Vanadium $L_{2,3}$ XANES experiments and first-principles multielectron calculations: Impact of second-nearest neighboring cations on vanadium-bearing fresnoites

THOMAS HÖCHE,1,* HIDEKAZU IKENO,2 MARISA MÄDER,3 GRANT S. HENDERSON,4 ROBERT I.R. BLYTH,5 BRIAN C. SALES,6 AND ISAO TANAKA7

1Fraunhofer-Institut für Werkstoffmechanik IWM, Walter-Hülse-Strasse 1, D-06120 Halle, Germany
2Fukui Institute for Fundamental Chemistry, Kyoto University, Takano-Nishihiraki, Sakyo, Kyoto 606-8103, Japan
3Leibniz-Institut für Oberflächenmodifizierung e.V., Permoserstrasse 15, D-04318 Leipzig, Germany
4Department of Geology, University of Toronto, 22 Russell Street, Toronto, M5S 3B1, Canada
5Canadian Light Source, University of Saskatchewan, 101 Perimeter Road, Saskatoon, S7N 0X4, Canada
6Correlated Electron Materials Group, Materials Sciences and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6056, U.S.A.
7Department of Materials Science and Engineering, Kyoto University, Yoshida, Sakyo, Kyoto 606-8501, Japan

ABSTRACT

Transition-metal $L_{2,3}$ XANES spectra are widely used to determine coordination and valence of the target ion. For decades, experimental fingerprinting, i.e., the comparison with spectra obtained from known reference compounds was the way to interpret spectral features. This approach was based on the common understanding that only anions in the first coordination sphere would determine the near-edge structure, and crystalline references were selected accordingly. Using ab initio charge-transfer multiplet calculations, we demonstrate that there is also a significant impact on spectral features from the second-nearest neighbor cations. This finding is exemplified for three fresnoite-type vanadates, namely Ba$_2$VSi$_2$O$_8$ (BVS), K$_2$VV$_2$O$_8$ (KVV), and Rb$_2$VV$_2$O$_8$ (RVV). The theoretical treatment provides evidence that for the three compounds studied it is not variable bond lengths or bond angles between vanadium and oxygen that make the V-$L_{2,3}$ XANES spectra different, but the interaction of the target vanadium ions with its neighboring cations (Si for BVS, V for KVV and RVV), which dominates. Therefore, we conclude that simple fingerprinting can result in misleading interpretations when interactions with second-nearest neighboring cations are not taken into account. Ab initio charge-transfer multiplet calculations of spectral shapes (theoretical fingerprinting) should be employed instead to get a deeper understanding of structure-spectra relationships, or the choice of reference spectra should take into account second-nearest neighbors. Our findings are similarly important for the interpretation of electron energy-loss near-edge (ELNES) spectra.

Keywords: X-ray absorption spectroscopy (V-$L_{2,3}$ XANES), first-principles multielectron theory, fresnoites, Ba$_2$VSi$_2$O$_8$, K$_2$VV$_2$O$_8$, Rb$_2$VV$_2$O$_8$

INTRODUCTION

The spectroscopy of unoccupied states, either excited by X-rays (X-ray absorption near-edge structure, XANES) or electrons (electron energy-loss near-edge structure, ELNES), has been gaining increasing interest due to its sensitivity toward subtle changes in the electronic structure accessible at a spectral resolution below 100 meV, or more precisely $10^{-4}$ times the excitation energy (Regier et al. 2007).

It has been known for many years that departures in coordination around the probed transition-metal ion (see e.g., Brydson et al. 1989) result in changes to the spectral shape of transition-metal $L_{2,3}$ edges. This is because the energetic position of unoccupied 3d states is sensitively influenced by the crystal-field splitting essentially caused by the anions in the first coordination sphere around the probed cation (Höche et al. 2004). Another source of spectral differences is the valence state. For transition metals, it is found that lowering the valence causes a chemical shift toward lower photon energies or electron energy losses, respectively (Leapman et al. 1982). This chemical shift is due to more effective screening of the core potential for reduced species. In parallel, upon decreasing the valence of a given element, the number of unoccupied states is decreased as well. For example, chemical shifts of the Ti $L_{2,3}$ edges toward lower energy losses have been observed by Leapman et al. (1982), while La$_{1-x}$Sr$_x$TiO$_3$ was studied by Abbate et al. (1991) using Ti-$L_{2,3}$ XANES to demonstrate the influence of altering Ti valence while keeping the Ti coordination unchanged (via the substitution of strontium by lanthanum). Höche et al. (2003b) also proved this effect using ELNES spectroscopy of barium oxo-titanates (III/IV) Ba$_4$Ti$_{12}$O$_{16}$. Eventually, Coulomb and exchange interactions (Zaanen et al. 1985) have to be taken into account for understanding departures from the ideal $L_3/L_2$ intensity ratio for 3d transition metals (Thole and Laan 1988).

While the experimental assessment of transition-metal $L_{2,3}$ edges has been brought to a very high level of sophistication in terms of spectral, as well as, spatial resolution, the simulation of transition-metal $L$-edges has only recently reached a state...