NEXAFS EXPERIMENT AND MULTIPLE SCATTERING CALCULATIONS ON KO₂: EFFECTS ON THE π RESONANCE IN THE SOLID PHASE

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Abstract

The high-energy resolution O K-edge absorption NEXAFS spectrum has been measured for *in situ* prepared potassium superoxide. The experimental data have been analyzed in detail by multiple scattering calculations using self-consistent field potentials. In particular the so-called π resonance at rising edge, which presents a double peaks structure, has been totally resolved and reproduced by the calculations. This analysis indicates that the grown material is arranged in a KO₂ structure with an O-O distance between 1.31Å and 1.34Å. Moreover, the calculation demonstrates both a complete ionic character of the bound between the O^{2-} anion and the K atoms and a strong interaction between the anion and the solid-state matrices.

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Introduction

The interest in the oxygen interaction with simple systems is related to the understanding of the early stages of molecular dissociation and in particular of the oxidation processes of surfaces.

The oxidation of alkali metals has being attracted much interest due to the properties of these metals as promoters of many surface reactions. The simple electronic structure of alkali atoms facilitates the investigation of the atomistic aspects of the oxidation process. The alkali-oxides phase-diagrams [1] indicate that the interaction of oxygen with alkali metals leads to the formation of different oxide species, that contain from the atomic O^{2-} to molecular O_2^- and O_2^{2-} anions. A systematic study of these compounds makes it possible to monitor the geometrical distortion of the molecular bond and the changes of the electronic properties due to the interaction with the solid matrices.

Previously NEXAFS studies [2,3] of the O K-edge of Cs oxides found a considerable distortion of the O-O distance with respect to the free ion case in the CsO_2 compound, contrary to the Cs_2O_2 system that results slightly affected by the solid state interaction.

Pure forms of different potassium oxides are more difficult to prepare than the cesium compounds. A simple exposure of K thin film to oxygen leads to a mixture of different molecular ions [1]. Nevertheless pure KO_2 system can be obtained [4] following a different growth method that is described in the experimental section.

We present here the oxygen K-edge NEXAFS study of the pure phase system performed at High Energy Resolution. The experimental data have been analyzed on the basis of *"ab initio"* Multiple Scattering (MS) calculations using potentials and charge densities generated by self-consistent field (SCF) procedure [5]. The comparison between experimental data and MS calculations indicates that the grown material is in the pure $K^+O_2^-$ phase with an O-O distance ranging between 1.31Å and 1.34Å, i.e. a distance larger than the value in the free anion (1.29 Å). Our analysis excludes both different structural models and fractional charge transfer from K atoms to O anions.

Moreover, the so-called π resonance feature, which is located below the rising edge due to the transitions to the continuum levels, has been analyzed in details. This has a fine structure formed by two peaks. Special care has been taken in measuring the π resonance energy range in order to obtain the best signal to noise ratio. Although the polarization dependence analysis indicates a π character of this resonance, the large energy splitting shows a strong interaction between the anion and the solid state matrices.

Experimental

The experiment was performed at the VUV beam line of ELETTRA (Italy). Near-edge X-ray absorption fine structure (NEXAFS) measurements were performed in the Auger Yield electron mode of detection, with the sample held at 120 K. The photon energy resolution was below 0.2 eV at the O K-edge [6]. The base pressure of the experimental chamber was about 8×10^{-10} mbar.

Potassium was evaporated from carefully outgassed SAES getter chromate sources onto a clean substrate (Si (100) and polycrystalline Cu). The thickness of alkali metal films was calibrated

from a quantitative analysis of the XPS peak intensity of the K 2p and a substrate peak (Si 2p, Cu 3p) as a function of the time of exposure.

