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Temperature dependence of the pre-edge structure in the Ti K-edge x-ray absorption spectrum of rutile

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Abstract. The temperature dependence of the pre-edge features in x-ray absorption spectroscopy is reviewed. Then, the temperature dependence of the pre-edge structure at the K-edge of titanium in rutile TiO_2 is measured at low and room temperature. The first two peaks grow with temperature. The fact that these two peaks also correspond to electric quadrupole transitions is explained by a recently proposed theory.

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1. Introduction

Pre-edge peaks often arise at the K-edge of transition metal elements. This pre-edge structure is sensitive to the metal valence, to the symmetry of its surroundings and to the atomic species of the neighbours (see [1] for a recent review). As a consequence, the measurement and analysis of the pre-edge peaks are widely used in earth sciences [2], biology [3], chemistry [4] and physics [5, 6].

Because of their practical importance, pre-edge features have to be well understood and they were the object of detailed theoretical works using various approaches: multiplets [7, 8], Bethe-Salpeter equation [9], multiple-scattering [10], pseudopotential theory [5, 11]. Vedrinskii and his group were particularly active to extract information from the pre-edge structure [12, 13, 14].

In section 2, we make a short review of the literature to show that the temperature dependence of pre-edge peaks is not a rare property of x-ray absorption spectra. However, this dependence is usually attributed to static off-center displacements or to phase transitions. Therefore, our preliminary investigation [15] showing a temperature dependence of the pre-edge peaks at the titanium K-edge in TiO_2 (rutile) came out as a surprise because the pre-edge variation was observed in a temperature range where no phase transition occurs and where many high-precision structural studies [16, 17, 18, 19, 20] indicate that no off-center atomic displacement takes place. Soft modes have indeed been reported [21] but the calculated phonon spectrum shows excellent agreement with experiment and no imaginary mode is present [22, 23, 24, 25] when the proper functionals are used [26].

Thus, we carried out detailed experiments to confirm and analyze this temperature dependence. The results of these experiments are presented in section 3. Section 4 describes why such a temperature dependence is a priori surprising and sketches a theoretical interpretation that enables us to understand why the temperature dependence is restricted to the first two peaks and why no energy shift is observed. A conclusion summarizes our results and provides possible extensions of this work.

2. A short review

In this section, we present a short and non-exhaustive review of the temperature dependence of pre-edge peaks.

As far as we know, such a temperature dependence was first observed by Durmeyer and coll. [15] at the K-edge of titanium in TiO_2 (rutile), $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ and LiTi_2O_4 . It was subsequently measured at the titanium K-edge of a several perovskite crystals: PbTiO_3 [27, 28, 12, 29, 30], SrTiO_3 [31, 30], BaTiO_3 [30], CaTiO_3 [30].

A similar temperature dependence was observed at other edges in perovskite crystals: at the niobium K-edge of KNbO_3 [32, 33], NaNbO_3 [34], $\text{PbIn}_{1/2}\text{Nb}_{1/2}\text{O}_3$ [35], at the zirconium K-edge of PbZrO_3 [14], $\text{PbZr}_{0.515}\text{Ti}_{0.485}\text{O}_3$ [14], BaZrO_3 [14], at the K-edge of Mn in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ [36, 37] and at the K-edge of Fe in $\text{La}_{0.8}\text{Sr}_{0.2}\text{FeO}_3$

and $\text{La}_{0.7}\text{Sr}_{0.2}\text{FeO}_3$ [38]. In most cases, the temperature effect was interpreted in terms of a phase transition or of a static off-center atomic displacement due to the presence of very soft modes in the crystal.

However, the effect is not restricted to the perovskite structure. Apart from the results of Durmeyer and coll. [15], it was observed at the K-edge of titanium in TiO_2 and Mg_2TiO_4 [30], at the L-edges of La in Sr-doped La_2CuO_4 [39] and at the K-edge of V in VO_2 [40]. A temperature dependence of XANES spectra was also observed at the K-edge of oxygen in water [41] and in doped LaMnO_3 [42, 43]. Finally, the Mahan-Nozières-Dominicis singularity can also give rise to a temperature dependence of the x-ray absorption spectra of metals (see Ref. [44] for a review).

We come now to our experimental temperature dependence at the K-edge of titanium in rutile.

3. Experiment

The x-ray absorption experiments were performed at the D11 (energy dispersive) and at the EXAFSII stations of the DCI storage ring of the Laboratoire pour l'Utilisation du Rayonnement Synchrotron in Orsay (France).

