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

O Durmeyer¹, E Beaurepaire¹, J-P Kappler¹, Ch Brouder² and F Baudelet³

¹ IPCMS, UMR 7504 CNRS-ULP, 23 rue de Loess, BP 43, F-67034 Strasbourg Cedex 2, France
² Institut de Minéralogie et de Physique des Milieux Condensés, CNRS UMR 7590, Universités Paris 6 et 7, IPGP, 140 rue de Lourmel, F-75015 Paris, France
³ Synchrotron SOLEIL, L’Orme des Merisiers, Saint-Aubin-BP 48, F-91192 Gif-sur-Yvette Cedex, France

E-mail: christian.brouder@impmc.jussieu.fr

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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 TiO₂ 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.

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 neighbors (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 work using various approaches: multiplets [7, 8], Bethe–Salpeter equation [9], multiple scattering [10] and pseudopotential theory [5, 11]. Vedrinskii and his group were particularly active in extracting information from the pre-edge structure [12–14].

In section 2, we give 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 TiO₂ (rutile) came 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 [16–20] 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 experiments and no imaginary mode is present [22–25] 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 et al [15] at the K-edge of titanium in TiO₂ (rutile), Li₄/₃Ti₅/₃O₄ and LiTi₂O₄. It was subsequently...
measured at the titanium K-edge of several perovskite crystals: PbTiO₃ [27, 28, 12, 29, 30], SrTiO₃ [31, 30], BaTiO₃ [30] and CaTiO₃ [30].

A similar temperature dependence was observed at other edges in perovskite crystals: at the niobium K-edge of KNbO₃ [32, 33], NaNbO₃ [34] and PbIn₁₂Nb₁₂O₃ [35], at the zirconium K-edge of PbZrO₃ [14], PbZr₀.₅₁T₀.₄₉O₃ [14] and BaZrO₃ [14], at the K-edge of Mn in La₀.₈Sr₀.₂MnO₃ [36, 37] and at the K-edge of Fe in La₀.₉Sr₀.₁FeO₃ and La₀.₉Sr₀.₁FeO₃ [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 Durmeye et al. [15], we observed at the K-edge of titanium in TiO₂ and Mg₂TiO₄ [30], at the L-edges of La in Sr-doped La₂CuO₄ [39] and at the Mn-edge of VO₂ [40]. A temperature dependence of the XANES spectra was also observed at the K-edge of oxygen in water [41] and in doped LaMnO₃ [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 [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 × 4 mm × 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 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 of a curved Si(111) crystal focusing the x-ray beam at the center of the cryostat sample holder. Higher harmonics were rejected by an SiO₂ plane mirror. The x-ray intensity was measured by a photodiode array detector. Each spectrum was obtained as a result of four measurements: I₀ (without sample and with the beam), Iₜₐₙ (without sample and without beam), I (with sample and with the beam) and Iₜₐₙ (with sample and without beam). The absorption spectrum was then obtained from the formula \( \sigma = \log(I₀ - Iₜₐₙ) - \log(I - Iₜₐₙ) \). 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 Si(311) monochromator, an ionization 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 at 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 c axis of the crystal.
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 [48–50], in which the intensity of the vibronic peak varies as $1 + e^{-\theta/\theta'}$, where $\theta$ is the energy of the first vibrational level. Figure 2 shows the variation of the $A_2$ peak with temperature, fitted to the function $a(1 + e^{-\theta/\theta'}) + (1 - a)$, where $a(1 + e^{-\theta/\theta'})$ represents the fraction of the $A_2$ peak that is purely vibrational and $1 - a$ as 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 $\theta$ compares favorably to the energy of the first odd vibrational level at the $\Gamma$-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 [53–56], for which the temperature dependence is $\coth(\theta/2T) / (1 - a)$.