The compound has been grown *in situ*, directly on the clean substrates or on the K film by means of deposition of K in oxygen atmosphere, $p_{O2} \geq 5 \ 10^{-5}$ mbar. A subsequent annealing at 400K was performed in order to get a pure superoxide thin film [4]. These procedures lead to the formation of pure KO_2 species. XPS measurements of the O 1s core level performed *in situ*, showed only one component with a binding energy of 534.0 eV, confirming the presence of only one pure phase, in agreement with Ref. [4]. We have performed the XAS measurements at different incident angles. The resulting spectra are independent to such angle showing the polycrystalline nature of the grown compound.

The experimental spectra have been normalized to the incident photon flux (I_0), which has been evaluated by the drain current of a copper grid simultaneously measured with the experimental points. The energy range of the π resonance (shown in the inset of figure 1) has been carefully measured summing up several scans and increasing the acquisition time of single energy point.

The use of different substrates for growing the KO_2 films did not affect the NEXAFS spectra.

Results and discussion

Fig. 1 shows the normalized experimental NEXAFS data at the oxygen K-edge for a sample grown by the method described in the previous section. The inset shows in detail the first feature, the so-called π -resonance that presents a double-peak structure. Using photoemission spectroscopy we have found a value of the oxygen 1s binding energy of about 534 eV in agreement with the fact the binding energy of the superoxide anion O_2^- in alkali compounds has larger values than the binding energy of the other oxygen species O_2^{2-} and O^{2-}. In particular, the XPS spectrum (not shown here for brevity) exhibits a strong single peak at about 534 eV and a very weak peak at about 530.5 eV related to the peroxide species. The ratio of the area under the peak is about 16 indicating an almost pure superoxide phase, in agreement with the results reported in Ref. [4] and Ref. [7].

The O K-edge spectrum for the KO_2 system shows a sharp feature at 531.8 eV and a group of three features between 534 and 545 eV. This spectrum is similar to the one of CsO_2 system. In this last case SCF-MS calculations [2,3] have assigned π-like and σ-like characters to the resonances at about 531 eV and 537 eV respectively.

In Fig. 2 the comparison between the experimental spectrum and a set of MS calculations is reported. The energy step is 1.3 eV in this case. The theoretical spectra are obtained by changing the O-O distance in the central oxygen molecule conserving the crystal structure. The atomic cluster used in the calculations is formed by 82 atoms around the absorber and it has been built following the KO_2 symmetry with the lattice constants given by a= 4.03Å c=6.69Å [7]. The simulations have been performed by using the programs developed by the theory group of the LNF Laboratories **[5]** within the muffin-tin approximation for the shape of the potential. The exchange and correlation part has been calculated on the basis of Hedin-Lundqvist approximation. Following the same method used in the cesium case, the central O_2^- potential has been calculated for each cluster by SCF method imposing the formal valence of the anion and the presence of the core hole. Subsequently this potential has been embedded in the total cluster to perform the whole calculation [3,8].
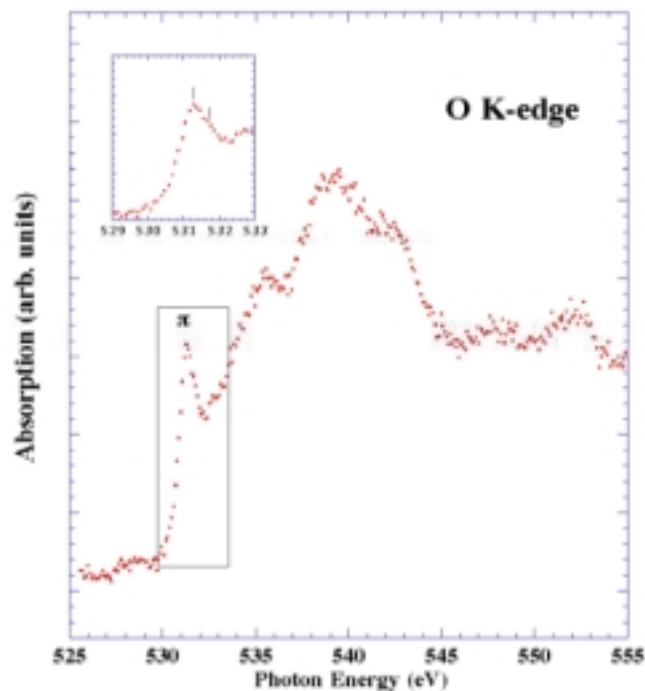
Figure 1. Oxygen K-edge NEXAFS spectrum of the sample grown by codeposition of oxygen and potassium. In the inset the π resonance region is reported in detail.
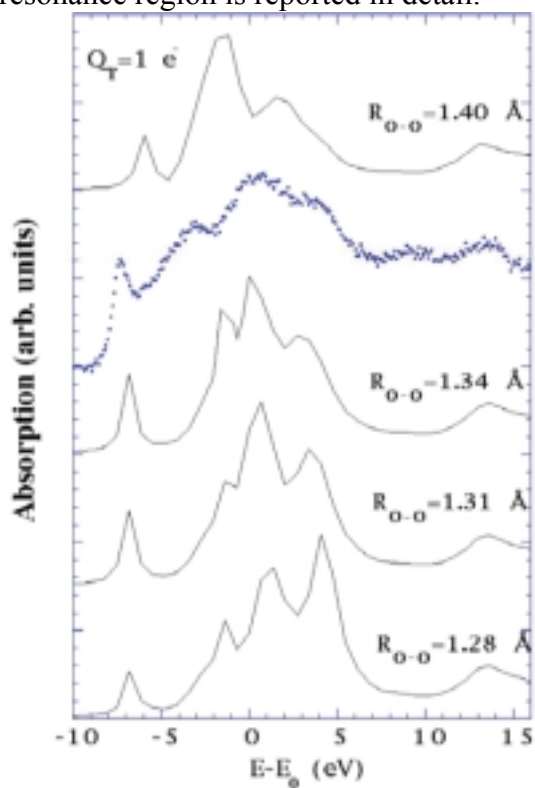

