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1990 J. Phys.: Condens. Matter 2 6127

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## Ti K XANES in superconducting $\text{LiTi}_2\text{O}_4$ and related compounds

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Received 9 October 1989, in final form 16 March 1990

**Abstract.** The mixed valence spinel  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$  ( $0 \leq x \leq 0.33$ ) compounds are superconducting for  $x \leq 0.12$  ( $T_{c\text{max}} = 12.7$  K) and present a metal or semiconductor-like transition for  $x \approx 0.2$ . In order to study the context of such interesting electronic properties, we performed Ti K edge measurements in these compounds and in the related systems  $\text{MgTi}_2\text{O}_4$  and  $\text{TiO}_2$ .

The evolution of the intensity, position and shape of the pre-edge and main edge features is reported. We show that these data do not support a one-electron description and suggest that  $\text{LiTi}_2\text{O}_4$  is a correlated d electron metal ( $U \approx W$ ).

Modifications in the pre-edge spectra as a function of temperature have been observed for  $\text{LiTi}_2\text{O}_4$ ,  $\text{Li}_{1.33}\text{Ti}_{1.67}\text{O}_4$  and  $\text{TiO}_2$ . We discuss possible interpretations of this effect (vibronic coupling or thermally induced lattice deformation).

### 1. Introduction

The mechanism for explaining superconductivity in high  $T_c$  superconductors is still a matter of debate. The study of spinel compounds, and especially of  $\text{LiTi}_2\text{O}_4$ , seems to be particularly attractive as previously pointed out [1, 2]. In fact many similarities between the behaviour of  $\text{LiTi}_2\text{O}_4$  compounds and the new copper oxide superconductors can be found: (i) the Ti atoms are in an octahedral coordination with the O atoms, as in the ideal perovskite structure; (ii) the presence of a mixed formal valence  $\text{Ti}^{3.5+}$  is similar to that, for instance of Y–Ba–Cu–O; (iii) the calculated density of states per Ti atom for the distorted spinel structure is comparable with that of the La–Sr–Cu–O system per Cu atom. From these remarks, it has been suggested that the RVB theory could explain the superconductivity in  $\text{LiTi}_2\text{O}_4$  [3]. However strong differences between the electronic structures of these compounds must also be pointed out:

- (i)  $\text{LiTi}_2\text{O}_4$  is a three-dimensional system;
- (ii) previous experimental results and electronic band structure calculations have shown that the states around  $E_F$  have predominant Ti d character, with a substantial hybridisation with O p states [3, 4]. The Ti d bands are separated from the O p states by an energy gap of 2.6 eV, and are further split into  $t_{2g}$  and  $e_g$  bands; in fact, the degree of

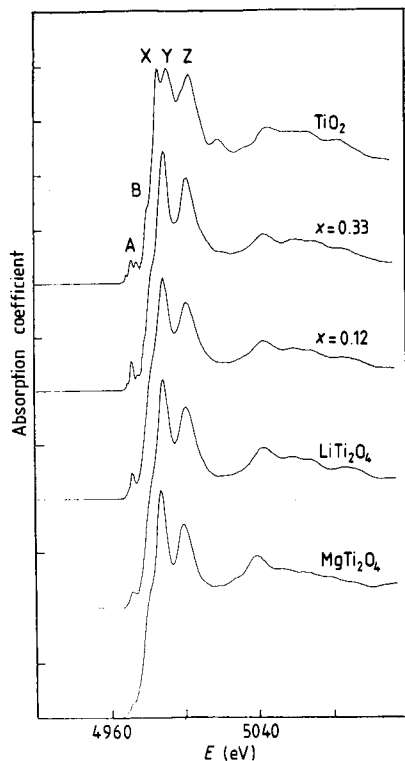
metal–oxygen hybridisation is therefore different in high  $T_c$  superconductors where the Cu d- and O p-like bands strongly overlap.

