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X-Ray Photoelectron Spectra of Defective Nickel Oxide

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Cation-deficient nickel oxides have been investigated by X-ray photoelectron spectroscopy. The high-binding-energy features in the O(1s), Ni(2p) X.p.s. of defective NiO are described as multielectron final states, induced by defective sites. These sites are described as $(NiO_6)^{9^-}$ molecular clusters because of the d hole. The energy shift between the main peak and the satellite, in both the O(1s) and Ni(2p) X.p.s. spectra, is due to a change in the ionic charge and in the oxygen coordination induced by cation vacancies.

X-Ray photoelectron spectroscopy (X.p.s.) is now extensively used to study the electronic structure of solids and the mechanism of surface reactions, such as chemisorption, heterogeneous catalysis and electrochemical reactions on electrodes. This technique allows the measurement of a final state in which one electron is removed from the ground state. The system under investigation tends to screen the photohole^{1, 2} produced in the photoelectron emission. In this process satellites can occur because by the excitation of the core (valence) electron, charge transfer from the ligand to the metal ion might be induced.^{3, 4} NiO is a cation-deficient semiconductor as well as being an excellent oxidation catalyst.⁵ It is also a prototype material for the investigation of highly correlated electronic systems.⁶

Multielectron excitations in NiO have been studied via core-level X.p.s.,^{7,8} valenceband photoelectron emission,^{3,7} bremsstrahlung isochromat spectroscopy (BIS)⁹ and Xray absorption spectroscopy.¹⁰ Stoichiometric NiO is described as an intermediatevalence system, as proposed by Fujimori and Minami,¹¹ with a large hybridization between the localized 3d states and the O(2p) valence band.^{9,11} Because of Ni(3d)-O(2p) hybridization the NiO (and also Ni dihalide) ground state is described as $\phi_{g} = a | 3d^{8} \rangle$ $+b|3d^{9}L\rangle$ where L stands for a hole on the oxygen (halogen) site.¹² Owing to the interaction between the 2p core hole and the valence electrons, strong satellite structures are observed in the core X.p.s. of NiO and Ni dihalides.^{13,14} While in the ground state the d⁸ and d⁹L configurations are degenerate, two different final states, 2p3d⁸ (satellite) and 2p3d⁹L (main line), are core-hole induced. This result is also obtained in Cu²⁺ dihalides, where the main line is unambiguously assigned to the fully relaxed 2p3d¹⁰L multielectron configuration.⁴ Nickel oxide has been extensively investigated by using core-level X.p.s. $^{8,14-18}$ In the last few years much interest has been focused on the identification of species having high-binding-energy components in the O(1s) spectra at 531.4 eV and in the Ni(2p) X.p. spectra at 856.1 eV.^{15,18}

The 1.6 eV satellite accompanying the sharpest Ni($2p_{3/2}$) main line has been assigned to an electronic transition into an excited 3d state on the basis of the optical absorption data.^{15,18} A similar argument ($t_{2g} \rightarrow e_g$ transition) has been used in order to justify the O(1s) high-energy feature at 1.6 eV from the main line. It has been observed recently¹⁹ that the O(1s) peak exhibits asymmetry when oxygen ions are created which do not have the proper ligand environment of the lattice oxygens. Actually the presence of ion vacancy point defects, produced by Ar⁺-ion bombardment on the NiO surface, produces



Fig. 1. X.p. spectra from the Ni(2p) core level of the different oxide samples. Inset: comparison between Ni(2p) and O(1s) X.p.s. spectra of a defective sample.

asymmetry in the originally symmetric O(1s) peak.¹⁹ In addition, no 1.6 eV satellite has been observed in the core-level X.p.s. of Ni dihalides.²⁰

