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MULTIELECTRON CONFIGURATIONS IN THE X-RAY ABSORPTION NEAR-EDGE STRUCTURE (XANES) OF NiO AT OXYGEN K THRESHOLD

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ABSTRACT

The oxygen K edge XANES (X-ray Absorption Near Edge Structure) of stoichiometric NiO has been measured, by partial electron yield, at the "Grasshopper" line of the Frascati synchrotron radiation facility. The main features of the spectrum in the multiple scattering region over the 50 eV energy range beyond threshold are well predicted by the full multiple scattering one-electron theory. The interpretation of fine details of the spectrum requires a many body picture, in fact the results are in agreement with a description of NiO as an intermediate valence system where the charge transfer gap is smaller than the Hubbard correlation.

INTRODUCTION

In the last few years much interest has focused on the investigation of multielectron excitations in core levels spectroscopies[1]. The multielectron excitations in a correlated electronic system like NiO has been object of extensive experimental investigation via core level X-ray photoemission spectrocopy XPS[2] valence band photoemis-

sion[2,4-6], resonant photoemission[7,8], bremsstrahlung isochromat spectroscopy BIS[4,5] and angular resolved photoemission[9]. Band structure theoretical approaches to NiO electronic structure have found no[10-12] or only 0.3 eV[13] gap within the 3d valence band, in contrast with evidence of an optical gap of 4.3 eV[14,4,5]. The role of electron correlation in NiO has been pointed out since the work of Mott[15]. A recent approach using the formalism of configuration interactions[16] has been shown to account for the valence band photoemission and BIS data[4,5].

Here we investigate the electronic structure of NiO via XANES. It can be shown that the inner shell absorption cross section can be separated into an atomic-like part and a part arising from multiple scattering of the photoelectron by neighboring atoms[17,18]. XANES is actually used to obtain information on the geometrical atomic arrangement of neighbor atoms[17,19] from the unoccupied electronic states of selected symmetry at selected sites[20,21]. The single particle picture for the main features of the XANES spectrum of metals[22,23], molecules[18], and molecular compounds[19] is well established. On the other hand, in correlated electronic system, like valence fluctuating compounds, where the ground state is described by mixing of atomic-like configurations, the XANES spectra at threshold show a splitting of localized atomic-like resonances due to multielectron configurations and provide a measure of ground state properties[20,24,25].

We have measured the high resolution oxygen K-XANES spectra of NiO and compared it with the one-electron full multiple scattering theory[26,27]. We show that the high resolution XANES data of stoichiometric NiO is well predicted by one-electron full multiple scattering theory.

The role of the configuration interaction due to the large electronic correlation effects in NiO gives rise to extra features in the oxygen K edge spectrum. We have identified these features and the results are discussed in the frame of a simple model for NiO. NiO is described as an intermediate-valence system, as first proposed by Fujimori and Minami[16], with a large hybridization[4-6,16,28-30] between the localized 3d states (the width of the 3d bands can be neglected,in fact, it is only about 0.5 eV[13]) and the oxygen 2p valence band (the dispersional bandwidth of the oxygen band is about 3.5 eV[9] and therefore cannot be neglected). In a simple model for NiO we consider localized $3d^n$ states at the Ni sites with large d-d Coulomb interaction U (U has been found to be between 5 eV and 10 eV[5,28,30]. The charge transfer energy needed to create a hole in the oxygen 2p valence band (which can be called $\underline{L}$ extending the meaning of the notation proposed by Fujimori in the framework of the ligand field theory for a cluster model, where the width of the oxygen 2p band is neglected) and to promote an electron in the 3d states is assumed to be $\delta E = 5$ eV[28] or 4.6 eV[30]. This can be consi-

dered the energy separation between the configuration $3d^8$ and the mean energy of the broad $3d^9\underline{L}$ configuration in the ground state in a many-body language. Because of Ni(3d)--O(2p) hybridization the mixing parameter v between the two configurations is non zero, v = 1.75 eV as found experimentally[30], and thre ground state is described as $\psi_0 = a|3d^8> + b|3d^9\underline{L}>$. The hybridization mixing parameter v determines the intermediate valence (i.e. b is not zero), in fact if v were zero the $3d^9\underline{L}$ configuration will be unoccupied in the ground state and the system will be an integer valent $3d^8$ system. This type of electronic structure, where $U > \delta E$,, is common to a class of materials such as CeO_2, which we call "interatomic-intermediate-valence (IIV) systems"[31,32].

