DFT+\(U\) calculation of the Cr \(K\) pre-edge structures in \(\text{ZnCr}_2\text{O}_4\)

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Abstract. Zinc chromite \(\text{ZnCr}_2\text{O}_4\) has been investigated by X-ray absorption near edge structure (XANES) spectroscopy at the Cr \(K\)-edge, with the objective of better understanding the origin of the electronic excitations giving rise to the pre-edge features. In particular, the origin of a third feature visible only in Cr-rich compounds of the \(\text{ZnAl}_2\text{O}_4\)-\(\text{ZnCr}_2\text{O}_4\) solid solution is studied. Standard density functional theory (DFT) XANES calculations were first performed, then a Hubbard \(U\) parameter was included in an attempt to improve the relative peak positions by increasing the localization of the Cr 3\(d\) states. The origin of the pre-edge features in \(\text{ZnCr}_2\text{O}_4\) has been analyzed using DFT+\(U\) calculations, local projected densities of states and the assignment of the spectral features for the dilute \(\text{ZnAl}_2\text{O}_4\):Cr\(^{3+}\) compound. We show that DFT+\(U\) does not overcome the limitations of standard DFT in modeling the relative peak positions, and that approaches including advanced description of the electron-hole interaction are needed.

1. Introduction

Spinels exhibit a wide range of solid solutions, the color of which has been studied extensively, since the great variety of coloration make them the basis of most ceramic pigments \([1,2]\). In the gahnite-zincchromite \(\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4\) the change of color from pink to green through brownish pink upon increasing chromium content has been the subject of several studies \([2,3,4]\). X-ray absorption near edge structure spectroscopy (XANES) has been used in our previous work to interpret the influence of chromium on the color and structural changes for two compounds of the \(\text{ZnAl}_{2-x}\text{Cr}_x\text{O}_4\) series \([5]\). In this work the isotropic XANES spectra of a compound diluted in Cr, with composition \(\text{ZnAl}_{1.875}\text{Cr}_{0.125}\text{O}_4\), and of the end-member \(\text{ZnCr}_2\text{O}_4\) were calculated using density functional theory (DFT) and compared with the experimental spectra measured for \(\text{ZnAl}_{1.8}\text{Cr}_{0.2}\text{O}_4\) and \(\text{ZnCr}_2\text{O}_4\), respectively. The agreement with experiment has been considered fairly good for the dilute sample but only satisfactory for the concentrated one regarding the overall spectral features. To have a better agreement with experiment, a promising approach is to improve the description of electron correlation effects present in the \(\text{ZnCr}_2\text{O}_4\) spinel by the inclusion of the Hubbard \(U\) term \([6]\). This method often improves the description of the electronic structure for systems in which standard DFT fails \([7,8]\). Therefore, this paper reports the influence of the \(U\) parameter when simulating XANES within DFT in the case of \(\text{ZnCr}_2\text{O}_4\).
2. Computational methods

The first-principles analysis has been conducted within DFT using the PWscf and Xspectra [10, 11] codes included in the QUANTUM-ESPRESSO package [9], utilizing spin-polarized PBE generalized gradient approximation [12], and norm-conserving pseudopotentials. The parameters used for the pseudopotential generation are given in Ref. [13]. A plane-wave kinetic energy cut-off of 90 Ry was found to be optimal from convergence tests. At room temperature, ZnCr$_2$O$_4$ has a cubic structure ($Fd\bar{3}m$) with $a = 8.33$ Å [5]. Zn$^{2+}$ cations occupy tetrahedral sites while Cr$^{3+}$ with $S=3/2$ populate octahedral sites. We considered the cubic cell (56 atoms) and the collinear antiferromagnetic structure proposed by Chan et al. [14]. The atomic positions were allowed to vary to minimize the total energy and the interatomic forces while keeping the lattice parameter fixed to its experimental value. A Hubbard $U$ correction term, which is applied to the 3$d$ states of the Cr atoms to increase their localization, was added to the conventional DFT calculation. Singh et al. [15], for example, used $U=3.0$ eV for Cr $d$ orbitals in ZnCr$_2$O$_4$ with the local spin-density approximation (LSDA). However, the value of $U$ has not been reported relevant to this study and, consequently, different values have been chosen for $U$ in the 0-3 eV range. The Cr K-edge electric dipole (E1) and electric quadrupole (E2) absorption cross sections were then calculated including the Hubbard $U$ term. The charge density of the system was calculated self-consistently, with a 1$s$ core hole on one Cr among the 16 in ZnCr$_2$O$_4$. A single $k$-point was used to perform self-consistent spin-polarized charge-density calculation including the core-hole, and a Monkhorst-Pack grid of $2 \times 2 \times 2$ $k$-points in the Brillouin zone for the absorption cross section calculation. The energy dependent broadening parameter used for the XANES cross section calculation is identical to that used in Ref. [16]. The isotropic XANES spectrum is the sum of the E1 and E2 contributions. Local projected density of states (DOS) were calculated on the system with a core-hole, using Löwdin projections, $2 \times 2 \times 2$ Monkhorst-Pack $k$-points grid and a Gaussian broadening of 0.00368 eV.

