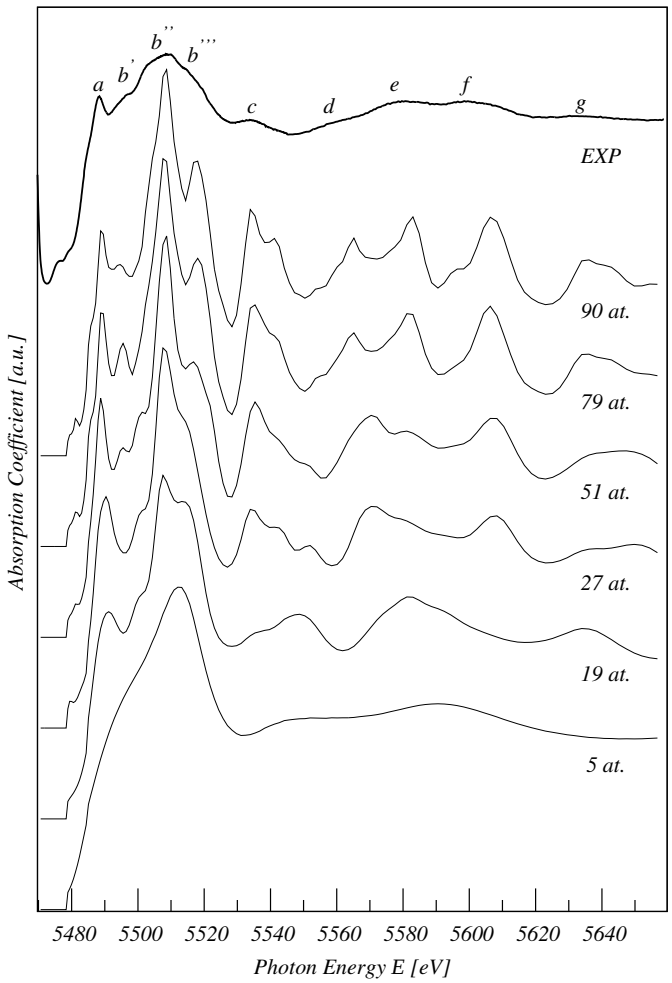

Figure 1: Palenzonaite MXAN calculations performed increasing the number of scattering atoms. The experimental spectrum is drawn on top.

Another way to assess the limits for the cluster size and the angular momentum cutoff can be derived by calculating the absolute difference between two consecutive spectra. In case of palenzonaite it was clear to choose the number of scatterers: the difference between the spectra calculated with 5 and 19 scatterers and 19 and 27 scatterers was in the order of 0.35, while dropping to around 0.25 for the next two calculations and finally to 0.1 when adding 90 atoms. At the same time the difference between $lmax = 2$ and 3 was in the order of 0.4, while the difference between $lmax = 3$ and 4 was again 0.1.

Since in our model the T site is fully occupied by V, instead of a combination of V, As and Si we decided to optimize the size of the first shell. Starting from a theoretical value of 1.714 Å we let the 4 V-O distances of the first shell to change coherently of about 5%. So the MS fit parameters were the MT overlap (*ovlp*), the interstitial potential ($V0_{imp}$) and the radius of the first shell (R1); the alignment parameters were an energy shift (*ensh*), a normalization factor (*norm*) and a factor to account for the residual slope of the experimental spectrum (*slope*); finally the broadening parameters were the core hole lifetime (fixed to the theoretical vale of 1.01, *broad*), the experimental resolution (*broad exp*), the plasmon onset energy (*epl*) and the plasmon intensity (*apl*). Since the RSMS theory may not be accurate for the calculation of the transitions to the bound states (the pre-edge peak), we decided to add a Θ-like function weight to the fit, whose onset starts at -2 eV with respect to E_0.

