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

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## 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 $Ba_2VSi_2O_8$ (BVS), $K_2VV_2O_8$ (KVV), and $Rb_2VV_2O_8$ (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, $Ba_2VSi_2O_8$, $K_2VV_2O_8$, $Rb_2VV_2O_8$