Figure 2. Oxygen K-edge SCF-MS calculations (solid lines) with O-O distance in the KO2 model structure (cluster of 83 atoms) as a parameter, compared with the NEXAFS of the codeposited system (dotted line).

All the structures present in the experimental spectrum are well reproduced by the calculation using the atomic cluster described before. This fact clearly indicates that in the film grown by co-deposition the structure of the potassium superoxide dominates in agreement with the XPS results. The O-O distance changes strongly affect the energy separation and relative intensities of the different features present in the simulations. We have found that the best accordance with the experimental spectrum is achieved for an O-O distance between 1.31Å and 1.34Å. This value is bigger than the one of the free anion species but lower than in CsO_2 case.

The polarization analysis of the features between 534 and 545 eV indicates that the central peak at about 540 eV is dominated by the z component, i.e. parallel to the intermolecular axis, of the total cross section. This feature can be therefore identified as a σ resonance. Notice that for an O-O distance of 1.40 Å the σ resonance becomes prominent and more similar to the CsO_2 case. The other two peaks at about 536 and 547 eV are formed by a mixture of xy and z-polarization components indicating a strong contribution of the atoms far from the absorber anion.
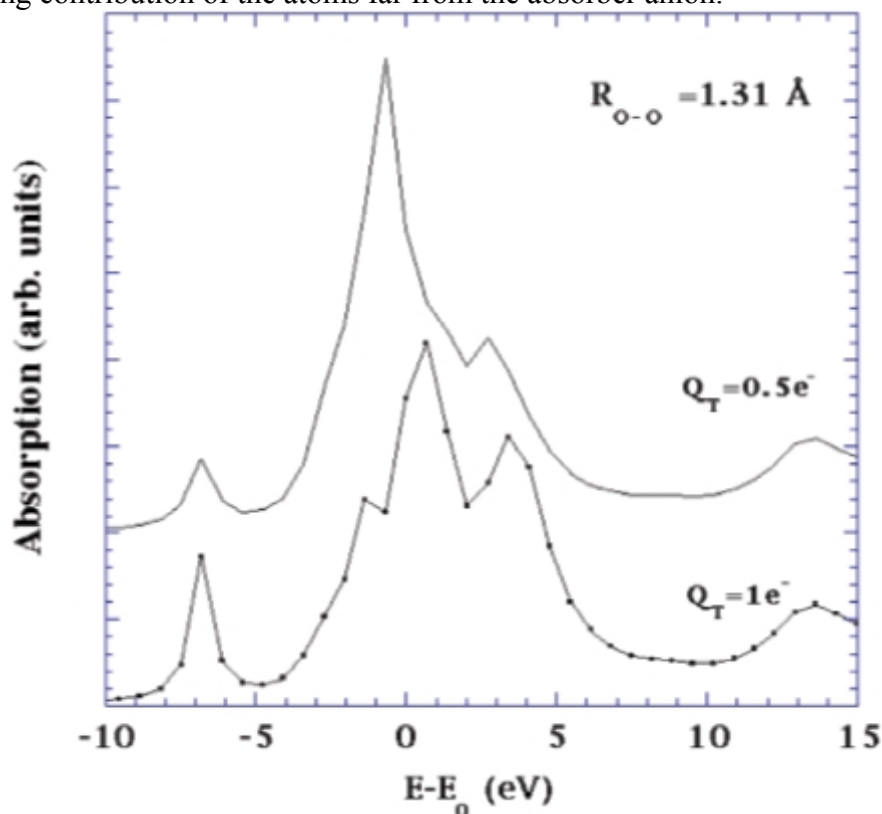

Figure 3. Oxygen K-edge SCF-MS calculations for an O-O distance of 1.31 Å and two different charge transfer amounts: $Q_T = 1\ e^-$ and $Q_T = 0.5\ e^-$.

In Fig. 3 we show the comparison between two SCF calculations performed with different charge transfer amount Q_T. Both correspond to the cluster with an O-O distance of 1.31 Å. Clearly the whole low energy region is strongly perturbed for a charge transfer amount that goes from $Q_T = 1\ e^-$ to $Q_T = 0.5\ e^-$. In particular, in the $Q_T = 0.5\ e^-$ case the σ resonance moves towards lower energies and the peak at –4 eV in the figure, which corresponds to the experimental feature at 536 eV, is completely absent. This last result is in contrast with the experimental findings, as already reported

in the Cs-oxides case [3]. This is not a surprising due to the strong ionic character of these compounds.

The complete discussion about the resonances at about 531 eV is reported in the next paragraph.

