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Novel Method for 3*d* Transition Metal $L_{2,3}$ ELNES by First Principles Multi-Electron Theory

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There have been two different kinds of approaches to reproduce ELNES by theoretical calculations. One is called a multiple scattering approach. The other is a quantum mechanical approach to compute unoccupied density of states for selected atoms. It has been demonstrated that most of *K*-edge ELNES can be reproduced by such methods. Using a standard first principles method within the one-electron approximation, *K*-edge ELNES can be well reproduced if the effect of a core-hole is properly taken into account [1,2].

On the other hand, the $L_{2,3}$-edge ELNES cannot be reproduced using such methods. It is sometimes misunderstood that $L_{2,3}$-edge ELNES can be obtained simply by overlaying the spectrum by the one-electron calculations with proper L_3-L_2 splitting and L_3/L_2 intensity ratio. However, strong correlation among electrons and that between the core-hole and the excited electron totally changes the spectral shape when the atomic orbital of the excited electron is spatially localized as in the case of 3*d* orbital for transition metal compounds. The 3*d* electrons show widely spread multiplet structures even at the ground state because of the strong correlation. The presence of the 2*p* core-hole introduces further complexity into the spectra. Therefore, theoretical spectrum by the one-electron calculations cannot be used to reproduce the experimental spectrum in general.

Multiplet structures of isolated atoms were well studied both by experiment and theory. Crystal field effects have been incorporated into an atomic multiplet program using group theoretical formalism, which is called crystal field atomic multiplet program [3]. Although this approach has been successful for reproducing multiplet structures of many transition-metal compounds, it uses a number of adjustable parameters. It cannot be used to predict multiplet structures *a priori*. Another problem resides in the treatment of the ligand orbitals. Contribution of the ligand orbitals as a result of covalent bonding can be included in the crystal field theory only in an indirect manner. A first principle calculation beyond one-electron approximation to take account multi-electron interactions is therefore desirable. In order to treat the electronic transition from a core orbital, relativistic effects should also be considered. A part of the relativistic effects is known as spin-orbit coupling. It can be automatically included by solving four-components Dirac equations instead of Schrödinger equations.

In the group of the present authors, a novel calculation technique that can directly deal with both multi-electron problem and the relativistic effect has been developed [4]. Electronic correlations among 3*d* electrons and a 2*p* hole are rigorously calculated by taking Slater determinants of all electronic configurations made by molecular orbitals. In other words, configuration interactions (CI) among molecular orbitals are computed. The new technique can be used to predict $L_{2,3}$-edge spectra quantitatively without any adjustable parameters. Some of recent results including Ni $L_{2,3}$ ELNES of NiO, $LiNiO_2$ and NiO_2 (Li-extracted $LiNiO_2$) and Mn-doped ZnO and GaN are presented [5].

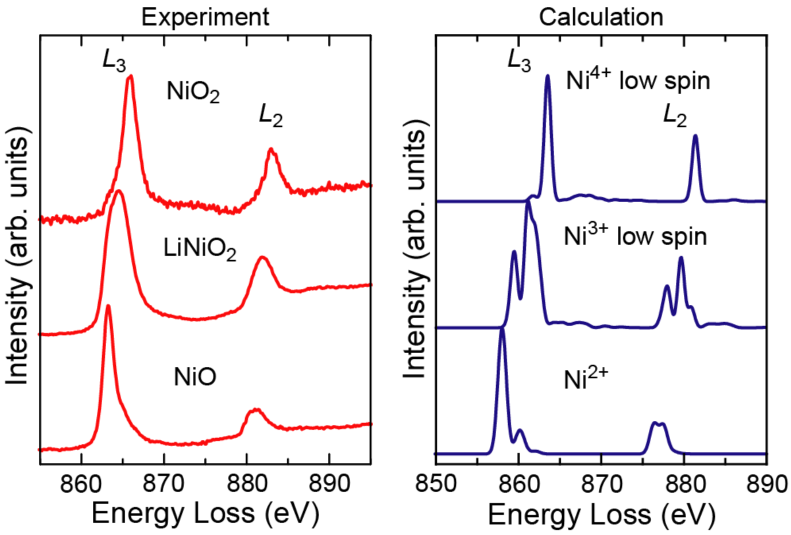

Fig. 1 Comparison of experimental and theoretical Ni-$L_{2,3}$ ELNES of NiO, $LiNiO_2$ and NiO_2 (Li-extracted $LiNiO_2$)

References

[1] S. D. Mo et al. Phys. Rev. B 62, 7901 (2000).

[2]T. Mizoguchi et al. Phys. Rev. B. 70 045103 (2004).

[3] F. M. F. de Groot, J. Electron Spectrosc. Relat. Phenom. 67, 529 (1994).

[4]K. Ogasawara et al. Phys. Rev. B 64, 155413 (2001).

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