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

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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 Co\(^{2+}\).

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 Co\(^{2+}\) symmetry (Oh, Td, C\(_{4v}\), D\(_{3h}\)) and calculate the p-d hybridization, which is expected to vary for 6-, 5- and 4-fold coordinated 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 Co\(^{2+}\) in various symmetries for which we expected the p-d hybridization to vary. We chose two different spinels: CoCr\(_2\)O\(_4\) (4-fold coordinated Co\(^{2+}\) in T\(_d\)) and Co\(_2\)GeO\(_4\) (6-fold coordinated Co\(^{2+}\) in D\(_{3d}\) that we approximate to O\(_h\)) and two compounds containing 5-fold coordinated Co sites: BaCoP\(_2\)O\(_7\) (C\(_{4v}\)) and LiCoBO\(_3\) (D\(_{3h}\)). CoCr\(_2\)O\(_4\) was synthesized by coprecipitation [5], BaCoP\(_2\)O\(_7\) by precipitation-calcination [3] and 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 Quany [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 β = 0.6 to the Slater integrals calculated for an isolated ion and spin-orbit coupling at 80% of its free ion value [13]. 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 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\(^2\)3d\(^7\)4p\(^0\) and 1s\(^2\)3d\(^6\)4p\(^1\) that describes the initial state. The p-d hybridization Hamiltonian depends on the difference Δ between the average energies of these two electronic configurations. For Co\(^{2+}\), the \textit{ab initio} value is Δ = 13.5 eV. Depending on the symmetry, the hybridization Hamiltonian is described by one (T\(_d\) and D\(_{3h}\)) or two (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: 2γ = 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 10\(^{-4}\)Å\(^2\) [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 Co\(_2\)GeO\(_4\). We used the centrosymmetric
Oh 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 Oh 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 Oh and T_d cases. The symmetry of the ground state (Table I) agrees with the energy level diagrams [3].

![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 (Oh).](image)

**Fig.1**

**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                   | V_{p-d}(a_1) = 0.25          | ^E                   | 26                      |
| LiCoBO_3    | D_{3h} (5)    | D_q = -0.087                  | V_{p-d}(e) = 0.84            | ^4A_2'                | 61                      |
| CoCr_2O_4   | T_d (4)       | D_q = -0.055                  | V_{p-d} = 5.5                | ^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, Galoisy L, Lelong G and Newville M 2014 Local Ordering Around Tetrahedral Co^{2+} in Silicate Glasses J. Am. Ceram. Soc. 97 60–2
[2] Hunault M, Bauchau F, Loisel C, Hérol M, Galoisy 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, Galoisy L and Calas G 2014 Spectroscopic properties of five-coordinated Co^{2+} in phosphates Spectrochim. Acta. A. Mol. Biomol. Spectrosc. 117 406–12
[4] Arrio M-A, Rossano S, Brouder C, Galoisy 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 Rousse G 2013 Magnetic structures of LiMBO_{3} (M = 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 Quany - a quantum many body script language, http://www.quanty.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_{3d}^{2} = 11.60483 eV, F_{3d}^{4} = 7.20942 eV, \zeta_{3d} = 0.066 eV;
[14] The hybridization Hamiltonian mixes d and p functions of same symmetry: t_{e} for T_{2g}, e’ for D_{4h}, and \alpha 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