First-Principles Study of Co $L_{2,3}$ XANES and ELNES
of Trivalent Cobalt Compounds

Yu Kumagai[1], Hidekazu Ikeno[1], Fumiyasu Oba[1], Katsuyuki Matsunaga[1], and Isao Tanaka[1,2]

[1]*Department of Materials Science and Engineering, Kyoto University*
Yoshida, Sakyo, Kyoto 606-8501, Japan
[2]*Nanostructures Research Laboratory, Japan Fine Ceramics Center*
Nagoya 456-8587, Japan

X-ray-absorption near-edge structures (XANES) and electron-energy-loss near-edge structures (ELNES) at transition metal (TM) $L_{2,3}$ edges correspond to the electronic dipole excitation of $2p_{1/2}$ and $2p_{3/2}$ core electrons to unoccupied $3d$ orbitals. Therefore TM $L_{2,3}$ XANES/ELNES spectra have plenty of information about the TM-$3d$ elements such as oxidation and spin states. TM $L_{2,3}$ XANES/ELNES show clear multiplet structures due to the strong correlation among the spatially localized $3d$ electrons and a $2p$ core-hole. On the other hand, the effects of crystal structure are considered to be less important for the spectral shape. However, some compounds do not follow this opinion. For example, there are clear differences between the spectra of $LaCoO_3$ and $LiCoO_2$, in which trivalent Co are low-spin state and surrounded by six oxygen ions. To clarify the effects of crystal structure on TM-$L_{2,3}$ XANES/ELNES spectra, theoretical investigations are needed.

In general, it is impossible to reproduce TM $L_{2,3}$ XANES/ELNES spectra using mean-field method such as the local density approximation. The authors' group has developed a relativistic configuration interaction calculation technique based on four-component molecular orbitals for model clusters [1]. The strong correlation among TM $3d$ electrons and a $2p$ core-hole and the spin-orbit coupling, which splits $2p$ core orbitals into $2p_{1/2}$ and $2p_{3/2}$, are calculated explicitly. We used a CoO_6^{9-} model cluster and incorporated the effects of crystal structure by embedding the cluster into the array of point charges.

First, we verified that our calculation method reproduces the spectra of $LaCoO_3$ and $LiCoO_2$. Next, to elucidate the origin of the differences, we investigated the effects of the Madelung potential on the spectral shape using the models for four crystals, i.e., layered rock salt (LRS), perovskite (PE), rock salt (RS), and spinel (SP), in which the Co-O bond length is fixed at 1.92 Å. The spatial distribution of the relative Madelung potential, $\Delta V^{MP}(r)$, is shown for these crystals in Fig. 1. The white zone of the potential maps indicates the space with $\Delta V^{MP} \approx 0$, and it appears to be the largest in PE and the second largest in RS. The theoretical spectra of these structures are shown in Fig. 2 together with the spectrum of an isolated CoO_6^{9-} cluster. As can be seen, the spectral shape does not change markedly in PE from that of the isolated cluster. On the other hand, in the other crystals, the intensity of subpeaks b and e decreases and subpeak c vanishes. The results show that the Madelung potential acting on respective orbitals is one of the main factors in determining the trivalent Co $L_{2,3}$ XANES/ELNES [2].

References
[1] H. Ikeno, T. Mizoguchi, Y. Koyama, Y. Kumagai, and I. Tanaka, Ultramicroscopy **106,** 970 (2006).
[2] Y. Kumagai, H. Ikeno, F. Oba, K. Matsunaga, and I. Tanaka, Phys. Rev. B (in press).
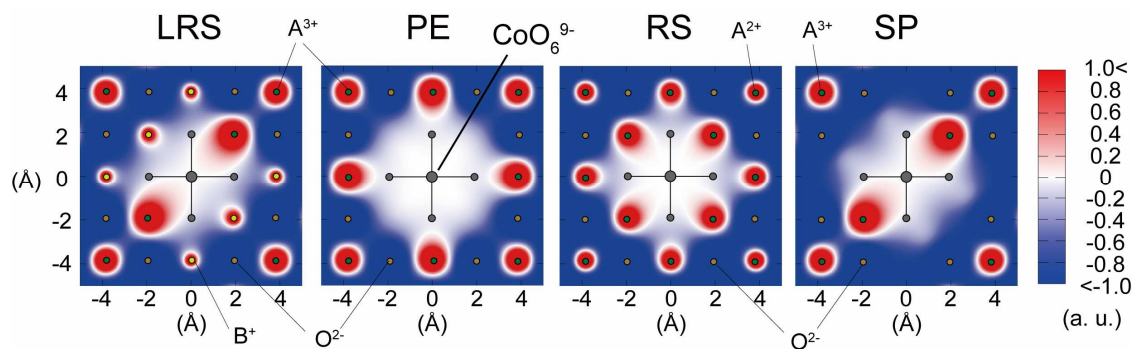
FIG. 1. Madelung potential around the CoO_6^{9-} cluster for layered rock salt (LRS), perovskite (PE), rock salt (RS), and spinel (SP) on the (100) plane.
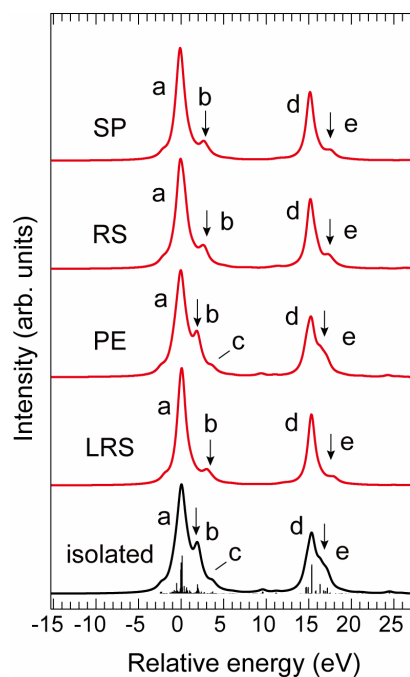

FIG. 2. Theoretical Co $L_{2,3}$ XANES with low-spin initial state for SP, RS, PE, LRS, and an isolated cluster.