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Oxygen 1s and cobalt 2p x-ray absorption of cobalt oxides*

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Abstract. The oxygen 1s and cobalt 2p x-ray absorption spectra of CoO, Li-doped CoO and LiCoO₂ have been measured with 0.1 eV resolution. The cobalt 2p spectra are analysed with a ligand-field multiplet model and the inclusion of charge-transfer effects is discussed. The oxygen 1s spectra are interpreted as transitions to empty oxygen p states and it is concluded that the effects of correlations in the 3d band possibly are too small to be detectable. The symmetries and the electronic configurations of the cobalt ions in the oxides are determined. It is concluded that, in contrast to for example NiO and La₂CuO₄, the doping-induced states are possibly of ¹A₁ symmetry, which would imply that the quasi-particles have spin $\frac{3}{2}$ and are most likely trapped.

1. Introduction

In this study we focus on the difference in analysis of oxygen 1s and cobalt 2p x-ray absorption spectra (XAS) of a series of cobalt oxides. The final goal is to add to the knowledge of the electronic structure of these oxides and of transition-metal oxides in general. The recent interest in the electronic structure has been partly stimulated by progress in electron and x-ray spectroscopies, which have been made possible as a result of a series of technological innovations. Owing to the increased resolution the theoretical descriptions can be tested in far more detail.

A series of models are currently in use for the interpretation of spectroscopic data related to the electronic and magnetic structure of transition-metal oxides. The main models are schematically given in table 1. Two extreme models are: (1) density-functional theory, mostly treated within the local-density approximation (LDA); LDA treats all electrons alike and the *N*-electron distribution of states obtained from a ground-state calculation is used for comparison with x-ray absorption spectra; (2) the ligand-field multiplet (LFM) approach, which explicitly accounts for the 3d electrons only. LDA is empirically adequate for the analysis of weakly correlated systems and for those experiments which are not too sensitive for correlation effects.

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Up to now, oxygen 1s XAS spectra of transition-metal oxides have been analysed with LDA, preferably with the final-state core hole included. The reason is that, apart from the 3d band, the spectrum probes rather delocalized bands. Ligand-field multiplet analysis is adequate for those experiments which stimulate action mostly of the 3d electrons, such as dd transitions and metal 2p x-ray absorption spectra. Ligand-field multiplet analysis works best for strongly correlated 3d bands. Both LDA and LFM calculations can be performed in a rather routine and straightforward manner.

Table 1. Overview of models currently in use for the interpretation of experiments related to electronic structure of transition-metal oxides.

Model	Electrons	Empirically adequate	Ref.
Band structure (LDA)	All, bands	Oxygen 1s XAS	[1,2]
Ligand-field multiplet (LFM)	Only 3d, local (incl. multiplets)	dd transitions 2p XAS	[3,4] [5-7]
Anderson impurity (CI)	Local 3d, plus band	2p XPS, PES, IPES	[8-10]
CI+LFM	Local 3d, plus band (incl. multiplets)	2p XPS	[11]
LDA+SIC	Test of localization	Band gap, moment	[12]
LDA+U	including U in LDA		[13]

Other more complex, though, in principle, more accurate and general, models are the short-range model Hamiltonians like the Anderson impurity model and LDA calculations with discontinuous potentials. The short-range models, in either the cluster mode or the impurity mode, are used mainly to give a description of the spectral shapes of photoelectron spectroscopy (PES), inverse photoelectron spectroscopy (IPES) and x-ray photoelectron spectroscopy 2p (XPS) experiments, yielding empirical values of the Coulomb repulsion (U_{dd}) and the charge-transfer (CT) energy (Δ). The LDA calculations using discontinuous potentials, under the heading of 'self-interaction correction' (SIC) [12] and LDA+U [13] aim at an *ab initio* method for the description of the electronic structure of transition-metal oxides. The results obtained so far give good agreement with experimental band gaps and magnetic moments, though many questions remain with respect to their validity as well as the obtained density of states. The short-range model including multiplets is becoming more and more effective and can possibly replace the ligand-field multiplet analysis for 2p XAS particularly for covalent materials [9,11].