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 the 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 a 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 [57–61]. If we use this factor to describe 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 = $ 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 dependence 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 non-equilibrium 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] led 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 does 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 does 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 final states. The initial state is taken to be the core state centered at 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 $R$ is small compared to the electronic variable $r$ and we obtain, to first order in $R$ and for a spherical core state $\phi_0(r)$, the shifted function

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

When multiplied by $\epsilon \cdot r$, the additional term gives us a factor $\epsilon \cdot r \cdot R \cdot r$ that can be transformed into the sum of a monopole term proportional to $(\epsilon \cdot R)^2$ and a quadrupole term. The monopole term gives rise to transitions towards $s$ states, the quadrupole term to transitions towards $d$ states. The transitions towards $s$ states are observed at the aluminum or silicon K-edge [71], while 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 that the temperature-dependent pre-edge peaks grow with temperature is due to the corresponding increase in thermal vibration amplitudes.

Of course, equation (1) is not sufficient because the integration over $r$ 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 only changes 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 and (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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References

[1] Yamamoto T 2008 Assignment of pre-edge peaks in K-edge x-ray absorption spectra of 3d transition metal compounds: dipole or quadrupole? X-Ray Spectrom. 37 572–84
[2] Chalmin E, Farges F and Brown G E Jr 2009 A pre-edge analysis of Mn K-edge XANES spectra to help determine the speciation of manganese in minerals and glasses Contrib. Mineral. Petrol. 157 111–26
[3] Arfaoui M, Cabaret D, Della Longa S, Seitsonen A and Mauri F 2007 First-principles full-potential calculations of the Fe K pre-edge and near-edge structure in carbonmonoxy-myoglobin AIP Conf. Proc. 882 331–3
[4] Getty K, Delgado-Jaime M U and Kennepohl P 2008 Assignment of pre-edge features in the Ru K-edge x-ray absorption spectra of organo metallic ruthenium complexs Inorg. Chim. Acta 361 1059–65
[5] Gougoussis C, Calandra M, Seitsonen A, Brouder Ch, Shukla A and Mauri F 2009 Intrinsic charge transfer gap in NiO from Ni K-edge x-ray absorption spectroscopy Phys. Rev. B 79 045118
[6] Vedrinskii R V, Kraizman V L, Lemeshko M P, Nazarenko E S, Novakovich A A, Reznichenko L A, Fokin V N and Shuvaeva V A 2009 Local atomic structure of niobates and titanates from x-ray absorption spectroscopic data Phys. Solid State 51 1394–8
[7] Arrio M A, Rossano S, Brouder Ch, Galais 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. 51 454–60
[8] de Groot F M F, Vankó G and Glatzel P 2009 The 1s x-ray absorption pre-edge structures in transition metal oxides J. Phys.: Condens. Matter 21 104207
[9] Shirley E 2004 Ti 1s pre-edge features in rutile: a Bethe–Salpeter calculation J. Electron Spectrosc. Relat. Phenom. 136 77–83
[10] Wu Z Y, Natoli C R, Marcelli A, Paris E, Bianconi A and Saini N L 2003 Unified interpretation of pre-edge-x-ray absorption fine structures in 3d transition metal compounds AIP Conf. Proc. 652 497–506
[11] Juhin A, Brouder Ch, Arrio M A, Cabaret D, Saincavit P, Balan E, Bordage A, Calas G, Eckhout S G and
Glatzel P 2008 X-ray linear dichroism in cubic compounds: the case of Cr$^{3+}$ in MgAl$_2$O$_4$. Phys. Rev. B 78 195103

[12] Vedrinskii R V, Kraizman V L, Novakovitch A A, Demekhin P V, Urazhzhin S V, Ravel B and Stern E A 1997 Pre-edge fine structure (PEFS) of the K-XAS for the 3d atoms in compounds: a new tool for quantitative atomic structure determination. J. Phys. Condens. Matter 7 C2 107–10

[13] Vedrinskii R V, Kraizman V L, Novakovitch A A, Demekhin P V and Urazhzhin S V 1998 Pre-edge fine structure of the 3d atom K x-ray absorption spectra and quantitative atomic structure determinations for ferroelectric perovskite structure crystals. J. Phys.: Condens. Matter 10 R951–80

[14] Vedrinskii R V, Nazarenko E S, Lemeshko M P, Nassif V, Proux O, Novakovitch A A and Joly Y 2006 Temperature dependent XAFS studies of local atomic structure of the perovskite-type zirconates. Phys. Rev. B 73 134109