$\text{LiTi}_2\text{O}_4$  is one end member of the homogeneity range of the spinel phase  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$  ( $0 < x < \frac{1}{3}$ ) and is superconducting at temperatures up to 12.7 K. This system has the highest observed  $T_c$  among the four superconducting compounds that crystallise in the spinel structure (together with  $\text{CuRh}_2\text{S}_4$ ,  $\text{CuRh}_2\text{Se}_4$  and  $\text{CuV}_2\text{S}_4$  where  $T_c$  is in the range 3–4 K). Several careful investigations have been made on this superconducting system. They established  $\text{LiTi}_2\text{O}_4$  as a d-band superconductor; specific heat data have shown that the samples verified all features of a conventional BCS (Bardeen–Cooper–Schrieffer) weak coupling superconductor. Conversely, the mechanism of superconductivity has been shown to be more complex when off-stoichiometric compounds like  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$  and  $\text{Li}_{1-y}\text{Mg}_y\text{Ti}_2\text{O}_4$  are considered. The substitution of titanium by a monovalent ion  $\text{Li}^+$  on the Ti-octahedral sites decreases the  $\text{Ti}^{3+}/\text{Ti}^{4+}$  ratio whereas the substitution of lithium by a divalent ion  $\text{Mg}^{2+}$  on the Li-tetrahedral sites increases the  $\text{Ti}^{3+}/\text{Ti}^{4+}$  ratios in the spinel sublattice. It has also been shown that only 2% of magnesium produce a significant change in both  $T_c$  and  $\Delta T_c$ , and simultaneously for Li substitutions it has been noted that there is a sizable disappearance of superconductivity for  $x = 0.12$  in the vicinity of the metal insulator transition (MIT), but the insulator features ( $\gamma = 0$ ) are only reached for  $x = \frac{1}{3}$  [1]. High pressure studies also suggested that the superconductivity in this oxide system is of d character associated with the Ti sublattice, and that the composition induced disappearance of superconductivity is caused by the accompanying change of Ti ions rather than by a volume reduction. More recently, experimental results reported on spinel compounds and related mixed valent systems confirmed all the above conclusions. A better sample quality, i.e. (i) a normal resistivity lower by a factor 100 in comparison with previous results, (ii) a very narrow specific heat transition, (iii) no residual specific heat linear contribution below  $T_c$  [1], allowed us to establish  $\text{LiTi}_2\text{O}_4$  as a conventional BCS weak coupling superconductor, but some characteristic features emphasise the occurrence of spin fluctuation effects or electronic correlation effects. In fact, the comparison between the bare DOS, the measured DOS at the Fermi level and the electron–phonon coupling constant, as well as the valence photoemission data and the presence of a narrow  $t_{2g}$  band, suggest that in  $\text{LiTi}_2\text{O}_4$  electronic correlation effects cannot be disregarded.

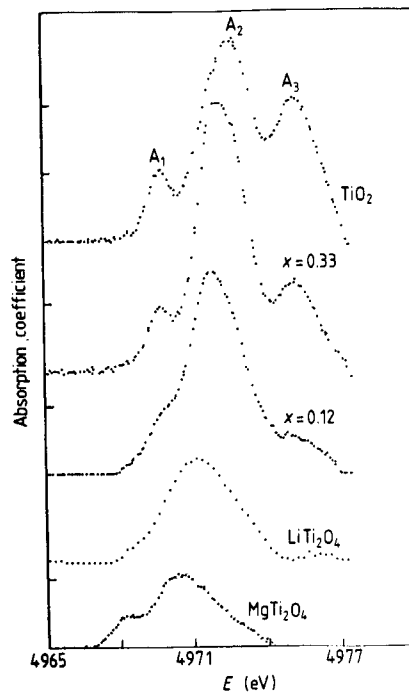
In order to study the context of such interesting electronic properties, we performed Ti K edge measurements in Li–Ti–O compounds and in the related systems:  $\text{MgTi}_2\text{O}_4$  and  $\text{TiO}_2$ . In this paper we show that the evolution of the intensity, position and shape of the pre-edge and main-edge features do not support a one-electron description and are directly connected to the disappearance of superconductivity. By analogy with rare earth systems [5] an estimation of the correlation energy  $U_{\text{dd}}$  is found to be 1.5 eV, which suggests that  $\text{LiTi}_2\text{O}_4$  is a correlated d electron metal ( $U \approx W$ ). Furthermore, modifications in the pre-edge spectra as a function of temperature have been observed for  $\text{LiTi}_2\text{O}_4$ ,  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  and  $\text{TiO}_2$ . A qualitative interpretation of this effect is discussed (vibronic coupling or thermally induced lattice deformation).