2. Experimental details

The x-ray absorption spectra have been measured at beamline U4B of the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. The monochromator, the AT&T-built DRAGON [14], has been used with a resolution of about 0.1 eV full width at half-maximum at the oxygen 1s edge at 530 eV. The energy scale is calibrated by measuring the titanium 2p and oxygen 1s spectra of

SrTiO_3 and TiO_2 , which have been compared with data published previously [1, 6]. The spectra were recorded in total electron yield mode.

With electron yield methods it is not possible to determine absolute absorption cross sections. To present the spectra, a constant background absorption has been subtracted and the electron yield intensity has been normalized to unity for all spectra taken [1, 15]. The samples, sintered pellets, were scraped with a ruby file to ensure surface cleanliness. The pressure was 5×10^{-10} Torr. To test the reproducibility of the results, the samples were measured at two different sample positions and with renewed scraping.

The $\text{Li}_{0.1}\text{Co}_{0.9}\text{O}$ and $\text{Li}_{0.2}\text{Co}_{0.8}\text{O}$ samples are prepared by grinding together the proper amounts of Li_2CO_3 and CoO . The pressed powders were kept at 950°C under a dry oxygen flow for 16 h, reground and kept at 1050°C in argon atmosphere for 24 h. By fast cooling the metastable high-temperature phases were preserved. X-ray diffraction showed a homogeneous phase with less than 1% of LiCoO_2 . The Li content found from the lattice parameter (table 2) was consistent with a wet chemical analysis [10, 16]. The LiCoO_2 sample was prepared from Li_2CO_3 and CoO by keeping the pressed powders at 950°C in dry oxygen for 16 h. X-ray diffraction showed a homogeneous single-phase sample.

Table 2. Compounds: unit-cell parameters and symmetry.

Compound	Symmetry	Unit-cell parameters (Å)	Ref.
CoO	O_h^1	$a = 4.26$	[10]
$\text{Li}_{0.2}\text{Co}_{0.8}\text{O}$	O_h^1	$a = 4.20$	[16]
LiCoO_2	$D_{3d} (R\bar{3}m)$	$a = 2.82, c = 14.05$	[10]

3. Results and interpretation

Figure 1 shows the cobalt 2p x-ray absorption spectra of the lithium cobalt oxides. Two structures are visible related to respectively the L_3 and L_2 edge, split by the 2p spin-orbit coupling.

The spectra show a large amount of fine structure, which is related mainly to the multiplet structure of the final state. The spectra of 10% and 20% lithium-doped CoO are similar to that of pure CoO. The spectral shape of LiCoO_2 is markedly different, which is an indication of a different symmetry state. The overall shift to higher energy is a mark of the higher valency, which has, for example, been demonstrated for a series of manganese compounds in [17].

Figure 2 shows the oxygen 1s x-ray absorption spectra of the lithium cobalt oxides. The structures at threshold relate to the transitions of oxygen p character hybridized with cobalt 3d states and above 533 eV to oxygen p character in the cobalt 4sp band, as has been discussed in detail in [1]. In contrast to the metal 2p edges the effects of lithium doping are directly visible as the growth of a peak at threshold. Again the LiCoO_2 spectrum is markedly distinct from the others, which is an indication of a different crystal structure.

