

**Unoccupied density of states of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$   
studied by polarization-dependent x-ray-absorption spectroscopy  
and bremsstrahlung isochromat spectroscopy**

P. Kuiper,\* J. van Elp, and G. A. Sawatzky

*Department of Solid State Physics of the Materials Science Centre, University of Groningen,  
Nijenborgh 18, NL-9747 AG Groningen, The Netherlands*

A. Fujimori

*Department of Physics, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113, Japan*

S. Hosoya

*Institute for Materials Research, Tohoku University, Sendai 980, Japan*

D. M. de Leeuw

*Philips Research Laboratories, P.O. Box 80000, NL-5600 JA Eindhoven, The Netherlands*

(Received 15 October 1990; revised manuscript received 21 February 1991)

Oxygen 1s x-ray-absorption measurements of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  ( $0 \leq x \leq 1.15$ ) are presented, together with O 1s polarization-dependent x-ray absorption on single-crystal  $\text{La}_{1.85}\text{Sr}_{0.15}\text{NiO}_4$ . It is concluded that the charge-compensating holes have mainly oxygen 2p character. The Ni 3d<sup>9</sup> final states reached because of the p-d hybridization in the ground state are strongly polarized in the (a,b) plane. The Sr-induced O 2p holes are found to be distributed equally over in-plane  $p_x, p_y$  and out-of-plane  $p_z$  orbitals. Possible explanations for this are presented. The intrinsic band gap of  $\text{La}_2\text{NiO}_4$  is found to be at least 4 eV. The bremsstrahlung-isochromat-spectroscopy results show that the Sr-induced states are spread out over a large portion of the band gap and are not concentrated at the top of the valence band.

## INTRODUCTION

Since the discovery of superconductivity at unprecedented temperatures in doped  $\text{La}_2\text{CuO}_4$ ,<sup>1</sup> interest has grown in the properties of related compounds like  $\text{La}_2\text{NiO}_4$ . Although searches for superconductivity in Ni-based compounds have been in vain and Ni substitution for Cu in  $\text{La}_2\text{CuO}_4$  superconductors suppresses superconductivity,<sup>2</sup> there have been some recent reports<sup>3,4</sup> of diamagnetism and decreasing resistivity at low temperatures in  $\text{La}_2\text{NiO}_4$ , with and without Sr doping. Our interest in this material stems from the possibility of comparison with data on  $\text{La}_2\text{CuO}_4$  and  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  and from the opportunity it gives to investigate the influence of strontium impurities and oxygen interstitials on the nature and symmetry of induced holes in charge-transfer-like, strongly correlated insulators.

$\text{La}_2\text{NiO}_4$  has the orthorhombic distorted  $\text{K}_2\text{NiF}_4$  crystal structure. The compound is a layered perovskite with the  $\text{NiO}_2$  layers separated by two LaO layers. While in NiO the six nickel-oxygen bonds have a length of 2.08 Å, in  $\text{La}_2\text{NiO}_4$  there are four shorter 1.95-Å bonds in the plane, and two longer 2.26-Å bonds perpendicular to it, which gives a ratio of 1.16 (Jorgensen, Ref. 5). This is considerably smaller than the value of 1.28 for  $\text{La}_2\text{CuO}_4$ . A report about two Ni positions with bond ratios of 1.32 and 1.07 was shown by Rodríguez-Carvajal *et al.*<sup>6</sup> to be due to an incorrect identification of a magnetic reflection as arising from nuclear scattering. Neutron diffraction has shown that  $\text{La}_2\text{NiO}_4$  is antiferromagnetic with a three-dimensional Néel temperature of about 320 K.<sup>7,8</sup>

The crystal structure can accommodate excess oxygen in interstitial positions in the LaO plane;<sup>5</sup> samples annealed in oxygen have the composition  $\text{La}_2\text{NiO}_{4.18}$ .<sup>4</sup> The reduced stoichiometric compound is reported to rapidly take up oxygen from air at room temperature.<sup>9</sup> More than half of the trivalent lanthanum can be replaced by divalent strontium without important changes in the crystal structure, but the rhombohedral distortion disappears. Up to  $\text{Sr}_2$  seems to be possible.<sup>10</sup> Strontium doping reduces the tendency of the material towards oxygen nonstoichiometry.<sup>11</sup>

