

## Electronic State of Nickel in Barium Nickel Oxide, BaNiO<sub>3</sub>

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An attempt is made to draw conclusions on the binding situation and the electronic state of nickel in the hexagonal perovskite BaNiO<sub>3</sub> characterized by chain units of face sharing NiO<sub>6</sub> octahedra by means of XPS, IR, and Mössbauer spectroscopy and susceptibility measurements. Although the results of Mössbauer measurements appear to favor the existence of quadrivalent Ni, the photoelectron spectroscopy data suggest the description of BaNiO<sub>3</sub> in terms of trivalent Ni and oxygen anion holes. In terms of a local ionic model the idealized description of this high-valent oxometalate would correspond to Ba<sup>2+</sup>Ni<sup>3+</sup>(O<sup>2-</sup>)<sub>2</sub>O<sup>•-</sup>. A binding model was formulated by taking into account the structural and electronic properties of the compound.

### Introduction

Oxometalates with transition metals in high formal valence states exhibit a variety of interesting physical and chemical properties. An example of actual interest are oxocuprate type superconductors with Cu<sup>II</sup>Cu<sup>III</sup> mixed valence.

Similar high oxidation states of the transition metal are found for oxides of the neighboring element nickel, e.g. BaNiO<sub>3</sub> and SrNiO<sub>3</sub>, which have been less well investigated under this aspect. The metal/oxygen sublattice of BaNiO<sub>3</sub> (Figure 1) can be described by NiO<sub>6</sub> octahedra sharing faces to form chain units (NiO<sub>6/2</sub>)<sub>∞</sub><sup>•-</sup> oriented parallel to each other.<sup>1,2</sup> The face sharing of the polyhedra leads to an unusually short distance between the nickel atoms within one chain unit; the Ni–Ni distance is actually below that found for nickel atoms in the element. This fact appears rather extraordinary from the viewpoint of a simple ionic bonding model involving Ni<sup>4+</sup> ions with respect to the consequence of a strong Coulomb repulsion between the metal ions. It must be assumed therefore that the Ni/O bonding is partially covalent, which would reduce the effective charges and the repulsion between the metal atoms.<sup>2</sup> An alternative model is based on the assumption that nickel is trivalent (Ni<sup>3+</sup> ions) while the charge balance is achieved by a partial reduction of the anion valence. In the simple ionic description the two models are characterized by the correlation

$$\text{Ni}^{4+}/\text{O}^{2-} \text{ vs } \text{Ni}^{3+}/\text{O}^{\bullet-}$$

The latter case involves either localized or delocalized oxygen anion holes.

Here we want to emphasize that the chosen ionic description is not meant to describe the real charge distribution because covalent bonding contributions reduce the ionic charge.

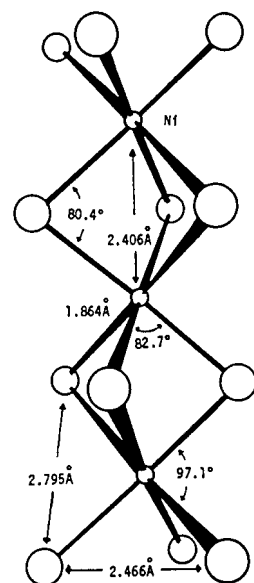


Figure 1. Structure scheme of Ni/O chain elements in BaNiO<sub>3</sub>.<sup>2</sup>

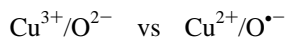
The aim of the present work is to find experimental evidence for an answer to the question which of the two models is a better representation for the description of the bonding state Ni/O in BaNiO<sub>3</sub>. This question is also of interest with respect to the bonding situation in superconducting oxocuprates, where it has been shown that the transition temperature, *T<sub>c</sub>*, depends on the concentration of defect electrons. So far it is still unclear whether the defect electrons have essentially d or p character (copper holes or oxygen holes);<sup>3–5</sup> the situation is basically similar in an ionic model to that described above for nickel,

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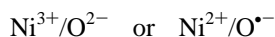
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i.e.



To obtain information on bonding strength and valence states in  $\text{BaNiO}_3$  we used infrared, Mössbauer, and photoelectron spectroscopy as well as susceptibility measurements and X-ray diffraction. For a reasonable interpretation it appears necessary to investigate appropriate reference compounds. The requirement that the bonding in the latter should be well-known while their structures should be related to  $\text{BaNiO}_3$  turned out, however, to be a problem. For those compounds which could in principle be used as standards for trivalent nickel, e.g.  $\text{LaNiO}_3$  or  $\text{BaNi}_{0.86}\text{O}_{2.36}$ , it is again unclear if there is a coexistence between valence states, i.e.



The investigation of these phases presented therefore a chance, however, to also approach this question.