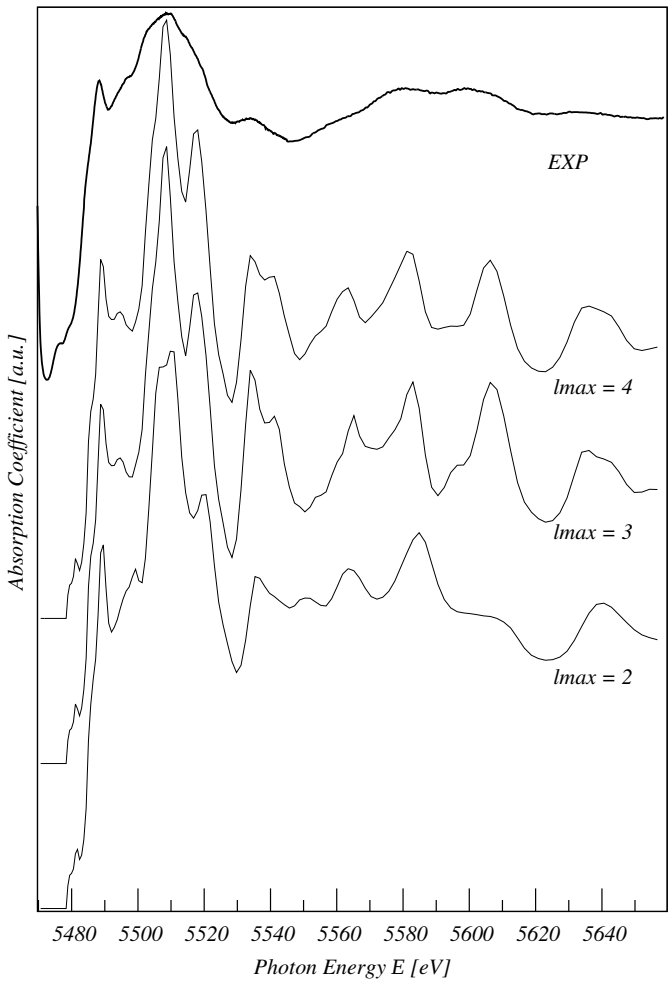

Figure 2: Palenzonaite MXAN calculations performed increasing *lmax*. The experimental spectrum is represented on top.

2 Fit details for all model compounds

Structural data and MT parameters			
	V-O (Å)	1.689(2)	
	ovlp	0.202(1)	
	V0inp (eV)	-12.5(8)	
	sq.res.	3.9	
	nsca	90	
	lmax	3	

Alignment and broadening parameters			
ensh (eV)	5478.9	norm	0.039
fermi (eV)	-2.82	Broad (eV)	1.0+0.5
Epl (eV)	12.12	Apl	11.16

Muffin-tin radii (Å)		
	V	1.090
	O	0.945
	Na	1.810

Table 1: Palenzonaite fit results. The number in brackets represents the error on the last digit. No error is available for broadening and alignment parameters since they have been calculated using the Monte-carlo method. The two values for the broad parameters refer to the core-hole lifetime (fixed for simplicity to 1 eV instead of the theoretical value of 1.01 eV, since there is no difference in the calculated spectra) and the experimental resolution. The value of sq.res. represents the sum of the square of the residual and gives an indication of the goodness of the fit.

Structure and MT parameters			
	V-O (Å)	2.03(1)	
	ovlp	0.078(5)	
	V0inp (eV)	-9.3(6)	
	sq.res.	9.5	
	nsca	123	
	lmax	3	

Alignment and broadening parameters			
ensh (eV)	5478.86	norm	0.043
fermi (eV)	-2.76	Broad (eV)	1.0+0.5
Epl (eV)	20.2	Apl	12.2

Muffin-tin radii (Å)		
	V	1.248
	O_1	0.821
	O_2	0.827
	Ca	1.554

Table 2: Goldmanite fit results. The number in brackets represents the error on the last digit. No error is available for broadening and alignment parameters since they have been calculated using the Monte-carlo method. The two values for the broad parameters refer to the core-hole lifetime (fixed to the theoretical value of 1) and the experimental resolution.