Stoichiometric  $\text{La}_2\text{NiO}_4$  is an electrical insulator.<sup>12</sup> Although optical spectra measured by Tajima *et al.*<sup>13</sup> indicate an onset of the absorption at about 1.5–2 eV, the authors seem inclined to estimate a charge-transfer energy of about 4 eV. However, the oxygen content of the sample was not accurately known, so the gap of pure  $\text{La}_2\text{NiO}_4$  remains uncertain. Doping decreases the electrical resistivity; metallic behavior is observed for  $x \geq 0.8$ .<sup>14,15</sup>

Band-structure calculations<sup>16,17</sup> in the local density approximation incorrectly predict  $\text{La}_2\text{NiO}_4$  to be a metal, a problem similar to that encountered in NiO (Ref. 18) and  $\text{La}_2\text{CuO}_4$ .<sup>19</sup> It is now well understood that this discrepancy is caused by the large d-d Coulomb interactions and the discontinuity<sup>20</sup> in the exchange correlation potential when comparing ground- and excited-state properties. Similar to NiO (Ref. 21) and  $\text{La}_2\text{CuO}_4$ ,<sup>22,23</sup> we would expect the gap in  $\text{La}_2\text{NiO}_4$  to be of a charge-transfer nature<sup>24</sup> falling in class B of the Zaanen-Sawatzky-Allen (ZSA) phase diagram.<sup>25</sup> In this case, the first ionization state would be of primarily O 2p character

TABLE I. Stoichiometry parameters and lattice parameters of the measured samples of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$ ; the first entry is of a single crystal, the rest are ceramic samples.

$x$	$\delta$	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )
0.14		5.441	5.466	12.628	375.6
0	0.13	5.465		12.68	378
0.25	0.02	5.428		12.70	374
0.5	-0.01	5.391		12.74	370
0.8	-0.01	5.402		12.55	366
0.925	-0.01	5.412		12.47	365
1.15	-0.02	5.416		12.36	363

and the first electron affinity state of Ni 3d character, corresponding to nominal electron configurations  $d^8\bar{L}$  and  $d^9$ , respectively.

Band-structure calculations are useful, however, for obtaining parameters for model Hamiltonian calculations.<sup>26,27</sup> This has been done for  $\text{La}_2\text{NiO}_4$  with a slightly too small apical bond to in-plane ratio of 1.12.<sup>28</sup> The result was a gap of 3.0 eV, 1 eV larger than calculated for  $\text{La}_2\text{CuO}_4$ . The first ionization states were found to have mainly O 2p character. Recently, more complete model calculations gave a gap of 4 eV.<sup>29</sup>

An experimental method well suited to study the nature and symmetry of the states above the Fermi level for both pure and doped materials is x-ray-absorption spectroscopy, as has been amply demonstrated for  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  (Ref. 30) and the high- $T_c$  superconductors.<sup>31</sup>

### EXPERIMENT

Samples of  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$  with  $x$  ranging from 0 to 1.2 were prepared by a solid-state reaction starting from  $\text{La}_2\text{O}_3$ , NiO, and  $\text{Sr}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . The samples were pre-fired for 1 h at 600 °C. The powders were then cold pressed at 100 bar, fired for 13 h in pure oxygen of 1 bar at 1100–1300 °C, and subsequently cooled at about 100 °C/h to room temperature. Samples with  $x > 0.5$  especially required firing temperatures as high as 1300 °C in order to obtain single-phase materials.

The ceramic samples were checked by x-ray diffraction to be single phase. The cell was tetragonal, the lattice parameters are listed in Table I. There is reasonable agreement with published structure data.<sup>12,13,32</sup> The oxygen content was determined iodometrically and from the weight loss by hydrogen reduction. These methods agreed except for the influence of adsorbed water in some samples on the weight loss. Results are shown in Table I.  $\text{La}_2\text{NiO}_{4+\delta}$  had  $\delta=0.13$ , while for higher strontium contents the oxygen excess in oxygen-annealed samples decreases in agreement with Ref. 10.

Single crystals of  $\text{La}_2\text{NiO}_{4+\delta}$  and of  $\text{La}_{1.85}\text{Sr}_{0.15}\text{NiO}_4$  were grown by the floating-zone method; the exact oxygen content is not known. The lattice parameters of the doped crystal were determined during a determination of the crystal orientation. The structure of these  $\text{La}_2\text{NiO}_{4+\delta}$  crystals has been investigated by Kajitani *et al.*<sup>33</sup>

X-ray-absorption experiments at the oxygen  $K$  edge

were done at BESSY using the SX-700-I monochromator. The slit size used was 10  $\mu\text{m}$  resulting in a linewidth of about 0.4 eV. The absorption was measured by dividing the total photoelectric yield by the ring current. The photon energy was calibrated by measuring the absorption edges of vanadium and chromium metal samples and comparing them to electron-energy-loss measurements by Fink *et al.*<sup>34</sup> The samples could be scraped in vacuum with an alumina file.