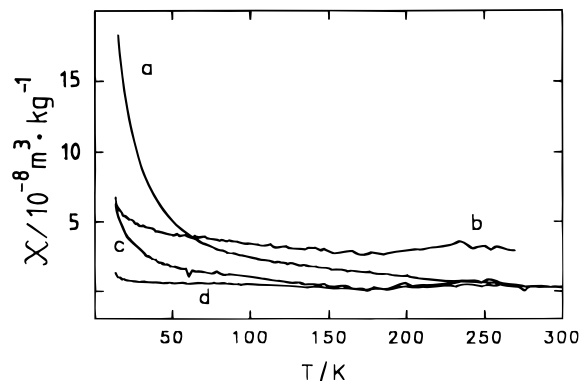
### Experimental Section

The preparation of the polycrystalline compounds  $\text{BaNiO}_2$ ,  $\text{LaNiO}_3$ ,  $\text{BaNi}_{0.86}\text{O}_{2.36}$ , and  $\text{BaNiO}_3$  was performed by the conventional sintering process. Educts were green  $\text{NiO}$ ,  $\text{La}_2\text{O}_3$ , and  $\text{BaCO}_3$  (analytical grade). The procedure for preparing  $\text{BaNiO}_3$  and  $\text{BaNiO}_2$  is described by Krischner.<sup>6</sup>  $\text{BaNi}_{0.86}\text{O}_{2.36}$  was obtained by sintering  $\text{BaNiO}_3$  at 900 °C in a nitrogen atmosphere with subsequent quenching to room temperature.<sup>7</sup>  $\text{BaNi}_{0.86}\text{O}_{2.36}$  was synthesized by us in the context of investigations on  $\text{BaNiO}_3$ .<sup>7</sup> With modification of the preparation procedure of  $\text{LaNiO}_3$  a stoichiometric mixture of  $\text{La}_2\text{O}_3$  and  $\text{NiO}$  was heated with  $\text{Na}_2\text{CO}_3$  (50 wt %) for 7 d at 900 °C.<sup>8</sup> After removal of the alkali carbonate by working with water, the powder obtained was annealed at 600 °C for 2 d in oxygen atmosphere. Except for  $\text{BaNi}_{0.86}\text{O}_{2.36}$ , which contains traces of  $\text{NiO}$ , the oxometalates prepared in this way were black single-phase compounds (X-ray diffractogram) easily soluble in dilute mineral acids. Lattice parameters are as follows:  $\text{LaNiO}_3$ , hexagonal,  $a = 5.456$  Å,  $c = 13.138$  Å;  $\text{BaNiO}_3$ , hexagonal,  $a = 5.635$  Å,  $c = 4.8041$  Å;  $\text{BaNi}_{0.86}\text{O}_{2.36}$ , orthorhombic,  $a = 5.599$  Å,  $b = 9.945$  Å,  $c = 4.422$  Å;  $\text{BaNiO}_2$ , orthorhombic,  $a = 5.737$  Å,  $b = 9.190$  Å,  $c = 4.760$  Å.

The structural characterization of the product was performed by X-ray diffractometry (powder diffractometer with primary monochromator, position sensitive detector,  $\text{Cu K}\alpha 1$  radiation). Magnetic susceptibilities were measured with an ac susceptometer (23–325 K) for paramagnetic phases and a Faraday balance (78–350 K) for the diamagnetic compounds. KBr pressed pellets served for the measurement of the IR spectra.

Mössbauer spectra were recorded with a conventional vertical spectrometer with helium cryostat in transmission geometry with a sample mass of 200–300 mg. The  $^{61}\text{Co}$  source was prepared by activation of a  $^{62}\text{Ni}_{0.85}\text{Cr}_{0.15}$  alloy.

X-ray photoelectron spectroscopy (XPS, nonmonochromatized  $\text{Mg K}\alpha$  radiation,  $h\nu = 1253.6$  eV) was carried out in a Leybold-Heraeus LH 200 MCD system equipped with hemispherical analyzer, which was operated in the constant pass energy mode. The base pressure of the apparatus was  $2 \times 10^{-10}$  mbar. The energy scale was calibrated using  $E_B(\text{Au } 4f_{7/2}) = 84.0$  eV. The resolution of the XPS data was 1.2 eV (fwhm of  $\text{Ag } 3d_{5/2}$ ). The samples were transferred into the preparation chamber (base pressure  $10^{-9}$  mbar) as loose powder in a mortarlike stainless steel sample holder. A wobble stick equipped with a stainless



**Figure 2.** Temperature-dependent magnetic susceptibilities of  $\text{BaNi}_{0.86}\text{O}_{2.36}$  (a),  $\text{LaNiO}_3$  (b),  $\text{BaNiO}_2$  (c), and  $\text{BaNiO}_3$  (d).

**Table 1.** Correlation of Formal Oxidation State ( $\text{Ni}^{n+}$ ), Magnetic Properties, and Bond Length of Oxonickelates

	$\text{Ni}^{n+}$ (a)	magnetic susceptibility $\chi$ (200 K)( $\text{m}^3 \cdot \text{kg}^{-1}$ ) <sup>b</sup>	$d(\text{Ni}-\text{O})$ (Å)	$\nu(\text{Ni}-\text{O})$ ( $\text{cm}^{-1}$ )
$\text{BaNiO}_2$	2	diam/ $6 \times 10^{-9}$	$2.01^{10}$	570
$\text{LaNiO}_3$	3	Pauli/param/ $3 \times 10^{-8}$	$1.925^{11}$	
$\text{BaNi}_{0.86}\text{O}_{2.36}$	3.17	param/ $1.2 \times 10^{-8}$		585
$\text{BaNiO}_3$	4	diam/ $3.5 \times 10^{-9}$	$1.864^{11}$	595

<sup>a</sup> Formal valency  $n+$  derived from ionic model with  $\text{O}^{2-}$  anions.

