

Density Functional Theory study of the core-hole effect in simulations of core-loss spectra.

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Keywords: core-hole, DFT, ELNES, XANES

The core-hole (CH) effect in simulations of Electron Energy-Loss Near Edge Structures (ELNES) or X-Ray Absorption Near Edge Structures (XANES) is a long standing problem in solid state physics. Several very different explanations can be found in the literature to justify a weak/strong CH effect at a given edge. The aim of the present paper is to give a clear analysis of the underlying mechanisms governing the CH strength at a given edge.[1] *Ab initio* calculations based on the Density Functional Theory (DFT) were performed using WIEN2k [2] and FEFF [3] codes at different edges for the following compounds: rutile TiO₂ (r-TiO₂), MgO and some transition metals (Ti, Fe, Co, Cu and Zn). Such model compounds cover all classes of materials from metals to insulators.

We demonstrate that the CH strength at a given edge is not driven by the metallic or insulating nature of the sample or by the density of valence electron as usually thought. It is always present in any core-level spectroscopy experiment but not always observable. The mechanism governing the core-hole strength is found to be the same in all class of materials and is analyzed under several aspects.

First, the localization of the first empty states above the Fermi level is an important criterion to determine if these states should be strongly affected by the CH or not. If they have a strong character of the excited atom, then an important CH effect is expected. If the excited atom only weakly participates to the first empty states then, the CH effect on these states is shown to be small.

Second, the compensation charge mechanism occurring inside the solid due to the creation of the core-hole is analyzed. It is found to be similar in WIEN2k and FEFF calculations. The positive charge induced by the creation of the CH is more or less entirely compensated by an extra-electron (added in the calculation to maintain the crystal neutrality) localized in the first empty states of the excited atom. The perturbation on the excited atom Local Density Of States (LDOS), and thus on the corresponding ELNES or XANES structures, is then directly linked to the symmetry of the compensating charge. Only the LDOS having the same character as the compensating charge is affected by the CH. Figure 1 illustrates this point in the case of a CH on the titanium $1s$, $2s$ or $2p_{3/2}$ core states in r-TiO₂. In all cases, the extra electron is localized in the titanium $3d$ states (first atomic empty states), so that only the titanium d LDOS is perturbed by the creation of the CH. This figure also illustrates that whatever the CH depth (*i.e.* the eigenenergy of the excited core level), the response of the system is the same.

Following these arguments, the CH strength at any edge in r-TiO₂ can be understood. As shown by figure 2, no CH effect is observed at the O K edge since the conduction band has mainly Ti character. No CH effect is observed at the Ti K edge whereas a strong one appears at the Ti L₃ edge since only the Ti d DOS is perturbed by the creation of the CH. The

CH effect at the O and Mg K edges in MgO, at the metal K edges in the transition metal series as well as in other examples of the literature will be discussed. The limits of DFT when considering semi-core states will be illustrated.

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2. P. Blaha *et al.*, WIEN2k, An augmented plane wave plus local orbital program for calculating crystal properties, Technical University Wien, Austria, 2001.
3. A.L. Ankudinov *et al.*, Phys. Rev. B **58**, 7565 (1998).

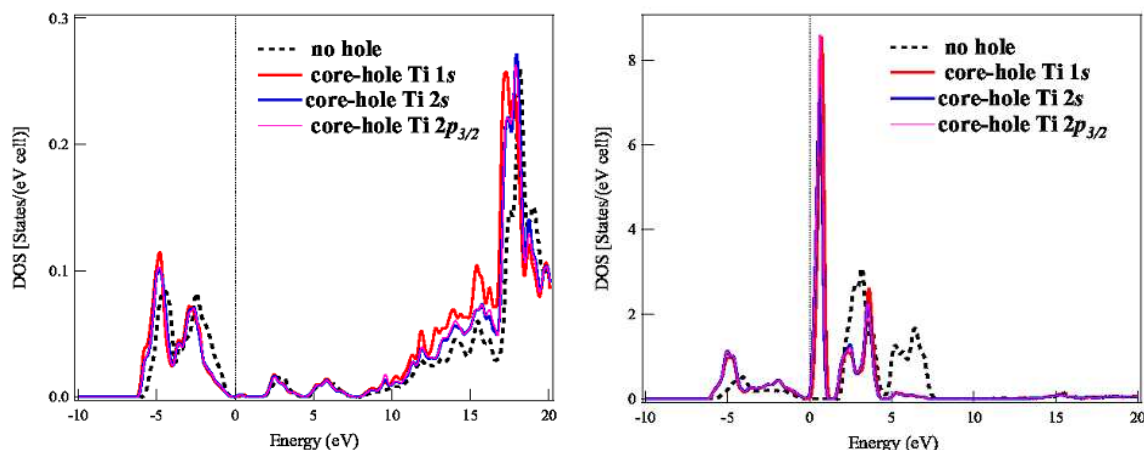


Figure 1. (Colour) Comparison of the projected titanium ($s+p$) (left) or titanium d (right) LDOS in r -TiO₂ when considering the ground state or different core-holes. Calculations were performed with WIEN2k.

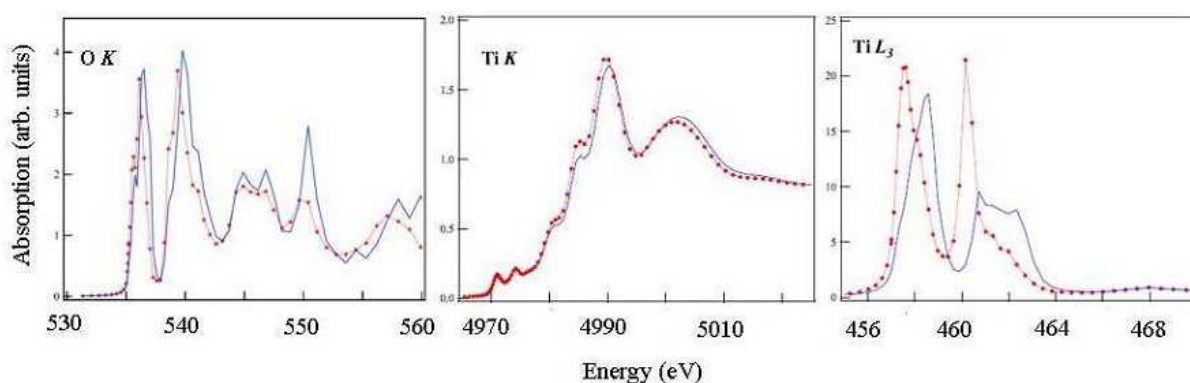


Figure 2. (Colour) Calculations of the O K, Ti K and L₃ edges in r -TiO₂ including (dotted lines with circles) or not (full lines) a CH. Calculations were performed with FEFF.