An accurate study concerning the defect structure of NiO, as revealed by core X.p.s., has been carried out by Roberts and Smart,¹⁷ who suggest that the high-binding-energy features observed with the NiO surface evacuated at room temperature arise from the OH group, in agreement with the observation for nickel hydroxide.¹⁴ As water is removed, Ni³⁺ species are formed, together with Nickel vacancies, which account for the high-energy components in the X.p. spectra.¹⁷ On this basis, it should be possible to obtain nickel oxides with different surface stoichiometry if the chemisorbed water is removed from the sample surface. The final surface stoichiometry depends on the oxide preparation, since OH chemisorbtion on NiO is energetically promoted by defects but not by a 'perfect' surface.²¹ However, the assignment of excited electronic states to high-energy features is not well established. In this paper a study of the electronic structure of defective nickel oxide, as detected by core X.p.s., is reported. In particular, the surfaces of cation-deficient nickel oxides, produced by thermal treatment, have been

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Fig. 2. X.p. spectra from the O(1s) core level of the various defective oxides.

studied. The aim of this paper is to give an explanation, in terms of multielectron configurations, of the core X.p.s. high-energy features.

Experimental

In order to obtain oxides with different surface stoichiometries, NiO specimens prepared by various methods were heated during evacuation. Sample (a) was obtained after evacuation at 500 °C for 2 h of a high-purity Ni sheet oxidized at 1100 °C in air, while sample (b) was obtained after evacuation, at 250 °C for 2 h, of a nickel sheet oxidized at 700 °C in air. Sample (c) was an Li-doped nickel oxide evacuated at 350 °C for 3 h and was obtained by heating a 4% Li₂O-NiO powder mixture in air at 800 °C.

When a monovalent ion, *e.g.* Li⁺, enters the crystal lattice of NiO, an increase in the hole concentration is expected. Owing to the presence of Ni³⁺ point defects in the oxide bulk, the NiO-Li₂O mixture is black, in contrast to the stoichiometric oxide, which is green.

Sample (c) was evacuated at a selected temperature in such a way as to promote the evaporation of lithium oxide. After heating in air the lithium oxide is on the surface of a solid $\text{Li}_x \text{Ni}_{1-x} O$ solution.²² Upon heating the sample up to 300 °C in vacuum, lithium

oxide dissociates and the Li^+ ions are uniformly distributed over the surface interstices of nickel oxide.²²

In fig. 1 and 2 are shown the d measurements (see above) for the same (c) sample in different positions. In particular, the angle between the normal to the sample surface and the direction of the analysed electrons was increased by 40° with respect to the previous one. A decrease in thickness of the oxide investigated should be representative of defects high concentration, since a decrease of the vacancy density is expected from the surface to the bulk of sample.

The evacuation temperatures were chosen in order to promote only water desorption and vacancy generation. This choice was dictated by the experimental evidence for Ni²⁺ reduction at high evacuation temperatures.¹⁷

The pressures in the spectrometer chamber were lower than 7×10^{-8} mbar during heating. In our experimental set-up no mass spectrometer was fitted to the analysis chamber. Therefore, monitoring of the gas-phase composition during evacuation and heating was not performed. However, after thermal treatment, none of the Ni(2p) spectra showed any extra features at 865.5 eV binding energy, as expected after dehydroxylation.¹⁷ After thermal treatment it is expected to obtain oxides containing cation vacancies and holes as point defects.

Results and Discussion

X.p.s. from Ni($2p_{3/2}$) and O(1s) core levels of nickel oxides was performed using a Vacuum Generators ESCALAB MKII spectrometer coupled with a PDP/11 computer for data acquisition and analysis. Spectra were detected by operating in the constant analyser energy mode, at a pass energy of 25 eV, using an Al K_a X-ray source.

In fig. 1 Ni(2p) X.p. spectra of the oxide samples are reported. The typical spectra are constituted by features A, B and C, respectively, at 854.5, 856 and 861.5 eV. These spectra are in agreement with previously reported¹⁶⁻¹⁹ Ni(2p) X.p.s. data.