## 2. Experimental details

Samples were prepared following two types of chemical procedures both described elsewhere [1]. The absorption experiments have been obtained at the EXAFS II station set up at Laboratoire pour l'Utilisation du Rayonnement Electromagnétique (LURE),



**Figure 1.** Normalised Ti K edge spectra of  $\text{TiO}_2$ ,  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$  and  $\text{MgTi}_2\text{O}_4$  at room temperature.



**Figure 2.** Pre-edge structures of  $\text{TiO}_2$ ,  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$  and  $\text{MgTi}_2\text{O}_4$  at 300 K, obtained after subtracting from normalised spectra, between 4960 and 4980 eV, a  $\tan^{-1}$  background.

Orsay. The experimental equipment, as usual for transmission measurements, consists of a monochromator Si (311) and ionisation chambers in front and behind the sample. The sample absorption is expressed as a function of the energy of the incident photons:  $\mu(E) = \log(I_0/I)$ ,  $I_0$  and  $I$  being the ionisation currents. Additional premirrors are used in order to reject parasite harmonics. For the EXAFS data acquisition the energy is scanned from 200 eV below the absorption edges to 1000 eV above. The energy resolution in the 5–6 keV range, is typically 0.8 eV. Normalisation of the energy scale for the different spectra were made using a Ti foil. The first edge structure which occurs at  $E = 4964.75$  eV (figure 1) corresponds to a  $1s \rightarrow 4p$  dipole allowed transition [6].

### 3. Edge results at room temperature

The Ti K edge absorption spectra in  $\text{TiO}_2$ ,  $\text{MgTi}_2\text{O}_4$  and  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$  for  $x = 0, 0.12, 0.33$ , recorded at room temperature are given in figure 2. Our data for  $\text{TiO}_2$ , which correspond to a six-fold titanium  $\text{Ti}^{4+}$  in a distorted octahedral configuration, are in good agreement with those reported in the literature [6]. Two energy regions are usually distinguished in such spectra: above about 4980 eV where the structures are assigned to

the dipole transitions  $1s \rightarrow np$  and below 4980 eV corresponding to the so called pre-peak region [7].

In the case of  $\text{TiO}_2$ , three peaks labelled X, Y, Z in figure 1 are observed in the first spectral region for  $4980 \text{ eV} < E < 5020 \text{ eV}$ . Their usual interpretation is as follows: the X and Y peaks are due to the  $1s \rightarrow 4p$  allowed transitions taking into account a partial degeneracy raise of  $p_{x,y}$  and  $p_z$  orbitals due to the distortion [6]. Recently, strong light polarisation effects on these two peaks have been observed on a  $\text{TiO}_2$  single crystal [8]. The third peak Z is usually attributed to  $1s \rightarrow np$  ( $n > 4$ ) dipole-allowed transitions [6].

In the case of spinel compounds, where the Ti environment corresponds to a better approximation of the octahedron, the main Ti-edge structure presents only one peak due to a  $1s \rightarrow 4p$  transition and one peak due to  $1s \rightarrow np$  ( $n > 4$ ) dipolar transitions, while a weak structure is also visible in the main absorption ramp. Some authors identified this feature with a monopole  $1s \rightarrow 4s$  transition to the  $3a_{1g}$  molecular orbitals (MO). Other investigations using the MO approach also assign this transition in an octahedral configuration to the  $4t_{1u}$  levels. We will not discuss further the origin of this feature.

In all the studied samples, we observed small pre-peaks (labelled A in figure 1) in the energy range  $4960 < E < 4980 \text{ eV}$ . The simplest approach for explaining these edge features can be made by reference to the local symmetry around the absorbing atom. In the case of the tetrahedral configuration, an intense peak is observed in this spectral region due to transition towards molecular orbitals  $t_{2g}$  with a large Ti p character [9]. The situation of the quasi-octahedral configuration is more confused since non-negligible structures are observed below the  $1s \rightarrow 4p$  transitions though the first unoccupied molecular orbitals do not have the local Ti p symmetry. The occurrence of these pre-peaks is often attributed to dipole forbidden transitions  $1s \rightarrow 3d$  involving either a quadrupolar or a vibronic mechanism. However, to our knowledge, no quantitative estimation taking into account these mechanisms has been performed.

Recent polarisation dependent experiments performed on  $\text{TiS}_2$  [10] provide new information on this problem since they show that in this case the polarisation dependence of the pre-peak intensity is mainly characteristic of dipolar transitions. The authors proposed to interpret this finding according to the dipolar approximation and taking into account that the Ti 3d band states near the Brillouin zone boundaries are in fact p and d mixed states due to hybridisation effects. In a first step, we assume that the same mechanism can interpret the pre-peaks in spinel compounds.