A rutile single-crystal plate (9 mm x 4 mm x 50 μm) was measured at the D11 station in the transmission mode. The crystal plate was placed inside a liquid-helium cryostat operating between 4.2 K and 300 K. Measurements were carried out for two orientations, with the (110) face of the crystal perpendicular to the x-ray beam and the c -axis either parallel or perpendicular to the linear polarization vector of the beam. The polychromator consisted in a curved Si(111) crystal focusing the X-ray beam at the center of the cryostat sample holder. Higher harmonics were rejected by a SiO_2 plane mirror. The x-ray intensity was measured by a photodiode array detector. Each spectrum was obtained as a result of four measurements: I_0 (without sample and with the beam), I_{black} (without sample and without beam), I (with sample and with the beam), I_{black} (with sample and without beam). The absorption spectrum was then obtained from the formula $\sigma = \log(I_0 - I_{\text{black}}) - \log(I - I_{\text{black}})$. The x-ray energy corresponding to each detector pixel was determined by comparing the spectra with a spectrum measured on a two-crystal monochromator beamline. The energy resolution was typically 0.8 eV.

Our preliminary study [15] showed us that the pre-edge structure could exhibit a low signal to noise (S/N) ratio when the crystal thickness was optimized for the edge-jump. Therefore, we optimized the crystal thickness for the pre-edge structure and cut an approximately 50 μm thick crystal plate. As a consequence, we obtained excellent spectra in the pre-edge region but the XANES spectra after the edge had a rather low S/N ratio and, for each polarization direction, we normalized the spectrum at the inflection point of the absorption edge instead of at the edge jump.

To check the validity of this procedure, we carried out additional experiments at the EXAFSII station. The experimental equipment consisted of a two-crystal

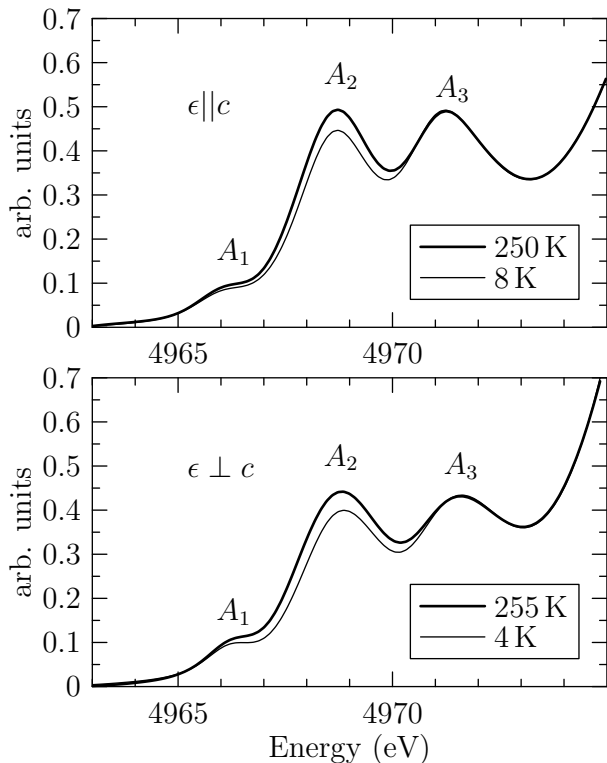


Figure 1. Temperature variation of the pre-edge peaks at the K-edge of titanium in rutile, with the x-ray polarization vector parallel and perpendicular to the c -axis of the crystal.

Si(311) monochromator, an ionisation chamber to measure the incident beam and an electron-yield detector. We measured a bulk rutile single crystal with the (110) face perpendicular to the x-ray beam and with the c -axis of the crystal either parallel or perpendicular to the x-ray polarization vector. The S/N ratio of the pre-edge region was comparable to that of the Ti K-edge spectra of rutile measured on the same beamline in similar conditions [45, 46]. The experimental spectra were normalized by the standard procedure and, as in our previous work [15], the temperature dependence was found to be negligible except in the pre-edge region. Moreover, the observed spectra and temperature dependence agreed well with the transmission experiments of the D11 station. In the present paper we show only the results of the transmission experiments because of their better S/N ratio.

4. Experimental results

Figure 1 shows the pre-edge features of rutile recorded at different temperatures with the polarization vector perpendicular and parallel to the crystal c -axis. A decrease of the first two peaks A_1 and A_2 is observed at low temperature, whereas the third peak A_3 does not show any significant variation. It is important to notice that temperature induces a change in the intensity but not in the energy position of the peaks.

