Origin of the pre-edge structure at the Al $K$-edge: the role of atomic vibrations

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Abstract. We present a detailed analysis of the pre-edge peak present in the Al $K$-edge XANES spectra of corundum ($\alpha$-Al$_2$O$_3$) and diaspore ($\alpha$-AlOOH), as measured at room temperature. This is achieved by XANES and DOS calculations performed using the density functional theory in a pseudopotential plane-wave framework. The XANES calculations carried out for the equilibrium atomic positions do not reproduce the pre-edge of corundum and partially reproduce it in the case of diaspore. It is shown that the electronic transitions occurring in the pre-edge involves the $3s$ empty states of the aluminium absorbing atom. The Al $3s$ states can be probed in the electric dipole approximation via a $p$-$s$ mixing, which is possible only if the Al site is not centrosymmetric. Although Al does not occupy an inversion center in the two minerals under study, the $p$-$s$ mixing is too weak to provide a pre-edge feature in good agreement with experiment. The deviation from centrosymmetry can be enhanced by the atomic vibrations. We develop a theory that takes into account the atomic vibrations directly in the calculation of the absorption cross section, based on the Born-Oppenheimer approximation. This theory is applied to corundum and diaspore and yields satisfactory results in the pre-edge region.

1. Introduction
A pre-edge is quite often present at the $K$-edge of low-Z cations in X-ray absorption near-edge structure (XANES) spectra of minerals or other oxides. For instance, a pre-edge feature is visible at the Mg $K$-edge in enstatite (Mg$_2$Si$_2$O$_6$) [1], in pyrope (Mg$_3$Al$_2$Si$_3$O$_{12}$) [2], in Mg(OH)$_2$ [3] and in farringtonite (Mg$_3$P$_2$O$_8$) [4]. At the Al $K$-edge, a pre-edge feature has notably been observed in corundum ($\alpha$-Al$_2$O$_3$) [5], in topaz (Al$_2$SiO$_4$F$_2$) [6], in kyanite (Al$_2$SiO$_5$) [6], in spodumene (LiAlSi$_2$O$_6$) [6], in diaspore ($\alpha$-AlOOH) [7], in boehmite ($\gamma$-AlOOH) [8], in K-alum (KAl(SO$_4$)$_2$.12H$_2$O) [8] in albite (NaAlSi$_3$O$_8$) [5], in berlinite (AlPO$_4$) [7], and in LaAlO$_3$ [3]. A pre-edge is also well-resolved at the Si $K$-edge of stishovite (SiO$_2$ with rutile-type structure) [6, 9]. In most of the compounds cited above, the absorbing cation is six-fold coordinated to oxygen atom. In the case of the Si and Al $K$-edges, Dien Li et al. [6] have assigned this pre-edge feature to a dipole forbidden $3s$-like transition. In the case of diaspore, corundum and enstatite, the pre-edge has been reproduced by muffin-tin multiple scattering XANES calculations in the electric dipole approximation and attributed to medium range order [7, 1]. However for corundum, the muffin-tin calculations have been refuted by full-potential calculations that do not exhibit any pre-edge feature [10, 11]. Recently, at the Mg $K$-edge, full-potential calculations have permitted the reproduction of the pre-edge feature for enstatite and farringtonite, but not
for pyrope [4]. For farringtonite and enstatite, the calculations have shown that the pre-edge is due to the contribution of the five-fold Mg site and the strongly distorted six-fold Mg site, respectively. Consequently, the distortion of the site seems to play an important role in the pre-edge. But its precise origin is still unclear, notably for corundum. In this paper, we focus our attention on two minerals, corundum (\(\alpha\)-Al\(_2\)O\(_3\)) and diaspore (\(\alpha\)-AlOOH), that both exhibit a well-resolved pre-edge at the Al K-edge. Our aim is notably to understand why pure 1s \(\rightarrow\) p transition computed in a full-potential framework does not allow to account for the pre-edge feature observed in corundum experimental XANES spectrum.

At the transition metal K-edge in perovskites, it has been shown that the intensity of the pre-edge depends on the temperature [12, 13, 14, 15], so bringing to light the influence of atomic vibrations in X-ray absorption spectroscopy. Moreover, atomic vibrations have been detected by x-ray resonant elastic scattering experiments at the K-edge of germanium [16, 17]. Thus, we suspect that vibrations could also play a significant role at the K-edge of low Z cations, especially in the case of corundum. In this paper, we summarize a theoretical approach to include the atomic vibrations in XANES calculations [18]. Then we show that the 3s states of Al are probed at the Al K-edge, as the atomic vibrations are considered.