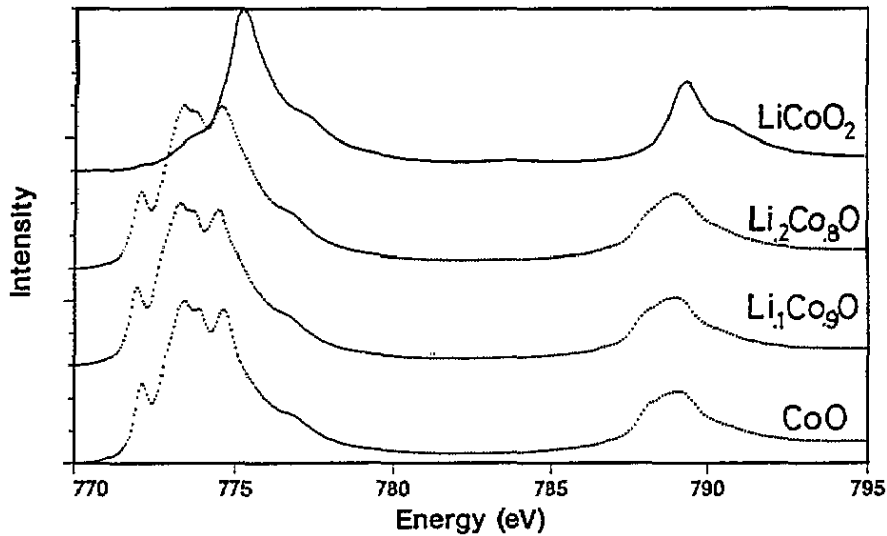


Figure 1. The cobalt 2p x-ray absorption spectra of CoO, $\text{Li}_{0.1}\text{Co}_{0.9}\text{O}$, $\text{Li}_{0.2}\text{Co}_{0.8}\text{O}$ and LiCoO_2 .

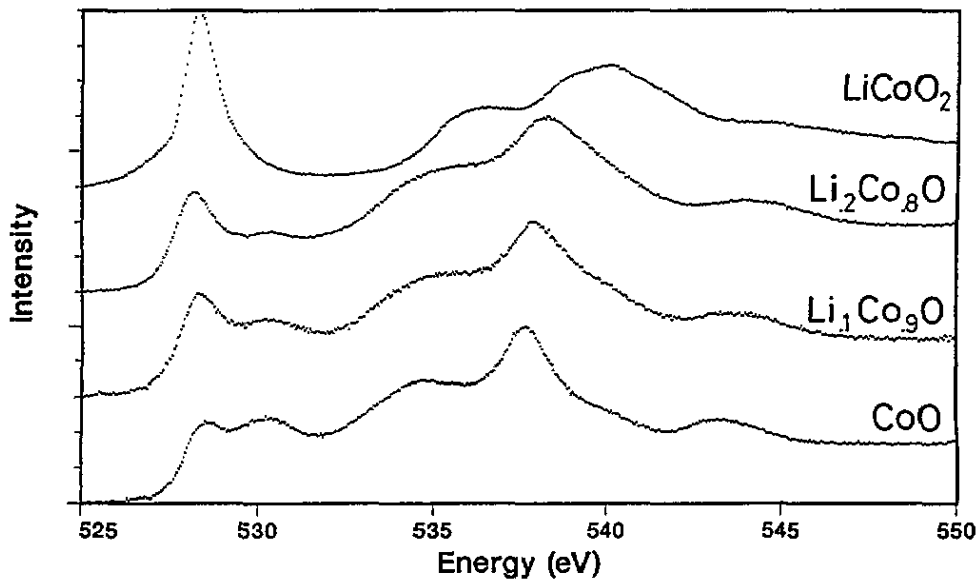


Figure 2. The oxygen 1s x-ray absorption spectra of CoO, $\text{Li}_{0.1}\text{Co}_{0.9}\text{O}$, $\text{Li}_{0.2}\text{Co}_{0.8}\text{O}$ and LiCoO_2 .

3.1. CoO

The electronic structure of CoO has been discussed on the basis of the Anderson impurity model [10, 18]. Recently Okada and Kotani included multiplet effects, for

the analysis of both 2p XPS and 2p XAS spectra [11]. They show that within the charge-transfer model, 2p XPS is dominated by hybridization effects, whereas 2p XAS is dominated by multiplet effects. The important merit of this study is that the combined charge-transfer plus multiplet approach is able to simulate both spectra within a unified model.

A problem that still has to be solved is the reliability of the parameters as used in the various short-range models. Because of this uncertainty, we prefer to analyse 2p XAS with a ligand-field multiplet model, neglecting charge-transfer effects. In the ligand-field multiplet model, the ground state of CoO is described as $3d^7$. The electrostatic interactions (Slater integrals) determine the 4T_1 symmetry of the ground state. From the optimization of the spectral shape of the $3d^7[{}^4T_1] \rightarrow 2p^53d^8$ transition, an effective cubic crystal field strength of 1.05 (± 0.05) eV is found to give the best agreement with experiment. A T_1 symmetry ground state is susceptible for 3d spin-orbit coupling [19] and the effect of 3d spin-orbit coupling on the spectral shape is studied in figure 3.