Fig. 2 shows the O(1s) X.p.s. of the oxide specimens. Features are present at 529.7 eV (peak A') and 531.4 eV (peak B'). Comparison between fig. 1 and fig. 2 shows that the intensities of the B and B' peaks are correlated. This is also shown in table 1, where the experimental ratio of the peak intensities are reported [obtained after curve-fitting procedures (using Gaussian and Lorentzian functions), background subtraction and deconvolution (to remove line-broadening due to the X-ray source and to the analyser). The background subtraction was performed using a routine that allows a non-linear background to be removed from all points of a given region of the spectra, with reference to the Shirley method.²³ The curve-fitting procedure was used in order to evaluate the peak intensities. In particular, the function used for a given peak was of the type:

$$f(x) = hp(x)$$

where h is the peak height and p(x) is the Gaussian-Lorentzian product function in which the M mixing ratio[†] between the Lorentzian and the Gaussian functions is in the range 0-1 (M = 1 for a Lorentzian peak, M = 0 for a Gaussian peak). The least-squares method was applied by retaining as variable parameters M, h and both the peak f.w.h.m. and the energy at the same peak centre.

In order to reduce the observed widths of spectral lines in photoelectron spectroscopy, a deconvolution routine was used. This routine removes the line-broadening due to the analyser and to the X-ray source by sequential deconvolution. The analyser broadening function is represented by a Gaussian function and the X-ray broadening is taken as a combination of two Lorentzian functions. The parameters for the Lorentzian function are taken from the ref. (24) and the method used was an iterative approach, as suggested

[†] $p(x) = (\{1 + M[x - x(0)]^2/b^2\} \exp\{(1 - M)[x - x(0)]^2/b^2\})^{-1}$, where x(0) is the peak centre and b = 0.5 f.w.h.m.

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Table 1. Experimental ratio of the peak intensities				
as obtained after curve-fitting, background sub-				
traction and deconvolution				

e B'/A	B/A	C/A	
0.2	0.4	0.8	
0.4	0.7	1.1	
0.7	1.0	1.5	
0.9	1.2	1.7	
	e B'/A 0.2 0.4 0.7 0.9	e B'/A B/A 0.2 0.4 0.4 0.7 0.7 1.0 0.9 1.2	e B'/A B/A C/A 0.2 0.4 0.8 0.4 0.7 1.1 0.7 1.0 1.5 0.9 1.2 1.7

by Cittert.²⁵ An Ni/O ratio less than one is obtained for all samples, as expected for a non-stoichiometric oxide surface. The Ni/O atomic ratio has been obtained from comparison of the peak intensities corrected for the photoionisation cross-section ratios deduced from Scofield's data;²⁶ corrections were also made for the escape depth and the kinetic-energy response of the analyser. The uncertainty in the values obtained for the Ni/O ratios is *ca.* 20%.

Since hydroxyl species are removed during the thermal treatment, the high-energy peaks B and B' are related to the point defects of the oxide surface. A change in the defect concentration is expected on going from sample (a) to sample (d).

The B' feature in the O(1s) spectra is located at the same energy for all the samples. In the Li-doped sample an A'-B' energy separation of 1.7 eV was found. An optical absorption peak at 0.43 eV was observed only for Li-doped oxide²⁷ (with respect to NiO for which absorption at 1.5 eV was measured²⁸). Therefore a clear correlation between the satellite feature and the absorption data is not apparent.

Stoichiometric Nickel Oxide

As previously shown, the ground state of a stoichiometric NiO is described as a mixture of $|3d^8\rangle$, $|3d^9L\rangle$ configurations. The symmetry of the p-like states at the oxygen site, in the frame of the ligand-field theory for an octahedral cluster (ONi₆), is a T_{1u} symmetry; therefore the ligand hole can be also indicated by T⁵_{1u}. Accordingly, the ground-state configuration is given by:

$$\phi_{g} = a_{0} |O(1s^{2}T_{1u}^{6}) Ni(3d^{8})\rangle + b_{0} |O(1s^{2}T_{1u}^{5}) Ni(3d^{9})\rangle$$

