

## Tracking the signature of low symmetry environments in the XAS $K$ pre-edge

M Hunault<sup>1,\*</sup>, V Vercamer<sup>1,2</sup>, M W Haverkort<sup>3</sup>, M-A Arrio<sup>1</sup>, C Brouder<sup>1</sup>, G Calas<sup>1</sup> and A Juhin<sup>1</sup>

<sup>1</sup> Sorbonne Universités, UPMC Univ Paris 06, CNRS, IRD, MNHN, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, 4 place Jussieu, 75252 Paris cedex 05, France

<sup>2</sup>AGC France SAS, 100 rue Léon Gambetta, 59168 Boussois, France

<sup>3</sup>Max-Planck-Institut für Chemische Physik fester Stoffe Nöthnitzer Str. 40, 01187 Dresden, Germany

\*E-mail: myrtille.hunault@impmc.upmc.fr

**Abstract.** For Co-containing crystalline compounds measured by XAS, the influence of the local symmetry on the  $K$  pre-edge features is studied using advanced Ligand Field Multiplet (LFM) calculations, which accurately take into account the  $p$ - $d$  hybridization. The LFM theory is used to calculate the  $K$  pre-edge spectra of  $\text{Co}^{2+}$  in various environments and the absolute intensities of electric-quadrupole and -dipole transitions involved in the pre-edge. This enables to reproduce the spectra for cubic ( $O_h$ ,  $T_d$ ) and lower symmetries ( $C_{4v}$ ,  $D_{3h}$ ), and allows quantitative derivation of the local  $p$ - $d$  mixing.

### 1. Introduction

Site geometry of transition metal (TM) ions substituted in crystals is a crucial characteristic, which drives their properties and related applications, from solid-state physics to coordination chemistry. In particular, exotic geometries like 5-fold coordinated sites are often predicted or suspected in coordination complexes, surfaces and interfaces, glasses and amorphous compounds. However their presence is difficult to assess because the spectral signature is largely unknown. X-ray absorption spectroscopy and in particular,  $K$  pre-edge features are powerful tools to determine the local structure of TM. In the case of cobalt(II), a widely used coloring agent, its coordination number (CN) plays a major role in the coloration of crystals and glasses [1,2]. Understanding how the local structure controls the properties in crystals is a motivation for applying core level spectroscopy to investigate the local geometry of  $\text{Co}^{2+}$ .

$\text{Co}^{2+}$  can be found in 4-, 5- or 6-fold coordination with a large diversity of site symmetries, which can be distinguished according to the intensity, and shape of the pre-edge [3]. The variation of the intensity of the pre-edge depends on the  $3d$ - $4p$  hybridization that, when it is allowed by the absence of an inversion center, enables an electric dipole contribution in addition to the electric quadrupole transitions. This effect is well-known for the cases of  $T_d$  site geometry and has been reproduced for iron ions by calculations in the Ligand Field Multiplet model [4]. In order to describe



exotic sites, it is necessary to consider lower symmetries though it is challenging. In this paper we compare the influence of  $\text{Co}^{2+}$  symmetry ( $\text{O}_h$ ,  $\text{T}_d$ ,  $\text{C}_{4v}$ ,  $\text{D}_{3h}$ ) and calculate the  $p$ - $d$  hybridization, which is expected to vary for 6-, 5- and 4-fold coordinated  $\text{Co}^{2+}$ . A good agreement is obtained between calculations and experimental Co K-edge XANES spectra.

## 2. Experimental

Our work focuses on a benchmark set of four crystalline samples bearing  $\text{Co}^{2+}$  in various symmetries for which we expected the  $p$ - $d$  hybridization to vary. We chose two different spinels:  $\text{CoCr}_2\text{O}_4$  (4-fold coordinated  $\text{Co}^{2+}$  in  $\text{T}_d$ ) and  $\text{Co}_2\text{GeO}_4$  (6-fold coordinated  $\text{Co}^{2+}$  in  $\text{D}_{3d}$  that we approximate to  $\text{O}_h$ ) and two compounds containing 5-fold coordinated Co sites:  $\text{BaCoP}_2\text{O}_7$  ( $\text{C}_{4v}$ ) and  $\text{LiCoBO}_3$  ( $\text{D}_{3h}$ ).  $\text{CoCr}_2\text{O}_4$  was synthesized by coprecipitation [5],  $\text{BaCoP}_2\text{O}_7$  by precipitation-calcination [3] and  $\text{LiCoBO}_3$  by a traditional ceramic route [6]. All samples were characterized by x-ray diffraction. Samples were prepared as powders sandwiched between two Kapton® tapes.