<sup>b</sup> diam = diamagnetic; param = paramagnetic.

steel pestle was used to grind the samples in UHV until bulk stoichiometry was obtained. In the preparation chamber oxygen exposures (purity 99.9999%) at 10 mbar were performed at temperatures up to 873 K followed by rapid transfer in UHV to the measurement chamber.

### Results and Discussion

**General Characterization.** In Figure 2 the susceptibilities measured are given as a function of temperature. The results confirm the diamagnetic behavior expected for  $\text{BaNiO}_2$  and  $\text{BaNiO}_3$ <sup>6</sup> and the Pauli paramagnetism of  $\text{LaNiO}_3$ .<sup>9</sup> A value of  $n_B = 0.66$  (Bohr magnetons) resulted from a  $1/\chi$  vs  $T$  curve for  $\text{BaNi}_{0.86}\text{O}_{2.36}$ . The susceptibilities observed at 200 K are given in Table 1 for the four samples. In a first approximation the magnetic behavior appears to be consistent with the observation of diamagnetism for low-spin  $\text{Ni}^{2+}/d^8$  and  $\text{Ni}^{4+}/d^6$ . For the  $d^7$  configuration of  $\text{Ni}^{3+}$  paramagnetism is to be expected for the high-spin as well as the low-spin case. Both compounds, which can be assigned to  $\text{Ni}^{3+}$ , i.e.,  $\text{LaNiO}_3$  and  $\text{BaNi}_{0.86}\text{O}_{2.36}$ , exhibit, in fact, paramagnetism. The low values observed can be explained by covalence effects; in the case of  $\text{LaNiO}_3$  in addition the metallic character has to be taken into account (Pauli paramagnetism).

The IR spectra of the  $\text{Ba}/\text{Ni}/\text{O}$  compounds are given in Figure 3. With increasing formal charge of the nickel ions the absorption maximum of the  $\text{Ni}/\text{O}$  stretching vibration is shifted to higher wavenumbers (Table 1).<sup>10</sup> This behavior confirms the increase in  $\text{Ni}/\text{O}$  bond order with increasing formal valence. The relative broad absorption band of  $\text{BaNi}_{0.86}\text{O}_{2.36}$  appears to be composed of the signals of  $\text{BaNiO}_2$  and  $\text{BaNiO}_3$ . An explanation of this observation could be based on the assumption that  $\text{Ni}^{2+}$ ,  $\text{Ni}^{3+}$ , and  $\text{Ni}^{4+}$  coexist in  $\text{BaNi}_{0.86}\text{O}_{2.86}$ . This unusual assignment is based on earlier investigations of the compound

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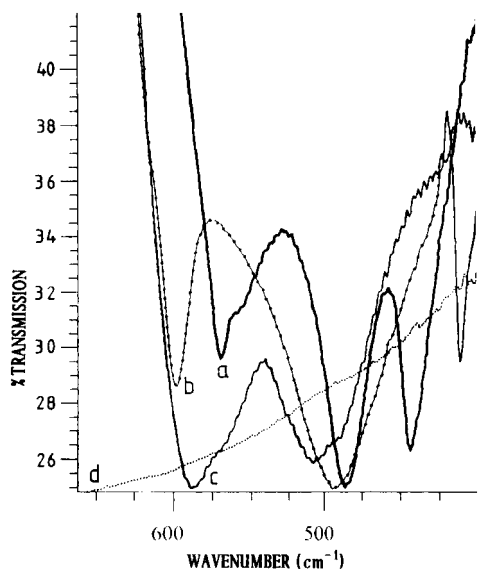
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**Figure 3.** IR spectra of BaNiO<sub>2</sub> (a), BaNiO<sub>3</sub> (b), BaNi<sub>0.86</sub>O<sub>2.36</sub> (c), and LaNiO<sub>3</sub>(d).

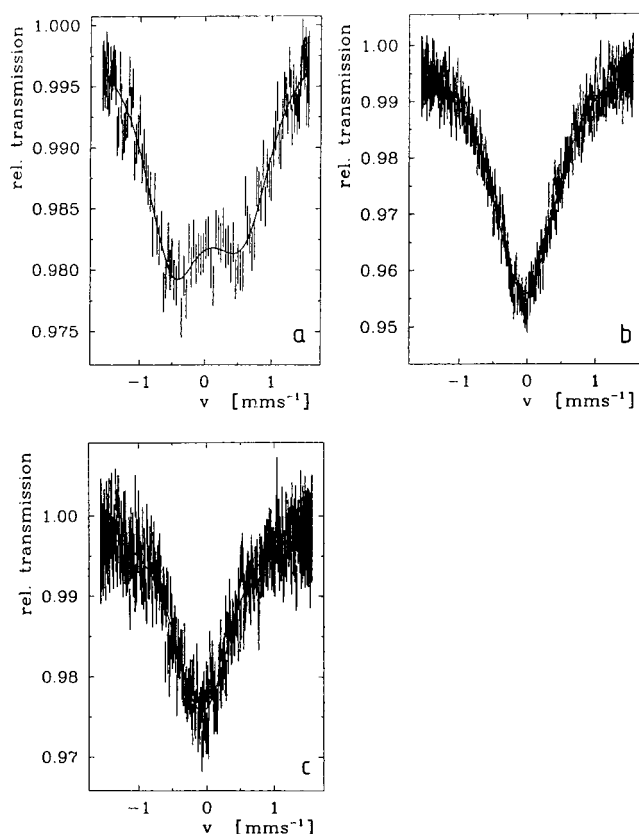
BaNi<sub>0.86</sub>O<sub>2.50</sub>, which provide evidence for the simultaneous presence of all three valence states of nickel.<sup>12</sup>

The dependence of the bonding strength Ni/O upon the formal nickel valence as described above is supported by literature data on the Ni/O interatomic distances: with increasing formal nickel oxidation state the Ni/O bond length (Table 1) is decreasing.