The following of the paper comprises two main sections. The first one is dedicated to the analysis of the pre-edge feature of the aluminium K-edge spectra of corundum and diaspore, by using Density Functional Theory (DFT) calculations in a plane-wave framework. Calculated XANES spectra are presented, and the pre-edge is interpreted in terms of local and partial density of states (DOS) calculations. The influence of site distortion is emphasized. The role of atomic vibrations is introduced and preliminary XANES calculations performed with the absorbing atom displaced from its equilibrium position are shown. In the second section, a theory for including the atomic vibrations into the absorption cross section in the electric dipole approximation is summarized. This theory is then applied to the two minerals under study and the results are discussed. Conclusions of this work are given in a last section.

2. Pre-edge analysis
2.1. Computational details
The calculations presented in this work were performed using the Quantum-espresso suite of codes [19], where the implementation of XANES has been recently achieved (XSpectra package) [20], by following the framework of Taillefumier et al. [21]. Quantum-espresso is based on DFT, uses plane-wave basis set, pseudopotentials and periodic boundary conditions. The calculation is performed in two steps: (i) the minimization of the total energy of a supercell including a 1s core hole on the absorbing atom, so leading to a self-consistent charge density of the system under study, (ii) the absorption cross section computation. This second step comprises the reconstruction of the all-electron wave function of the absorbing atom using the Projector Augmented Wave (PAW) method [22], and the construction of a Lanczos basis set that allows the calculation of XANES as a continued fraction. More details can be found in Refs. [21, 11].

Supercells have been built from the experimental diffraction data of Refs. [23] and [24] for corundum and diaspore, respectively. Corundum (\(\alpha\)-Al\(_2\)O\(_3\)) crystallizes in the trigonal system (space group R\(3c\)) with \(a = 5.128\) \(\text{\AA}\) and two Al\(_2\)O\(_3\) per unit cell. We have built a 2 \(\times\) 2 \(\times\) 2 trigonal supercell, since it was previously shown that this size of supercell was sufficient to avoid interaction between core-holes belonging to neighboring cells [11]. Diaspore (\(\alpha\)-AlOOH) crystallizes in the orthorhombic system (space group Pbam) with \(a = 4.401\) \(\text{\AA}\), \(b = 9.421\) \(\text{\AA}\), \(c = 2.845\) \(\text{\AA}\), and four AlOOH per unit cell. In that case, we have used a 2 \(\times\) 1 \(\times\) 3 supercell, which was found to be large enough to isolate the absorbing atom.

We have used norm-conserving Troullier-Martins pseudopotentials [25] with the same parameterization as in Ref. [11]. The pseudopotential of the absorbing atom is generated with a core-hole on the 1s level. The exchange and correlation potential was modeled in the Generalized
Gradient Approximation in the formulation given by Perdew, Burke and Ernzerhof [26]. The wave functions were expanded to an energy cutoff of 80 Ry. The total energy minimization (first step of the calculation) is performed at the Γ point of the Brillouin zone. The computation of the XANES spectra (second step of the calculation) was performed in the electric dipole approximation on a 4×4×4 k-point grid. One Blöchl projector was used for the PAW all-electron reconstruction of the final state wave-function, with a 2 Bohr radius augmentation sphere. The calculated spectra are broadened using a constant $\gamma$ parameter (0.7 eV) in the continued fraction. The empty local and partial DOS were calculated on the supercells using Löwdin projections and a Gaussian broadening of 0.3 eV.

2.2. XANES calculations at the equilibrium atomic positions

Figure 1a compares the experimental Al K-edge XANES spectrum of corundum with the calculated one obtained from the experimental equilibrium atomic positions of Ref. [23]. Except, in the pre-edge, all the experimental features are satisfactorily reproduced by the calculation. As shown in the inset (Fig. 1a), no pre-edge feature is displayed neither in the calculated isotropic spectrum, nor in angular-dependent contributions. For crystals with $3m$ ($D_{3d}$) point group symmetry like corundum, the isotropic spectrum is given in the electric dipole approximation by $\sigma_{\text{iso}} = (2\sigma_\parallel + \sigma_\perp)/3$, where $\sigma_\parallel$ and $\sigma_\perp$ correspond to the polarisation vector $\hat{\varepsilon}$ of the photon beam parallel and normal to the $C_3$ symmetry axis of the crystal, respectively [27].