which a large $d^{8}-d^{9}L$ energy difference due to the Ubbard correlation energy. Therefore the O(1s) photoelectron emission process of a stoichiometric oxide provides two mixed final states at the oxygen site:

$$\begin{array}{l} \phi_{\rm f}^{\rm M} = a_1 \,|\, {\rm O}({\rm s} \,\, 2{\rm p}^6) \,{\rm Ni}(3{\rm d}^8) \rangle + b_1 \,|\, {\rm O}({\rm s} \,\, 2{\rm p}^5) \,{\rm Ni}(3{\rm d}^9) \rangle \\ \phi_{\rm f}^{\rm s} = a_2 \,|\, {\rm O}({\rm s} \,\, 2{\rm p}^6) \,{\rm Ni}(3{\rm d}^8) \rangle + b_2 \,|\, {\rm O}({\rm s} \,\, 2{\rm p}^5) \,{\rm Ni}(3{\rm d}^9) \rangle \end{array}$$

where s stands for a hole in the 1s oxygen core level. The energy separation between the main line and satellite peaks is given (neglecting the overlap between configurations) by $\delta E = (\Delta E_t^2 + 4T_t^2)^{\frac{1}{2}}$

where $T_{\rm f}$ is the off-diagonal matrix element in the final state and $\Delta E_{\rm f} = E({\rm s} {\rm d}^9 {\rm L}) - E({\rm s} {\rm d}^8)$.

In the sudden approximation the intensity ratio of the satellite and main peak is⁴

$$\frac{I_{\rm s}}{I_{\rm M}} = \tan^2 \left(\frac{\theta_{\rm f}}{2} - \frac{\theta_{\rm g}}{2} \right)$$

$$\tan \theta_{\rm f(g)} = \frac{2T_{\rm f(g)}}{\Delta E_{\rm f(g)}}$$
(1)

where

in which the labels g and f stand for the ground state and the final state, respectively. In the limit $T/\Delta E < 1$, eqn (1) gives:

$$\frac{I_{\rm s}}{I_{\rm M}} = \left(\frac{T_{\rm f}}{\Delta E_{\rm f}} - \frac{T_{\rm g}}{\Delta E_{\rm g}}\right)^2.$$
(2)

We must consider the covalent mixing of a state $3d^8$ with strong term splitting with a state $3d^8L$ with small term splitting.¹¹ The matrix element connecting these states is ca. 1.75 eV, as is found experimentally.²⁹ Furthermore, in the core satellite the same oneelectron transfer integral can be retained for the initial state as well as for the final state when the core hole is localized. A change in the energy difference between the two mixed configurations, in the initial and final states, is not expected to be large. The satellite intensity is predicted to be negligible, since $T/\Delta E < 1$ and differences in ΔE and hybridization are not core-hole induced. This is in agreement with the experimental spectra, in which core emission asymmetry is not observed in O(1s) X.p.s. for a stoichiometric material.

The X.p.s. from the Ni(2p) core level of stoichiometric NiO shows strong satellite structures. The core hole produced in the photoelectron emission event acts differently on the d⁸, d⁹L ground-state configurations and two final states are induced.⁴ The sharp main line (peak A, fig. 1) is assigned to the $c3d^9L$ final state in which the c(2p)photohole is screened by an oxygen 2p electron.³ The satellite (peak C) is assigned to the $c3d^8$ unscreened high-energy configuration.³ The energy difference between features A and C can be evaluated according to:

$$E_{\rm c} - E_{\rm A} \approx E(cd^8) - E(cd^9L) \approx E(d^8) - E(d^9L) - q(c3d)$$

where q(c, 3d) is the Coulomb interaction between a 3d electron and a 2p core hole.