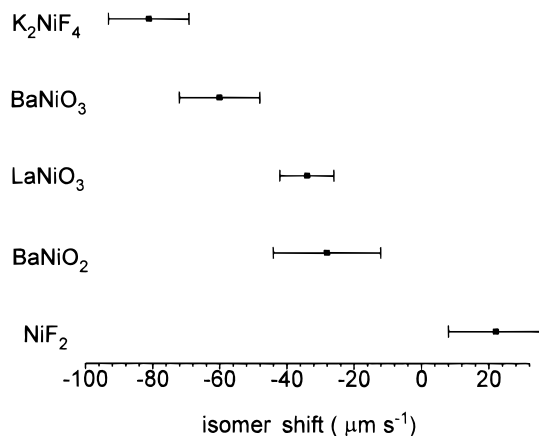
**Mössbauer Spectroscopy.** The <sup>61</sup>Ni Mössbauer spectra of BaNiO<sub>2</sub>, LaNiO<sub>3</sub>, and BaNiO<sub>3</sub> are given in Figure 4. From these measurements two different aspects relevant for the description of the chemical bonding can be derived.

The first aspect concerns the signal splitting which is weak for BaNiO<sub>3</sub> but rather strong for BaNiO<sub>2</sub>. This quadrupole splitting is observed when the electric field gradient (efg) which is controlled by valence and lattice contributions is unequal to zero at the nucleus. The quadrupole splitting measured for BaNiO<sub>2</sub> corresponds to  $V_{zz} = -1.5 \times 10^{18} \text{ V cm}^{-2}$  and belongs thus to the highest values measured so far for nickel compounds.<sup>13</sup> In contrast with the 4-fold coordination of nickel by oxygen in BaNiO<sub>2</sub> the octahedral ligand field of Ni<sup>4+</sup> in BaNiO<sub>3</sub> is not expected to result in quadrupole splitting. The fact that weak signal splitting is observed for BaNiO<sub>3</sub>, however, could be explained by an asymmetric charge distribution in the case the valence state is not +4 but lower; a perturbed quasi-octahedral environment causes d-orbital splitting and can then lead to noncubic valence electron distribution. Another possibility is that the lattice contribution to the efg results from the quasi-one-dimensional structure.

The second aspect concerns the isomer shift  $\delta$ , which represents a measure for the electron density in the nuclear region and provides thus indirect evidence for the oxidation state of the corresponding species. In the case of Ni a shift of  $\delta$  in negative direction suggests a reduced occupation of the d-orbitals. Beside the conventional isomer shift an additional quadratic Doppler shift originating from lattice vibrations may appear. All compounds investigated in this study are expected to have similar Debye–Waller factors, however, so that this



**Figure 4.** Mössbauer spectra of BaNiO<sub>2</sub> (a), LaNiO<sub>3</sub> (b), and BaNiO<sub>3</sub> (c).



**Figure 5.** Comparison of the Mössbauer isomer shifts  $\delta$  of BaNiO<sub>2</sub>, LaNiO<sub>3</sub>, BaNiO<sub>3</sub>, and the reference compounds NiF<sub>2</sub> and K<sub>2</sub>NiF<sub>6</sub>.

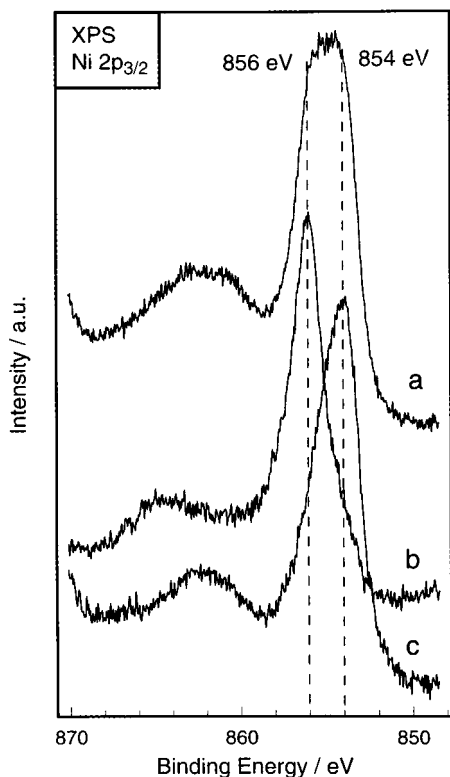
effect should be approximately equal for all compounds and can be neglected. The  $\delta$  values ( $\mu\text{m s}^{-1}$ ) measured were as follows: BaNiO<sub>2</sub>, -28(16); LaNiO<sub>3</sub>, -34(8); BaNiO<sub>3</sub>, -60(12); NiF<sub>2</sub>, 22(14); K<sub>2</sub>NiF<sub>6</sub>, -81(12). The fluorides which are considered as the most ionic Ni compounds were taken for comparison. The graphical presentation of these values (Figure 5) shows that the  $\delta$  value of BaNiO<sub>3</sub> is situated between the isomer shifts of K<sub>2</sub>NiF<sub>4</sub> and LaNiO<sub>3</sub>. With the assumption that K<sub>2</sub>NiF<sub>4</sub> presents a compound with Ni<sup>4+</sup> these results suggest an effective Ni oxidation state between +3 and +4.