EXPERIMENTAL

Experiments were performed at the Frascati National Laboratories using the storage ring Adone operated at 1.5 GeV. We used the Grasshopper grazing incidence monochromator, equipped with a 1200 line/mm holographic grating, and variable slits from 15 to 400 μm. We obtained an energy resolution ΔE = 1.5 eV operating with 15 μm slits at 530 eV. The light emerging from the monochromator was refocused on the sample by a 2° grazing incidence toroidal mirror. The radiation incidence angle on the sample surface was 45°. The spot size was about 2x2 mm.

The emitted electrons were detected by use of a two-stage cylindrical mirror analyser (CMA). The axis of the detector was normal to the incident radiation. The surface XANES spectra[33,34] were measured by the partial electron yield method where the CMA was operated in a constant final state (CFS) mode selecting out electrons at 2 eV) (maximum of secondary electron energy distribution).

Nickel oxide NiO was grown on a nickel metal surface kept at the temperature of 950°C in a high partial pressure of oxygen about 152 Torr. In this condition the growth of the oxide layer is stoichiometric. We have found in our conditions that the thickness of the oxide layer grows according with the parabolic rate growth of NiO 1.38×10^{-9} ($g\cdot cm^2\cdot sec^{-2}$). This is consistent with both graviometric and electron microscopy measurements. X-ray diffraction, Auger spectroscopy and EXAFS spectra at the Ni K-edge were used to check the purity and stoichiometry of the NiO oxide layer.

RESULTS AND DISCUSSION

a) One-electron excitations

Fig. 1 shows the experimental oxygen K-edge XANES of NiO layer on nichel. Because we collect secondary electrons at very low kinetic energy,with a very long escape depth, our data have to be considered giving bulk NiO properties. The oxide layers were thick

enough (d > 5000 Å) that no electron emission from the substrate was observed.

Our data are in good agreement with electron-energy loss experiments[35,36]. The spectrum in Fig. 1 shows peaks predicted by the theory which were not resolved in the XANES spectrum reported in ref.(26).

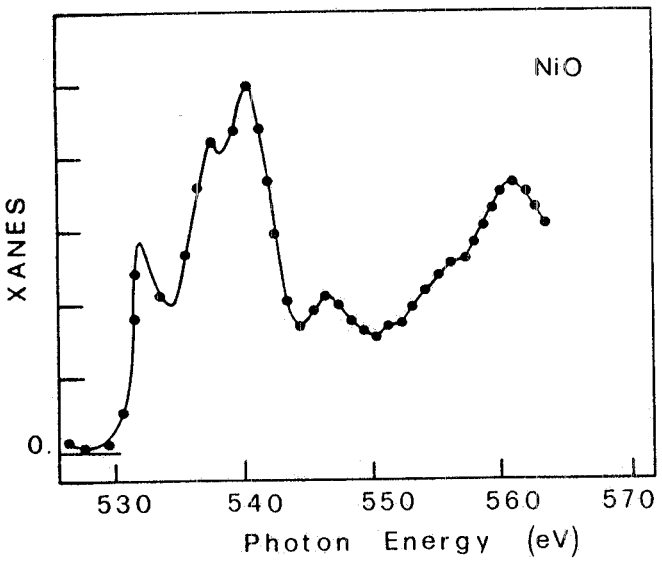

Fig. 1 - Oxygen K-XANES of NiO measured by electron partial yield at a constant final state $E^* = 2$ eV.