![Figure 1. Comparison between experimental and calculated Al K-edge XANES spectra in corundum (a) and in diaspore (b). The experimental spectra, measured at room temperature, were already published in [7]. The calculated spectra have been obtained from the equilibrium atomic positions. In the insets, that are zooms on the pre-edge region, angular dependent calculated spectra are also displayed. While no pre-edge is distinguishable in the calculated XANES of corundum, a pre-edge feature clearly appears in the $\hat{\varepsilon} \parallel \hat{b}$ contribution in the case of diaspore.](image)

The existence of the experimental Al K pre-edge feature has been however demonstrated by numerous experimental data [6, 8, 28, 29, 11, 30, 31, 3, 32]. In the literature, there are some quite ancient theoretical XANES spectra of corundum that exhibit a pre-edge [7, 28]. It should be emphasized that they have been carried out using a non self-consistent muffin-tin potential and such an approximation is now well known to give inaccurate results in the pre-edge region. More recently, full-potential calculations have confirmed the absence of a theoretical electric dipole pre-edge as in Figure 1a [10, 11, 30, 33]. Therefore, the pre-edge feature at the Al K-edge in corundum is manifestly not due to pure $1s \rightarrow p$ electric dipole transitions.
Figure 1b compares experimental and calculated Al K-XANES spectra of diaspore. The calculated spectrum has been performed from the experimental atomic positions of Ref. [24]. The agreement between experiment and theory is satisfactory. Unlike the case of corundum, a pre-edge is visible in the calculated spectrum, but is too weak as compared to experiment. In the inset, we observe that the calculated pre-edge feature comes from the $\hat{\varepsilon} \parallel [010]$ contribution of the isotropic spectrum. In the case of diaspore, which crystallizes in the orthorhombic system, the isotropic spectrum is the mean average of the $\hat{\varepsilon} \parallel [100]$, $\hat{\varepsilon} \parallel [010]$ and $\hat{\varepsilon} \parallel [001]$ contributions. The inset shows that the pre-edge feature of diaspore seems to be strongly anisotropic. To our knowledge, no experimental data are available to attest the validity of this theoretical result. A previous study has shown a well-defined calculated pre-edge feature at the Al K-edge of diaspore, but the method employed uses again a non self-consistent muffin-tin framework [7].

2.3. DOS calculations and pre-edge interpretation

The aim of this subsection is to give an explanation of the presence (resp. absence) of an electric dipole $1s \rightarrow p$ pre-edge feature in the theoretical XANES spectrum of diaspore (resp. corundum).

First, we want to determine the symmetry of the states that are involved in the pre-edge region in both minerals. Figure 2 presents partial and local DOS of corundum (a) and of diaspore (b). The DOS have been obtained from the same self-consistent potential as the one used for the XANES calculations. We have plotted the $s$, $p$ and $d$ partial empty DOS of the aluminium absorbing atom, the $s$ and $p$ ones of the oxygen first six neighbours and the $s$, $p$ and $d$ ones of the aluminium second neighbours.

The empty DOS of corundum and diaspore are similar. The noticeable differences are weak and essentially concern the Al absorbing atom DOS: a broader and less intense Al 3$p$ peak in diaspore than in corundum, and the presence of Al 3$p$ weak contribution at the same energy as the one of the Al 3$s$ peak in diaspore. In both cases, the position of the experimental pre-edge peak (top panels) coincides with the 3$s$ projected DOS of the Al absorbing atom. The first main XANES feature essentially has an Al 3$p$ character, and the 3$d$ Al states mainly arise at higher energies.

The 3$s$ states of the absorber are hybridized with the $s$ and $p$ empty states of the oxygen neighbours. On the contrary, the Al second neighbours do not significantly contribute to the pre-edge. The 3$s$ empty states of non excited aluminium atoms are not localized in the bottom of the conduction band as is the case when a 1$s$ core-hole is present. In other words, the 1$s$ core-hole attracts the 3$s$ and 3$p$ states, leading to the pre-edge peak and the first main feature of XANES (the influence of the core-hole on all the XANES features, except pre-edge has notably been shown in Ref. [11]). Consequently, it seems that the pre-edge is a local effect tightly related to the presence of the 1$s$ core-hole.

As mentioned before, one can notice a weak overlap between the 3$s$ and 3$p$ DOS of the Al absorber, so explaining the weak $1s \rightarrow p$ pre-edge feature in the calculated XANES of diaspore. Since $1s \rightarrow 3s$ electric dipole and quadrupole transitions are strictly forbidden, the experimental pre-edge peak can be due to $1s \rightarrow p$ transitions where $p$ states are hybridized with Al 3$s$ states. This $p-s$ mixing is only possible if the absorbing atom site is not centrosymmetric, and that is the case in both corundum and diaspore crystallographic structures. The point symmetry of Al site is $C_3$ (one three-fold axis along the [111] of the trigonal cell) for corundum and $C_s$ (one mirror $\perp [001]$) for diaspore. Thus the symmetry order is greater in corundum than in diaspore. The distortion from a regular octahedron is equivalent in both structures: the quadratic elongation as defined in Ref. [34] is 1.02 for the two Al sites, and the angular variance slightly differs (66.6° and 64.0° for corundum and diaspore, respectively). Consequently the distortion of the octahedron is not a relevant parameter to explain the absence $p-s$ mixing in corundum DOS calculations and its presence in diaspore ones. But, above the octahedron, the corundum and diaspore
structures strongly differs. In diaspore, three of the six oxygen atoms are linked to hydrogen atoms, that are located in some kinds of channels extending along the [001] direction. The AlO$_6$ octahedra share edges to form some kinds of double strings (along [001]), and these double strings are connected to each other by sharing corner oxygens, so forming a three-dimensional network [24]. In corundum the oxygen positions approximate hexagonal close packing, with Al occupying two thirds of the octahedral interstices. The charge density anisotropy should be then more pronounced in diaspore than in corundum, and equally within the coordination sphere of Al (even if the Al site distortion is similar in both compounds). Consequently, these differences of charge density anisotropy between corundum and diaspore provide an explanation of the differences observed in the Al absorbing atom DOS calculations in both minerals (i.e. the $p$$-$s mixing in the pre-edge region and the broader Al 3p peak in diaspore than in corundum).