In figure 2 we present the different pre-edge structures obtained after subtracting from experimental spectra for  $4960 < E < 4980 \text{ eV}$  a  $\tan^{-1}$  background simulating the absorption ramp. A large variation of the pre-peaks shape and intensity is observed as a function of the Ti valence.

The pre-edge structure of  $\text{TiO}_2$  is characterised by three peaks  $A_1$ ,  $A_2$ ,  $A_3$  with different weights, already observed in many other  $\text{Ti}^{4+}$  pseudo-octahedrally coordinated systems [6]. Previous experimental (Ti  $L_{2,3}$ , Ti K and O K edges measurements) and theoretical investigations (band structure calculations) [11] performed on this system, seem to confirm the dipolar attribution  $1s \rightarrow 3pd$  for the A pre-peak. In fact invoking the dipole approximation ( $\Delta l = \pm 1$ ), it has been shown that all the fine structures of the Ti- $L_{2,3}$ , Ti K and O K edges in  $\text{TiO}_2$  present two peaks that can be aligned to construct an empirical MO energy level diagram: the peak  $A_2$  ( $A_3$ ) in this approximation is assigned to the transition towards the  $t_{2g}$  ( $e_g$ ) band; in agreement with the MO scheme and the calculated bands structure, it is suggested that these orbitals have mainly the Ti 3d symmetry and a weaker O p and Ti p character.

On the other hand the presence of the weak  $A_1$  feature on the Ti K edge could not be interpreted in a simple band structure model (extended Hückel). The origin of this

small peak  $A_1$  at lower energy is still controversial since it does not correspond to mono-electronic features: some authors assume that it is a shake-down process involving a hole in  $t_{1g}$  orbitals; other authors associate the peak  $A_1$  either to a vibronic coupling, or to a Frenkel exciton. We performed simulation of our spectra taking into account the experimental resolution and core hole lifetime. In all compounds, the intrinsic width of  $A_1$  is found to be very small ( $<0.1$  eV) and consistent with a bound state created by the core hole potential. However, recent theoretical investigations did not confirm this excitonic interpretation [11]: in fact taking into account a multiple-scattering approach using a muffin-tin form for the potential of each atom Brydson *et al* [12] have recently shown that such a one-electron theory seems able to reproduce the main features of the Ti K edges. The calculation corresponds only to the rate of dipolar transitions. A good agreement between theory and experiment is observed only for the position of the peak (but not intensity): this allows the authors to suggest that all the peaks A, B, X, Y, Z represent transitions to states having at least a significant amount of p symmetry which corroborates the dipolar interpretation for the  $A_2$  and  $A_3$  pre-peaks. Furthermore the peak  $A_1$ , alternately attributed to an excitonic mechanism is also present in the calculated spectra, even though core hole effects have been neglected. However, since the peak  $A_1$  is not present in the calculated  $\text{TiO}_2$  density of states [11], this sets the problem of the consistency between a band structure and a multiple scattering approach so that, in our opinion, the origin of  $A_1$  remains an open question.

The pre-edge structure of  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  is also characterised by the three peaks  $A_1$ ,  $A_2$ ,  $A_3$  already observed for  $\text{TiO}_2$  but with different weights. For the spectral attribution of these pre-peaks the same point of view as discussed above for  $\text{TiO}_2$  has been adopted. In fact in a rigid band model, with a varying Fermi level so as to respect the charge neutrality, the width and energy separation of the pre-peaks correspond qualitatively to the density of d states calculated for  $\text{LiTi}_2\text{O}_4$  [3, 4] (the Ti p density of states was not calculated):

(i) the octahedral field splits these Ti 3d states into  $t_{2g}$ - and  $e_g$ -like bands which are non-overlapping in this compound and are separated by 2 to 3 eV.

(ii) the calculated density of states exhibits a partially filled conduction band (about 2 eV above the oxygen 2p bands) which contains one electron per formula unit (none for  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ ) and has predominantly Ti 3d character with a small amount of O 2p character [4]. In this model it therefore seems reasonable to attribute respectively the peaks  $A_2$  and  $A_3$  (separated by about 2.7 eV) to the transitions towards band states constructed on  $t_{2g}$  and  $e_g$  orbitals respectively, whereas, as in the  $\text{TiO}_2$  system, no simple attribution of the  $A_1$  peak can be proposed.