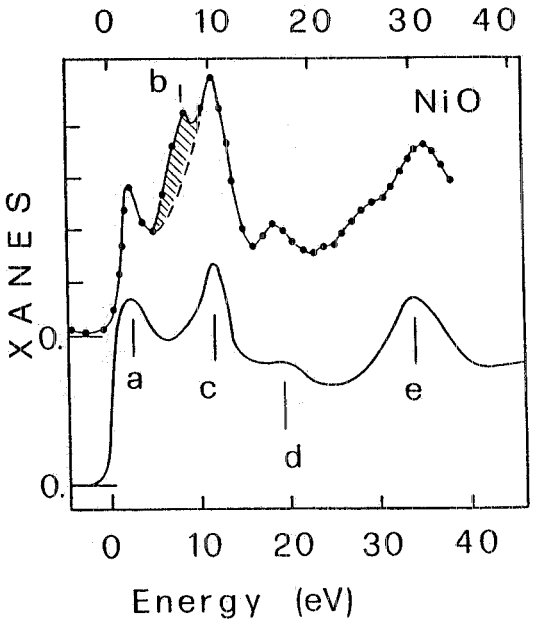

Fig. 2 - Theoretical oxygen K-XANES of NiO calculated by Norman et al.[26] compared with the experimental spectrum where the energy scale has been compressed by a factor CF = 1.1.

The experimental XANES spectrum is compared in Fig. 2 with the theoretical XANES of NiO calculated by Norman et al.[26] using the one particle full multiple scattering theory for a cluster around the central oxygen atom formed by ten neighbor atoms. The agreement between the theory and experimental data is quite good, showing that comparing good-quality XANES data with full multiple-scattering XANES theory leaves no place for speculations about the role of multiple scattering in XANES.

In Fig. 2 we have aligned the first peak a and we have compressed the theoretical spectrum to obtain a good alignement between the theoretical and experimental spectra using a compression factor for the experimental energy scale. The need of this type of correction (first observed by Grunes[37]) in the comparison between the experimental XANES spectra and XANES theory is due to the energy-dependent exchange correlation between the photoelectron and the valence electrons, which was not taken into acount in the XANES calculations.

The agreement between the theoretical and experimental spectrum shows that the features a,c,d and e can be assigned unambigously to one-electron excitations. These states

are due to multiple-scattering resonances of the p-photoelectron in the continuum, i.e. the maxima of the local density of states at the oxygen site of p-type, selected by the dipole selection rule ($\Delta l = +1$)

Feature c is at the threshold of the p conduction band. This is demonstrated in Fig. 3 where the NiO spectrum is compared with MgO spectrum measured using energy loss spectroscopy by Colliex[36]. MgO has the same crystal structure of NiO but there are not unoccupied d-states at threshold. All the multiple scattering peaks determined by the same local atomic arrangement are observed in both spectra. The lack of peak A in MgO demonstrates that peak A in NiO is due to transitions to the unoccupied states due to the mixing of O-2p orbitals with Ni-3d orbitals.

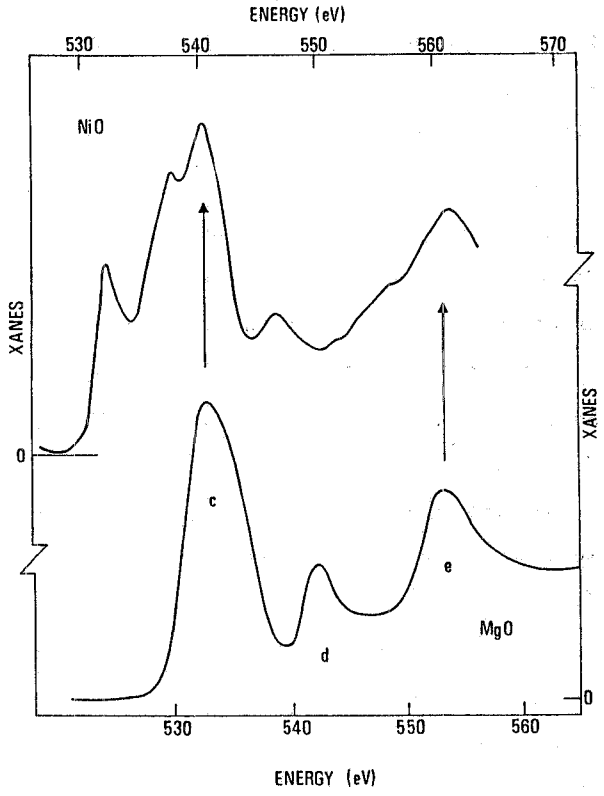

Fig. 3 - Comparison between the oxygen K-XANES of NiO and MgO. In the MgO spectrum there are no unoccupied d states, therefore the first absorption feature has been aligned with peak C of NiO.

