

Short communication

X-ray absorption spectra of the spinel $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$

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Abstract

X-ray absorption spectra of the spinel $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$ were recorded at the Cu K and L_3 , Mn K and L_3 , and O K edge. The spectra are aligned on a common energy scale with the aim to establish an experimental picture of the conduction band structure. The fine structures observed a few electron volts around the absorption thresholds are discussed in terms of hybridisation of cation and anion orbitals. Emphasis is put on the identification of spectral features correlated with the presence of lithium on the tetrahedral sites of the spinel structure. The consequences of lithium insertion/extraction on the intensities of these spectral structures are discussed. Previous studies by X-ray absorption spectroscopy of lithium insertion/extraction in various spinels are found to agree with our expectations.

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1. Introduction

Several years ago, the spinel LiMn_2O_4 has been proposed as an interesting cathode material for rechargeable Li-ion cells [1,2] and its electrochemical properties have been studied extensively [3,4]. However, the behaviour of LiMn_2O_4 under repeated charge/discharge cycling turned out to be unsatisfying. To overcome this problem the partial substitution of Mn by other transition metals has been suggested to give $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$, where M can be Ti, Cr, Co, Ni, Cu, or a mixture of them [5–10]. Numerous studies have thus been devoted in recent years to lithium insertion/extraction reactions in $\text{LiM}_x\text{Mn}_{2-x}\text{O}_4$ compounds.

A comprehension of the chemical and electronic processes caused by lithium insertion and extraction in an electrode material necessitates not only a detailed analysis of the structural modifications a material undergoes, but also knowledge of the redox reactions in which the various elements in the material are involved. The determination of oxidation states is thus a crucial point. In this context X-ray absorption spectroscopy (XAS) has been shown to be an experimental technique of particular importance. Each element in the material can be probed individ-

ually by tuning the X-ray wavelength to its characteristic X-ray absorption edges. The position of the edge on an energy scale is correlated with the oxidation state. A shift of the absorption edge is thus usually attributed to a redox process. Further information on the probed atom can be gained from the fine structure a few electron volts around the absorption edge (X-ray absorption near edge structure, XANES) which reflects the density of electronic states at the bottom of the conduction band. This band structure is determined by the chemical bonds the absorbing atom is involved in, i.e. by the nature and the positions of the surrounding atoms. Making use of the selection rules for dipolar transitions allows scanning of empty states in the conduction band separately for the different final state symmetries (s, p, d, . . .) and provides deeper insight into the charge transfer processes induced by insertion/extraction. XAS has therefore been used extensively to investigate redox processes in pure and partially substituted LiMn_2O_4 [5–14].

However, the analysis of XANES spectra necessitates a profound comprehension of the various spectral features, which can be achieved by comparison with calculated partial densities of accessible electronic states in the conduction band for the probed element. Several calculations of the band structure have been carried out for both pure and partially substituted LiMn_2O_4 [15,16] but none of these calculations provides sufficient details on the partial densities of states of all elements to allow a comprehensive interpretation of the XANES spectra. Analysis of XANES

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data of spinel electrode materials remained therefore in many cases limited to the evaluation of chemical shifts induced by redox reactions.

An interpretation of XANES data despite lacking band structure calculations is, however, made possible by recording a maximum number of absorption spectra scanning the most relevant final state symmetries of all elements. The hybridisation between electronic states of the different elements leads to the appearance of spectral features at identical relative energies in the corresponding X-ray spectra of all involved atoms. An alignment of all spectra on a common relative energy scale provides thus a rather precise picture of the conduction band structure and allows a fully coherent interpretation of the XANES spectra.

In the present work we chose the substituted spinel $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$ for a complete study of the bottom of the conduction band over a range of approximately 20 eV. X-ray absorption spectra were recorded at the Cu K and L_3 , Mn K and L_3 , and O K edges corresponding, respectively, to electronic transitions $\text{Cu } 1s \rightarrow 4p$ and $2p_{3/2} \rightarrow (3d,4s)$, $\text{Mn } 1s \rightarrow 4p$ and $2p_{3/2} \rightarrow (3d,4s)$, and $\text{O } 1s \rightarrow 2p$. In this way the most relevant states building up the bottom of the conduction band are scanned. An alignment of all spectra on a common relative energy scale will be presented and the structural informations that can be obtained from the spectra will be discussed with reference to previously published experimental work.

2. Experimental

The spinel compound $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was prepared by a sol–gel procedure. Stoichiometric mixtures of Cu, Mn, and Li acetates were added to a water–ethanol (75:25, v/v) solution. Five percent lithium was added in excess. The slurries were slowly heated up to 200 °C to dryness. The product was then heated to 800 °C for 24 h and then reannealed for 24 h at 750 °C. X-ray diffraction showed that a high purity spinel phase was obtained.