Several interesting features can be noted in the evolution of the spectra as a function of Ti valence reported on figures 2 and 3:

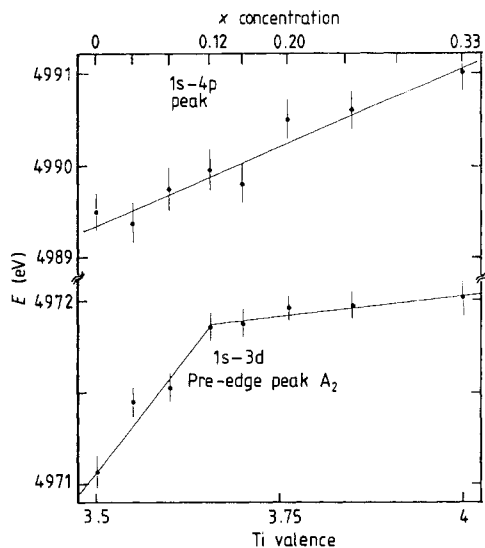
(i) peak  $A_1$  nearly vanishes in going from  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  to  $\text{LiTi}_2\text{O}_4$  and then seems to reappear shifted at a 1.7 eV-lower energy for  $\text{MgTi}_2\text{O}_4$ ;

(ii) peak  $A_2$  broadens, is shifted by 1.7 eV, and its intensity decreases by at least a factor of 3;

(iii) peak  $A_3$  nearly disappears for  $x < 0.12$ ;

(iv) the absorption ramp is shifted at a 3 eV-lower energy on going from  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$ .

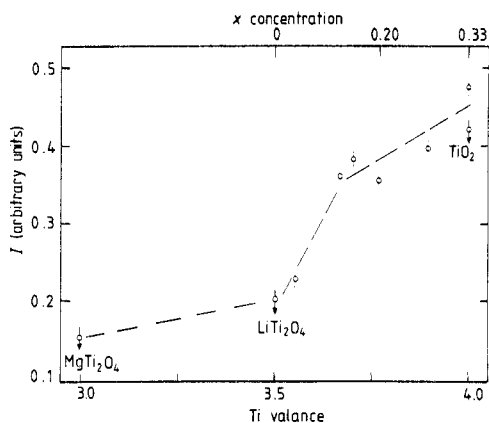
We believe that the disappearance of  $A_3$  is mainly an artifact of our subtraction procedure since the absorption ramp is shifted in energy more rapidly than the pre-peaks. As a consequence we will not discuss this structure further.



**Figure 3.** Oxidation state versus energy positions of various absorption features in the Ti K edge spectra of various titanium oxides, exhibiting the same symmetry.

Generally, the energy positions of various absorption features are also found to be correlated with the oxidation state (formal valence) as demonstrated e.g. at the V K edge in the oxides [13]. From the Ti-experimental data, it is shown that an increase in oxidation state shifts: (i) the energy of the pre-edge  $A_2$  peak by an amount of 1.7 eV and (ii) the  $1s \rightarrow 4p$  transition above the absorption edge to higher energies by 3 eV. The positive shifts in the threshold (so called chemical shifts) with respect to the valence increase can be conceptually interpreted by an increase of the attractive potential of the nucleus upon the  $1s$  core electron and a reduction in the repulsive core Coulomb interaction with all the other electrons in the compound. However the observed discrepancy in figure 3 between the chemical shifts related to localised final states, i.e. pre-peak, and to the extended final states, i.e. absorption ramp, seems to emphasise the occurrence of electronic correlation effects in the narrow  $t_{2g}$  band. By analogy with rare earth systems [5], a qualitative estimation of the Coulomb interaction  $U_{dd}$  between d electrons can be extracted from the different XAS final states: if we assume a shift  $\Delta \epsilon_d$  at the position of the d level from  $Li_{4/3}Ti_{5/3}O_4$  to  $MgTi_2O_4$ , and the Coulomb potentials  $U_{dd}$  ( $U_{sd}$ ) between two d electrons (the core hole and d electrons) we then write as a first approximation (i) the difference  $E(1s-3d^0 4p^1) - E(1s-3d^1 4p^1) \approx U_{sd} - \epsilon_d$ , (ii) the difference  $E(1s-3d^1 4p^0) - E(1s-3d^2 4p^0) \approx U_{sd} - \epsilon_d - U_{dd}$ . We corrected all the energy positions of the peaks and pre-peaks obtained for the two spinel compounds  $MgTi_2O_4$  and  $Li_{4/3}Ti_{5/3}O_4$  by expanding the energy scale of each spectrum by a factor  $d^2(\text{sample})/d^2(LiTi_2O_4)$  where  $d$  is the interatomic distance and using the law  $(E(1s-3d^0 4p^1) - E(1s-3d^1 4p^0)) d^2$  [14]. In fact this correction takes into account the effects of bond-length variations of titanium in an octahedral coordination. From these considerations we obtain a value of  $U_{dd}$  of about 1.3 eV which leads to a value of  $U_{dd}/W_{t_{2g}} = 0.6$  [4] and then point out the role played by electronic correlation effects in such a narrow  $t_{2g}$  conduction band.