The absorption edge in NiO can be determined experimentally by knowing that the binding energy E(1s) of the O-1s level is at $E_b(1s) = 530$ eV[3]. In the one-electron scheme the photoionization absorption threshold is predicted to be at $E_o = E_b(1s) + E(gap) = 534$ eV, where E(gap) is the gap energy 4.3 eV measured using BIS[4]. Therefore, using this one-electron scheme the peak a in the oxygen K-XANES at 532 eV is a bound state with a 2 eV binding energy. Because of the current controversy on the assignement of the 4.3 eV gap an alternative extimate of E_o can be obtained. Where the 4.3 eV gap is interpreted in the one-electron picture[13] as the function from the O(2p) at $\sim$ - 2 eV to Ni(3d) unoccupied band, the absorption threshold is predicted to be at $\sim$ 532 eV. A more detailed discussion of this point comparing the different final states of different spectroscopies will be published later.

In conclusion the one-electron interpretation of the XANES of NiO, together with the dispersion of the O(2p) valence bands probed by angle-resolved photoemission[9], shows that a set of states of NiO can be well described by one-electron theory: the oc-

cupied O(2p) bands and the p-like high-energy conduction bands. The one-electron scheme cannot account for features b and f in the XANES spectrum, which will be discussed in Sect. b.

b) Multielectron configuration interaction

Important many body effects in the XANES appear when the electronic structure of the studied system exhibits configuration interaction in the initial state. In fact the core hole is screened not only by the passive electrons, as in core level photoemission (XPS), but also by the excited photoelectron, therefore final charge transfer state "shake up" (or final state configuration interaction) are usually quenched in XANES[32,38,39]. Moreover, at the oxygen K-edge the oxygen core hole is generally well screened by oxygen 2p valence band electrons. Therefore the O K-XANES is a good local probe of initial-state properties and it should be consistent with BIS data.

In an intermediate valent system like NiO the ground state is described in a many body language as a mixture of two configurations $|3d^8\rangle$ and $|3d^9\underline{L}\rangle$ therefore in the final state with a core hole in the oxygen is level O($\underline{1s}$) (or $\underline{h}$) and one photoelectron in an unoccupied state, two possible final-state configurations for each one-electron excitation could be excited corresponding to the two configurations of the passive valence electrons.

At threshold the lowest energy-allowed final-state configuration is $|Ni(3d^9)\text{-}O(\underline{1s})\rangle$ and it is assigned to peak a in Fig. 2. The symmetry of the p-like states at the oxygen site in the frame of ligand field theory for a octahedral cluster ONi_6 is T_{1u} symmetry, therefore the ligand hole $\underline{L}$ can be also indicated by T_{1u}[5]. The peak a final state can be reached with a transition from the ground state configuration:

$$\psi_g = a|O(1s^2, T_{1u}^6)Ni(3d^8)\rangle + b|O(1s^2, T_{\underline{1u}}^5)Ni(3d^9)\rangle$$

to the final state

$$O(\underline{1s}^1, T_{1u}^6)Ni(3d^9).$$

This is the lowest-energy fully relaxed configuration where the excited photoelectron neutralizes the ligand hole. This final state is similar to the final state of charge-transfer excitation at the optical band gap $d^9\underline{L}$ where the hole in the O(2p)states has been transferred to the core O(1s) level.

In one electron language this is the transition to the first unoccupied state which is dipole allowed because of strong Ni(3d) and O(2p) hybridization. This is demonstrated by the strong oscillator strenght for peak a predicted by a full multiple scattering

calculation which gives the p-component of the local density of states at the oxygen site.

At high energies the final state excited multielectron configurations are those with the core hole $O(\underline{1s}^1)$ and one extra electron in each of the p maxima of the local density of states called here c*, at the oxygen site determined by the intermediate valence state,

$$\text{i)} \quad O(\underline{1s}^1, T_{1u}^6)Ni(3d^8)c^{*1}$$

$$\text{ii)} \quad O(\underline{1s}^1, T_{1u}^5)Ni(3d^9)c^{*1} \ .$$

This effect determines the presence of an extra feature for each one-electron transition to each c*. We interpret the experimental features b and f in the NiO XANES spectrum, not accounted by the full multiple scattering theory, as due to this many body effect.