Co K-edge (7709 eV) XAS spectra were collected at beamlines 13-BM-D and 13-ID-E at the Advanced Photon Source (Chicago IL, USA – 7 GeV and 102 mA injected positron). The incident beam was monochromated using Si(111) or Si(311) double crystal monochromators. XANES spectra were recorded in transmission mode at room temperature. The energy calibration was achieved using a Co foil as reference. All XANES spectra presented here result from the average of four successively obtained spectra. The spectra were normalized to an absorption step of 1 using the "ATHENA" software [7]. The pre-edge features presented in this paper are given after background removal, using an arctangent function.

## 3. Theory and calculations

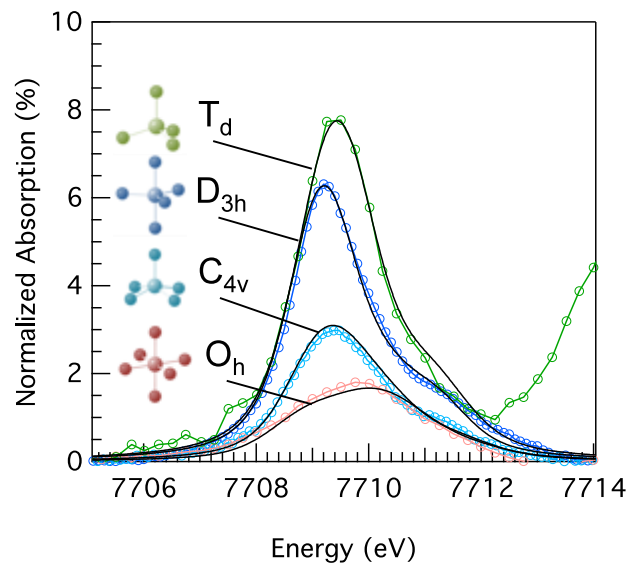
In order to extract quantitative information from  $p$ - $d$  hybridization of the pre-edge, we performed LFM calculations using the method developed by Thole et al. [8] in the framework established by Cowan [9] and Butler [10]. Here, this approach is implemented in the code Quanty [11], in which operators are defined using second quantization and spectra are calculated using Green functions [12]. It takes into account all the  $3d$ - $3d$  and  $1s$ - $3d$  electronic Coulomb interactions, as well as the spin-orbit coupling on every open shell of the absorbing atom. For all sites, we applied a reduction factor of  $\beta=0.6$  to the Slater integrals calculated for an isolated ion and spin-orbit coupling at 80% of its free ion value [13].  $\text{Co}^{2+}$  is considered as an isolated ion and its geometrical environment is treated through a parameterized crystal-field potential defined by the point group symmetry of the absorbing site. These parameters were fitted in agreement with the optical spectra of the compounds. For non-centrosymmetric sites, hybridization is allowed between  $3d$  and  $4p$  orbitals of  $\text{Co}^{2+}$  and is described by an hybridization Hamiltonian built from the  $U^{(1-)}$  and  $U^{(3-)}$  unit tensor operators as derived in [4], which mixes the electronic configurations  $1s^23d^74p^0$  and  $1s^23d^64p^1$  that describes the initial state. The  $p$ - $d$  hybridization Hamiltonian depends on the difference  $\Delta$  between the average energies of these two electronic configurations. For  $\text{Co}^{2+}$ , the *ab initio* value is  $\Delta = 13.5$  eV. Depending on the symmetry, the hybridization Hamiltonian is described by one ( $\text{T}_d$  and  $\text{D}_{3h}$ ) or two ( $\text{C}_{4v}$ ) parameters [14]. The hybridization parameters are adjusted in order to fit the experimental intensity of the  $K$  pre-edge. The absolute intensities are calculated at  $T = 300$  K and the population of the initial state levels is given by the Boltzmann law. The spectra are convoluted by a Lorentzian (full width half maximum, FWHM:  $2\gamma = 1.33$  eV) and a Gaussian (FWHM: 0.4 eV), which respectively accounts for the lifetime of the  $1s$  core hole of Co and the instrumental resolution. Finally, the transitions are normalized by the edge jump at the Co K-edge, calculated for a Co atom as  $3.0 \cdot 10^{-4} \text{ \AA}^2$  [15]. Hence, the calculated spectra can be directly compared to the normalized experimental ones.