Non-stoichiometric Nickel Oxide

The homogeneity range of NiO includes only excess oxygen. Thus non-stoichiometric samples have nickel vacancies, each of them leading to the formation of two holes to obtain neutrality. In a cation-deficient NiO, a nickel site is also at the centre of a distorted octahedral cluster. In contrast, in the lattice of a defective oxide several oxygen sites, (first neighbours to Ni³⁺) will be surrounded by cation vacancies and Ni³⁺ in a fivefold coordination site. Moreover, the deviation from stoichiometry in samples (a)-(d) is expected to be large. Particularly (see text) for all the oxides investigated, the δ values (where δ is the deviation from the stoichiometry in Ni_{1- δ}O) are *ca.* 1/6: on average all the oxygen atoms are in a fivefold coordination site. Therefore, the C_{4v} point group is representative of the oxygen coordination in these defective samples, if cluster distortion is neglected.

In a non-stoichiometric oxide Ni³⁺ sites are also expected at the centre of distorted octahedral clusters. These coordination sites are described as $(NiO_6)^{9-}$ molecular clusters because of the d-hole. These are the photoemission clusters,¹¹ since 3d-photoemission final states are given by

$$\phi_{\rm f} = a_1 | {\rm d}^7 \rangle + a_2 | {\rm d}^8 {\rm L} \rangle + a_3 | {\rm d}^9 {\rm L}^2 \rangle.$$

The stabilization of holes on Ni sites is due to the presence of charged nickel vacancies, in contrast to stoichiometric oxides where charge transfer is d-hole induced. In fact, the main line in the 3d photoemission of stoichiometric oxide is unambiguously assigned to the 3d⁸L configuration, in which a d-hole is screened by a ligand electron, while satellites are assigned to the unscreened d⁷ states.³ A positive difference between d⁷ and d⁸L multielectron state energies is obtained for an $(NiO_6)^{9^-}$ cluster in a stoichiometric lattice. Also, in a non-stoichiometric NiO the d⁷–d⁸L energy difference is expected to be M. Tomellini

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Fig. 3. Scheme of a non-stoichiometric lattice: the vacancy, indicated by a square, leads to the formation of two holes (Ni^{3+}) at distance R. Inset: equivalent scheme used in order to evaluate the vacancy-hole interaction (see text).

small because of the Coulomb interaction between a d-hole and a vacancy. The evaluation of this difference provides:

$$[E(d^{7}) - E(d^{8}L)]_{d} = [E(d^{7}) - E(d^{8}L)]_{s} - 2\left(\frac{2e^{2}}{kR}\right)$$
(3)

where the label d(s) stands for a defective (stoichiometric) material, and $2e^2/kR$ (ca. 0.8 eV in NiO) is the Coulomb interaction between a double charge vacancy and a d-hole, as shown in fig. 3. Using the photoemission data³ for the evaluation of the $E(d^7)-E(d^8L)$ energy separation, eqn (3) provides degenerate d^7-d^8L configurations that are also in agreement with the optical data.²⁴

The ionic reaction, providing a $d^7 \rightarrow d^8L$ transition, which can occur in a nonstoichiometric material, takes much less energy than the analogous process for an intrinsic oxide:

$$Ni^{2+} + O^{2-} \rightarrow Ni^+ + O^-(d^8 \rightarrow d^9L).$$

Then the ground state of a defective nickel cluster can be described as

$$\phi'_{g} = a | d^{7} \rangle + b | d^{8}L \rangle$$

with degenerate d⁷ and d⁸L configurations. In particular, the relation

$$[E(d^{8}L) - E(d^{7})]_{d} \approx [E(d^{8}) - E(d^{7}) + E(L)]_{d}$$

holds, where E(L) is the ligand energy. On this basis two mixed final states are expected from the photoemission of a 'defective' oxygen site. Accordingly we have:

$$\phi_{f}^{\prime M} = a_{1} | O(sA_{1} E^{4}) Ni(3d^{7}) \rangle + b_{1} | O(sA_{1} E^{3}) Ni(3d^{8}) \rangle$$

$$\phi_{f}^{\prime S} = a_{2} | O(sA_{1} E^{4}) Ni(3d^{7}) \rangle + b_{2} | O(sA_{1} E^{3}) Ni(3d^{8}) \rangle$$