**Photoelectron Spectroscopy.** In connection with the question of the charge distribution of the Ni–O bond photoelectron spectroscopy data are of particular interest, since they yield direct information on the bonding energy of the electrons on nickel and oxygen. A reasonable interpretation of the data requires again a comparison with known values of related

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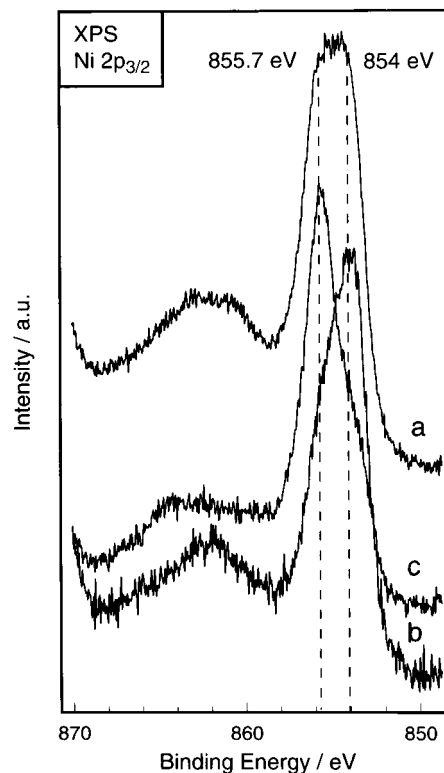
**Table 2.** Binding Energy (eV) for Ni 2p<sup>2/3</sup> and O 1s Electrons of Selected Nickel Compounds

	Ni <sup>14</sup>	NiO <sup>15</sup>	Ni(OH) <sub>2</sub> <sup>15</sup>	Ni <sub>2</sub> O <sub>3</sub> <sup>15</sup>	NiCl <sub>2</sub> <sup>16</sup>	K <sub>2</sub> NiF <sub>6</sub> <sup>16</sup>
Ni 2p <sub>3/2</sub>	852.8	854.5	855.3	856.0	856.8	861.0
O 1s		529.8	531.0	531.2		

**Figure 6.** Ni 2p<sub>3/2</sub> XPS spectra of BaNi<sub>0.86</sub>O<sub>2.36</sub> (a), BaNiO<sub>3</sub> (b), and BaNiO<sub>2</sub> (c).

compounds. For this purpose a series of appropriate phases was collected from the literature; the data are listed in Table 2. They provide an empirical relationship on the grounds of XPS measurements between the bonding energy (eV) of the Ni 2p<sub>2/3</sub> and the O 1s electrons and the chemical environment.

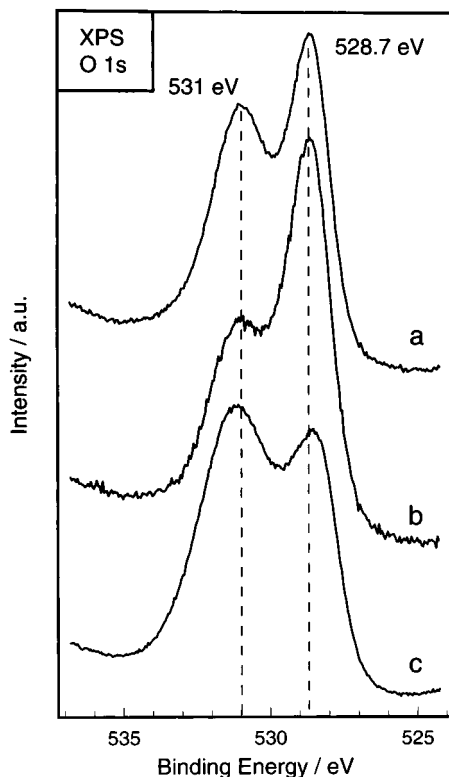
The data allow an evaluation of the position of the Ni 2p<sub>3/2</sub> signal for a hypothetical compound with Ni<sup>4+</sup> in octahedral oxygen coordination. A comparison of the values for NiO and NiCl<sub>2</sub> shows that the binding energy for Ni<sup>2+</sup> compounds differs by ca. 2 eV on the transition from the oxide to the halide. If a similar conclusion is made for Ni<sup>4+</sup> compounds, then the value expected for a hypothetical Ni<sup>4+</sup> oxide should be close to ca. 859 eV since the value measured for K<sub>2</sub>NiF<sub>6</sub> corresponds to 861 eV. The Ni 2p<sub>2/3</sub> spectra of BaNiO<sub>2</sub>, BaNi<sub>0.86</sub>O<sub>2.36</sub>, and BaNiO<sub>3</sub> are given in Figure 6. Since the overlap of La 3d<sub>3/2</sub> and Ni 2p<sub>3/2</sub> signals in LaNiO<sub>3</sub> prevent the data extraction, we used BaNi<sub>0.86</sub>O<sub>2.36</sub> as a reference compound with a high formal Ni<sup>3+</sup> fraction. The Ni 2p<sub>2/3</sub> signal of BaNiO<sub>2</sub> exhibits a value of 854.3 eV typical for Ni<sup>2+</sup> in octahedral coordination. For BaNiO<sub>3</sub> a substantial shift to 856 eV is found which has to be assigned to Ni<sup>3+</sup> as it is clearly below the value expected for Ni<sup>4+</sup> (nickel hydroxide, Ni(OH)<sub>2</sub>, exhibits a shift value of 854 eV; its presence as impurity is most unlikely, however, as discussed below). The shoulder observed at the high-energy side of the BaNiO<sub>2</sub> signal can be interpreted in terms of the presence of a small amount of Ni<sup>3+</sup> while a minor amount of Ni<sup>2+</sup> (shoulder at the lower energy side) is visible for BaNiO<sub>3</sub>. The signal of BaNi<sub>0.86</sub>O<sub>2.36</sub> is broadened, which is attributed to the presence of comparable amounts of Ni<sup>2+</sup> and Ni<sup>3+</sup>.