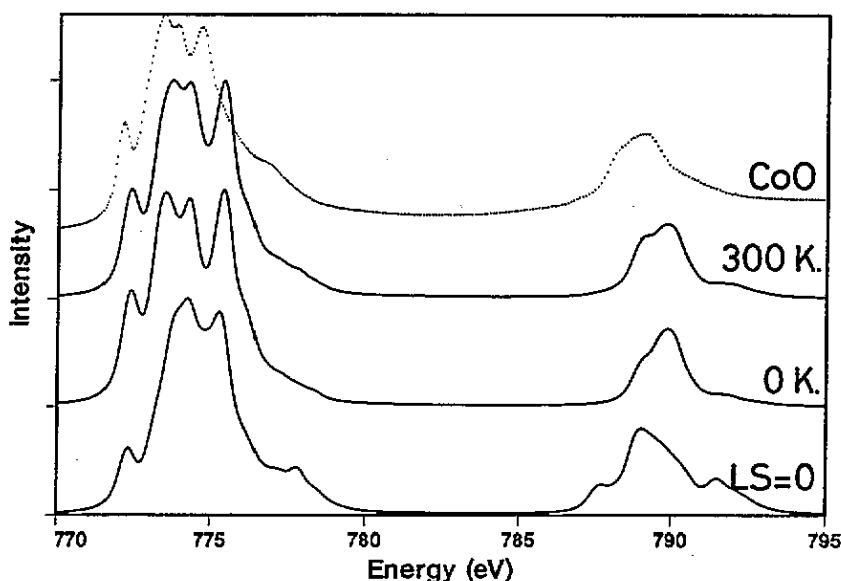


Figure 3. The cobalt 2p x-ray absorption spectrum of CoO, compared with ligand-field multiplet calculations of the $3d^7[{}^4T_1] \rightarrow 2p^53d^8$ transition. In the bottom spectrum 3d spin-orbit coupling is neglected. The two middle spectra are calculated with the atomic 3d spin-orbit coupling for respectively 0 and 300 K.

The ligand-field multiplet consists of discrete lines [6, 7] and to compare with experiment they have been broadened with a Lorentzian of 0.1 eV for the L_3 edge and 0.3 eV for the L_2 edge in order to simulate the lifetime broadening. Moreover the spectra are convoluted with a Gaussian broadening of 0.1 eV in order to simulate the experimental resolution. The spectra obtained as such have been normalized to unity. For clarity it is noticed that this implies that no information concerning absolute cross sections can be obtained and as such only the spectral fine structure is simulated.

The calculated spectrum in which the 3d spin-orbit coupling is neglected is given at the bottom. It appears that especially in the L_2 region the agreement with the experimental spectrum (given at the top) is not good. For the second and third spectra from the bottom the 3d spin-orbit coupling has been included with the same strength as in Co^{2+} atoms. The splittings induced by the 3d spin-orbit coupling are of the order of 100 meV and the simulations are given for 0 and 300 K respectively. It is clear that if 3d spin-orbit coupling is included a better agreement is obtained. The solid-state value of the 3d spin-orbit coupling could in principle be determined accurately from a series of temperature-dependent experiments.

The remaining discrepancy, mainly the too wide L_3 spectral region, is related to the neglect of charge transfer [11]. A compression of the spectrum cures these discrepancies, which shows that the effects of charge transfer are not too disturbing in the present case.

3.2. The oxygen 1s x-ray absorption spectrum of CoO

As the model for the analysis of the oxygen 1s x-ray absorption spectra we will use LDA band-structure calculations. A transition is made from the 1s core level to unoccupied oxygen p states, which are hybridized with the metal 3d as well as 4sp states, and a mapping of the oxygen p character is obtained.

What can be the effects of electron correlation? To answer this question, we can first remark that electron correlation effects are only to be considered in the 3d band. For this 3d band an answer will be sought using the charge-transfer model as a guide. The ground state of CoO can be written as $3d^7 + 3d^8\bar{L}$. In the oxygen 1s x-ray absorption process an electron is excited to a state of oxygen p character, or in other words it fills a ligand hole state. In [10] the oxygen 1s core hole has been neglected and under that approximation the final state of oxygen 1s x-ray absorption is identical to that of IPES. The oxygen 1s XAS spectrum is then given by the transition matrix elements related to $3d^8\bar{L} \rightarrow 3d^8$. The cluster calculation of [10] shows a distinct structure at about 4 eV from the first peak. This peak is not detectable as a distinct peak in the experimental spectrum and from this we conclude that a closer study of the model is needed in order to solve this discrepancy. The basic problem is the identification of final states of oxygen 1s XAS and IPES. The creation of the core hole will affect the effective charge-transfer parameters to be used in the final state [20].