[15] Durmeyer O, Kappler J P, Beurepaire E, Heintz J M and Drillon M 1990 Ti K XANES in superconducting Li$_2$TiO$_3$ and related compounds. J. Phys.: Condens. Matter 2 6127–36

[16] Burdett J K, Hughbanks T, Miller G J, Richardson J W Jr and Smith J V 1987 Structural-electronic relationships in inorganic solids: powder neutron diffraction studies of the rutile and anatase polymorphs of titanium dioxide at 15 and 295 K J. Am. Chem. Soc. 109 3639–46

[17] Howard C J, Sabine T M and Dickson F 1991 Structure and thermal parameters for rutile and anatase Acta Crystallogr. B 47 462–8

[18] Sakata M, Uno T, Takata M and Howard C J 1993 Maximum-entropy-method analysis of neutron-diffraction data J. Appl. Crystallogr. 26 159–65

[19] Sabine T M, Kennedy B J, Garrett R F, Goran G J and Cookson D J 1995 The performance of the Australian powder diffractometer at the photon-factory Japan. J. Appl. Crystallogr. 28 513–7

[20] Kumazawa S, Takata M and Sakata M 1995 An accurate determination of the thermal vibration of rutile from the nuclear density distribution of the maximum-entropy analysis Acta Crystallogr. A 51 651–8

[21] Jiang B, Zuo J M, Jiang N, O’Keeffe M and Spence J C H 2003 Charge density and chemical bonding in TiO$_2$. Acta Crystallogr. A 59 341–50

[22] Montanari B and Harrison N M 2004 Pressure-induced instabilities in bulk TiO$_2$ rutile. J. Phys.: Condens. Matter 16 273–92

[23] Rignanesi G M, Rocquefelte X, Gonze X and Pasquarrello A 2005 Titanium oxides and silicates as high-k dielectrics: a first-principles investigation Int. J. Quantum. Chem. 101 793–801

[24] Rignanesi G M, Rocquefelte X, Gonze X and Pasquarrello A 2005 Erratum: Titanium oxides and silicates as high-k dielectrics: a first-principles investigation Int. J. Quantum. Chem. 103 354

[25] Sikora R 2005 Ab initio study of phonons in the rutile structure of TiO$_2$. J. Phys. Chem. Solids 66 1069–73

[26] Montanari B and Harrison N M 2002 Lattice dynamics of TiO$_2$ rutile: influence of gradient corrections in density functional calculations Chem. Phys. Lett. 364 528–34

[27] Ravel B, Stern E A, Yacobi Y and Dogan F 1993 Lead tinate is not a classic case of a displaceable ferroelectric phase transition Japan. J. Appl. Phys. Suppl. 32-2 782–4

[28] Engel E, Dreizler R and Malzacher P 1987 Density functionals on the basis of the relativistic field theory J. Physique Coll. 48 C2 321–8

[29] Sato K, Miyanaga T, Ikeda S and Diop D 2005 XAFS study of local structure change in perovskite titanates Phys. Scr. T115 359–61

[30] Hashimoto T, Yoshiassa A, Okube M, Okudera H and Nakatsuka A 2007 Temperature dependence of XANES spectra for ATiO$_3$, A$_2$Ti$_2$O$_7$ and TiO$_2$ compounds with structural phase transitions AIP Conf. Proc. 882 428–30

[31] Nozawa S, Iwashin T and Osaka H 2005 Direct observation of the quantum fluctuation controlled by ultraviolet irradiation in SrTiO$_3$. Phys. Rev. B 72 121101

[32] Shuvaeva V A, Yanagi K, Yagi K, Sakauke T and Terauchi H 1999 Polarized XAFS study of the atomic displacements and phase transitions in KNBO$_3$. J. Synchrotron Radiat. 6 367–9

[33] Shuvaeva V A, Pirog I, Azuma Y, Yagi K, Sakauke T, Terauchi H, Raevskii I P, Zhuchkov K and Antipin M Y 2003 The local structure of mixed-ion perovskites J. Phys.: Condens. Matter 15 2413–21

[34] Shuvaeva V A, Azuma Y, Yagi K, Sakauke T and Terauchi H 2001 Polarized XAFS study of high-temperature phases of NaNBO$_3$. J. Synchrotron Radiat. 8 833–5