In Figure 1b (diaspore), the inset has shown that the calculated pre-edge only comes from the $\epsilon$ $\parallel$ [010] contribution. The [010] direction differs from the others in the sense that one of the six oxygen first neighbours of Al lies quite along the [010] axis (at 19.7°). Therefore, the
calculated pre-edge is mainly due to the mixing between $3p_y-3s$ of the absorber and the $p_y$ of the oxygen atom lying nearly in the [010] direction.

2.4. The effect of the displacement of the absorbing atom

We have shown that the experimental pre-edge indirectly comes from the $3s$ empty states of the absorbing atom. The $3s$ can be probed at the Al K edge if they overlap with the $p$ empty states of the absorbing atom. In diaspore the overlap is weak and the resulting pre-edge is not intense enough when compared with experiment. In corundum, there is no overlap. The atomic vibrations can therefore play a key role in the existence of an experimental pre-edge.

![Figure 3. Theoretical XANES polarized spectra of corundum for $\hat{e} \parallel C_3$ ($\sigma_\parallel$), calculated for three distinct positions of the absorbing atom, along the three-fold axis: $\Delta z = 0.0$ Bohr, the equilibrium position (black solid line) $\Delta z = 0.1$ Bohr (blue dashed line) and $\Delta z = 0.2$ Bohr (green dashed-dotted line).](image)

As a first approximation, XANES calculations have been performed with the absorbing atom displaced from its equilibrium position. Figure 3 shows calculated $\sigma_\parallel$ XANES spectra of corundum obtained with two values of displacement of the absorbing atom along the three-fold axis direction: $\Delta z = 0.1$ Bohr and $\Delta z = 0.2$ Bohr. The displacement of the absorbing atom has been operated in order to enhance the site distortion (i.e. increasing the longest Al-O distance and decreasing the shortest one). A pre-edge slightly appears for $\Delta z = 0.1$ Bohr and is clearly visible for $\Delta z = 0.2$ Bohr. One should notice that the 0.1 Bohr value is consistent with the experimental thermal parameter while 0.2 Bohr is quite large. Besides, when $\Delta z$ is increased, one notices a shift of the first main feature to lower energy. This will lead to a broadening of the first main peak when averaged with the $\sigma_\perp$ contribution, which is unchanged when Al is moved along the $C_3$ axis. Same kinds of calculations should also be performed for displacement of Al in a direction normal to the $C_3$ axis. The resulting isotropic spectrum will then be characterized by a rather weak pre-edge and by a broadened main peak. In other words, it is not possible to take vibrations into account by calculating an average of x-ray absorption spectra over an ensemble of nuclear positions.

In constrast we now show that, by using reasonable approximations, we can set up a theory of the influence of vibrations on XANES such that the pre-edge peak shows up without broadening the main absorption peak.
3. Including the atomic vibrations into the absorption cross section

3.1. Theory

To calculate the influence of atomic vibrations on the absorption cross section, we must a priori compute the effect of the core-hole. Mader and Baroni [35] showed that the core-hole can considerably modify lattice vibrations and gives rise to strong anharmonic effects. Taking these effects into account for complex materials would be beyond our present capabilities.

However, Thole and coll. showed that the influence of the core-hole can be removed by using sum rules [36]. A similar simplification is possible if the lattice vibration energies are small with respect to the energy resolution (due to core-hole lifetime and experimental resolution). This assumption is realistic at the K-edge of transition metals and, as we shall see, even at the K-edge of aluminium. However, the calculation remains rather demanding if no other approximation is made and we make the further hypothesis that the crude Born-Oppenheimer approximation is valid in the final state.