## 4. Results and discussion

The normalized background-corrected resulting spectra are presented in Fig.1. They reveal the influence of the site symmetry on the intensity and shape of the pre-edge transitions. As expected, the lowest intensity is observed for the 6-fold coordinated site in  $\text{Co}_2\text{GeO}_4$ . We used the centrosymmetric

$O_h$  approximation to model for the symmetry of the slightly distorted  $D_{3d}$  site. In this case, hybridization is symmetry-forbidden and only electric quadrupole transitions contribute to the pre-edge feature. For the other point groups, we observe an increase in the intensity from  $C_{4v}$  to  $D_{3h}$  to  $T_d$ , which is in line with the effect of the  $p-d$  hybridization allowed for non-centrosymmetric cases.

On Fig.1, we compare the experimental results with the calculated pre-edge for each case. The hybridization parameters are given in Table I. These calculations enable to reproduce the measured intensities and shapes of pre-edge features as shown in Fig.1. This validates the use of ideal point group symmetry to model the symmetry of the slightly distorted sites. For  $O_h$  and  $T_d$  symmetries, the range of the fitted parameters agrees with that found for Fe K-edge XANES spectra [4]. Furthermore we observe that the fraction of the dipole contribution to the total pre-edge area for Co and Fe in  $T_d$  are similar (68%). For the cases of  $C_{4v}$  and  $D_{3h}$ , the fraction of electric dipole contribution to the pre-edge is intermediate between  $O_h$  and  $T_d$  cases. The symmetry of the ground state (Table I) agrees with the energy level diagrams [3].



**Fig.1** Normalized Co K pre-edge spectra for each of the four symmetries of this study: experimental (colored line and markers) and respective calculation (plain black line). Green:  $CoCr_2O_4$  ( $T_d$ ), dark blue:  $LiCoBO_3$  ( $D_{3h}$ ), light blue:  $BaCoP_2O_7$  ( $C_{4v}$ ) and pink:  $Co_2GeO_4$  ( $O_h$ ).

Table I: Parameters used for the calculation of the Co K pre-edge features.

Sample	Symmetry (CN)	Crystal field parameters (eV)	Hybridization parameters (eV)	Ground state symmetry	Dipole contribution (%)
$Co_2GeO_4$	$O_h$ (6)	$D_q = 0.11$	-	${}^4T_{1g}$	0
$BaCoP_2O_7$	$C_{4v}$ (5)	$D_q = 0.148$ $D_s = -0.087$ $D_t = 0.055$	$V_{p-d}(a_1) = 0.25$ $V_{p-d}(e) = 0.84$	${}^4E$	26
$LiCoBO_3$	$D_{3h}$ (5)	$D_\mu = 0.0$ $D_\nu = -0.096$	$V_{p-d} = 5.5$	${}^4A_2'$	61
$CoCr_2O_4$	$T_d$ (4)	$D_q = -0.055$	$V_{p-d} = 8.5$	${}^4A_2$	68

## 5. Conclusion

In this work, we calculated and quantified the influence of hybridization on the K pre-edge spectral features. The good agreement obtained between calculations and experiment demonstrates the validity of our model and of the Ligand Field Multiplet approach. It offers the possibility to interpret quantitatively the pre-edge features of  $Co^{2+}$  or other TM ions in terms of spectral characteristics and of

degree of admixture between  $4p$  and  $3d$  levels in the ground state. This information can be further used to interpret the optical absorption spectra of Co-bearing materials, in which the energy and intensity of the  $3d$ -transitions strongly rely on the  $p$ - $d$  hybridization. This aspect will be further discussed in an upcoming paper. The rationalization of the relation between the local structure and the spectroscopic properties offers a powerful tool to help determining the speciation of TM in amorphous materials as for instance in glasses, which show a strong influence of glass composition on its color.