X-ray absorption spectra were recorded using the synchrotron radiation of the LURE facilities, Orsay, France. Cu and Mn K edge spectra were recorded on beamline D21 of the DCI storage ring in transmission geometry using ionisation chambers for the measurement of incident (I_0) and transmitted (I) beam intensity. The monochromator was a $\text{Si}(311)$ double crystal giving a spectral resolution of 1.7 and 2.0 eV at the Mn and Cu K edges, respectively. Harmonics were rejected by mirrors. The monochromator was calibrated by setting the first inflection points in the spectra of Mn and Cu foils to 6539 and 8979 eV, respectively [17]. Cu L_3 edge spectra were recorded on beamline SA32 of the SuperACO ring in the total electron yield mode using a beryl double crystal monochromator allowing a spectral resolution of 0.4 eV. The monochromator was calibrated by setting the absorption maximum of the L_3 edge of a cleaned Cu metal plate to 931.2 eV. The O K and Mn L_3 absorption edges were recorded in the partial electron yield mode on beamline SA22 of the SuperACO ring using a channeltron detector. The beamline was equipped with a lattice monochromator and entrance slits, allowing a spectral resolution of 0.1 eV. The monochromator was calibrated by setting the first inflection

point of the L_3 edge spectrum of metallic Mn to 638.7 eV [18]. The spectral resolution at all edges is further limited by broadening induced by the finite lifetime of the core hole (Cu K 1.55 eV, Mn K 1.16 eV, Cu L_3 0.56 eV, Mn L_3 0.32 eV [19]). The absorption spectra were obtained by step scanning with energy steps of 0.4 eV (Cu K), 0.3 eV (Mn K), 0.2 eV (Cu L_3 , O K), and 0.1 eV (Mn L_3). All spectra were corrected for a linear baseline which was fitted to the pre-edge part.

3. Results

Fig. 1 shows the X-ray absorption spectra obtained at the Cu K and L_3 , Mn K and L_3 , and O K edges of $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$ aligned on a common energy scale. The zero of this scale has been chosen arbitrarily at the energetically lowest absorption peak of the O K edge spectrum. The absolute energies of the various spectral features to be discussed below are given in Table 1. The following interpretation of the spectra is based on the theoretical band structure and the XANES spectra of the spinel compound $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [20] and several systematic studies of the X-ray absorption spectra of binary transition metal oxides [21,22].

Let us first consider the O K edge. Each anion in the spinel lattice is surrounded by one cation on a tetrahedral site and three cations on octahedral sites. In $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$ the tetrahedral sites are occupied exclusively by lithium, while manganese and copper are found on the octahedral sites in statistical distribution. In this way the anion forms chemical bonds with all cations present in the compound and we can expect the anion X-ray absorption spectrum to be the most important for the analysis of the electronic structure. The O K edge spectrum of

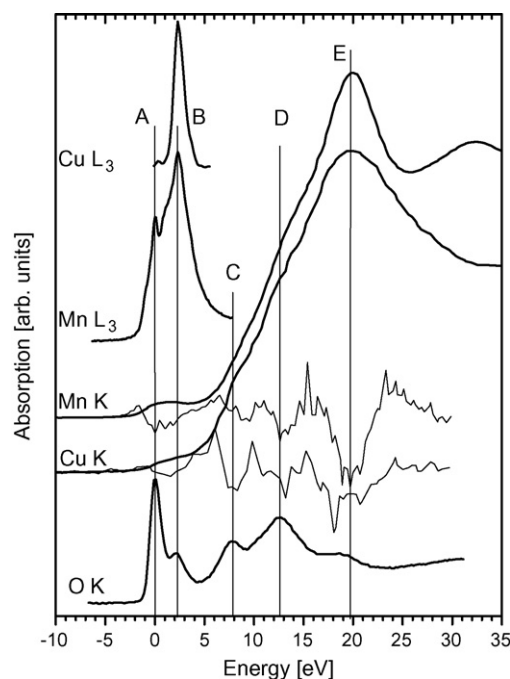


Fig. 1. X-ray absorption spectra of $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$ recorded at the O K, Mn K and L_3 , and Cu K and L_3 absorption edges, aligned on a common relative energy scale, together with the Mn K and Cu K edge second derivatives.