3.1.1. XANES formula within the Born-Oppenheimer framework

According to the Born-Oppenheimer approximation [37, 38], the wavefunction of a system of interacting electrons and nuclei can be written as the product \( \chi_n^f(\mathbf{R})\psi_n(\mathbf{r}; \mathbf{R}) \), where \( \mathbf{r} \) is the electronic position vector and \( \mathbf{R} = (\mathbf{R}_1, \ldots, \mathbf{R}_N) \) collectively denotes the position vectors of the \( N \) nuclei of the system. The electronic wavefunction \( \psi_n(\mathbf{r}; \mathbf{R}) \), with energy \( \epsilon_n(\mathbf{R}) \), describes a state of an electron in the potential where the nuclei are fixed at positions \( \mathbf{R} \). The ground state corresponds to \( n = 0 \). The origin of the nuclear variables is chosen so that \( \mathbf{R} = 0 \) is the equilibrium position, i.e. \( \epsilon_0(0) \) is the minimum of \( \epsilon_0(\mathbf{R}) \).

For each \( n \), the vibrational wavefunctions \( \chi_j^f(\mathbf{R}) \) are the orthonormal solutions of the Schrödinger equation \( (H_{\text{kin}} + \epsilon_n(\mathbf{R}))\chi_j^f(\mathbf{R}) = E_j^f\chi_j^f(\mathbf{R}) \), where \( E_j^f \) is the total energy of the system of electrons and nuclei and \( H_{\text{kin}} \) is the nuclear kinetic energy. Within the Born-Oppenheimer approximation, the x-ray absorption cross-section becomes

\[
\sigma(\omega) = 4\pi^2\alpha_0\hbar\omega \sum_{fj} \left| \int d\mathbf{R} d\mathbf{r} \chi_j^f(\mathbf{R})^* \psi_f(\mathbf{r}; \mathbf{R})^* \hat{\mathbf{e}} \cdot \mathbf{r} \chi_0^0(\mathbf{R}) \psi_0(\mathbf{r}; \mathbf{R}) \right|^2 \delta(E_j^f - E_0^0 - \hbar\omega),
\]

where the unit vector \( \hat{\mathbf{e}} \) describes the direction of the photon beam polarisation, and where the indexes \( f \) and \( 0 \) denote the final and initial states, respectively. To take the effect of temperature into account, \( \chi_0^0(\mathbf{R}) \) is replaced by a Boltzmann density matrix.

The core-hole lifetime and the experimental resolution can be represented by a convolution of the absorption cross-section with a Lorentzian function \( (\Gamma/\pi)/(\omega^2 + \Gamma^2) \). This gives us

\[
\sigma_\gamma(\omega) = 4\pi\alpha_0 \sum_{fj} \left| \int d\mathbf{R} d\mathbf{r} \chi_j^f(\mathbf{R})^* \psi_f(\mathbf{r}; \mathbf{R})^* \hat{\mathbf{e}} \cdot \mathbf{r} \chi_0^0(\mathbf{R}) \psi_0(\mathbf{r}; \mathbf{R}) \right|^2 \frac{(E_j^f - E_0^0)\gamma}{(E_0^0 + \hbar\omega - E_j^f)^2 + \gamma^2},
\]

where \( \gamma = \hbar\Gamma \).

The total energy is written \( E_j^f = \epsilon_f + E_{\text{vib}}^{fj} \), where \( \epsilon_f \) is the electronic energy at equilibrium position and \( E_{\text{vib}}^{fj} \) the vibrational energy. When \( \gamma \) is much larger than the vibrational energy we can neglect the contribution of \( E_{\text{vib}}^{fj} \) and carry out the sum over the vibrational index \( j \); the completeness relation \( \sum_j \chi_j^f(\mathbf{R})^* \chi_j^f(\mathbf{R}) = \delta(\mathbf{R} - \mathbf{R}') \) gives us

\[
\sigma_\gamma(\omega) = 4\pi\alpha_0 \int d\mathbf{R} \sum_j \left| \int d\mathbf{r} \psi_f(\mathbf{r}; \mathbf{R})^* \hat{\mathbf{e}} \cdot \mathbf{r} \chi_0^0(\mathbf{R}) \psi_0(\mathbf{r}; \mathbf{R}) \right|^2 \frac{(\epsilon_f - \epsilon_0)\gamma}{(\epsilon_0 + \hbar\omega - \epsilon_f)^2 + \gamma^2},
\]

where we also replaced \( E_0^0 \) by \( \epsilon_0 \). Note that we derived this result without making the harmonic approximation. Therefore, the strongly anharmonic behavior due to the core-hole [35] is taken
The integral over electronic variables depends only on the position $\mathbf{R}$, so that eq. (1) is not the average of standard XANES spectra over various nuclear positions $\mathbf{R}$. Note at last that the effect of vibrations is taken into account by using the distribution of positions $|\chi_0^0(\mathbf{R})|^2$ in the initial state.

3.1.2. The crude Born-Oppenheimer approximation The expression for $\sigma_L(\omega)$ is still fairly challenging because we must sum over the displacements of a large (in principle infinite for a crystal) number of atomic position vectors $\mathbf{R}$. We now make a further approximation where the initial and final states are treated differently.