**Figure 7.** Ni 2p<sub>3/2</sub> XPS spectra of BaNi<sub>0.86</sub>O<sub>2.36</sub>: (a) untreated; (b) reduced in a vacuum at 600 °C; (c) treated with O<sub>2</sub> at 600 °C.

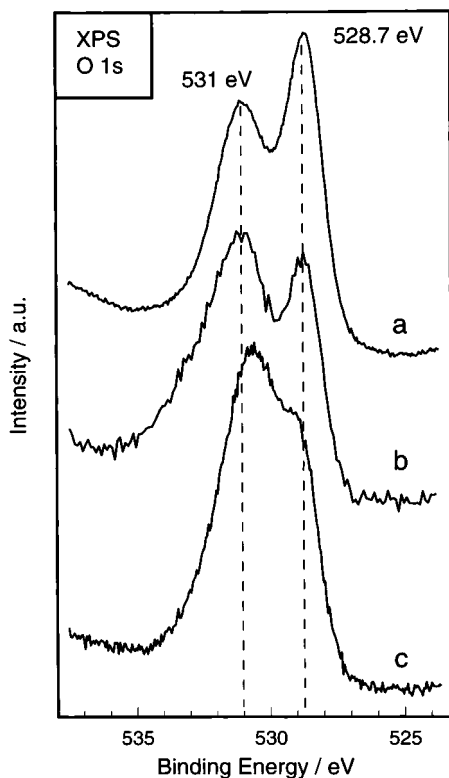
On grounds of three spectra of BaNi<sub>0.86</sub>O<sub>2.36</sub> obtained under different conditions we can show principally (Figure 7) that the signal position variation is influenced by oxygen and not by hydroxide (or carbonate). In the upper section of Figure 7 the spectrum of the untreated sample is given with the characteristic signal broadening. Two different signal components in approximately similar weight can be identified here. The signal fraction of the species with higher oxidation state is diminishing under reducing conditions (treatment under UHV at 600 °C, for 30 min, Figure 7b). Upon subsequent oxidation (600 °C, p(O<sub>2</sub>) = 10 mbar, 30 min) this signal component is increasing again beyond the original ratio (Figure 7c).

In Figure 8 the O 1s signals of the reaction sequence described are given. The signal peaks at lower binding energy (528.7 eV) correspond to O<sup>2-</sup> in metal oxides while the peak at higher binding energy (531.0 eV) could correspond to OH<sup>-</sup>, CO<sub>3</sub><sup>2-</sup>, or O<sup>-</sup>.<sup>17</sup> Similar to the situation found for the Ni signals (Figure 7) the ratio of the two components at higher and lower binding energy is diminishing under reducing conditions and is increasing beyond the original value upon subsequent oxidation. Since under the reaction conditions applied (UHV and high-purity oxygen) a contamination with CO<sub>2</sub> or H<sub>2</sub>O can be excluded, the increase of the signal at 531 eV in the oxidation step can only originate from the reaction with oxygen. Because of the high binding energy of the signal the assignment to O<sup>-</sup> appears to be reasonable. The O 1s lines of BaNiO<sub>3</sub> and BaNiO<sub>2</sub> are compared with those of BaNi<sub>0.86</sub>O<sub>2.36</sub> in Figure 9. As compared to BaNi<sub>0.86</sub>O<sub>2.36</sub> the barium compound BaNiO<sub>3</sub> exhibits clearly

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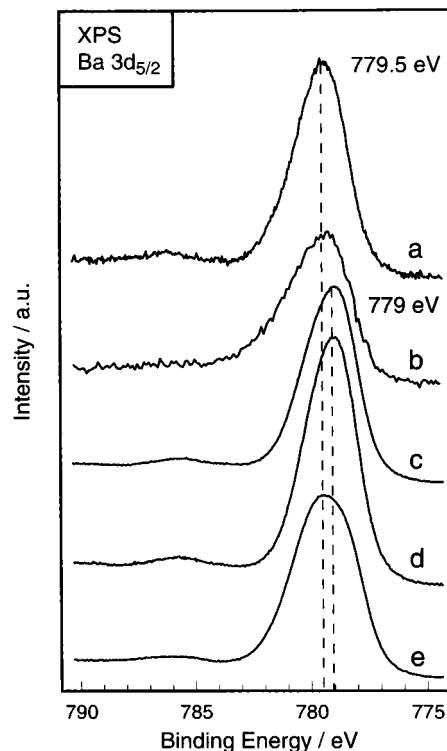
**Figure 8.** O 1s XPS spectra of BaNi<sub>0.86</sub>O<sub>2.36</sub>: (a) untreated; (b) reduced in a vacuum at 600 °C; (c) oxidized with O<sub>2</sub> at 600 °C.