Table 1
Composition of bands of unoccupied states and their relative positions

Absorption band	A	B	C	D	E
Band character (principal contributions)	Mn d + O p	Mn d + Cu d + O p	Li p + O p + Mn p + Cu p	Mn p + Cu p + Li p + O p	Mn p + Cu p + Li p + O p
Relative position	0	2.2	8	12.5	20
Cu L ₃ edge	–	930.8	–	–	–
Mn L ₃ edge	640.1	642.4	–	–	–
O K edge	528.8	531.0	536.6	541.3	548
Mn K edge	6540.7	6542.5	6549	6552	6560.7
Cu K edge	–	8978.0	8984	8988	8996

Absolute energies of the corresponding spectral features on the X-ray absorption spectra. All energies in eV.

LiCu_{0.5}Mn_{1.5}O₄ shows five absorption bands, labeled A to E, and agrees in shape with that obtained at the O K edge for the spinel Li₄Ti₅O₁₂ [20]. The origin of these bands is now well understood [20–22]. The first two peaks, A and B, separated by 2.2 eV, reflect transitions to oxygen 2p states hybridised with transition metal 3d orbitals, which are split by the crystal field into t_{2g} and e_g states. In LiCu_{0.5}Mn_{1.5}O₄ the spectral shape is mainly determined by the distribution of manganese 3d states due to the stoichiometric Mn to Cu ratio of 3:1. Manganese is expected to be in the 4+ oxidation state [11], corresponding to an electron configuration 3d⁵t_{2g}³e_g⁰ and we have to distinguish between the majority(↑)- and minority(↓)-spin states. The 3d t_{2g}(↑) band of Mn⁴⁺ is filled. Concerning the remaining states it has been shown by several authors [22,23] that in oxides of Mn⁴⁺ the e_g(↑) and t_{2g}(↓) bands of the electronic ground state may coincide in such a way that only two bands of Mn d–O p mixed states are discerned in the O K edge spectrum: this combined e_g(↑)–t_{2g}(↓) band, appearing with high intensity, and the e_g(↓) band. The observed energy difference of 2.2 eV between peaks A and B can thus be attributed to the crystal field splitting between the t_{2g}(↓) and e_g(↓) states. The appearance of peak C at +8 eV in the O K edge spectrum is characteristic for spinel compounds containing lithium in tetrahedral coordination and reflects the hybridisation of oxygen p orbitals with the p states of these lithium atoms [20]. The absolute energy at which it is found on the oxygen K edge spectrum is independent of the nature of the transition element contained in the sample (536.6 eV for LiCu_{0.5}Mn_{1.5}O₄ as compared to 536.7 eV for Li₄Ti₅O₁₂ [20]) whereas the energy of the two lowest bands A and B is determined by the dominant transition element (528.8 and 531.0 eV here as compared to 529.6 and 532.4 eV for Li₄Ti₅O₁₂ [20], see Fig. 2). The last two peaks of the O K edge spectrum, D and E, reflect the hybridisation between transition metal p, lithium p, and oxygen p states [20].

The dipolar approximation associates the Mn L₃ absorption spectrum with transitions from the Mn 2p_{3/2} core level to empty states in the conduction band of d and s symmetry. The spectral shape is, however, essentially determined by the accessible d states due to the much smaller matrix elements of 2p → 4s transitions as compared to 2p → 3d [24]. The crystal field induced by the surrounding anions splits the Mn 3d states into a t_{2g} triplet and an e_g doublet. This metal–ligand interaction competes with an intra-atomic Coulomb interaction between all 3d electrons (3d–3d) and between the 3d electrons and the 2p core hole (3d–2p). These intra-atomic effects give rise to a multiplet

of electronic levels. The spectral shape is a result of the sum of all these interactions. In weak crystal fields the shape is determined by line splitting induced by intra-atomic effects. In stronger crystal fields a splitting into two peaks separated by approximately 10Dq, the crystal field parameter, may be observed. The Mn L₃ edge spectrum of LiCu_{0.5}Mn_{1.5}O₄ reveals two major peaks separated by 2.3 eV. This value agrees well with the splitting of 2.2 eV between bands A and B of the O K edge spectrum, suggesting that the two principal peaks of the Mn L₃ edge spectrum result essentially from the crystal field splitting. Thus, the Mn L₃ edge spectrum is placed in Fig. 1 in such a way that the two main structures match with bands A and B.