where Mulliken's notation is used to describe $p_z(A_1)$ and $p_{x,y}(E)$ orbital symmetry. The $\phi_f^M, \phi_f'^M$ final states involve photoelectron emission from oxygen sites in a nearest-

neighbour position of a stoichiometric and defective Ni site, respectively. We assign ϕ_f^M , $\phi_f'^M$ final states to the A' and B' features in the O(1s) X.p. spectra. Accordingly the A'-B' energy separation is given, neglecting hybridization, by

$$\Delta E' = [E(\phi_t^{\prime M}) - E(\phi_t^M)] + [E(\phi_g) - E(\phi_g^{\prime})] + \Delta E_c(1s) \approx \Delta E_c(1s)$$

in which ΔE_c is the energy difference between the oxygen core levels. In order to identify feature B in Ni(2p) spectra, X.p.s. data of both the O(1s) and Ni(2p) core levels were aligned. This is shown in the insert of fig. 2, where a good correspondence between A–B and A'–B' structures is observed. We assigned the 856 eV high-binding-energy feature to the fully relaxed $c3d^9L^2$ final state, localized on a 'defective' nickel site. The relaxed $c3d^9L^2$ final state is related to the $3d^9L^2$ state describing, with the degenerate configurations $3d^8L$ and $3d^7$, the ground state of the (NiO₆)⁹⁻ cluster. These two states are resolved in the Ni(2p) X.p.s. of the defective sample, where charge transfer from the ligand to the cation is induced by the core hole. Stabilization of holes in NiO lattices provides (NiO₆)⁹⁻ coordination clusters, which are energetically stable because of the cation vacancies. The energy difference between peaks A and B is given by:

$$\begin{split} E_{\rm B} - E_{\rm A} &\approx [E(\mathrm{d}^{9}\mathrm{L}^{2})_{\rm d} - E(\mathrm{d}^{9}\mathrm{L})_{\rm s}] + [E(\phi_{\rm g}) - E(\phi_{\rm g}')] + \Delta E_{\rm c}(2\mathrm{p}) \\ &\approx \Delta E_{\rm c}(2\mathrm{p}) + U(\mathrm{L},\mathrm{L}) \end{split}$$

in which U(L, L) is the ligand-hole correlation energy. One expects two separate states $3d^9L^2$, corresponding to configurations with the two ligand holes at the same or different ligand atoms. In the latter case the difference $E_A - E_B$ is ca. $\Delta E_c(2p)$, since U(L, L) is negligible.⁴ Furthermore, the evaluation of the chemical shift (in the ionic limit) between ϕ_g and ϕ'_g mixed states, for both the O(1s) and Ni(2p) core levels respectively, provides:

$$\Delta E_{\rm c}(1{\rm s}) \approx q^{\prime 2} \left\langle \frac{1}{r_{\rm p}} \right\rangle - \frac{q^{\prime 2} \sqrt{2}}{kR} \tag{4}$$

$$\Delta E_{\rm c}(2{\rm p}) \approx q^2 \left\langle \frac{1}{r_{\rm d}} \right\rangle - \frac{(e^2 + q^2)}{kR} \tag{5}$$

where $r_{d(p)}$ is the Ni_{3d}(O_{2p}) orbital radius, $q^2/e(q'^2/e)$ is the effective positive charge of a nickel (oxygen) site of an (NiO₆)⁹⁻ cluster in a defective lattice. The last two terms in the right-hand side of eqn (4) and (5) are the first-order contributions arising from a modification of the molecular potential. In these computations only first-neighbour interactions were taken into account. Moreover, by making use of the ($\langle 1/r_{p(d)} \rangle$) values³⁰ by considering that $q^2 = (ae)^2$ and $q'^2 = (be)^2$, where e is the electronic charge, we have:

$$(E_{\rm B'} - E_{\rm A'}) - (E_{\rm B} - E_{\rm A}) \approx b^2 e^2 \left(\left\langle \frac{1}{r_{\rm p}} \right\rangle + \frac{1 - \sqrt{2}}{kR} \right) - a^2 e^2 \left(\left\langle \frac{1}{r_{\rm d}} \right\rangle - \frac{2}{kR} \right). \tag{6}$$