This value of  $U_{dd}/W_{t_{2g}}$  in the Li-Ti-O system can explain why the 3d XAS final states are not well resolved. In comparison with rare earth system [5], with  $U_{ff}/W \gg 1$ , where all the  $4f^n$  XAS final states are clearly resolved.



**Figure 4.** Intensity of the sum of the  $A_1$  and  $A_2$  pre-edge peak versus the Ti formal valence (i.e. the concentration  $x$ ) at 300 K.

In the present system final state effects are also perceptible in the variation of the pre-peak intensity weight, i.e. as a function of the  $3d^1/3d^0$  ratio in the XAS ground state. Simulations have shown that the  $\text{LiTi}_2\text{O}_4$  ( $\text{Ti}^{3.5+}$ ) main-edge structure ( $1s \rightarrow np$ ) could be reproduced with a 50% amount of  $\text{Ti}^{3+}$ , i.e.  $\text{MgTi}_2\text{O}_4$ , and a 50% amount of  $\text{Ti}^{4+}$ , i.e.  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ . The same simulations have shown that the shape of the  $\text{LiTi}_2\text{O}_4$  pre-edge could be reproduced, with 20% of  $\text{Ti}^{4+}$  and 80% of  $\text{Ti}^{3+}$ . This effect suggests that  $\text{LiTi}_2\text{O}_4$  is not a simple mixed valence system (as for instance in some Sm or Eu compounds), but on the contrary, the hybridisation between Ti 3d and O 2p orbitals should also be taken into account in order to describe the ground state.

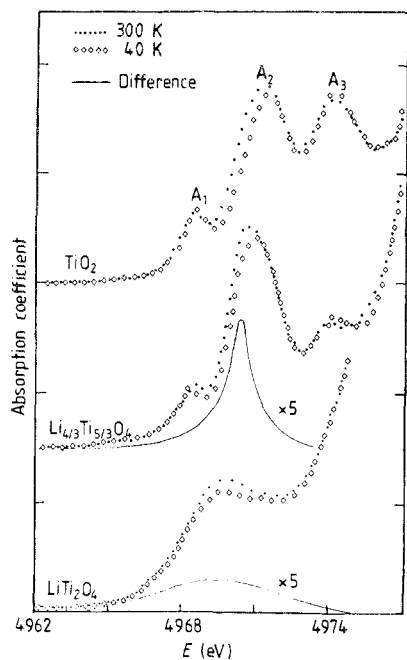
Furthermore if we report either the sum  $I$  of the  $A_1$  and  $A_2$  peak intensities or the energy position of the  $A_2$  peak versus the Ti formal valence (figures 3 and 4) we clearly distinguish two kinds of regime; the first for  $0 < x < 0.12$  with a high positive value of  $dI/dv$ , corresponds to the superconducting domain and the second occurs for the non-superconducting domain  $0.12 < x < 0.33$ , including the  $\text{MgTi}_2\text{O}_4$  compounds characteristic of ( $\text{Ti}^{3+}$ ), with a lower  $dI/dv$  value. Interestingly, the variation of the low temperature contribution  $\gamma$  to the specific heat versus  $x$  [1] exhibits a similar fracture around  $x = 0.12$ , i.e. in the vicinity of the MIT. The same behaviour has already been observed in the pre-peaks of some vanadium oxides [13]: in  $\text{VO}_2$ , a discontinuous change of the shape of the XAS spectra and a discontinuous decrease of the peaks' heights show up at the MIT temperature.