For a $K$-edge, the 1s core level wavefunction is strongly localized around the nucleus and it weakly depends on the surrounding atoms. Therefore, we can approximate $\psi_0(\mathbf{r}; \mathbf{R})$ by $\phi_0(\mathbf{r} - \mathbf{R})$, where $\mathbf{R}$ is the position vector of the absorbing atom and where $\phi_0$ is the 1s wavefunction of the absorbing atom at equilibrium position. For the final states, we make the standard crude Born-Oppenheimer approximation [38], according to which the final state electronic wavefunctions do not significantly vary with $\mathbf{R}$ for the small vibrational motions of the system in the initial state. In other words, $\psi_f(\mathbf{r}; \mathbf{R}) \approx \phi_f(\mathbf{r})$, where $\phi_f(\mathbf{r}) = \psi_f(\mathbf{r}; 0)$.

This gives us

$$\sigma_L(\omega) = 4\pi\alpha_0 \int d\mathbf{R} |\chi_0^0(\mathbf{R})|^2 \sum_f |\int d\mathbf{r} \phi_f(\mathbf{r})^* \mathbf{r} \phi_0(\mathbf{r} - \mathbf{R})|^2 \frac{(\epsilon_f - \epsilon_0)\gamma}{(\epsilon_0 + \hbar\omega - \epsilon_f)^2 + \gamma^2}. $$

The integral over electronic variables depends only on the position $\mathbf{R}$ of the absorbing atom. Therefore, we can integrate over the other nuclear variables and the expression becomes

$$\sigma_L(\omega) = 4\pi\alpha_0 \int d\mathbf{R} \rho(\mathbf{R}) \sum_f |\int d\mathbf{r} \phi_f(\mathbf{r})^* \mathbf{r} \phi_0(\mathbf{r} - \mathbf{R})|^2 \frac{(\epsilon_f - \epsilon_0)\gamma}{(\epsilon_0 + \hbar\omega - \epsilon_f)^2 + \gamma^2}, $$

(2)

where $\rho(\mathbf{R})$ is obtained by integrating $|\chi_0^0(\mathbf{R})|^2$ over the displacement variables of the all the nuclei except those of the absorbing atom.

In the harmonic approximation, $\rho(\mathbf{R}) = \text{exp}(-\frac{1}{2} \mathbf{R} \cdot U^{-1} \cdot \mathbf{R})$, where $U$ is the thermal parameter matrix used in x-ray crystallography [39, 40].

3.1.3. Calculation of the matrix element The core-hole wavefunction $\phi_0(\mathbf{r})$ is first fitted with a linear combination of exponentials $e^{-a r}$. For a hydrogenoid atom, $a = Z/a_0$, where $Z$ is the atomic number and $a_0$ the Bohr radius. Each shifted exponential is described by the Barnett-Coulson expansion [41] 

$$e^{-a|\mathbf{r} - \mathbf{R}|} = \sum_{n=0}^{\infty} (2n + 1)P_n(\hat{\mathbf{r}} \cdot \hat{\mathbf{R}}) c_n(\mathbf{r}, \mathbf{R}), $$

(3)

where $P_n(\hat{\mathbf{r}} \cdot \hat{\mathbf{R}})$ are Legendre polynomials and with

$$c_n(\mathbf{r}, \mathbf{R}) = -\frac{1}{\sqrt{\mathbf{R}}} \left( r_< P_{n+\frac{1}{2}}(a r_<) K_{n+\frac{1}{2}}(a r_<) + r_> P_{n+\frac{1}{2}}(a r_<) K'_{n+\frac{1}{2}}(a r_<) \right), $$

where $r_< = \min(\mathbf{r}, \mathbf{R})$, $r_> = \max(\mathbf{r}, \mathbf{R})$, $I_{\nu}(z)$ and $K_{\nu}(z)$ are the modified Bessel functions and $I'_{\nu}(z)$ and $K'_{\nu}(z)$ their derivatives with respect to $z$. For notational convenience, we consider that the core wavefunction can be represented by a single exponential $\phi_0(\mathbf{r}) = Ce^{-a r}$.
To calculate the matrix element, we expand the final state wavefunction over spherical harmonics $\phi_f(r) = \sum_{\ell m} f_{\ell m}(r) Y_{\ell m}^m(\hat{r})$. The matrix element over the electronic variable is

$$\int \text{d}r \phi_f(r)^* \hat{\varepsilon} \cdot r \phi_0(r - \mathbf{R}) = \sum_{\ell m} X_{\ell m}^m(\mathbf{R}),$$

with

$$X_{\ell m}^m(\mathbf{R}) = C \sum_{n=0}^{\infty} \int \text{d}r f_{\ell m}^*(r) Y_{\ell m}^m(\hat{r})^* \cdot r (2n + 1) c_n(r, R) P_n(\hat{\varepsilon} \cdot \mathbf{R}).$$