[35] Shuvaeva V A, Azuma Y, Raevskii I P, Yagi K, Sakauke T and Terauchi H 2004 The local structure of PbIn$_{1/3}$Nb$_{1/3}$O$_3$ Ferroelectrics 299 103–8

[36] Qian Q, Tyson T A, Lee C C, Croft M, Cheong S W and Greenblatt M 2000 Thermal effects in the x-ray spectra of La$_{1-x}$Ca$_x$MnO$_3$. Phys. Rev. B 62 13472–81

[37] Bridges F, Booth C H, Kwei G H, Neumeier J J and Sawatzky G A 2000 Temperature dependent changes of the Mn 3d and 4p bands near Tc in colossal magnetoresistance systems: XANES study of La$_{1-x}$Ca$_x$MnO$_3$. Phys. Rev. B 61 R9237–40

[38] Deb A, Ralph J M, Cairns E J and Bergmann U 2006 Characterization of La$_{0.95}$Sr$_{0.05}$FeO$_3$ and La$_{0.9}$Sr$_{0.1}$FeO$_{3-δ}$ as a function of temperature by x-ray absorption spectroscopy Phys. Rev. B 73 115114

[39] Hidaka M, Tokiwa N, Oda M, Choi J Y and Lee J M 2003 Electronic states near Fermi level in superconductors La$_{2-x}$Sr$_x$CuO$_4$ by means of x-ray absorption spectra near Cu-K and La-L$_2$ phases Phase Transit. 76 905–21

[40] Pommellier B, Cortes R, Loisy E and Berthon J 1994 Polarization dependence of the V K edge in VO$_2$ through the phase transition at 68 °C Phys. Status Solidi b 183 335–50

[41] Wernet P, Nordlund D, Bergmann U and Terasaki P 2005 Ab initio study of La$_{0.9}$Sr$_{0.1}$MnO$_3$: Jahn–Teller distortion effects Phys. Rev. B 71 125117

[42] Mannella N, Rosenhahn A, Watanabe M, Sell B, Nambu A, Ritchey S, Arenholz E, Young A, Tomioka Y and Fadley C S 2005 Temperature-dependent x-ray absorption spectroscopy of colossal magnetoresistive perovskites Phys. Rev. B 71 125117

[43] Tsai Y T, Chang W J, Huang S W, Lin Y J, Lee J Y, Chen J M, Wu K H, Uen T M, Gou Y S and Jiang Y J 2009 Temperature-dependent x-ray absorption near edge spectroscopy of doped LaMnO$_3$ J. Appl. Crystallogr. 42 335–50

[44] Ohkawa K and Tanabe Y 1990 The soft-x-ray edge problem Rev. Mod. Phys. 62 929–91

[45] Brudner Ch, Kappler J P and Beurepaire E 1990 Theory and application of angle-resolved x-ray absorption spectra 2nd European Conf. on Progress in X-Ray Synchrotron Radiation Research (Conference Proceedings vol 25) ed A Balerna, E Bernieri and S Mobilio (Bologna: Italian Physical Society) pp 19–22

[46] Ohtaka K and Tanabe Y 1990 The soft-x-ray edge problem Rev. Mod. Phys. 62 929–91