3. Results and discussion

Figure 1 displays the experimental and calculated Cr K-edge spectra in ZnCr$_2$O$_4$. The theoretical spectra have been aligned with the experimental one with respect to the energy position of the main peak. The experimental pre-edge spectrum exhibits three main features at 5993, 5995 and 5996.5 eV, labeled $\alpha$, $\beta$ and $\gamma$, respectively. Based on Ref. [5] (Figs. 6 and 9), the assignment of these peaks is straightforward when comparing the calculated spectrum

![Figure 1. Comparison between experimental and calculated XANES spectra at the Cr K-edge of the spinel ZnCr$_2$O$_4$ using DFT with and without Hubbard U parameter, namely $U=0$, 1.5 and 3 eV. The standard DFT result corresponds to $U=0$ eV. The inset is a focus on the pre-edge region. The isotropic XANES spectrum calculated in standard DFT, and the experimental isotropic spectrum have been replotted from Ref. [5].](image-url)
of ZnCr$_2$O$_4$ with that of ZnAl$_2$O$_4$:Cr$^{3+}$. Accordingly, peaks $\alpha$ and $\beta$ are due to E2 transitions of the core electron to unoccupied 3$d$ states of the absorber. The $\gamma$ feature is due to non-local E1 transitions to empty 4$p$ states of the absorber, hybridized with empty 3$d$ states of the next-nearest Cr neighbors through empty $p$ states of O. As can be seen and also reported in Ref. [5], the calculated pre-edge peaks lie higher in energy than the analogous peaks in the experimental spectrum. Furthermore, two peaks can be well-distinguished in the calculated spectrum belonging to the feature $\gamma$, which are not as distinct in the experimental spectrum.

The identification of the pre-edge peaks observed in Cr K-edge calculated XANES spectrum of ZnCr$_2$O$_4$ seems not to be straightforward in the present case, and both local and non-local transitions noticed in the pre-edge regions are at too high energies compared to experiment. To assign these transitions, the pre-edge regions of the experimental and calculated spectra as well as their decompositions into E1 and E2 transitions are shown in the top panels of Figure 2 while the density of states (DOS) projected on the Cr absorber at $U=0$ (Figure 2 (a), middle panel), peak $\alpha$ is the result of two E2 transitions to minority spin $t_{2g}$ and majority spin $e_g$ orbitals while peak $\beta$ is due to E2 transitions to minority spin $e_g$ states. Also shown in Figure 2 (a), peak $\gamma$ is due to E1 transitions to the $p$ states of the absorbing Cr, orbitally mixed with the 3$d$ orbitals of the neighboring Cr. These observations are also presented briefly in Table 1.

The lower panels of Figure 2 (b) illustrate the impact of the Hubbard $U$ on the electronic DOS. When the $U$ term is added, the minority spin $t_{2g}$ and $e_g$ orbitals are found closer to each other. Furthermore, the majority spin states are separated from the minority spin ones leading to a decrease in intensity of peak $\alpha$, in disagreement with experiment. Similarly as in the previous case, the observed peaks in the pre-edge region at $U=3$ eV, shown in the top panel of Figure 2 (b), are assigned to specific transitions and listed in Table 1. Comparing the transitions at $U=0$ eV to the transitions at $U=3$ eV, it can be observed that the Cr 3$d$ $t_{2g}^{\text{min}}$ contribution is moved from peak $\alpha$ to peak $\beta$ as the Hubbard parameter $U$ is changed from 0 to 3 eV.

