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1989 J. Phys.: Condens. Matter 1 2147

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LETTER TO THE EDITOR

Evidence for holes on oxygen in some nickel oxides

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Received 3 January 1989

Abstract. Core-level spectroscopic studies show the presence of holes on oxygen in LaNiO_3 and LiNiO_2 . Nickel in these oxides seems to be essentially in the $2+$ state instead of the $3+$ state—where it would formally be expected to be on the basis of the stoichiometry.

Recent investigations of high-temperature superconducting cuprates such as $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$, $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$ and $\text{Bi}_2\text{CaSr}_2\text{Cu}_3\text{O}_{8+\delta}$ have established the absence of the Cu^{3+} species that is expected to be present on the basis of stoichiometry; instead, holes are present on oxygen (Chakraverty *et al* 1988, Fuggle *et al* 1988, Rao 1988, Sarma and Rao 1987, 1988). In the light of this observation, we considered it important to investigate a few transition-metal oxide systems to find out whether the presence of oxygen holes is a phenomenon that occurs generally and is not restricted to superconducting cuprates alone. For this purpose, we have investigated LiNiO_2 and LaNiO_3 where Ni is formally in the $3+$ state, by means of core-level x-ray photoelectron spectroscopy. The study has indeed revealed that, in these oxides, holes are present on oxygen giving rise to O^{1-} -type species while Ni is essentially present in the $2+$ oxidation state.

LiNiO_2 and LaNiO_3 were synthesised by the ceramic method and sintered in oxygen in the form of pellets. X-ray photoelectron spectra were recorded with a VG spectrometer using $\text{Mg K}\alpha$ (1253.6 eV) radiation after the surfaces had been scraped with a ceramic file in the sample preparation chamber (operating vacuum $\sim 10^{-10}$ Torr). The Ni 2p and O 1s regions of the spectra were recorded after monitoring the C 1s region in order to estimate the carbonate content of the surface, if any. It may be noted that carbonates give an O 1s feature in the 531 eV region as distinct from the 529 eV feature due to O^{2-} species; the O^{1-} -type species is also expected to have its characteristic binding energy in this region (Chang *et al* 1988, Ford *et al* 1988, Rao *et al* 1987). An independent study of several carbonates showed the O 1s/C 1s intensity ratio to be ≈ 7.2 .

The Ni $2p_{3/2}$ spectra of LiNiO_2 , LaNiO_3 and NiO are shown in figure 1. The Ni $2p_{3/2}$ spectrum of NiO is well understood (Hüfner and Wertheim 1973, van der Laan *et al* 1986), with a main feature at 854 eV and a weaker feature at 861 eV. The two features in the Ni $2p_{3/2}$ (or $2p_{1/2}$) spectra arise from configuration interaction in the initial and final states of the photoemission. The more intense or well screened $2p_{3/2}$ feature at 854 eV is due to the lowest-energy configuration possible in the core-hole state, primarily $2p^53d^9$. The second peak at 861 eV, often assigned to the poorly screened or satellite peak, represents excited configurations such as the $2p^53d^8$. The spectra of LiNiO_2 and

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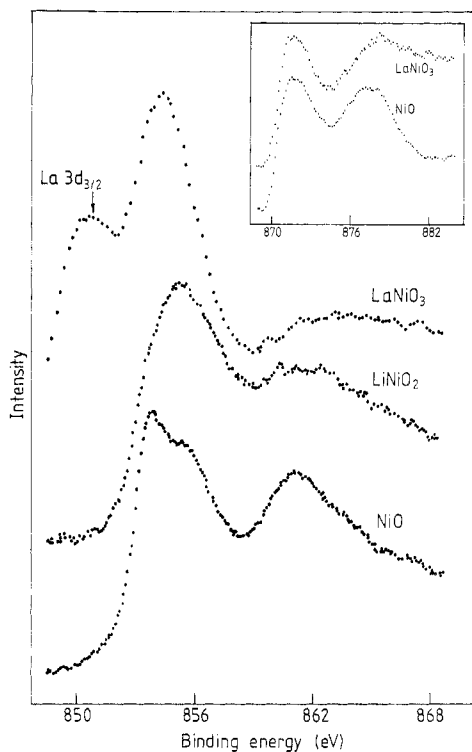


Figure 1. X-ray photoelectron spectra of the Ni $2p_{3/2}$ region of NiO, LiNiO₂ and LaNiO₃. The inset shows the Ni $2p_{1/2}$ region of NiO and LaNiO₃.

LaNiO₃ also show the doublet $2p_{3/2}$ feature, similar to that of NiO, with the main peak around 855.5 eV and the satellite peak around 862 eV. Since the La $3d_{3/2}$ spectrum in LaNiO₃ overlaps the Ni $2p_{3/2}$ spectrum, making it difficult to discern the spectral shape due to Ni, we have also given the Ni $2p_{1/2}$ spectra of NiO and LaNiO₃ in figure 1 (see the inset). The Ni $2p$ spectra do not exhibit any feature corresponding to the $2p^53d^7$ configuration of Ni³⁺, which is expected to appear at a considerably higher binding energy than the two features in the spectra in figure 1.