Standard angular momentum recoupling techniques [42] lead to

$$\hat{\varepsilon} \cdot r P_n(\hat{\varepsilon} \cdot \mathbf{R}) = \frac{(4\pi)^2 r}{3(2n + 1)} \sum_{\lambda p} (-1)^{\lambda + p} Y_1^{\lambda - p}(\hat{\varepsilon}) Y_n^{\lambda - p}(\hat{\varepsilon}) \sum_\alpha C_{1\lambda n p}^{\alpha a} Y_1^\alpha(\hat{r}),$$

where $C_{1\lambda n p}^{\alpha a}$ are Gaunt coefficients and $\alpha$ takes the values $\{n - 1\}$ and $n + 1$. Thus,

$$X_{\ell m}^m(\mathbf{R}) = \frac{(4\pi)^2 C}{3} \sum_{n = \ell \pm 1} \int r^3 \text{d}r f_{\ell m}^*(r) c_n(r, R) \sum_\lambda (-1)^m Y_1^{\lambda - m}(\hat{\varepsilon}) Y_n^{\lambda - m}(\hat{\varepsilon}) C_{\ell m}^{\lambda n m - \lambda},$$

where only $n = 1$ is allowed if $\ell = 0$. Equation (4) shows that all values of the final state angular momentum $\ell$ are now allowed. According to the Barnett-Coulson expansion, the shifted core level function is a sum over all angular momenta. Thus, all final state angular momenta can be reached in spite of the fact that only electric dipole transitions are taken into account. In particular, vibrations allow for dipole transitions to the $s$ and $d$ final states at the $K$-edge.

3.2. Application to the case of corundum and diaspore

The X-ray absorption cross section within the crude Born-Oppenheimer approximation has been implemented in the XSpectra package. The integral over $\mathbf{R}$ of eq. 2 is achieved by a 361 point integration procedure derived from eq. (25.4.68) of [43]. The calculations have been performed from the self-consistent charge density obtained for the supercells with the atoms at the equilibrium positions. The method allows the calculation of electric dipole transitions that are not necessarily of type $1s \rightarrow p$ since the initial wave-function has lost its exclusive $1s$ character (see eq. 3). For each crystal, we have used two different sets of $U$ thermal parameter matrix elements, the first one corresponding to experimental values extracted from X-ray diffraction data refinement [44, 45], and the second one being hypothetical and corresponding to values smaller than the experimental ones. The broadening parameter as well as the number of $k$-points for the Brillouin zone integration are identical to that used in the previous section.

The results are shown in figures 4a and 4b for corundum and diaspore, respectively. For comparison, the experimental spectra and the calculated ones of figures 1a and 1b are also displayed. When vibrations are taken into account, a pre-edge peak appears in the case of corundum and is more pronounced in the case of diaspore. Since these peaks are at the position of the $3s$ states, they are reachable by electric dipole transitions because the displaced core level gets a small $p$ component. It could be also noticed that only the pre-edge region is affected by the atomic vibrations. The main peak is not broadened as in the calculation carried out with the absorber displaced from its equilibrium position (see Fig. 3). This is due to the fact that in eq.1, the $\epsilon_f$ and $\epsilon_0$ energies are obtained with a calculation performed at the equilibrium atomic positions. This result is corroborated by temperature experimental XANES measurements of corundum (298 K) and alumina in the supercooled (2278 K) and liquid (2362 K) phases [32].
Figure 4. Experimental and calculated Al K-edge isotropic XANES spectra in corundum (a) and in diaspore (b). For each compound, three calculated spectra are displayed: one obtained with the equilibrium atomic positions (black solid line) which is identical to that of Figure 1, and two others using the theory described in 3.1 (thin blue and thick green solid lines). These latter have been obtained with two different sets of values for the thermal parameter matrix elements of Al. In the first set (labeled U exp.), the \( U \) matrix elements are \( U_{11} = U_{22} = 0.00229 \, \text{Å}^2 \) and \( U_{33} = 0.00242 \, \text{Å}^2 \) for corundum [44], and are \( U_{11} = 0.00395 \, \text{Å}^2, \) \( U_{22} = 0.00267 \, \text{Å}^2, \) \( U_{33} = 0.00261 \, \text{Å}^2 \) and \( U_{12} = 0.00006 \, \text{Å}^2 \) for diaspore [45]. In the second set, the \( U \) diagonal matrix elements equal to 0.001 Å\(^2\), the off-diagonal ones being set to zero.

The intensity of the pre-edge increases with the temperature while the positions of the first two main peaks remain unchanged.