In summary, it appears that DFT+$U$ does not overcome the two main issues arising in the standard DFT calculation of the Cr K-edge spectrum of ZnCr$_2$O$_4$. First, the E1 peaks in the pre-edge are too close to the main edge peak, that is, the 3$d$ states of Cr are too close to the $p$ ones. Second, the E2 peaks are also found at too high energies, as the core-hole interaction is not well modeled by our calculations. As the distance between neighboring core-holes is 8.33 Å,
Table 1. Tentative assignment of α, β and γ peaks in terms of local (E2) and non-local (E1) transitions.

| peak | Assign. for $U=0$ eV | Assign. for $U=3$ eV |
|------|----------------------|----------------------|
| α    | E2: $1s \rightarrow 3d(e_{maj}^{maj} + t_{2g}^{min})$ of abs. Cr | E2: $1s \rightarrow 3d e_{min}^{maj}$ of abs. Cr |
| β    | E2: $1s \rightarrow 3d e_{maj}^{maj}$ of abs. Cr | E2: $1s \rightarrow 3d (t_{2g}^{min} + e_{g}^{min})$ of abs. Cr |
| γ    | E1: $1s \rightarrow p$ of abs. Cr | E1: $1s \rightarrow p$ of abs. Cr |

no improvement is expected by increasing the supercell size. Vibrational effects could affect the peak intensities rather than their splitting and are not responsible for the observed failure of the current calculation. Beyond DFT approaches could improve the modeling of the core-hole-electron interaction but the Bethe-Salpeter equation remains very challenging for such open-shell system, while the efficiency of TD-DFT relies on the choice of the used kernel. Besides, ligand field multiplet calculations could better reproduce the local α and β peaks but is unable to account from the non-local γ peak.

4. Conclusion

The evolution of the Cr K pre-edge features along the ZnAl$_2$O$_4$-ZnCr$_2$O$_4$ was first reported by Verger et al. [5] and interpreted using XANES calculations performed in standard DFT. In the present study, in an attempt to improve the agreement with the experimental spectrum for ZnCr$_2$O$_4$, DFT+$U$ calculations were carried out with different values chosen for $U$ on the Cr 3d states. Our findings show that the pre-edge features, and in particular their relative splitting, are however not better reproduced when taking into account the Hubbard parameter. Approaches including an improved modeling of the electron-hole interaction are expected to provide a better overall agreement with experiment, although correlated systems such as ZnCr$_2$O$_4$ represent a significant computational challenge. From the point of view of experiment, high energy resolution fluorescence detection could be used to better resolve the pre-edge features.

Acknowledgement

This work was partly granted access to the HPC resources of IDRIS under the allocation 2015-100172 made by GENCI (Grand Equipement National de Calcul Intensif). E.R. gratefully acknowledges the support of the Postdoctoral Fellowship of the Hungarian Academy of Sciences.

References

[1] Martos M, Martínez M, Cordoncillo E and Escribano P 2007 J. Eur. Ceram. Soc. 27 4561-67
[2] Prim S, García A, Galindo R, Cerro S, Llusar M, Folgueras M and Monró G 2013 Ceram. Int. 39 6981-89
[3] Halenius U, Andreozzi G B and Skoghy H 2010 Am. Mineral. 95 456-62
[4] Bosi F, Andreozzi G B, Halenius U and Skoghy H 2011 Am. Mineral. 96 594-8
[5] Verger L et al. 2015 Phys. Chem. Miner., DOI 10.1007/s00269-015-0771-8
[6] Anisimov V I, Aryasetiawan F and Lichtenstein A I 1997 J. Phys. Condens. Matter. 9 767
[7] Panchmatia P M, Sanyal B and Oppeneer P M 2008 Chem. Phys. 343 47-60
[8] Rivero P, Loschen C, Moreira I D P R and Illas F 2009 J. Comput. Chem. 30 2316-26
[9] Giannozzi P et al. 2009 J. Phys. Condens. Matter 21 395502
[10] Gouguissis C, Calandra M, Seitsonen A and Mauri F 2009 Phys. Rev. B 80 075102
[11] Taillefermier M, Cabaret D, Flank A M and Mauri F 2002 Phys. Rev. B 66 195107
[12] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77 3865-8
[13] Juhin A, Calas G, Cabaret D, Galois L and Hazemann J L 2007 Phys. Rev. B 76 054105
[14] Chan K, Sau J, Zhang P and Cohen M 2007 Phys. Rev. B 75 054304
[15] Singh N and Rhee J Y 2010 J. Korean Phys. Soc. 57 1233-7
[16] Bordage A, Rossano S, Horn A H and Fuchs Y 2012 J. Phys. Condens. Matter 22 225401