All these quantitative features lead us to suggest initially that the composition-induced disappearance of superconductivity can be caused by the accompanying valence change of Ti ions and that some electronic structure effects are present in such mixed valent systems characterised by distinct  $\text{Ti}^{3+}/\text{Ti}^{4+}$  ratios. A possible interpretation of these effects could rely on the localisation of Ti 3d orbitals due to disorder as Li is progressively substituted. Such a localisation produces the two regimes observed in the behaviour of  $\gamma$  [1] and the pre-peak intensity or position, allowing us to distinguish metallic (superconducting) and semiconducting-like samples.

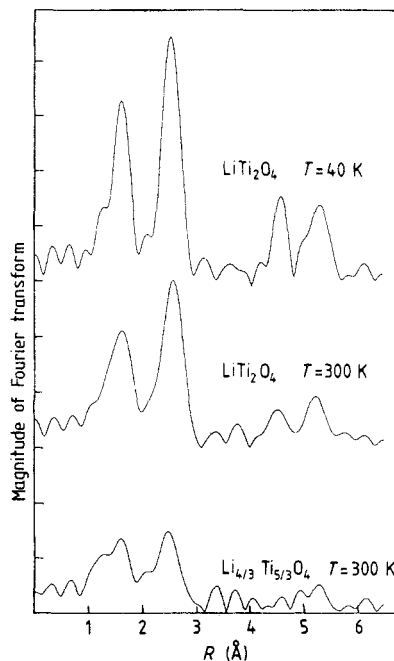
#### 4. Thermal variations of XANES and EXAFS

Thermal variations of the Ti-K edge, and especially of the  $A_2$  peak intensity in the  $\text{TiO}_2$ ,  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  and  $\text{LiTi}_2\text{O}_4$  compounds have been observed (figure 5). Indeed the intensity





**Figure 5.** Normalised pre-edge structures of  $\text{TiO}_2$ ,  $\text{LiTi}_2\text{O}_4$  and  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  at 300 K and 40 K.

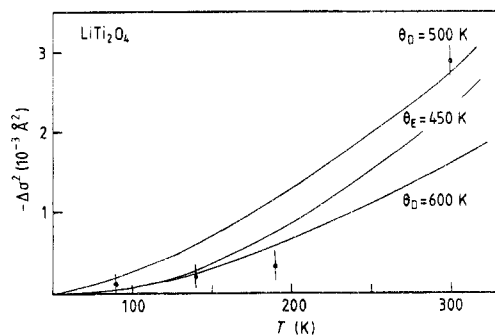


**Figure 6.** Fourier transforms of the EXAFS spectra at the Ti K edge.

of the  $A_2$  peak is reduced with decreasing temperature (5–10% of the intensity between room temperature and 45 K), whereas the  $A_1$  and  $A_3$  peaks do not seem to be really affected. This peculiar behaviour of the  $A_2$  peak is clearly observed in the difference spectra (see figure 5) that consists of a single peak broadened in going from  $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$  to  $\text{LiTi}_2\text{O}_4$ . At first sight, this temperature effect can be explained either by a weak distortion of the crystalline structure as a function of temperature (though we could not resolve it from x-ray diffraction data), or by the so-called vibronic coupling.

In order to discuss these mechanisms, we also performed EXAFS measurements above the Ti K edge in  $\text{LiTi}_2\text{O}_4$  as a function of temperature. The  $k^3$  weighted EXAFS signal (after a conventional background reduction) have been Fourier filtered between 100 and 750 eV above the edge in order to obtain the radial distribution function  $P(r)$  reported in figure 6. Several peaks extending up to  $\approx 5 \text{ \AA}$  representing Ti neighbours are clearly resolved. We focused our attention on the first peak at  $R = 1.7 \text{ \AA}$  which corresponds to the retrodiffusion by the six O first neighbouring atoms. Using calculated phase shifts and amplitudes [15], we checked that the increases of the intensity of this peak at low temperature are essentially due to the variation of the Debye–Waller factor and we can rule out strong modifications of Ti–O bond lengths within the EXAFS resolution ( $\pm 0.01 \text{ \AA}$ ) [16].