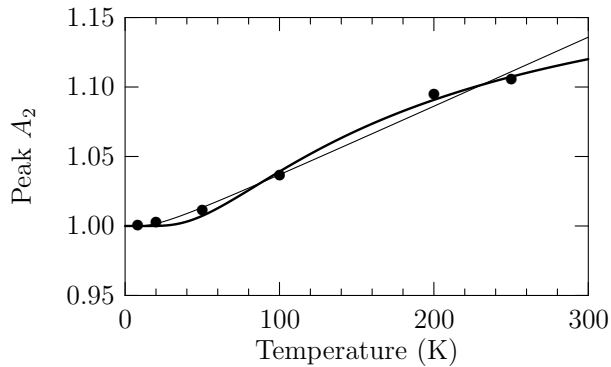


Figure 2. Relative intensity of peak A_2 as a function of temperature for $\epsilon||c$, normalized to 1 at 8K. Dots: experimental results; thick solid line: fit to the function $a(1 + e^{-\theta/T}) + (1 - a)$; thin solid line: fit to the function $a \cosh(\theta/2T) + (1 - a)$.

The physical origin of the pre-edge peaks of titanium in rutile is well known [47]. Peaks A_1 and A_2 correspond to electric quadrupole transitions towards $3d$ states of titanium with t_{2g} and e_g symmetry, respectively. Therefore, the peaks that vary with temperature are also the peaks corresponding to quadrupole transitions.

In the optical range, the effect of temperature is usually described by a simple model developed by Holmes and McClure [48, 49, 50], in which the intensity of the vibronic peak varies as $1 + e^{-\theta/T}$, where θ is the energy of the first vibrational level. Figure 2 shows the variation of the A_2 peak with temperature, fitted to the function $a(1 + e^{-\theta/T}) + (1 - a)$, where $a(1 + e^{-\theta/T})$ represents the fraction of the A_2 peak that is purely vibrational and $1 - a$ the fraction that is due to electric quadrupole transitions (and to the possible tail of the electric dipole peak A_3).

The result of the fit is $a = 0.21$ and $\theta = 168 \text{ K} \pm 10 \text{ K}$. Note that the value of θ compares favorably to the energy of the first odd vibrational level at the Γ point obtained by *ab initio* calculations (168 K [51], 150 K [26], 169 K [25] or 181 K [23]) or by neutron scattering 163 K [52]. However, the simplicity of the Holmes and McClure model implies that the quality of this agreement is probably fortuitous. Indeed, an alternative single-mode model is sometimes used [53, 54, 55, 56], for which the temperature dependence is $\coth \theta/2T$. For this second model the fit gives $\theta = 58 \text{ K} \pm 5 \text{ K}$ and $a = 0.014$.

5. Interpretation

It remains to understand why only the first two peaks vary with temperature while the rest of the XANES spectrum remains constant. We first describe the arguments that are usually given to explain the *absence* of temperature dependence of XANES spectra. Then, we show why, in some circumstances, this independence can be broken.

5.1. The temperature independence of XANES spectra

There are many reasons to believe that the pre-edge features of x-ray absorption spectra do *not* depend on temperature in the absence of structural transition. The first reason comes from the temperature dependence of the EXAFS part of x-ray absorption spectra, which is represented by a Debye-Waller factor $e^{-2k^2\sigma}$ in the EXAFS formula. The Debye-Waller factor accurately describes the temperature dependence of XAS in crystals, although it has to be supplemented with higher order cumulants in disordered materials. Moreover, it is well understood because it can be calculated *ab initio* with a good agreement with experiment [57, 58, 59, 60, 61]. If we use this factor to describes the temperature dependence near the edge, we must take an energy very close to the Fermi energy, so that k is very small and the factor is close to unity.

Of course, near the edge, the effect of temperature is not supposed to be described by a Debye-Waller factor and we must use a more sophisticated approach. Natoli's rule [62] gives good results near the edge. However, it describes an energy shift through the equation $kR = \text{Constant}$, and we do not observe any energy shift. More elaborate theoretical analyses were carried out. Brouder and Goulon [63, 64] used Lie group theory to describe the influence of a displacement on the multiple-scattering operator. However, the temperature evolution is expected to be small near the edge, essentially because of Natoli's rule. Poiarkova and Rehr [57] extended the Debye-Waller factor to multiple-scattering paths. Their formalism is not really valid in the pre-edge region, but if we try to extend it we find a very small temperature dependence because of the presence of the k^2 factor in the exponent. Fujikawa [65, 66] used Schwinger's technique to calculate the effect of the Franck-Condon factors on XAFS. He concluded that this effect was not important. In a later work [67], he investigated the effect of temperature through the Keldysh approach to nonequilibrium systems. He found that thermal vibrations could be represented by a convolution with the phonon spectral function. His result is valid in the pre-edge region but leads to a small temperature effect. Moreover, the convolution should give rise to a broadening of the pre-edge peaks with temperature. Again, this is not compatible with our experimental results. A further elaboration of his approach [68] lead to similar results.

