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First-principles study of phonon effects in x-ray absorption near-edge structure spectroscopy

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Abstract. Usually first-principles x-ray absorption near-edge structure (XANES) calculations are performed in the Born-Oppenheimer approximation assuming a static lattice, whereas the nuclear motion undoubtedly impacts XANES spectra notably at the K pre-edge of light elements in oxides. Here, an efficient method based on density-functional theory to account for quantum thermal fluctuations of nuclei is developed and is successfully applied to the K edge of corundum for temperatures up to 930 K. The zero-point motion influence is estimated. Comparison is made with previous theoretical approaches also developed to account for vibrations in XANES.

1. Introduction
Standard x-ray absorption near-edge structure (XANES) calculations rest upon the Born-Oppenheimer (BO) approximation, considering nuclei fixed at their equilibrium positions defined by the set of nuclear coordinates $\overline{\mathbf{R}}_{\mathrm{eq}}$. Yet, significant temperature-induced effects are noticed, particularly at the Al K-edge of corundum (α-Al$_2$O$_3$): the pre-edge peak can only be explained by $1s \rightarrow 3s$ forbidden transitions induced by lattice vibrations [1, 2, 3]. In this paper, the influence of quantum thermal fluctuations of nuclei on XANES is modeled within the BO approximation and quasiharmonic approximation (QHA) using a density-functional theory (DFT) framework. The dynamical matrix is determined to generate temperature-dependent sets of nonequilibrium nuclear configurations $\overline{\mathbf{R}}$ for which individual XANES spectra are calculated. Their average at a given temperature may be compared to the corresponding experimental spectrum. The method is applied at the Al K edge in corundum, which has been measured for temperatures up to 930 K [2]. The calculated spectra are compared with two previous theoretical approaches developed to account for thermal motion, either by small absorbing-atom displacements (AAD) [2] or by moving the $1s$ initial wave function in the crude Born-Oppenheimer (CBO) approximation [3].

2. Method
In the single-electron and electric-dipole approximations, the K-edge XANES cross section with x-rays of energy $\hbar\omega$, polarized along the $\hat{\mathbf{e}}$ vector is given by [4]

$$\sigma(\hbar\omega) = 4\pi^2\alpha\hbar\omega \sum_n |\langle \psi_n| \, \hat{\mathbf{e}} \cdot \mathbf{r} \, |\psi_{1s}\rangle|^2 \, \delta(\varepsilon_n - \varepsilon_{1s} - \hbar\omega), \qquad (1)$$

where α is the fine structure constant, and $|\psi_n\rangle$ and $|\psi_{1s}\rangle$ the final and initial monoelectronic states of energy ε_n and ε_{1s}, respectively. In Eq. (1) the nuclei are fixed in a given configuration, $\overline{\mathbf{R}}$, which is a parameter of the calculation: $\sigma(\hbar\omega) = \sigma(\hbar\omega; \overline{\mathbf{R}})$.

An expression accounting for the total system of nuclei and electrons is

$$\sigma_{\text{tot}}(\hbar\omega) = 4\pi^2 \alpha \hbar\omega \sum_{n,j} \left| \langle \Psi_n^j | \hat{\mathbf{e}} \cdot \mathbf{r} | \Psi_{1s}^0 \rangle \right|^2 \delta(E_n^j - E_{1s}^0 - \hbar\omega), \tag{2}$$

where the total Ψ_{1s}^0 initial and Ψ_n^j final states have energies E_{1s}^0 and E_n^j, respectively. Using the BO approximation and the first-order expansion of the Green's function of the total system as derived in Ref. [5], σ_{tot} can be written as

$$\sigma_{\text{tot}}(\hbar\omega) = \int d\overline{\mathbf{R}} \; \rho(\overline{\mathbf{R}}) \; \sigma(\hbar\omega; \overline{\mathbf{R}}), \tag{3}$$

with $\rho(\overline{\mathbf{R}})$ the QHA weighting displacement distribution. In Eq. (3), σ_{tot} is the average of individual configuration cross sections $\sigma(\hbar\omega; \overline{\mathbf{R}})$ using a probability distribution that takes into account temperature and quantum nuclear motion (see Ref. [5] for details).