The difference in energy between the two final state configurations is expected to be $\Delta E = (\delta E_f^2 + 4T^2)^{1/2}$ where T is the off-diagonal element of the final state Hamiltonian which determines the mixing between the final state configurations and $\delta E_f =$

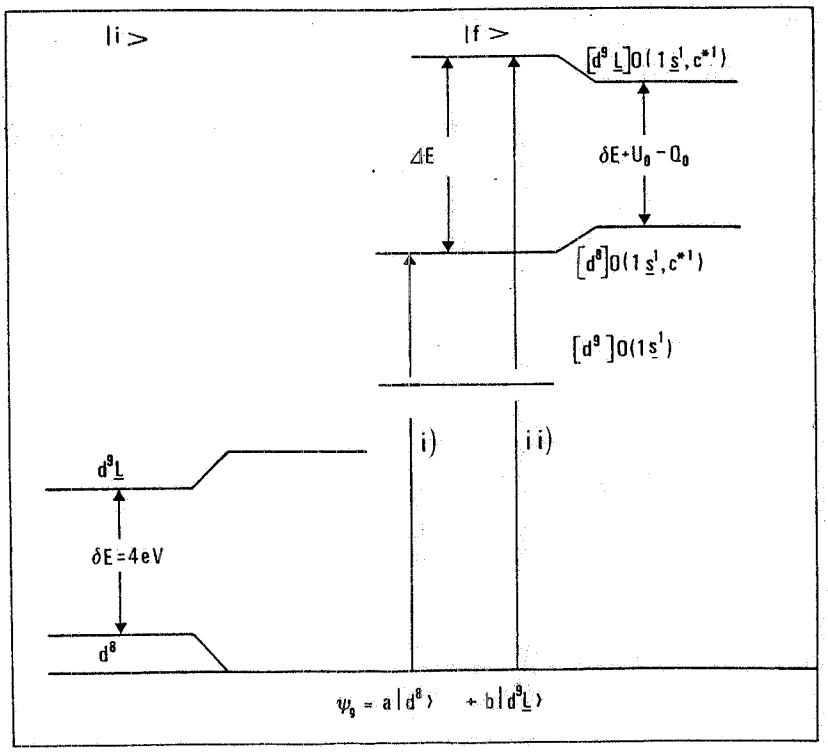

Fig. 4 - Scheme of multielectron configurations $|d^8\rangle$ and $|d^9\underline{L}\rangle$ in the ground state $|i\rangle$ and in the final state $|f\rangle$ in X-ray absorption. The arrows indicate direct transitions.

$= \delta E - U_o - Q_o$ where δE is the initial state separation of the d^8 and $d^9\underline{L}$ ionic configurations: $U_o = U_{dc^*} - U_{pc^*}$, where U^*_{dc} and U^*_{pc} are the Coulomb repulsion between c* and O(2p) of Ni(3d) electrons and $Q_o = Q_{\underline{L}c^*} + Q_{d\underline{h}}$, where $Q_{\underline{L}c} + Q_{d\underline{h}}$ are the Coulomb attraction between the ligand hole and the photoelectron and between Ni(3d) and O(1s) electrons, respectively.

The actual energy separation depends on many parameters which change for each state c* and therefore the mixing between the two configurations and their relative intensities also varies. We assign the pair of peaks c and b, and the pair of peaks e and f to the transitions associated with the mixing of configurations i) and ii) as described in Fig. 4.

CONCLUSION

In this work one-electron full-multiple-scattering theory has been shown to describe well the NiO XANES spectrum. The multielectron configuration interaction in the initial state of NiO is detected by extra multielectron features in the XANES spectrum. XANES is shown to be a new probe of localized states at the oxygen site, where in comparison other spectroscopies like BIS probe the unoccupied states, averaging over all sites of the material, and Ni(3d) XPS probes the states at the Ni site.

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