By setting $(E_{\rm B'} - E_{\rm A'}) - (E_{\rm B} - E_{\rm A})$ equal to zero, as is observed experimentally, we obtain $b/a \approx 1$. This is in a good agreement with the b/a value obtained in the limit of degenerate d^7-d^8L configurations, as expected in a non-stoichiometric oxide.

A rough evaluation of the defectiveness of the samples can be carried out by using the $R = I_{\rm B}/I_{\rm A}$ values as reported in table 1. In fact this value is approximately given by

$$R = C(h \cdot)/C(Ni^{2+}) = C[(NiO_6)^{9-}]/C[(NiO_6)^{10-}]$$

where $C(h \cdot)$ is the concentration of holes and $C(Ni^{2+})$ is the concentration of the regular Ni clusters. The mass balance, applied to the cation sub-lattice, gives

$$C(Ni^{2+}) + C(h \cdot) + C(V'') = 1$$
(7)

where V" stands for a charge vacancy. Finally, by using the electroneutrality condition

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 $2C(V'') = C(h \cdot)$, and the *R* expression in terms of $C(h \cdot)$ and $C(Ni^{2+})$, eqn (7) yields

$$\delta = C(\mathbf{V}'') = \left[3\left(1 + \frac{2}{3R}\right)\right]^{-1} \tag{8}$$

where δ is the concentration of vacancies referred to the nickel sub-lattice. This equation gives, for the measured samples [for samples (c) and (d) this estimate is within 0.02 because of the Li⁺ substitutional ions], values in the range 0.13–0.22 vacancies per nickel site, which satisfy the inequality $\delta \ge \frac{1}{6}$ as reported above. Furthermore, it is important to point out that the d⁷–d⁸L energy separation in the ground state of a defective cluster is a function of δ . Generally the eqn (3) should be rewritten according to the expression:

$$\Delta E_{\rm d} = \Delta E_{\rm s} - \left(\frac{2e^2}{kR} - \frac{e^2}{(2R)k}\right) 12\delta \tag{9}$$

where the hole-hole energy repulsion was also taken into account. However, in our case the ΔE variations, induced by a change in δ , are negligible as well as the b/a ratio. For a non-stoichiometric Li-doped NiO eqn (9) should be rewritten as

$$\Delta E_{\rm d} = \Delta E_{\rm s} - \left(\frac{2e^2}{kR} - \frac{e^2}{(2R)k}\right) 12\delta - \left(\frac{e^2}{kR}\right) 12x$$

where x is the concentration of Li^+ ions that are in a substitutional cationic position.

An increase in the ratio between the main line and the satellite is obtained on going from sample (a) to sample (d). It could be explained as a change of the hybridization parameter between $3d^8$ and $3d^9L$ configurations in the initial and final state, respectively. An increase in the T off-diagonal element ($\langle d^8 | H | d^9L \rangle$) in the energy matrix of the unperturbed system, induces a decrease of the satellite intensity. Distortion around the Ni site induces a change in T.³¹ Particularly, the T value decreased from (a) to (d) and, consequently, the observed intensity ratio between peaks C and A increased. This is in agreement with the description of the satellite intensity as an inverse function of Ni 3d occupation.³²

In conclusion, the high-binding-energy feature in Ni(2p) X.p.s. of defective oxide is assigned to a cd^9L^2 multielectron final state, induced by defective nickel sites. These sites are described as $(NiO_6)^{9-}$ molecular clusters, since d-holes are expected in a p-type semiconductor oxide. The ground state of this cluster is described as a mixing of degenerate d^7-d^8L configurations (with respect to a stoichiometric lattice) because of the charge vacancies. The chemical shift of the O(1s), Ni(2p) high-energy features is also explained as a change in the oxygen and nickel ionic charge due to the cation vacancies.