In this paper, temperature-dependent XANES cross sections [Eq.(3)] are calculated within DFT in the PBE approximation [6] using the QUANTUM ESPRESSO suite of codes [7]. The calculations are performed using ultrasoft pseudopotentials, with plane-wave energy cutoff of 60 Ry and 720 Ry for the wave-functions and charge density, respectively. Two Al pseudopotentials (one for the absorbing atom and one for the others) are constructed starting from a $3s3p3d$ valence configuration with a maximum cutoff radius of 2.10 Bohr. The O pseudopotential is the one of Ref. [5]. The experimental lattice parameters of corundum at 300, 650 and 930 K are used, while the 0 K calculation is carried out using the 100 K experimental parameters [8]. The dynamical matrices are obtained on a $3 \times 3 \times 3$ **k**-point grid. Fifty $2 \times 2 \times 2$ trigonal-supercell configurations of 80 atoms including one $1s$ core-hole are generated, upon which self-consistent charge densities are calculated at the Γ point, and XANES calculations are performed using the XSPECTRA package [9, 10] on a $4 \times 4 \times 4$ **k**-point grid with a broadening parameter of 0.4 eV. The 50 calculated XANES spectra are averaged by taking into account the core-level shift and the averaged spectra are shifted by 1565 eV so that the experimental and calculated main-edge peak energies match at 300 K.

3. Results and discussion

3.1. Comparison with experiments

The experimental and calculated temperature-dependent Al K-edge XANES spectra of corundum are presented in Fig. 1(a). As the temperature increases, the P pre-edge emerges and the A peak decreases, both peaks move down to lower energy. The B_1 and B_2 features are smoothed by temperature. The QHA calculation reproduces the experimental trends, as highlighted by the similarity of the difference of each spectrum with the room-temperature one shown in Fig. 1(b). From 300 to 930 K, the experimental and calculated A peak intensities decrease by 20 and 31%, respectively and the energy shift agreement between experiment and calculation is satisfactory. However, in the calculations, the P peak is less resolved and slightly underestimated. This discrepancy is expected to come from the fact that only the first order of the Green's function is considered in the calculation. An equivalent experiment-calculation matching is observed at the Mg K-edge in MgO [5].

It has been demonstrated that the P pre-edge emerges from forbidden $1s \rightarrow 3s$ electronic transitions induced by vibrations [1, 2]. The observation of the pre-edge in the 0 K calculation, where only residual zero-point motion subsists, emphasizes the importance of accounting for quantum vibrations in theoretical XANES.
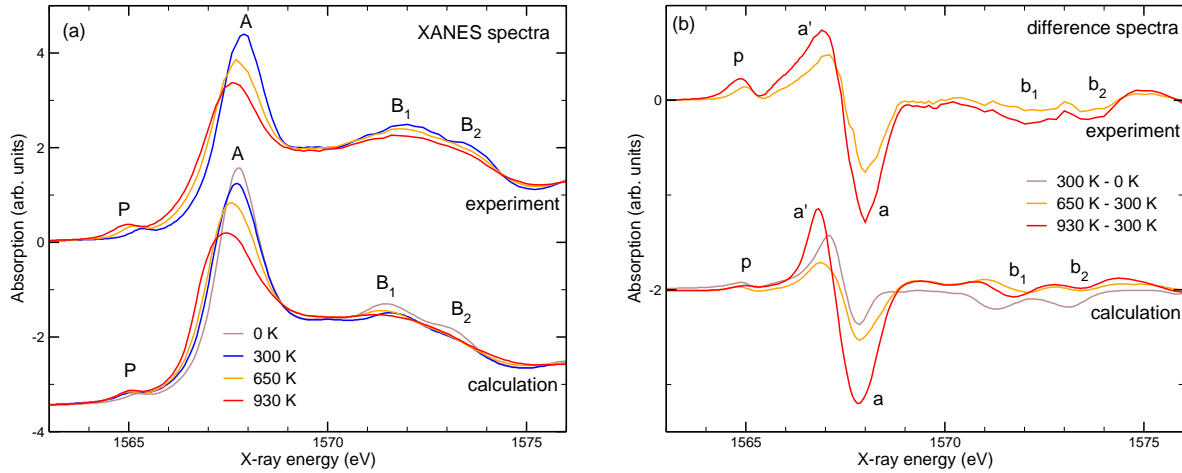
Figure 1. (a) Temperature-dependent experimental [2] and calculated Al K-edge XANES spectra of corundum. (b) Experimental and calculated difference spectra with the 300 K ones.