[47] Joly Y, Cabaret D, Renevier H and Natoli C R 1999 Electron population analysis by full-potential x-ray absorption simulations Phys. Rev. Lett. 82 2398–401
[48] Holmes O G and McClure D S 1957 Optical spectra of hydrated ions of the transition metals J. Chem. Phys. 26 1686–94
[49] McClure D S 1959 Electronic spectra of molecules and ions in crystals. Part II. Spectra of ions in crystals Solid State Physics vol 9, ed H Ehrenreich and D Turnbull (New York: Academic) pp 399–525
[50] Triest M, Davis M J and Reber C 1999 Absorption spectroscopy and time-dependent theoretical calculation of the intervalence band of FeIII-FeIIIBPMP(OPr)2(BPh4)2, a localized mixed-valence compound with a nonlinear metal-bridging ligand-metal core New J. Chem. 23 425–31
[51] Lee C, Ghosez P and Gonsé X 1994 Lattice dynamics and dielectric properties of incipient ferroelectric TiO2 rutile Phys. Rev. B 50 13379–87
[52] Traylor J G, Smith H G, Nicklow R M and Wilkinson M K 1971 Lattice dynamics of rutile Phys. Rev. B 3 3457–72
[53] Pisarev R V and Prokhorova S D 1969 The temperature dependence of optical absorption in the antiferromagnet KNiF3 Sov. Phys.—Solid State 10 1668–72
[54] Cieślak-Golonka M, Bartecki A and Sinha S P 1980 Vibrational fine structure in the electronic spectra of transition metal compounds. An experimental study Coord. Chem. Rev. 31 251–88
[55] McDonald R G and Hitchman M A 1986 Electronic ‘d–d’ spectra of the planar CuCl2− ions in bis(methadonium) tetrachlorocuprate(ii) and bis(creatinium) tetrachlorocuprate(ii): analysis of the temperature dependence and vibrational fine structure Inorg. Chem. 25 3273–81
[56] Taran M N, Langer K, Platonov A N and Indutny V V 1994 Optical absorption investigation of Cr4+ ion-bearing minerals in the temperature range 77–797 K Phys. Chem. Miner. 21 360–72
[57] Poilârkoa A V and Rehr J J 1999 Multiple-scattering x-ray-absorption fine-structure Debye–Waller factor calculations Phys. Rev. B 59 948–57
[58] Chun W J, Iijima K, Ohminami Y, Suzuki S and Asakura K 2004 Theoretical Debye–Waller factors of α-MoO3 estimated by an equation-of-motion method J. Synchrotron Radiat. 11 291–4
[59] Vaccari M and Fornasini P 2005 Thermal effects on EXAFS: ensemble averages and real-space approach Phys. Rev. B 72 092301
[60] Dimakis N 2007 Ab initio calculation of XAFS Debye–Waller factors for crystalline materials AIP Conf. Proc. 882 126–8
[61] Vila F D, Rehr J J, Rossner H H and Krappe H J 2007 Theoretical x-ray absorption Debye–Waller factors Phys. Rev. B 76 014301
[62] Natoli C R 1983 Near edge absorption structure in the framework of the multiple scattering model. Potential resonance or barrier effects? EXAFS and Near Edge Structure (Springer Series in Chemical Physics vol 27) (Berlin: Springer) pp 43–56
[63] Brouder Ch and Goulon J 1989 Influence of atomic displacements on XAFS Physica B 158 351–4
[64] Brouder Ch 1992 Lie group calculation of the Green function of disordered systems Applications of Multiple Scattering Theory to Materials Science (Materials Research Society Symp. Proc. vol 253) ed W H Butler, P H Dederichs, A Gonis and R L Weaver (Pittsburgh: Materials Research Society) pp 411–6
[65] Fujikawa T 1996 Debye–Waller and Condon factors in XAFS J. Electron Spectrosc. Relat. Phenom. 79 25–8
[66] Fujikawa T 1996 Theory of atomic displacement effects induced by core-hole production on EXAFS J. Phys. Soc. Japan 65 87–94
[67] Fujikawa T 1999 XAFS theory at zero and finite temperature J. Phys. Soc. Japan 68 2444–56
[68] Araî H, Ueno N and Fujikawa T 2007 Theory of electron–phonon interaction in XAFS and other spectroscopies AIP Conf. Proc. 882 108–10
[69] Mäder K A and Baroni S 1997 Vibrational broadening of x-ray emission spectra: a first-principles study on diamond Phys. Rev. B 55 9649–58
[70] Ankudinov A L and Rehr J J 2005 Nonspherical potential, vibronic and local field effects in x-ray absorption Phys. Scr. T 115 24–7
[71] Brouder Ch, Cabaret D, Juhin A and Sainctavit P 2010 Effect of atomic vibrations on the x-ray absorption spectra at the K-edge of Al in α-Al2O3 and Ti in TiO2 rutile Phys. Rev. B at press (Brouder C, Cabaret D, Juhin A and Sainctavit P 2009 arXiv:0912.0792)