The pre-edge calculated with the \( U \) matrix elements as determined by x-ray diffraction data refinements (blue thin lines) is too intense. As shown in Figure 4, this drawback can be circumvented by using smaller values of \( U \) matrix elements. Indeed, with 0.001 Å\(^2\) (thick green lines), the agreement with the experimental pre-edge becomes satisfactory. This reduction is familiar in x-ray absorption spectroscopy. It is well known that the Debye-Waller factor of x-ray diffraction and EXAFS are different because the former measures the distribution of displacements with respect to the equilibrium position whereas the latter describes the distribution of relative distances between the absorbing atom and the neighbours [46]. The same is true for XANES spectra. The vibration effect is mainly due to the relative displacement of the absorbing atom with respect to its first neighbours. In other words, the vibration modes that correspond to a global motion of the AlO\(_6\) “molecule” do not contribute to the XANES spectra. This explains the reduced value of the displacement parameter.

For diaspore, the equilibrium calculations have shown a particular anisotropy of the pre-edge (present only in the \( \vec{e} \parallel [010] \) contribution). This is invalidated by the inclusion of atomic vibrations within the cross section. Each polarized contribution to the isotropic spectrum does present a pre-edge feature.

To our knowledge, there is no experimental evidence of the role of atomic vibrations on the pre-edge at the Al K-edge. Only two papers have reported temperature dependent XANES spectra at the Al K-edge (in oxides). The first one is concerned with the influence of temperature (from 293 K to 673 K) on the Al coordination number in USY zeolite and in amorphous silica-alumina [31]. Unfortunately the resolution of the XANES spectra does not allow to reasonably distinguish the presence of a pre-edge. The second one has been mentioned before. It compares the XANES spectrum of corundum with the ones of supercooled and liquid alumina [32].
pre-edge is about twice more intense in the liquid phase than in corundum, the pre-edge intensity in the supercooled phase being intermediate. But in the supercooled and the liquid phases, the Al site is probably distributed and more distorted than in corundum. This can give, at least to a certain extent, an explanation for the augmentation of pre-edge intensity, and the influence of the atomic vibrations on the variations of the pre-edge intensity cannot be clearly established.

4. Conclusion

In this study, we have determined the origin of the pre-edge feature present in the Al K-edge XANES spectra of corundum and diaspore. To do so, we have performed calculations by using a pseudopotential plane-wave DFT framework.

First we have calculated XANES spectra and local and partial empty DOS for the equilibrium atomic positions. In the case of corundum, the theoretical XANES spectrum does not exhibit any pre-edge. In the case of diaspore, the calculated pre-edge peak is too weak. The DOS calculations have revealed the crucial role played by the 3s empty states of the Al absorbing atom in the origin of the pre-edge. This provides a justification for the assignation of the pre-edge peak to a 1s → 3s like transition as assumed by Dien Li et al. [6]. The local DOS have also shown that the pre-edge results from a local effect (within the coordination sphere) which strongly depends on the presence of 1s core-hole. The 3s states of Al can be probed at the Al K-edge only if the absorbing atom does not occupy an inversion center. That is the case in both minerals under study. The anisotropy of the charge density around the absorbing Al is more pronounced in the diaspore structure than in the corundum one, so explaining the weak calculated pre-edge in diaspore.

Then we have taken into account the atomic vibrations, since they can increase the deviation from centrosymmetry and so enhance the p-s mixing. As a first approximation, we have carried out calculations by displacing the absorbing atom from its equilibrium position. It was shown that this approach is not appropriate since it also leads to a substantial broadening of the first main XANES peak. Hence we have developed and implemented a method for including the atomic vibrations in the absorption cross section. By using reasonable approximations, we showed that only the vibrations of the initial state are relevant for the calculation, and that the transition energies are those of the crystal in its equilibrium position. The displacement parameters used in our calculations are different from the x-ray diffraction thermal parameters, they mainly consider the local distortion of the AlO$_6$ octahedron. For that reason, they could be relevant to study the effect of vibrations on the optical spectra of 3d transition metal impurities. The application of the method to corundum and diaspore provides satisfactory results, giving a theoretical evidence of the role of the atomic vibrations in the origin of the pre-edge. Note that Tinte and Shirley [47] recently investigated the influence of Jahn-Teller distortion on the Ti K-edge spectrum in SrTiO$_3$. This is different from the effect studied in the present paper.

For Mg or Si K-edge, the 3s empty states are probably involved in the pre-edge as well. For all the compounds listed in the introduction, it would be interesting to carry out a detailed analysis in order to distinguish the part due to the site distortion from the contribution of atomic vibrations. Experimental investigation of the temperature dependence of the pre-edges of these crystals would be quite useful to further test our theory.

Acknowledgments

We acknowledge A. Seitsonen, M. Calandra and Ch. Gougoussis for their assistance in the use of the XSpectra package. This work was performed using HPC resources from GENCI-[CCRT/CINES/IDRIS] (Grant 2009-[2015 and 1202]).

References

[1] Cabaret D, Sainctavit P, Ildefonse P and Flank A M 1998 Amer. Mineral. 83 300–304
