

# Theoretical Fingerprints of $M$ - $L_{2,3}$ XANES and ELNES for $\text{LiMO}_2$ ( $M=\text{Mn,Fe,Co,Ni}$ ) by *ab initio* Multiplet Calculations

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A large number of studies on lithium transition metal oxides have been performed for the cathode materials of lithium ion battery. Characterization of the transition metal ions in the cathodes during the charge/discharge cycles is one of the essential points for such studies. Among many techniques, spectroscopic methods to measure X-ray absorption near-edge structures (XANES) and electron energy loss near-edge structures (ELNES) at transition metal  $L_{2,3}$ -edges ( $M$   $L_{2,3}$ -edges), which is dominated by  $M$   $2p \rightarrow 3d$  transitions, are very powerful to selectively observe the electronic states and local environment of transition metal ions. It is known that  $M$ - $L_{2,3}$  XANES/ELNES show widely spread multiplet structure because of the strong electronic correlation among  $2p$  core-hole and  $3d$  electrons. For simulating these spectra, the present authors have developed an *ab initio* multiplet method based on the relativistic configuration interaction theory. Experimental  $M$ - $L_{2,3}$  XANES/ELNES with different  $d$ -electron numbers, coordination numbers, and symmetries have been successfully reproduced without any adjustable parameters[1,2].

In this work, we aim at providing theoretical fingerprints of  $M$ - $L_{2,3}$  XANES/ELNES for  $\text{LiMO}_2$  ( $M = \text{Mn, Fe, Co, Ni}$ ) and Li-extracted  $\text{MO}_2$  that should be useful for the analysis of experimental spectra. Theoretical spectra obtained by the *ab initio* multiplet method are given for six set of oxides with several different crystal structures. The effects of oxidation states, spin states, and crystal structures including that of the Jahn-Teller (JT) distortion on the  $M$ - $L_{2,3}$  XANES/ELNES are discussed[3].

Figure 1 shows theoretical  $M$ - $L_{2,3}$  XANES/ELNES of  $\text{LiMO}_2$  and Li-extracted  $\text{MO}_2$  with a layered structure ( $M=\text{Co, Ni}$ ). In the present work, both the high-spin (HS) and low-spin (LS) are considered as the initial state of  $M$ - $L_{2,3}$  XANES/ELNES. It is clearly seen that the spectral shape dramatically changes by choosing different spin state as the initial state. It is also clear that the spectral shape significantly changes due to the Li-extraction. These results demonstrate that the oxidation and spin state can be unambiguously determined using these theoretical fingerprints.

Figure 2 shows theoretical Mn- $L_{2,3}$  XANES/ELNES of  $\text{LiMnO}_2$  with layered structures. The  $\text{MnO}_6$  octahedron in the  $\text{LiMnO}_2$  is strongly distorted because of the JT effects on the  $\text{Mn}^{3+}$  ion in the  $d^4$  HS state. In order to extract the JT effects on the Mn  $L_{2,3}$ -edges, theoretical spectra of two compounds with and without JT distortion are compared. The changes in the spectral shapes due to the JT distortion can be recognized

from Fig. 2. It is also found that the JT distortion can be easily and clearly detected by measuring the orientation dependence of the spectra (not shown in Fig. 2). The capability of detecting the distortion around  $M$  ions would be extremely useful when characterizing the local environment of  $M$  ions in a complex host, such as in interface, surface, point defects, and amorphous structures.

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## References

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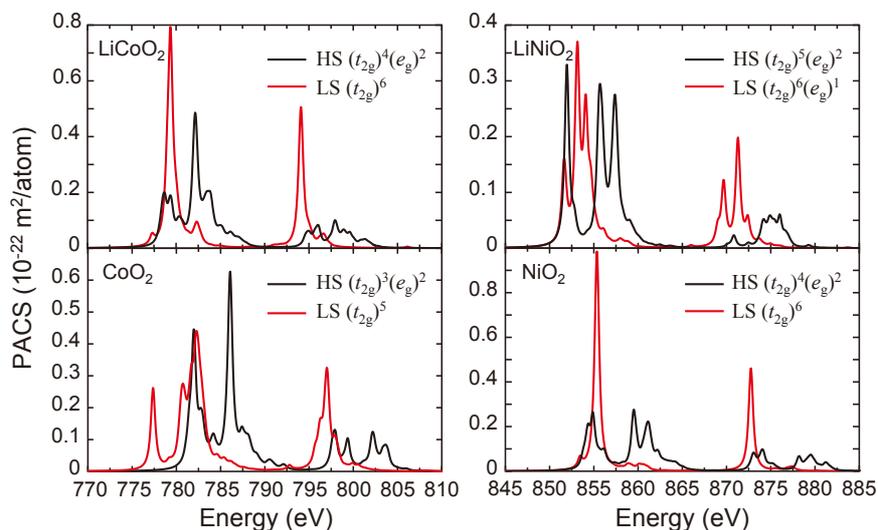


FIG. 1. Theoretical  $M$ - $L_{2,3}$  XANES/ELNES of  $\text{LiMO}_2$  and Li-extracted  $\text{MO}_2$  ( $M=\text{Co}, \text{Ni}$ ) with layered structures. Theoretical spectra from the high-spin (HS) and low-spin (LS) states are drawn in the black and red lines, respectively, for each compound.

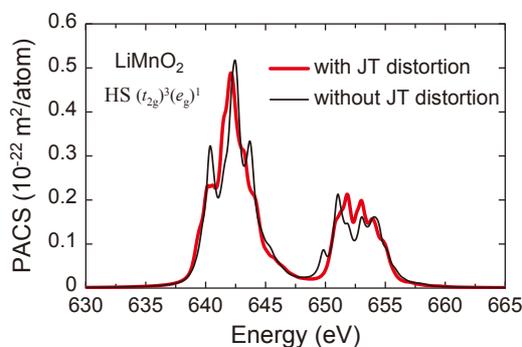


FIG. 2. Jahn-Teller effect on the theoretical  $\text{Mn}$ - $L_{2,3}$  XANES/ELNES of  $\text{LiMnO}_2$  with layered structures. Theoretical spectra are averaged over all directions.