The retrodiffusion amplitude for a Ti–O pair was extracted by an inverse Fourier filtering of the first peak of  $P(r)$ , so that the thermal variation of the Debye–Waller factor could be obtained using the ratio method [17]. From the temperature variation of the Debye–Waller factor  $\Delta\sigma^2$  between 300 K and 45 K and the assumption that the individual bonds can be treated as Einstein (Debye) oscillators [18], we could estimate



**Figure 7.** Variation of  $\Delta\sigma^2$  with temperature for the Ti–O interatomic distances. The solid lines represent respectively a Debye and an Einstein model fits ( $\theta_D = 500$  and  $600$  K,  $\theta_E = 450$  K).

the characteristic temperature  $\theta_E$  ( $\theta_D$ ). In figure 7 we present the fits of the data using the above models. From this figure, it appears that the experimental data do not allow us to choose between the Debye or the Einstein model. Anyhow, the value of the Debye or Einstein temperatures extracted from the fits ( $\theta_E \approx 450$  K,  $\theta_D \approx 550$  K) are in quite good agreement with the specific heat results between 4–15 K ( $\theta_D = 535$  K) [1].

The relevance of the vibronic mechanism to the explanation of the temperature dependence of the  $A_2$  pre-peak intensity can be now qualitatively discussed. If we use the Debye–Waller factor to perform a qualitative estimate of the degree of dynamic deformation of the Ti–O octahedron, the variation of the pre-peak intensity  $I(300 \text{ K})/I(45 \text{ K}) = 1.1 \pm 0.03$  is comparable to the mean relative atomic displacement ratio  $\sigma(300 \text{ K})/\sigma(45 \text{ K}) = 1.25$  calculated for an Einstein oscillator with  $\sigma^2 = (\hbar^2/2\mu k_B \theta_E) \coth(\theta_E/2T)$  [19]. This value of the mean relative displacement ratio shows that the atom motions at 45 K (or even at 0 K) are not negligible and agree with  $\frac{1}{3}$  of the mean relative atom displacement at room temperature.

However the observed effects could also be explained by the appearance of lattice deformations at low temperature. In order to check whether a vibronic mechanism or the existence of static distortions at low temperature are responsible for these variations of the pre-peak intensity, we now plan next to measure the x-ray absorption coefficient at various temperatures, since the intensity variations are expected to be continuous in the first case, and discontinuous in the second.

## 5. Conclusions

From the comparison of the x-ray absorption pre-edge spectra of  $\text{Li}_{1+x}\text{Ti}_{2-x}\text{O}_4$  ( $0 < x < \frac{1}{3}$ ) and related systems ( $\text{MgTi}_2\text{O}_4$ ,  $\text{TiO}_2$ ); the presence of electronic correlation effects has been suspected. While previous estimations indicated that the superconducting critical temperature  $T_c = 12.7$  K of  $\text{LiTi}_2\text{O}_4$  could be understood within the BCS theory based upon the electron–phonon interaction, we showed that electron–electron interactions cannot be disregarded. In fact, the evolutions of the intensity, the shape, the energy position of the pre-edge and main-edge features lead to a value of  $U_{dd}/W$  of about 1, and suggest that  $\text{LiTi}_2\text{O}_4$  can perhaps be understood within a correlated narrow d-band superconductivity framework.

Further considerations and conclusions could also be extracted from these Ti K edge pre-peak spectra, but no simple interpretation of the origin and the evolution of the  $A_1$  pre-peak has been given with respect to the  $\text{Ti}^{3+}/\text{Ti}^{4+}$  ratio. Moreover band structure

effects are expected to play a role in determining the observed absorptions features, but calculations do not reproduce the  $A_1$  near-edge absorption pre-peak of these titanium compounds ( $TiO_2$  and  $LiTi_2O_4$  at the Ti K edge).

We therefore point out that it is desirable to dispose of first principle calculated x-ray absorption spectra in order to understand the origin of the pre-peaks in transition metal compounds. From these calculations, experimental spectra in mixed valence systems could be simulated within the framework of many-body theories, allowing a description of the ground state.

Additionally, weak modifications in the pre-edge spectra as a function of temperature have been observed. From the comparison with EXAFS data we show that they do not contradict a vibronic description of the pre-peaks. However, further experimental study is in progress in order to decide between the possible mechanisms (static distortion or vibronic coupling). It is our hope that further theoretical and experimental work on this class of materials will be stimulated and definite conclusions drawn.

### Acknowledgments

It is a pleasure to thank Professors F Gautier, J Petiau, A Kotani and Drs A Khan, J C Parlebas and C Brouder for fruitful discussions.

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