The Mn K absorption spectrum reflects transitions from the Mn 1s core level to empty states of p symmetry. The spectrum shows two weak prepeaks below the absorption threshold, two shoulders in the arctan-like absorption step and a pronounced maximum above threshold. The prepeaks and the shoulders are clearly revealed by the second derivative which is also shown in Fig. 1. Prepeaks below the K X-ray absorption edge are observed for many transition metal compounds and are due to the excita-

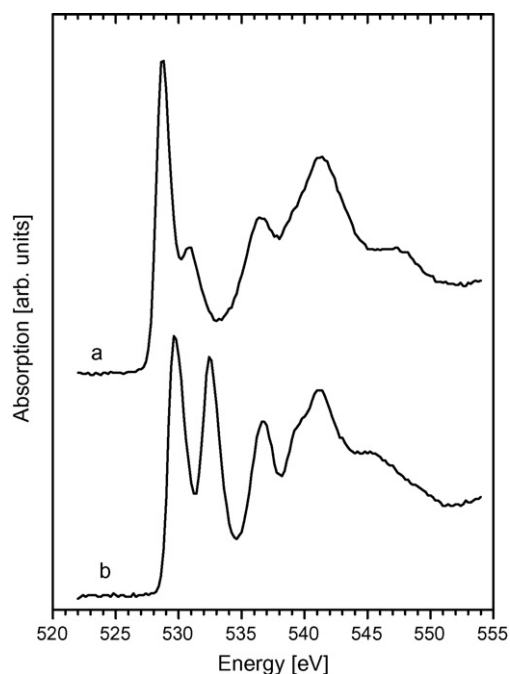


Fig. 2. Comparison of the oxygen K edge X-ray absorption spectra of (a) LiCu_{0.5}Mn_{1.5}O₄ and (b) Li₄Ti₅O₁₂.

tion of a 1s electron to the metal 3d states at the bottom of the conduction band. Transitions to these bands from the 1s core level become dipole-allowed by the admixture of some metal p character to the 3d states via hybridisation. The splitting between the two prepeaks of 1.8 eV agrees quite well with that of the two major L_3 edge structures. Accordingly, the Mn K edge prepeaks are aligned in Fig. 1 with bands A and B. It can be noted that this alignment gives coincidence of the O K edge peak C with the first shoulder of the Mn K edge, reflecting the admixture of Mn p states to this O p–Li p band. Furthermore, the second shoulder and the absorption maximum of the Mn K edge match with, respectively, the bands D and E of the O K edge. It is worth noting that two similar shoulders are observed on the Ti K edge of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [20].

The Cu K edge spectrum and its second derivative reveal a single prepeak below the threshold, two shoulders on the main absorption step and a pronounced maximum above threshold at identical relative energies as the Mn K edge spectrum. Identical shapes of transition metal K edges were also observed for partially Cr and Co substituted manganate spinels [6,7]. The p states of the substituting element mix with the Mn p–O p and Li p–O p bands. In Fig. 1 the Cu K edge spectrum is positioned such that structures C, D, and E match with those of the Mn K edge. The electron configuration $3d^9 4s^1$ of Cu^{2+} lets expect some Cu d density in the conduction band. The position of the prepeak suggests that these states lie in the domain of bands A and B, though apparently somewhat higher than the lowest Mn 3d states, if we take into account the fact that the onset of the Cu prepeak lies at a somewhat higher energy than that of the Mn prepeak and if we further take into account the higher line broadening at the Cu K edge as compared to the Mn K edge.

A more precise localisation of the empty Cu d states is, in principle, possible by considering the Cu L_3 edge, where the lower monochromator and core hole broadenings provide a better spectral resolution. However, due to the low copper concentration, the O K edge spectrum provides no distinctive structure that would allow determining the correct relative position. Thus, the Cu L_3 edge spectrum is placed in Fig. 1 relative to the Cu K edge, by deducting from the latter the known energy difference between the Cu 1s and $2p_{3/2}$ core levels in the copper oxide $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ of 8048.1 eV, given by the Cu $K\alpha_1$ X-ray emission line [25]. Aligned in this way the L_3 white line falls exactly on band B. Moreover, a small hump approximately 2 eV below the white line falls in the vicinity of band A. This result is, however, to be considered with some caution. The experimental errors in the calibration of the Cu K and L_3 absorption edges and of the Cu $K\alpha_1$ emission line sum up to approximately 1 eV. It will be sufficient for the purposes of the present paper to retain that the Cu 3d states form a narrow band at the bottom of the conduction band somewhat above the lowest Mn 3d states.