3.2. Comparison with previous theoretical approaches

Figure 2 compares the 300 K experimental XANES spectrum and four theoretical spectra, which are obtained using the $\overline{\mathbf{R}}_{\text{eq}}$ equilibrium configuration, the QHA method (Sec. 2) and two previous theoretical works, here called absorbing-atom displacement (AAD) [2] and crude Born-Oppenheimer (CBO) [3]. The calculated spectra are here all performed with the norm-conserving Troullier-Martins pseudopotentials used in Ref. [2]. The AAD method only considers the absorbing-atom displacement in the equilibrium configuration. In this approximation, the XANES spectra calculated for each off-center absorbing-atom displacement $\mathbf{R}_a$ are averaged with a weighting core harmonic displacement distribution function $\varrho(\mathbf{R}_a)$ (see Ref. [2] for details). In the CBO approximation, the electronic wave function of the final state is supposed to not significantly vary for small atomic motions. Therefore, the final states are calculated for the $\overline{\mathbf{R}}_{\text{eq}}$ configuration, and only the initial state is displaced. Then, with γ including both the core-hole lifetime and instrumental resolution, the CBO XANES cross section is expressed as [3]

$$\sigma_{\text{CBO}}(\hbar\omega) = 4\pi\alpha \int d\mathbf{R}_a \; \varrho(\mathbf{R}_a) \sum_n \left| \int d\mathbf{r} \; \psi_n^*(\mathbf{r}) \; \hat{\mathbf{e}} \cdot \mathbf{r} \; \psi_{1s}(\mathbf{r} - \mathbf{R}_a) \right|^2 \frac{(\varepsilon_n - \varepsilon_{1s})}{(\varepsilon_n - \varepsilon_{1s} - \hbar\omega)^2 + \gamma^2}. \quad (4)$$

All methods produce spectra in better agreement with the experiments than the equilibrium spectrum. Unlike the equilibrium calculation, each method induces a P pre-edge. The QHA and AAD spectra show a similar weak P peak. The displacement of either the absorbing atom or the whole nuclei configuration creates hybridizations between the Al s and p empty states, allowing to probe the absorbing Al $3s$ empty states through the electric-dipole approximation. The CBO approximation produces a strong P peak due to electric-dipole transitions towards absorbing Al s states from the $\psi_{1s}(\mathbf{r} - \mathbf{R}_a)$ displaced $1s$ initial state, which includes $\ell = 1$ components [3]. As observed at the Ti K-edge in rutile (TiO_2) [3], the CBO method significantly overestimates the pre-edge intensity.

Peak A varies according to the method used. Since the CBO method calculates the final states at $\overline{\mathbf{R}}_{\text{eq}}$, peak A almost matches the equilibrium one. Using AAD, peak A is slightly shifted to lower energy and this shift is even more pronounced using QHA. Such an energy shift results from the influence of the collective quantum dynamics on the band gap [5, 11].
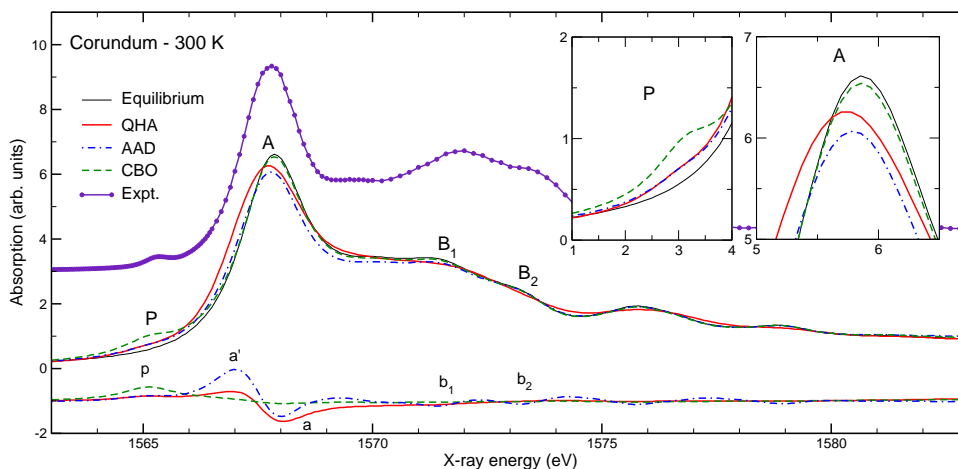
Figure 2. Calculated Al K-edge XANES spectra of corundum, at the 300 K volume, in the equilibrium case, using QHA method and previous approaches [2, 3]. The differences of theoretical spectra with respect to the equilibrium one are also displayed, as the well as the experimental 300 K XANES spectrum. The insets focus on the pre-edge and main peaks.

4. Conclusion

An efficient framework to account for temperature in XANES spectra is proposed. The good agreement between calculated and measured XANES spectra demonstrates that this approach successfully explains the temperature effects experimentally observed in XANES. Unlike standard equilibrium calculations, temperature-dependent theoretical spectra show the emergence of an additional P pre-edge peak, in good agreement with experiments. Our approach also reproduces other experimental trends, which are observed with increasing the temperature, such as the growth of the pre-edge peak, the intensity decrease of the main-edge peak and the shift towards lower energy of both peaks. The comparative analysis with former studies highlights the importance of accounting for the whole nuclear dynamics using a quantum treatment.

Acknowledgments

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