### Acknowledgements

This work is part of the « VITRAUX » project supported by a Sorbonne University Convergence grant (SU-14-R-ScPC-15-2). This research used resources of the Advanced Photon Source, a U.S. Department of Energy (DOE) Office of Science User Facility operated for the DOE Office of Science by Argonne National Laboratory under Contract No. DE-AC02-06CH11357. We acknowledge the support of GeoSoilEnviroCARS (Sector 13), which is supported by the National Science Foundation - Earth Sciences (EAR-1128799), and the Department of Energy, Geosciences (DE-FG02-94ER14466)

### References

- [1] Hunault M, Calas G, Galois L, Lelong G and Newville M 2014 Local Ordering Around Tetrahedral  $\text{Co}^{2+}$  in Silicate Glasses *J. Am. Ceram. Soc.* **97** 60–2
- [2] Hunault M, Bauchau F, Loisel C, Hérold M, Galois L, Newville M and Calas G 2015 Spectroscopic investigation of the coloration and fabrication conditions of medieval blue glasse *J. Am. Ceram. Soc.* doi:10.1111/jace.13783
- [3] Hunault M, Robert J-L, Newville M, Galois L and Calas G 2014 Spectroscopic properties of five-coordinated  $\text{Co}^{2+}$  in phosphates *Spectrochim. Acta. A. Mol. Biomol. Spectrosc.* **117** 406–12
- [4] Arrio M-A, Rossano S, Brouder C, Galois L and Calas G 2000 Calculation of multipole transitions at the Fe K pre-edge through  $p$ - $d$  hybridization in the Ligand Field Multiplet model *Europhys. Lett. EPL* **51** 454–60
- [5] Wang Y, Zhou Z, Jia M, Zhu X, Zhang W and Jiang D 2005 Spinel-Type Cobalt Chromites as Novel and Highly ortho-selective Catalysts for Phenol Alkylation *Catal. Lett.* **104** 67–71
- [6] Tao L, Neilson JR, Melot BC, McQueen TM, Masquelier C and Rouse G 2013 Magnetic structures of  $\text{LiMBO}_3$  ( $M = \text{Mn, Fe, Co}$ ) lithiated transition metal borates *Inorg. Chem.* **52** 11966–74
- [7] Ravel B and Newville M 2005 ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT *J. Synchrotron Radiat.* **12** 537–41
- [8] Thole B T, Cowan R D, Sawatzky G A, Fink J and Fuggle J C 1985 New probe for the ground-state electronic structure of narrow-band and impurity systems *Phys. Rev. B* **31** 6856–8
- [9] Cowan R D 1981 *The Theory of Atomic Structure and Spectra* (University of California Press)
- [10] Butler P H 1981 *Point group symmetry applications: methods and tables* (Plenum Press)
- [11] Haverkort M W Quanta - a quantum many body script language, <http://www.quanta.org/>
- [12] Haverkort M W, Zwierzycki M and Andersen O K 2012 Multiplet ligand-field theory using Wannier orbitals *Phys. Rev. B* **85** 165113-22
- [13] Slater integrals for Co free ion:  $F^2_{3d3d} = 11.60483 \text{ eV}$ ,  $F^4_{3d3d} = 7.20942 \text{ eV}$ ,  $\zeta_{3d} = 0.066 \text{ eV}$ ;
- [14] The hybridization Hamiltonian mixes  $d$  and  $p$  functions of same symmetry:  $t_2$  for  $T_d$ ,  $e'$  for  $D_{3h}$ , and  $a_1$  and  $e$  for  $C_{4v}$ . For each point group symmetry, one parameter corresponds to one symmetry.
- [15] Gullikson E M 2010 X-ray interactions with matter, CXRO, <http://www.cxro.lbl.gov>