This experimentally established picture of the conduction band is consistent with the behaviour of the compound under electrochemical reduction. When $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is used as cathode material versus lithium in an electrochemical discharge run, then lithium is inserted into the spinel lattice. This additional lithium is supposed to be ionised to Li^+ due to electron transfer to the conduction band of the host lattice, where the

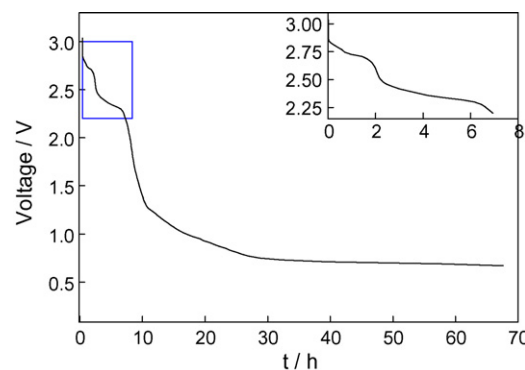


Fig. 3. Galvanostatic discharge curve of $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

electron occupies the lowest available state. Fig. 3 shows the discharge curve of $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$ versus lithium. The first plateau at ca. 2.72 V is observed in a series of spinels of composition $\text{LiNi}_x\text{Cu}_{0.5-x}\text{Mn}_{1.5}\text{O}_4$ ($0 \leq x \leq 0.5$) independently of x , while the second signal at 2.3–2.4 V is observed only in the presence of copper [10]. Thus, the first plateau can be attributed to the $\text{Mn}^{4+}/\text{Mn}^{3+}$ reduction, while the second can be ascribed to the $\text{Cu}^{2+}/\text{Cu}^+$ redox couple, which agrees with our picture of the lowermost part of the conduction band as being composed of Mn 3d states, while the empty Cu 3d band is situated somewhat above them. On further discharge, the electrode shows a complex reduction leading to the pure transition metals as found by XAS in other mixed spinel oxides [26]. These changes of the atomic arrangement induced by lithium intercalation lead to corresponding modifications of the electronic structure, so that the correlation between the discharge curve and the band structure of the starting material is progressively lost.

4. Discussion

While the analysis of chemical shifts of X-ray absorption lines has become a standard technique for the investigation of such redox reactions [6,7,10–12], the exploitation of variations of the spectral shape induced by the structural changes with the lithium insertion/extraction process is still rather scarce due to the limited comprehension of the origin of the various spectral features. Many authors observing changes in the spectral shape attribute them roughly to structural changes without further specifying them. The results and interpretations presented above should now open new possibilities in this field.

The appearance of shoulder C in the K edge X-ray absorption spectra of transition metals is characteristic for spinels containing lithium on tetrahedral sites [20]. It is observed in all transition metal K edge spectra of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [20], pure LiMn_2O_4 [12], and its partially substituted forms, whether the substituent being Cr [6], Co [7,8], Ni [8,10] or Cu, like in the present work. Extraction of lithium should cause this shoulder to disappear.

Corresponding observations were effectively made for pure LiMn_2O_4 [12] and its partially chromium [6] and nickel [10] substituted forms. On the other hand, Amundsen et al. [6] observed an enhanced shoulder C on both the Cr and Mn K edges after chemical lithium insertion via *n*-butyllithium in $\text{LiCr}_x\text{Mn}_{2-x}\text{O}_4$.

This might indicate that at least a fraction of the additional lithium occupies tetrahedral sites within the spinel structure. It has been shown recently that lithium inserted chemically in the spinel $\text{Li}_4\text{Ti}_5\text{O}_{12}$ occupies both octahedral and tetrahedral sites while lithium inserted electrochemically occupies octahedral sites exclusively, leading to a spinel–rocksalt phase transition [27].

The chemical bonds formed by the anion with tetrahedrally coordinated lithium give rise to the easily distinguishable peak C in the O K edge spectrum. The work of several authors shows that this peak disappears effectively when lithium is extracted from LiMn_2O_4 [13,14] while the other absorption peaks are conserved, proving again the common origin of this peak and shoulder C on the transition metal K edges.

5. Conclusion

X-ray absorption spectra of the spinel $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$ were recorded at the Cu K and L_3 , Mn K and L_3 , and O K edges. An alignment of all spectra on a common relative energy scale allowed a coherent interpretation of all spectral features near the absorption threshold and gave an experimental picture of the lowest 20 eV of the conduction band structure of the compound. Emphasis was put on the identification of distinctive spectral features correlated with the presence of lithium in the spinel lattice. A characteristic shoulder in the transition metal K edges and a characteristic peak in the oxygen K edge could be associated with a band of lithium p states mixed with oxygen and transition metal p orbitals. The consequences of lithium insertion/extraction on the intensities of these structures in cation and anion X-ray absorption spectra are discussed. Previous work from the literature studying lithium insertion/extraction by X-ray spectroscopy is found to agree with our expectations. It is shown that the principal points of the conduction band structure calculated for $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [20] can be transferred to similar spinels containing other transition metals than titanium. This improved insight into the origin of the various XANES features provides new possibilities in the study of lithium insertion/extraction processes in spinels.

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