**Figure 9.** O 1s XPS spectra of (a) BaNi<sub>0.86</sub>O<sub>2.36</sub>, (b) BaNiO<sub>3</sub>, and (c) BaNiO<sub>2</sub>.

a larger fraction of the component with the higher binding energy. Along with the results obtained under reducing/oxidizing conditions (cf. above) this observation suggests that the signal at 531 eV is at least in part to be assigned to O<sup>•-</sup>.

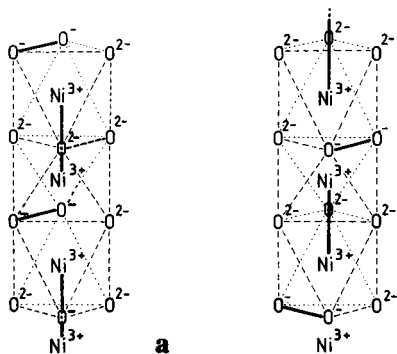
Line broadening related to two different Ba species is observed in the Ba 3d<sub>5/2</sub> spectra (Figure 10) for all compounds.



**Figure 10.** Ba 3d<sub>5/2</sub> spectra of (a) BaNiO<sub>2</sub>, (b) BaNiO<sub>3</sub>, (c) BaNi<sub>0.86</sub>O<sub>2.36</sub>, (d) BaNi<sub>0.86</sub>O<sub>2.36</sub> reduced in a vacuum at 600 °C, and (e) BaNi<sub>0.86</sub>O<sub>2.36</sub> oxidized in O<sub>2</sub> at 600 °C.

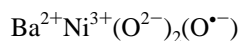
It is to be concluded therefore that besides the pristine phase additional barium impurity compounds such as BaCO<sub>3</sub>, Ba(OH)<sub>2</sub>, and BaO<sub>2</sub> may be present at the surfaces investigated. This observation could explain why in addition to the O<sup>2-</sup> signal at 529 eV a further signal appears at 531 eV in the O 1s spectrum of BaNiO<sub>2</sub>. As concerns the two other compounds studied, we assume that here also small concentrations of BaCO<sub>3</sub>, Ba(OH)<sub>2</sub>, or BaO<sub>2</sub> are present at the surface, simulating increased O<sup>•-</sup> concentrations. A further indication for the presence of surface impurities is the Ni<sup>3+</sup> signal fraction in BaNiO<sub>2</sub> (Figure 6). It is likely that the formation of those impurity phases occurred in the transfer step from the sample container (Schlenk tube, argon atmosphere) to the UHV chamber.

It is obvious thus that all samples measured were subjected to partial surface corrosion with the appearance of nickel-free barium phases as surface impurities. As another consequence, small amounts of Ni<sup>3+</sup> can be found in the spectra of BaNiO<sub>2</sub> and small amounts of Ni<sup>2+</sup> similarly in BaNiO<sub>3</sub>. Despite those experimental problems, several important results could be obtained. The existence of Ni<sup>4+</sup> in BaNiO<sub>3</sub> appears to be disproved; nickel seems to be trivalent in this compound if we neglect the small fraction of Ni<sup>2+</sup> present obviously as surface contamination. This agrees with the evidence for the presence of O<sup>•-</sup> in the O 1s spectra. We were able to prove that the signal measured at higher energy results from the interference of two components. One of these corresponds to the signal of the barium compound surface impurities; the other component whose fraction varies depending upon pretreatment (Figure 8) is clearly related with oxygen in a higher oxidation state (O<sup>•-</sup> or O<sub>2</sub><sup>2-</sup>). There is no final discussion on whether this oxygen is present as O<sup>•-</sup> in BaNiO<sub>3</sub> or as Ba<sub>2</sub>O<sub>2</sub> from the barium



**Figure 11.** Scheme of bonding model for  $\text{BaNiO}_3$  (two  $(\text{NiO}_{6/2})_{\infty}$  chain units) displaying Ni/Ni bonding, oxygen holes in the  $a/b$  plane, and (statistical) displacement of neighboring chain units.

compound impurity; the combination of the results favors, however, the first model, since the high oxidation potential determined via redox titration can only be explained by the presence of  $\text{O}^{\bullet-}$  when  $\text{Ni}^{4+}$  is absent. In a simple model of localized valences the ionic formula

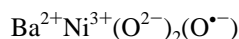


can thus be considered, which does not represent, however, the partially covalent character of the Ni/O bond. According to this formula the ratio of the two oxygen species should be 2:1  $\text{O}^{2-}/\text{O}^{\bullet-}$ . The fact that this ratio is not observed quantitatively for the integrated signal values of the O 1s lines at 529 and 531 eV (Figure 9) is a consequence of the fact that the signal at 531 eV consists of two components as described above.