Structure and MT parameters	
$V - O_1$ (Å)	1.62(2)
$V - O_2$ (Å)	2.00(2)
$V - O_3$ (Å)	2.02(2)
ovlp	0.27(2)
V0inp (eV)	-9.9(7)
sq.res.	1.6

Alignment and broadening parameters			
ensh (eV)	5478.6	norm	0.044
fermi (eV)	-4.2	Broad (eV)	1.0+0.5
Epl (eV)	22.0	Apl	18.1

Muffin-tin radii (Å)	
V	1.149
O_1	0.919
O_2	0.961
O_2	0.951
Wat	1.847
Si	1.085

Table 3: Cavansite fit results. The number in brackets represents the error on the last digit. No error is available for broadening and alignment parameters since they have been calculated using the Monte-carlo method. The two values for the broad parameters refer to the core-hole lifetime (fixed to the theoretical value of 1) and the experimental resolution.

Structure and MT parameters	
$V - O_1$ (Å)	1.68(1)
$V - O_2$ (Å)	1.68(2)
$V - O_3$ (Å)	1.68(5)
ovlp	0.21(4)
V0inp (eV)	-13.8(8)
sq.res.	1.9
nsca	90
lmax	4

Alignment and broadening parameters			
ensh (eV)	5476.1	norm	0.040
fermi (eV)	-3.2	Broad (eV)	1.0+0.5
Epl (eV)	15.5	Apl	17.0

Muffin-tin radii (Å)	
V	1.096
O_1	0.957
O_2	0.962
O_3	0.976
Pb_1	1.755
Pb_2	1.794

Table 4: Vanadinite fit results. The number in brackets represents the error on the last digit. No error is available for broadening and alignment parameters since they have been calculated using the Monte-carlo method. The two values for the broad parameters refer to the core-hole lifetime (fixed to the theoretical value of 1) and the experimental resolution.

Structure and MT parameters			
	ovlp	0.07(1)	
	V0inp (eV)	-14.0(6)	
	sq.res.	10.7	
	nsca	110	
	lmax	4	

Alignment and broadening parameters			
ensh (eV)	5479.6	norm	0.044
fermi (eV)	-4.7	Broad (eV)	1.0+0.8
Epl (eV)	22.2	Apl	24.8

Muffin-tin radii (Å)		
	V	1.196
	O	0.921

Table 5: V_2O_3 fit results. The number in brackets represents the error on the last digit. No error is available for broadening and alignment parameters since they have been calculated using the Monte-carlo method. The two values for the broad parameters refer to the core-hole lifetime (fixed to the theoretical value of 1) and the experimental resolution.

Structure and MT parameters			
	ovlp	0.14(1)	
	V0inp (eV)	-17.0(2)	
	sq.res.	10.6	
	nsca	102	
	lmax	4	

Alignment and broadening parameters			
ensh (eV)	5479.03	norm	0.042
fermi (eV)	-2.87	Broad (eV)	1.0+0.5
Epl (eV)	14.7	Apl	10.5

Muffin-tin radii (Å)		
	V	1.091
	O_1	0.919
	O_2	0.874

Table 6: V_2O_4 fit results. The number in brackets represents the error on the last digit. No error is available for broadening and alignment parameters since they have been calculated using the Monte-carlo method. The two values for the broad parameters refer to the core-hole lifetime (fixed to the theoretical value of 1) and the experimental resolution.

Structure and MT parameters			
	ovlp	0.28(2)	
	V0inp (eV)	-12.3(8)	
	sq.res.	3.4	
	nsca	119	
	lmax	4	

Alignment and broadening parameters			
ensh (eV)	5478.22	norm	0.043
fermi (eV)	-3.0	Broad (eV)	1.0+0.5
Epl (eV)	12.56	Apl	10.3

Muffin-tin radii (Å)	
V	1.105
O_1	0.921
O_2	1.047
O_3	1.0091

Table 7: V_2O_5 fit results. The number in brackets represents the error on the last digit. No error is available for broadening and alignment parameters since they have been calculated using the Monte-carlo method. The two values for the broad parameters refer to the core-hole lifetime (fixed to the theoretical value of 1) and the experimental resolution.