3.3. LiCoO_2

Before discussing the complicated Li-doped CoO samples, we first focus on the end member LiCoO_2 . LiCoO_2 has a well defined crystal structure and all trivalent cobalt ions are in equivalent sites. Again the cobalt 2p spectrum is analysed on the basis of the ligand-field multiplet model and the oxygen 1s spectrum is analysed with LDA calculations.

Figure 4 compares the cobalt 2p spectrum of LiCoO_2 with a ligand-field multiplet calculation of the $3d^6[{}^1A_1] \rightarrow 2p^53d^7$ transition. The main features are reproduced and the trivalent cobalt ions can be assigned to have low-spin 1A_1 symmetry. A charge-transfer model calculation for LiCoO_2 gives a ground state that is of strongly mixed $3d^6 + 3d^7\bar{L}$ character [10]. Within this charge-transfer model the

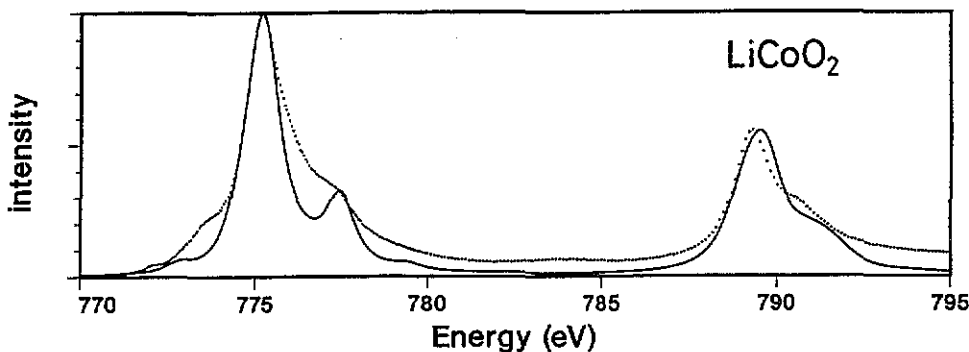


Figure 4. Cobalt 2p x-ray absorption spectrum of LiCoO_2 (dotted curve) compared with a ligand-field multiplet calculation of the $3d^6[{}^1A_1] \rightarrow 2p^53d^7$ transition (full curve).

overall transition is



It will be most interesting to see if a calculation that includes both multiplets and charge-transfer effects, like the one for CoO in [11], is able to reproduce the spectral features in more detail.

The oxygen 1s x-ray absorption spectrum of LiCoO_2 shows a sharp single peak at threshold. It is clearly separated from the other structures. For LiCoO_2 an accurate LDA band-structure calculation has been performed [2] and figure 5 shows a comparison with it. The ground-state calculation of the oxygen p projected density of states overestimates the intensity of the leading peak. If a core hole is included in a supercell calculation, the intensity of the first peak is reduced. It can be concluded that the overall agreement between the 1s x-ray absorption spectrum and the LDA band-structure calculation is good. In this respect it must be remarked that the 1A_1 symmetry of the initial state is special as the band gap is positioned in between the filled t_{2g} band and the empty e_g band, which is a fortunate case for one-electron models to work.

3.4. Li-doped CoO

We will now consider the effects of lithium doping in CoO . Given a compound $\text{Co}_{1-x}\text{Li}_x\text{O}$, the assumption can be that lithium is monovalent and goes substitutionally into the octahedral positions. Within a sample with 10% lithium, 12.5% of the cobalt ions are formally trivalent. The following questions concerning the trivalent cobalt ions can be asked: (1) what sites do they occupy, (2) what is their ground-state symmetry and (3) what is their electronic configuration?