## Conclusion

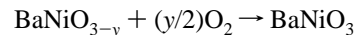
Simple experimental analytical data (redox titration) show that within the series  $\text{BaNiO}_2$ ,  $\text{LaNiO}_3$ ,  $\text{BaNi}_{0.86}\text{O}_{2.36}$ , and  $\text{BaNiO}_3$  the oxidation potential is increasing. Within the framework of an ionic model this result does obviously not provide any evidence whether the oxidizing species is  $\text{Ni}^{4+}$  or  $\text{O}^{\bullet-}/\text{O}_2^{2-}$ , respectively. By IR measurements it was possible to show that with increasing formal nickel valency an increasing strength of the Ni/O bonding is observed. Magnetic susceptibility measurements confirm the diamagnetic character of  $\text{BaNiO}_2$  and  $\text{BaNiO}_3$  while weak paramagnetic and Pauli paramagnetic behavior, respectively, was observed for  $\text{BaNi}_{0.86}\text{O}_{2.36}$  and  $\text{LaNiO}_3$ . These results agree in a first approximation well with the diamagnetic character of  $\text{Ni}^{2+}/d^8$  and  $\text{Ni}^{4+}/d^6$  and with a paramagnetic behavior of the  $\text{Ni}^{3+}/d^7$  low spin configuration of nickel ions. The results of Mössbauer spectroscopy measurements do not agree well with these conclusions because the presence of  $\text{Ni}^{4+}$  beside  $\text{Ni}^{3+}$  should lead to paramagnetism.

Like Mössbauer spectroscopy, XPS also gives evidence for  $\text{Ni}^{3+}$  but there is no indication for  $\text{Ni}^{4+}$ . In addition XPS provides evidence for the existence of  $\text{O}^{\bullet-}$  in this compound. The photoelectron spectroscopy data appear thus to provide a consistent model, which can be represented in an ionic formula as



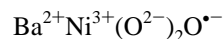
There are two additional arguments known from the literature which support the valence description of  $\text{BaNiO}_3$  by  $\text{Ni}^{3+}/\text{O}^{\bullet-}$ . One of these concerns the O/O bond length, which should be

equal in an ideal hexagonal close-packed Ba/O sublattice. Structural studies revealed, however, that the distance between two neighboring oxygen atoms within the hexagonal layers (2.4 Å) is significantly smaller as compared to the O/O distance (2.8 Å) between two layers.<sup>2</sup> One way to interpret the strong difference is to assume oxygen–oxygen interaction within the layers. A further indication for this is based on the results of calorimetric measurements on the enthalpy of the reaction:<sup>18</sup>

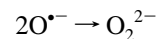


In a comparison with the enthalpies of related reactions leading to the formation of  $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ ,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ ,  $\text{La}_{2-x}(\text{Ba}/\text{Sr})_4\text{CuO}_y$ , and  $\text{La}_{2-x}\text{SrCuO}_y$ , it was concluded that the  $\Delta H_R$  value for the oxidation of  $\text{BaNiO}_{3-x}$  is typical for peroxide type compounds.

In Figure 11 the scheme for a model is given that represents an attempt to describe the Ni/O bonding for  $\text{BaNiO}_3$  on grounds of the evidence discussed above. As the starting point the ionic formula



was used, which seems to take into account the experimental facts better than the alternative possibility  $\text{Ba}^{2+}\text{Ni}^{4+}(\text{O}^{2-})_3$  with quadrivalent nickel. We assume a partial dimerization



of the anion fraction with p holes. In Figure 11a a  $(\text{NiO}_{6/2})_{\infty}^{2-}$  chain is given for an illustration of the scheme. According to the ionic description above we find in the hexagonal  $\text{BaO}_3$  layers  $\text{O}^{2-}$  as well as  $\text{O}_2^{2-}$  ions. The statistical orientation of these ions does not result in different oxygen positions; the selective orientation of the peroxide ions parallel to the hexagonal planes leads, however, to a reduced average O/O bond length relative to the O/O bond length in direction of the  $c$ -axis as observed experimentally. The diamagnetic behavior of  $\text{BaNiO}_3$  can be explained by localized metal/metal bonding with  $\text{Ni}_2$  cluster units in direction of the  $c$ -axis.<sup>7</sup> X-ray data yield only one single Ni position but a significantly increased temperature factor in the 001 direction;<sup>2</sup> this can be interpreted in terms of a statistical displacement of the  $(\text{NiO}_{6/2})_{\infty}^{2-}$  chain units in direction of the  $a$ -axis (Figure 11b). This model is further supported by a band structure calculation predicting bonding  $d_z^2$  orbitals and accounts for the semiconductor properties of  $\text{BaNiO}_3$ .<sup>9</sup>

The scheme described above is based upon a simple ionic model; it does not take into account the fact that Mössbauer data suggest a high covalency for the Ni/O bonding. In the hypothetical situation of 100% covalency all of the ionic charge of the  $\text{Ni}^{3+}$  would be reduced by 3 Ni/O atomic bonds.

In summary we have to conclude that the experimental evidence presented in this study cannot give an unequivocal answer to the question of the nickel valency in  $\text{BaNiO}_3$ . A balanced analysis turns out, however, to be in favor of a model with trivalent nickel with Ni/Ni bonding and anion holes. For  $\text{BaNiO}_2$  and  $\text{LaNiO}_3$  the Mössbauer data suggest that the valencies of the nickel ions agree with those derived from the formal charge in an ionic model with  $\text{O}^{2-}$  anions. For  $\text{BaNi}_{0.86}\text{O}_{2.36}$  one has to assume the coexistence of  $\text{Ni}^{2+}$ ,  $\text{Ni}^{3+}$ , and  $\text{O}^{\bullet-}$ .