The relative intensities of the two Ni $2p_{3/2}$ or $2p_{1/2}$ peaks are governed by the charge-transfer excitation energy, Δ , between Ni $3d$ - and O $2p$ -derived states and the hybridisation strength, V , between them. Roughly speaking, the intensity of the satellite peak is expected to decrease with increasing V and/or decreasing Δ , due to increasing covalency or metal- $3d$ -ligand- $2p$ admixture. The relative intensity of the satellite is significantly lower in LiNiO₂ and LaNiO₃ than in NiO. This reduction in the satellite intensity in these formal Ni³⁺ oxides is likely to be due to the value of V being higher than that for NiO. This is expected since the Ni-O bond is more covalent in these Ni³⁺ oxides.

Since Ni in LaNiO₃ and LiNiO₂ is not in the 3+ state, the excess positive charge should reside in the oxygen, giving rise to oxygen holes. In order to find evidence for the oxygen holes, we have carefully examined the O $1s$ spectra of LaNiO₃, LiNiO₂ and NiO (figure 2). The spectrum of NiO shows a main feature around 529 eV due to O²⁻ species and a very small shoulder around 531 eV. This 531 eV feature can almost entirely be accounted for by the small amount of carbonate impurity present on the surface as indicated by the C $1s$ feature. The feature around 531 eV in LiNiO₂ and LaNiO₃ is, however, intense and cannot be ascribed to the carbonate impurity. We find that at least

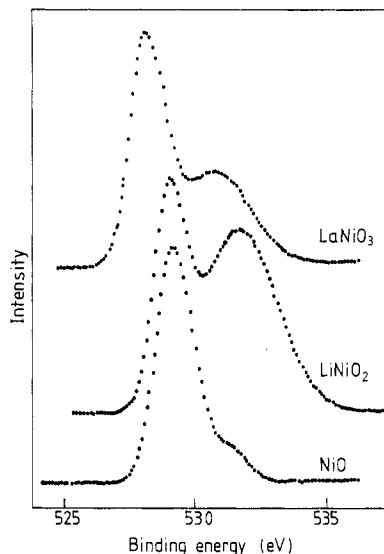


Figure 2. X-ray photoelectron spectra of the O 1s region of NiO, LiNiO₂ and LaNiO₃.

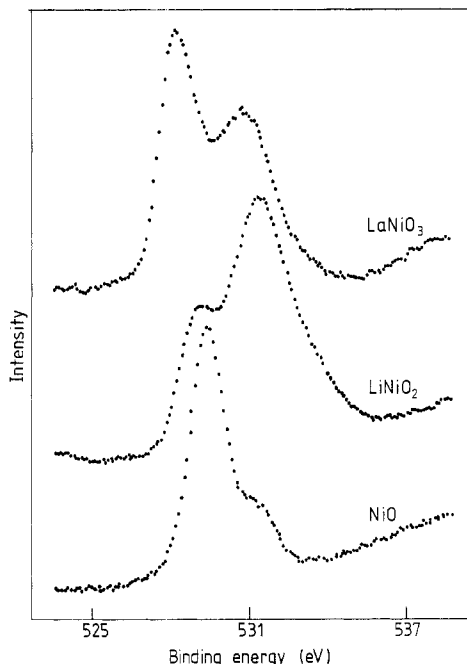


Figure 3. Constructed spectra of NiO, LiNiO₂ and LaNiO₃ in the O 1s region after subtraction of the background and the carbonate contribution. The remanent shoulder at 531 eV in the O 1s spectrum of NiO could be due to the defect oxide or OH⁻ species present on the surface (Wandelt 1982).

40% of the intensity of the 531 eV feature is due to a species other than carbonate. We attribute this to the oxygen holes or the O¹⁻ species. The spectra of O 1s after subtraction of the carbonate contribution are shown in figure 3. The assignment of the 531 eV feature to O¹⁻-type species finds support in recent studies of YBa₂Cu₃O_{7- δ} (Chang *et al* 1988, Ford *et al* 1988).

An important difference between the Ni 2p satellite peaks in the two formally Ni³⁺ oxides and NiO is that the satellite peak is considerably broader in the former. Furthermore, the main 2p_{3/2} feature at 854 eV shows considerable structure in NiO, but is featureless in the Ni³⁺ oxides. This is considered to be due to the fact that in the Ni³⁺ oxides there is one more hole present in the oxygen 2p level than there is in NiO. The presence of this extra hole in the ligand band considerably reduces the structure and increases the widths of both the peaks (Sarma 1988).

The present study shows that oxygen holes are formed in LaNiO₃ and LiNiO₂ instead of Ni being present in the 3+ state. It appears that the cation-anion charge-transfer energy in the trivalent nickel oxides is small compared to the Ni³⁺-Ni²⁺ charge-transfer energy. In other words, the reaction Ni³⁺ + O²⁻ → Ni²⁺ + O¹⁻ favours the formation of oxygen holes. Such charge transfer is favoured when the d electrons are itinerant or when the Ni-O bond is highly covalent.

We are grateful to the Department of Science and Technology for support of this research.

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