For the site occupancy the most obvious solution is octahedral Co^{3+} sites, substituting a divalent cobalt ion. Alternative solutions are that part of the trivalent cobalt ions go into interstitial tetrahedral sites. This alternative is suggested by theoretical studies of defect structures in the Co_{1-x}O system [21]. Also experimental data on Fe_{1-x}O and Co_{1-x}O pointed to tetrahedral cobalt vacancies of different types [22]. For the Li-doped systems it is possible that, similar to the defect structures in non-stoichiometric Co_{1-x}O , aggregates of trivalent cobalt ions with vacancies and/or complexes with the lithium ions will be formed.

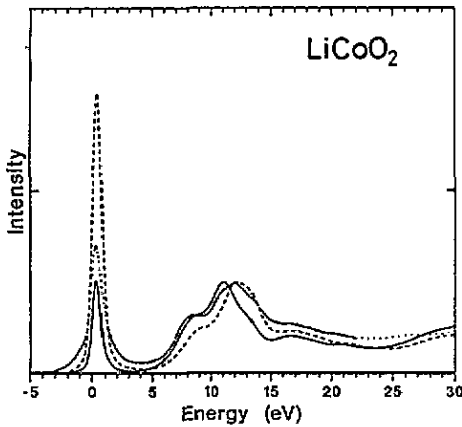


Figure 5. Oxygen 1s x-ray absorption spectrum of LiCoO_2 (dotted curve) compared with an LDA band-structure calculation. The full curve gives the density of states as calculated for the ground state. The broken curve relates to density of states after inclusion of the core hole (reproduced from [2]).

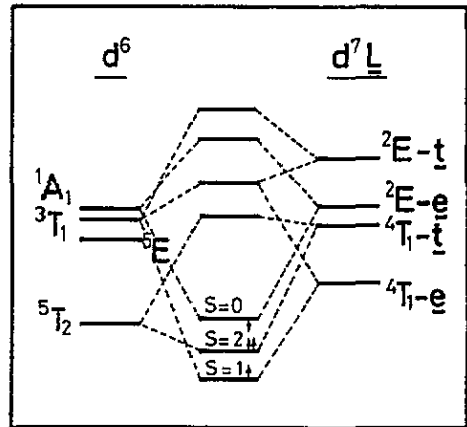


Figure 6. A possible energy diagram for the ground state of the lithium-doped states. The energy positions of the $3d^6$ states are taken from a Hartree-Fock calculation for a cubic crystal field strength of 1.2 eV. The relative energy positions of the respective $3d^7\bar{L}$ states are determined by addition of a ligand hole of respectively t_{2g} symmetry (\bar{t}) or e_g symmetry (\bar{e}) to the $3d^6$ -states of respectively 4T_1 symmetry and 2E symmetry.

The possible symmetries of octahedral sites are the 5T_2 high-spin state with the configuration $(t_{2g}^+)^3(e_g^+)^2(t_{2g}^-)^1$, and the 1A_1 low-spin state with configuration $(t_{2g}^+)^3(t_{2g}^-)^3$. An additional possibility is the 3T_1 intermediate spin state with the configuration $(t_{2g}^+)^3(e_g^+)^1(t_{2g}^-)^2$. In a Tanabe-Sugano diagram a direct transition from the high-spin to the low-spin state is observed and in this (ionic) picture the 3T_1 never constitutes the ground state [23]. However, it has been argued that this 3T_1 spin state could be the ground state because of its larger stabilization due to charge-transfer effects [10]. A diagram of all low-lying $3d^6$ and $3d^7\bar{L}$ states is given in figure 6. In the diagram an idealized situation is sketched in which the intermediate spin state 3T_1 is lowest in energy, mainly due to the relatively low energy position of its main $3d^7\bar{L}$ contribution. For the electronic configuration we note that the weight of the $3d^7\bar{L}$ states is higher than for divalent cobalt due to the increased covalency. A quantitative study into this matter would be welcome.

An important variable is the space that the different symmetries occupy. A cobalt ion of 5T_2 and 3T_1 symmetry will be slightly smaller than the original divalent cobalt ion, but a cobalt ion of 1A_1 symmetry has no e_g electrons and consequently occupies only little space, as is confirmed by the crystal structure of LiCoO_2 . It is found that with increasing lithium concentration the cell parameter decreases only slightly up to miscibility gap at $x_{\text{Li}} = 0.2$ [10], suggesting the doped states to have 3T_1 symmetry. $\text{Li}_x\text{Co}_{1-x}\text{O}$ is not stable for $x > 0.2$ because above this lithium concentration the small cation size of the 1A_1 symmetry state causes stress on the Li-doped CoO crystal and the crystal tends to phase segregate to LiCoO_2 and CoO (+ Li).