The π resonance

In Fig. 4 the high resolution O K-edge NEXAFS spectrum of KO_2 in the pre-edge region is presented. In order to test the doublet nature of the π resonance we performed several fits using both one and two lorentzian function and different backgrounds. One example of a doublet fit is also reported in the figure. The two lorentzian functions are separated of about 0.5 eV. It results that the fits obtained with two lorentzian is always better than the one obtained by a single function whatever background shape is used. This result clearly shows the presence of two peaks in this energy region, in contrast with a simple interpretation based on molecular orbital scheme.
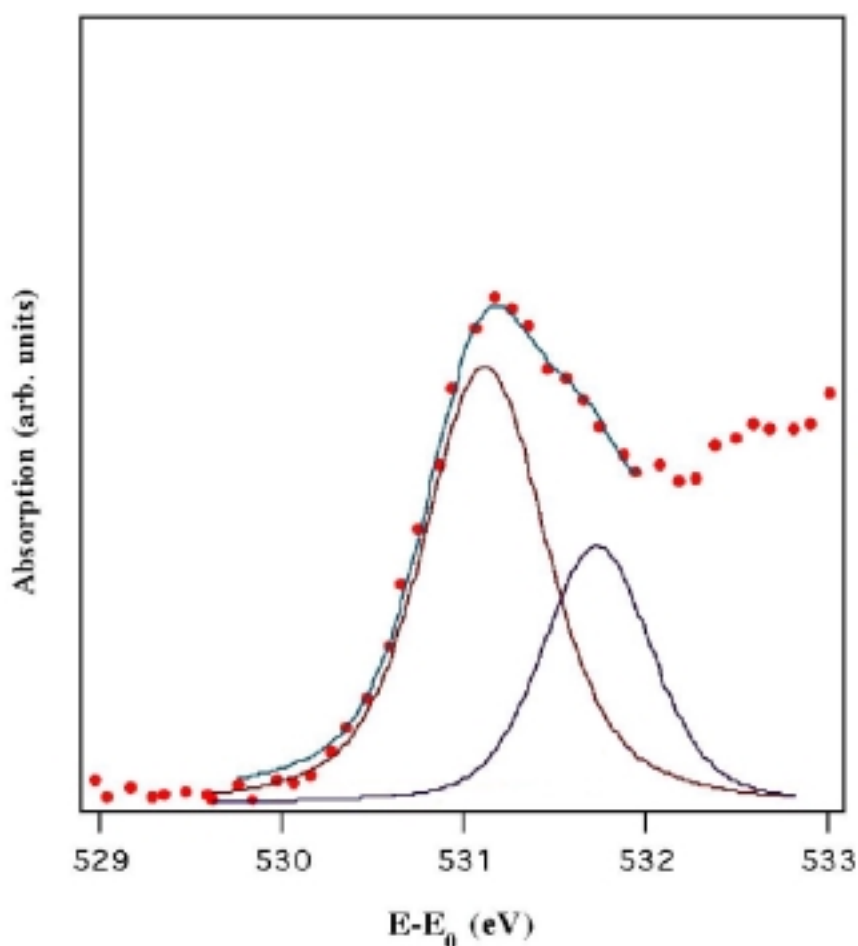
Figure 4. Fit of the π resonance region in the O K-edge NEXAFS spectrum. The two lorentzians are separated by about 0.5 eV.
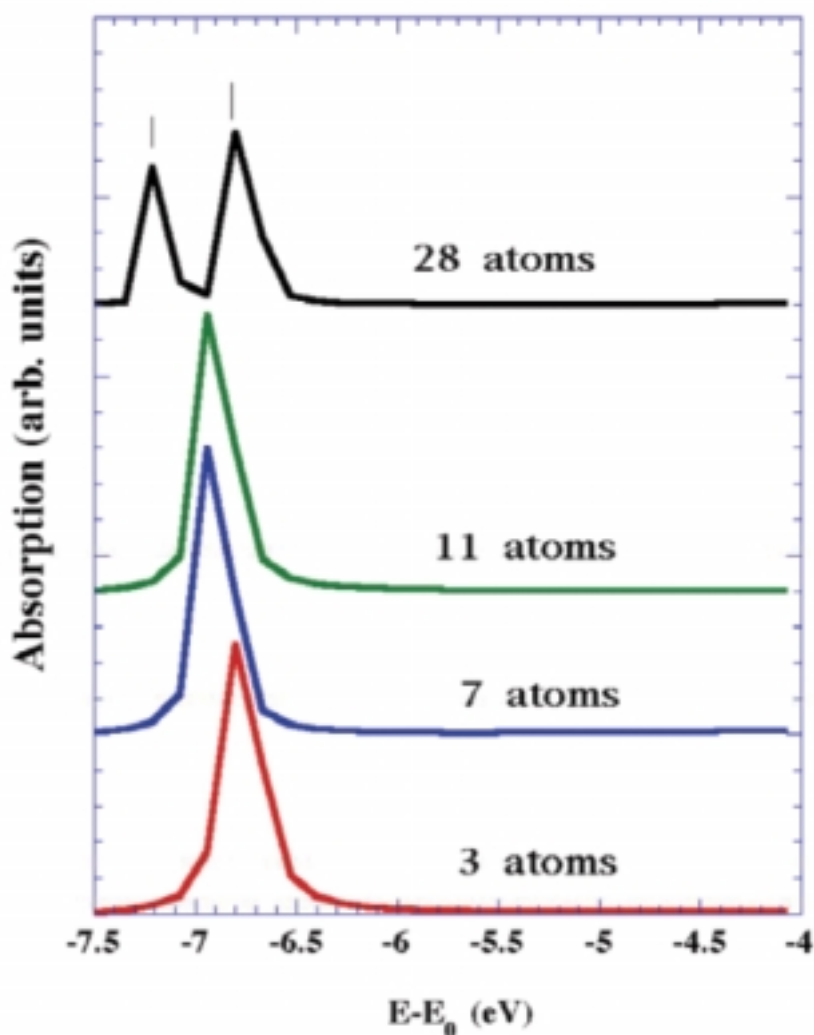
Figure 5. SCF calculations in the π resonance region by using different number of atoms around the absorber with the KO_2 geometry.