We can try to take vibrations into account by coming back to the Born-Oppenheimer approximation and writing the initial and final wavefunctions as a product of a vibrational and an electronic function. However, this approach looks like a dead end if we consider the work by Mäder and Baroni [69] who showed that, at the K-edge of carbon, the vibrations in the final state are strongly anharmonic and are deeply affected by the presence of the core-hole. Therefore, we are not allowed to consider the vibrations as similar in the initial and final states and we cannot use the harmonic approximation.

Ankudinov and Rehr [70] brought some hope by showing that the S K-edge spectrum of SF₆ is closer to experiment when the atomic positions are slightly shifted with respect to the equilibrium position. But, as can be seen in their figure, atomic displacements shift the position of the main lines and this shift is not experimentally

observed.

5.2. The temperature dependence of XANES spectra

We recently proposed a model that enables us to understand the observed temperature dependence [71]. Although a detailed account of this model would be beyond the scope of the present paper, we can give a physical description of the underlying physics.

We start from the Born-Oppenheimer approximation where the wavefunctions of the electron+nuclei system is the product of a vibrational function by a solution of the Schrödinger equation for clamped nuclei. The energy of these wavefunctions do not depend on the position of the nuclei (as the eigenvalues of the Schrödinger equation for an electron in a potential do not depend on position). The transitions are made between these wavefunctions. If we assume that the vibrational energies are small with respect to experimental resolution, we can sum over the final state vibrational functions and we obtain an average over the vibrational function of the initial state of transitions for which the transition energy do not depend on the atomic positions. This explains why the peak positions do not move while they move if we calculate the spectrum of a distorted structure.

The second step of the model consists in making a different approximation for the initial and the final states. The initial state is taken to be the core state centered at the position specified by the vibrational wave function. For the final state, we make the *crude* Born-Oppenheimer approximation, where the electronic wavefunction is assumed independent of the position of the absorbing atom. Then, the cross-section boils down to an average of the x-ray absorption spectra for a shifted core wavefunction (with fixed energies). What happens next can be sketched by an oversimplified model of the shifted core wavefunction. We assume that the displacement \mathbf{R} is small compared to the electronic variable r and we obtain, to first order in \mathbf{R} and for a spherical core state $\phi_0(r)$, the shifted function

$$\phi_0(|\mathbf{r} - \mathbf{R}|) \simeq \phi_0(r) - \frac{\mathbf{r} \cdot \mathbf{R}}{r} \phi_0'(r). \quad (1)$$

When multiplied by $\epsilon \cdot \mathbf{r}$, the additional term gives us a factor $\epsilon \cdot \mathbf{r} \mathbf{R} \cdot \mathbf{r}$ that can be transformed into the sum of a monopole term proportional to $(\epsilon \cdot \mathbf{R})r^2$ and a quadrupole term. The monopole term gives rise to transitions towards s states, the quadrupole term to transition towards d states. The transition towards s states are observed at the aluminium or silicon K-edge [71], the transitions towards d states are observed at the K-edge of transition metals because of the presence of a strong density of d states. This explains why the temperature variation occurs at the position of the quadrupole peaks. Finally, the fact the temperature-dependent pre-edge peaks grow with temperature is due to the corresponding increase in thermal vibration amplitudes.

Of course, eq. (1) is not sufficient because the integration over \mathbf{r} includes also a region where $r < R$. The full theory [71] is more complex but the physical idea is the same.

6. Conclusion

In this paper, we have presented the temperature-dependence of pre-edge features at the K-edge of titanium in rutile. This temperature dependence is not due to a phase transition or to a static distortion of the titanium site.

The temperature dependence changes only the intensities of the peaks and not their positions. Moreover, the peaks that vary with temperature are the electric quadrupole peaks of the spectrum. An explanation of this behavior was given in terms of the dynamic displacement of the absorbing atom.

Two conditions turn out to be crucial to observe temperature-dependent pre-edge peaks at the K-edge : (i) a large density of d states below the p states, so that the transitions to final d states are significant and visible; (ii) the existence of low-energy vibrational modes, so that the temperature effect can be observed at reasonable temperatures. Both of these conditions are satisfied in rutile and in perovskites containing transition metals. In that case, the temperature dependence provides information on the local vibrations around the absorbing atom. This can be particularly useful to investigate the vibrations of transition metal impurities.

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