By analysing the spectral shape of the cobalt 2p edges an answer with respect to the symmetry of the Li-doping-induced cobalt ions will be sought. The cobalt 2p edges

in figure 1 show on first observation that the spectra hardly change upon doping. The spectra are still dominated by the $3d^7 \rightarrow 2p^5 3d^8$ transition of CoO. Figure 7 gives the difference spectrum of $\text{Li}_{0.2}\text{Co}_{0.8}\text{O}$ with the CoO. The difference spectrum reveals the existence of extra intensity at about 776 eV, which is an indication for the presence of trivalent cobalt ions. The peak position is equal to that in the LiCoO_2 spectrum, which leads one to suggest that the states have 1A_1 symmetry, in contrast to the conclusion from the cell parameter variation.

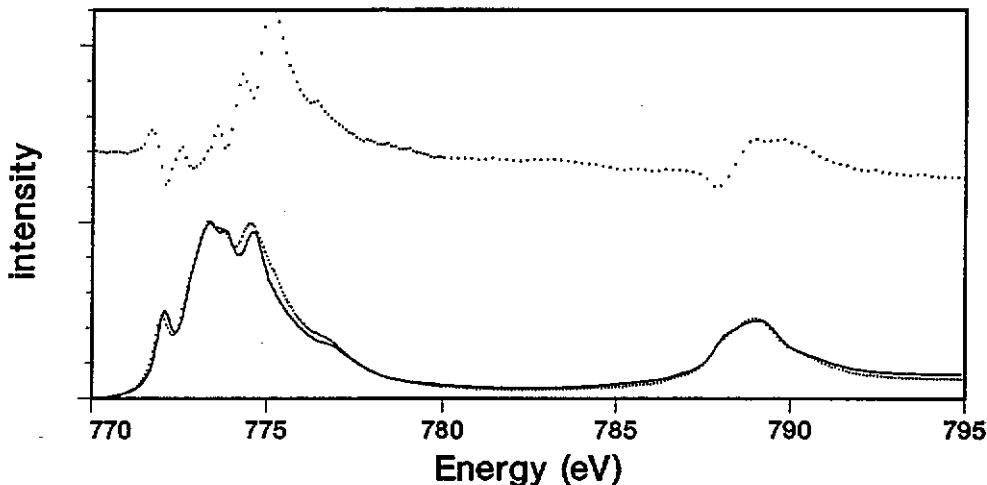


Figure 7. Difference spectrum of cobalt 2p x-ray absorption spectra of CoO (full curve) and $\text{Li}_{0.2}\text{Co}_{0.8}\text{O}$ (dotted curve). The top spectrum is the difference spectrum, which is smoothed with only half its points plotted.

In the oxygen 1s spectra (figure 2) the most remarkable change is the increase of intensity at the position of the first peak. Comparison with the LiCoO_2 spectrum again shows that the intensity increases at the position of the sharp peak of LiCoO_2 , adding to the evidence that the doped states have 1A_1 symmetry. In the case of 3T_1 symmetry the $(t_{2g}^+)^3(e_g^+)^1(t_{2g}^-)^2$ division of the 3d electrons does not agree with the existence of a single peak at threshold, though some precaution must be taken because the degree of observable structure in the oxygen 1s spectra does not entirely exclude this alternative.

In contrast to the $\text{Li}_x\text{Ni}_{1-x}\text{O}$ system [24], the peak related to Li-doping, is not growing in the gap but instead close to the energy position of the lowest unoccupied state in CoO, which can only be explained easily if the Co^{III} sites are attributed to 1A_1 symmetry. An important difference between the 3T_1 and 5T_2 symmetries and the 1A_1 symmetry is that the latter does not have $S = \frac{1}{2}$ hopping with the divalent cobalt ions, but can only couple by a $S = \frac{3}{2}$ quasi-particle [25]. Moreover the 1A_1 states are dominated by $3d^6$ character in contrast to the Ni^{III} impurity states in $\text{Li}_x\text{Ni}_{1-x}\text{O}$, which are dominated by $3d^8 \underline{L}$ character. This can be qualitatively understood as follows: a highly covalent Ni^{III} system will form a stable $3d^8(\underline{L})$ like situation. A Co^{III} system will have the same tendency but the alternative of a more stable low-spin state can form a state dominated by $3d^6$ like configuration.