In order to understand the origin of this splitting we have performed a set of theoretical calculations looking carefully in the π energy region. The energy step of the calculations is now 0.13 eV to check in details the presence of possible two peaks in the resonance. The SCF potential has been performed using the three atoms $O_2^-K^+$ cluster with a charge transfer $Q_T= 1$ e^-. Fig.5 shows detailed calculations in the π resonance energy region performed by using clusters with different number of atoms around the central $O_2^-K^+$ unit and an O-O distance of 1.31 Å. The splitting is absent for small cluster size, but it appears when the cluster radius is above 4 Å, i.e. including other O-O groups in the cluster. Further increasing the cluster size (up to 83 atoms) does not change the theoretical result. The splitting is always present with the same energy separation. This is a clear indication that in this ionic compound the splitting of the π resonance is due to solid-state effects. In fact, only calculations performed with a number of atoms above 28 present the splitting observed in the experimental data is reproduced with the right energy separation. A 28 atoms cluster is

composed by two complete plane of the KO_2 structure, resembling in this way the whole crystal with the same symmetry properties. The same result is achieved with an O-O distance of 1.34 Å.

Further calculations show that for a charge transfer $Q_T = 1$ e$^-$ leads to a single feature only for an O-O distances of 1.28 Å, while a charge transfer less than one electron induce a splitting only for an O-O distance greater than 1.40 Å. In any case the polarization analysis indicates a z component confirming a π-like symmetry.

Chemisorbed O_2 on a Pt (111) surface [9,10], is another example of a splitting in the π^* resonance involving the π empty orbitals. For that system a superoxo-like molecular configuration has been assigned, and the existence of the splitting was attributed to two different π states parallel and orthogonal to the O-O anion axis (and located at 530.3eV normal inc. and 530.9 eV at grazing respectively) due to a different amount of charge transferred from the substrate.

In the present case this picture must be excluded, because the complete ionic electronic configuration of the O_2^- molecular anion $[1s^2 (2\_g)^2 (2\_u^*)^2 (3\_g)^2 (1\pi_u)^4 (1\pi_g^*)^3]$ there is only one empty π molecular state. Moreover our sample is polycrystalline and the O_2^- axis orientation with respect to the light **E** vector cannot be fixed.

We conclude that the origin of the π^*-like resonance splitting in the KO_2 case is due to the scattering paths involving other oxygen atoms imbedded in a crystalline solid matrix and hence to a strong solid state effect revealed only by high resolution measurements.

Conclusions

We have shown that the structural and electronic changes of potassium-superoxide can be detected by NEXAFS technique. By comparison with MS H-L simulations we have determined that the O-O distance in the O_2 molecular group in the KO_2 compound is between 1.30 and 1.35 Å.

Multiple Scattering analysis of the O K-edge NEXAFS spectra, taking into account a model including atoms lying up to 8 Å from the central O atom, can give structural information on the O-O anion distances. The π resonance splitting above the O K-edge is found to be due to a multiple scattering path involving O atoms arranged in O-O groups, i.e. to a solid-state effect.

Acknowledgement

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