References

- 1 K. S. Kim, Phys. Rev. B, 1975, 11, 2177.
- 2 S. Hufner and G. K. Wertheim, Phys. Rev. Lett. A, 1975, 51, 299.
- 3 S. Hufner, F. Hulliger, J. Osterwalder and T. Riesterer, Solid State Commun., 1984, 50, 83.
- 4 G. van der Laan, C. Westa, C. Haas and G. A. Sawatzky, Phys. Rev. B, 1981, 23, 4369.
- 5 P. C. Gravelle and S. J. Teichner, Adv. Catal., 1969, 20, 167.
- 6 B. H. Brandow, Adv. Phys., 1977, 26, 651.
- 7 S. Hufner and G. K. Wertheim, Phys. Rev. B, 1973, 8, 4857.
- 8 P. R. Norton, R. L. Tapping and J. W. Goodale, Surf. Sci., 1977, 65, 13.
- 9 G. A. Sawatzky and J. W. Allen, Phys. Rev. Lett., 1984, 53, 2339.
- 10 I. Davoli, A. Marcelli, A. Bianconi, M. Tomellini and M. Fanfoni, Phys. Rev. B, 1986, 33, 2979.
- 11 A. Fujimori and F. Minami, Phys. Rev. B, 1984, 30, 957.
- 12 S. Hufner, Z. Phys. B, 1984, 58, 1.
- 13 S. Hufner, Solid State Commun., 1984, 49, 1177.

- 14 K. S. Kim and R. Davis, J. Electron. Spectrosc. Relat. Phenom., 1972-73, 1, 251.
- 15 K. S. Kim and N. Winograd, Surf. Sci., 1974, 43, 625.
- 16 M. W. Roberts and R. St C. Smart, Surf. Sci., 1980, 100, 590.
- 17 M. W. Roberts and R. St C. Smart, J. Chem. Soc., Faraday Trans. 1, 1984, 80, 2957.
- 18 G. K. Wertheim and S. Hufner, Phys. Rev. Lett., 1972, 28, 1028.
- 19 J. M. McKay and V. E. Henrich, Phys. Rev. B, 1985, 32, 6764.
- 20 M. Scrocco, J. Electron. Spectrosc. Relat. Phenom., 1980, 19, 311.
- 21 G. G. Wepfer, G. T. Surrat, R. S. Weidman and A. B. Kunz, Phys. Rev. B, 1980, 21, 2596.
- 22 A. E. Cherkashin, A. N. Goldobin, V. I. Savtchenko, P. N. Keyer and G. L. Smin, React. Kinet. Catal. Lett., 1974, 1, 411.
- 23 D. A. Shirley, Phys. Rev., 1972, 85, 4709.
- 24 N. Beatham and A. F. Orchard, J. Electron Spectrosc., 1976, 9, 129.
- 25 Van P. H. Cittert, Z. Phys., 1971, 69, 298.
- 26 J. H. Scofield, J. Electron Spectrosc., 1976, 8, 129.
- 27 I. G. Austin, B. D. Clay, C. E. Turner and A. J. Springthorpe, Solid State Commun., 1968, 53.
- 28 D. Adler and J. Feinleib, Phys. Rev. B, 1970, 2, 3112.
- 29 G. van der Laan, J. Zaanen and G. Sawatzky, unpublished results.
- 30 K. Siegbahn, D. A. Allison and J. H. Allison, in *Handbook of Spectroscopy* (CRC Press, Cleveland, Ohio, 1974), vol. 1, pp. 512-752.
- 31 M. Tomellini, D. Gozzi, A. Bianconi and I. Davoli, J. Chem. Soc., Faraday Trans. 1, 1987, 83, 289.
- 32 U. Hillebrecht, J. C. Fuggle, P. A. Bennet, Z. Zolnierek and Ch. Freiburg, Phys. Rev. B, 1983, 27, 2179.

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