Analyzing RIXS and RIXS-MCD of Iron Oxides by the *Ab-initio* Multiplet Method

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Background

Resonant inelastic x-ray scattering (RIXS) becomes a popular spectroscopic technique in modern science. RIXS is a *photon-in/photon-out* spectroscopy, which enable us to track all electronic and other elementary excitations in materials by tuning incident and outgoing photon energies. Recently, the magnetic circular dichroism of RIXS (RIXS-MCD) have also been investigated for characterization of magnetism in transition metal (TM) compounds. The spectral shapes of RIXS at the TM *K*-pre-edge (1s→3d) and TM $L_{2,3}$-edges (2p→3d) are dominated by the multiplet effects which originate from the strong electronic correlations between spatially localized 3*d* electrons. In this work, we have developed the *ab-initio* multiplet method to simulate RIXS and RIXS-MCD spectra.

Methods

The *ab-initio* multiplet method is based on the relativistic configuration interaction (CI) theory in quantum chemistry, where the molecular orbitals obtained by the relativistic density functional calculations are used to span the Hilbert space [1]. The many electron wavefunctions corresponding to the initial, intermediate and final states of transitions are obtained by fully diagonalizing a many-electron Hamiltonian matrix. Then, the differential scattering cross-section (DSCS) is calculated following the Kramers-Heisenberg formula. The RIXS-MCD spectra can also be calculated by introducing the Zeeman terms in the CI Hamiltonian, where the exchange interactions between magnetic moments were treated within the framework of the molecular field theory.

Results

Fe-*K*-pre-edge RIXS-MCD spectra of ferromagnetic spinel ferrite (Fe_3O_4) were calculated by the *ab-initio* multiplet method. An Fe^{2+} and Fe^{3+} ion can occupy either a tetrahedral site (*A*-site) and octahedral site (*B*-site) in spinel structures. Clear dependence of spectral shapes on the oxidation state and occupation site were predicted by our calculations. The with the theoretical spectrum of Fe^{3+} in *A*-site shows good agreement with experimental spectra reported by Sikora *et al.* [2]. The results indicate the strong Fe-*K*-pre-edge RIXS-MCD signal can mainly be ascribed to the Fe^{3+} in *A*-site. The method was also applied to interpret the RIXS-MCD at Fe $L_{2,3}$-edges of α-Fe_2O_3 which exhibits weak ferromagnetism induced by the Dzyaloshinskii-Moriya (DM) interaction between Fe ions [3]. The spectral features observed in experimental spectra were

reproduced well. We also found that RIXS-MCD signal is observed when excitation energy is tuned so that the electronic transitions occurs via spatially localized e_g orbitals that contribute to DM interactions.

Conclusions

We have developed the ab-initio multiplet method for simulating-edge RIXS and RIXS-MCD, and applied it to Fe *K*-pre-edge and Fe $L_{2,3}$-edges of several iron oxides. Main features appearing in experimental spectra were successfully reproduced by the *ab-initio* multiplet method. The origin of peak can also be analyzed from the properties of CI wavefunctions. We also demonstrated that RIXS-MCD is expected to be applied for investigation of various kind of magnetism that XMCD cannot be accessed.

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References

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