4. Concluding remarks

4.1. The interpretation of the x-ray absorption spectra

The cobalt 2p x-ray absorption spectra can be analysed in detail with a ligand-field multiplet model. Some improvement might be obtained if charge-transfer effects are also included in an accurate manner, but obstructions to the actual inclusion of charge-transfer effects for the analysis of x-ray absorption spectra are that for oxides the effects are small and also the model parameters, specifically the hopping, are modified in a largely unknown manner in the final states of 2p XPS, valence bond (VB)-PES and 2p XAS.

The oxygen 1s spectra do show large similarities to the oxygen p projected density of states as obtained from one-electron models. The influence of correlation effects on the 3d part of the spectrum is found to be rather small, possibly too small to be detectable.

4.2. The symmetry of the cobalt ions

From the interpretation of the cobalt 2p and oxygen 1s x-ray absorption spectra we come to the conclusion that CoO contains divalent cobalt ions with 4T_1 symmetry. This configuration is affected by the 3d spin-orbit coupling and the actual ground state is of E_1 symmetry. The strength of the 3d spin-orbit coupling cannot be determined accurately from the present data but is found to be of the same order as the atomic value. LiCoO_2 is found to contain trivalent cobalt ions with 1A_1 symmetry. For the spectra of the Li-doped CoO samples the changes in the shape of the spectra can be best explained assuming the trivalent cobalt ions to have 1A_1 symmetry. However other observations, for all the cell parameter variation, indicate 3T_1 symmetry. We have found no definitive answer to this question.

4.3. The electronic configuration of the cobalt ions

From the analysis in [10] it is found that CoO has about 80% $3d^7$ and about 20% $3d^8\bar{L}$ character. This is consistent with the finding that the spectral shape of its cobalt 2p x-ray absorption spectrum shows good agreement with a ligand-field multiplet calculation for the $3d^7$ configuration. In contrast for LiCoO_2 it has been found that the contributions of $3d^6$ and $3d^7\bar{L}$ are both about 45%. In the assignment of the Li-doping-induced states as having 1A_1 symmetry, the divalent cobalt ions are equivalent to those in CoO, and the trivalent ions to LiCoO_2 .

4.4. The miscibility gap in the Li-doped materials

The miscibility gap is a direct consequence of the much smaller ion size of the low-spin trivalent cobalt ions (compared to the high-spin divalent cobalt ions). This difference in ion-size causes apparently too much stress for $x \geq 0.2$ and, for these values of x , phase separation to LiCoO_2 and CoO (+Li) occurs. This does not directly answer the question for the concentration range between 0.0 and 0.2 and in principle allows for both the 1A_1 and the 3T_1 solutions.

4.5. The impurity states induced by Li doping

It has been found that hole doping in NiO, La₂CuO₄, MnO and LaFeO₃ creates impurity states in the band gap. This phenomenon has been explained consistently if a ground state dominated by 3d⁸ \underline{L} character is assumed (in the case of trivalent nickel). The trivalent nickel ions belong to the class of ions with a negative charge transfer and its related divalent ion belongs to the class of so-called charge-transfer insulators, which have a (considerably) smaller charge-transfer energy than Coulomb repulsion energy. From analogy it could be inferred that also hole doping in CoO would create similar impurity states. These impurity states have to be coupled to their parent states, which have high-spin 4T_1 character. With $S = \frac{1}{2}$ quasi-particles this makes possible triplet or quintet states, the latter of which can be excluded from magnetization measurements. However, apart from these states, the trivalent cobalt ions have an alternative not available for their nickel and copper analogues, that is to change their symmetry to 1A_1 . This state couples only via $S = \frac{3}{2}$ quasi-particles to its divalent parent states with the consequence that the quasi-particles are likely to be self-trapped. In other words the 1A_1 symmetry doped states in CoO are of a rather different nature than, for example, the impurity states in NiO.

Acknowledgments

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