### RESULTS

In Fig. 1 we present polarization-dependent x-ray-absorption (XAS) measurements on a single crystal of  $\text{La}_{1.85}\text{Sr}_{0.15}\text{NiO}_4$  at the O 1s edge. The crystal was measured as received. It had a flat shiny surface perpendicular to the  $c$  axis. Dipole transition selection rules dictate that, for perpendicular incident radiation, only states of  $p_x$  or  $p_y$  symmetry will be seen [ $x$  and  $y$  in the  $(a, b)$  plane of the crystal], while for grazing incidence and linear polarized light the geometry is chosen so that only  $p_z$  orbitals are accessible. Since all the structures have some polarization dependence it is difficult to choose a suitable normalization procedure. In Fig. 1 we see that a reasonable choice is to normalize to the intensity at 542 eV.

Starting our discussion of the spectra at high energies, we see above 538-eV oscillations in the absorption to continuum states. The structure at 544 eV is strongly polarization dependent with the highest intensity for in-plane polarization. This structure probably is related to the in-plane oxygen coordination. It would be interesting to have detailed polarization-dependent multiple-scattering calculations or high-energy band-structure calculations to compare with.

The dominant absorption peak at 536 eV is due to transitions to oxygen states hybridized with La 5d and 4f states. The intensity of this structure does not seem to be very polarization dependent, which can be understood by the quite isotropic coordination of the lanthanum atoms by nine oxygens. A calculation on  $\text{La}_2\text{CuO}_4$  shows that this absorption is almost equally due to O(1) and O(2) atoms.<sup>35</sup>

The absorption at 532 eV, however, is polarization dependent: it is most intense at perpendicular incidence, which means that there is a large density of  $p_{x,y}$  derived states. In this region there will be La 5d states, but they are not likely to be very polarization dependent, although

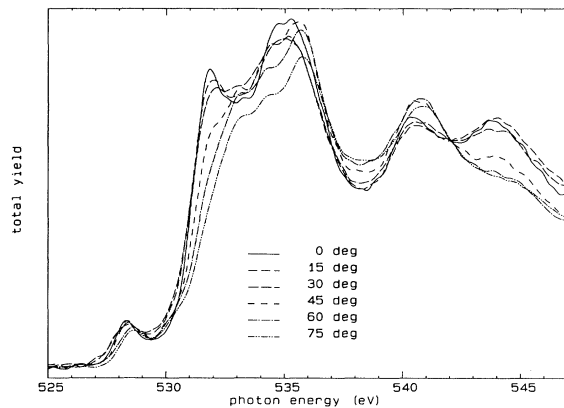


FIG. 1. Oxygen 1s x-ray-absorption spectra of an unscrapped single crystal of  $\text{La}_{1.85}\text{Sr}_{0.15}\text{NiO}_4$  with the surface perpendicular to the  $c$  axis at different angles of incidence of the polarized light.

according to Ref. 35 they are hybridized more strongly with oxygen atoms in the lanthanum planes so that some  $x,y$  polarization might be expected. In this region we also expect Ni  $3d^9$  final states. The  $d^9$  final states can be reached because of hybridization by  $pd(\sigma)$  bonds between empty Ni  $d$  orbitals and in-plane O  $2p_{x,y}$  orbitals. The  $pd(\sigma)$  hybridization with the apex oxygen  $p_z$  orbitals is expected to be a lot smaller because of the 16% larger interatomic distance. The peak intensity is proportional to the square of the  $d$  transfer integrals which, according to Harrison,<sup>36</sup> scale as  $R^{3.5}$ . The expected intensity ratio is then 0.36. So we expect the Ni  $3d^9$  final states reached by O 1s excitation to be enhanced in perpendicular incidence, while they should be reduced in grazing incidence. This leads us to believe that the polarization-dependent part in the absorption at 532 eV is at least partly due to Ni  $3d^9$  final states. This assignment finds support in a comparison with polarization-dependent XAS measurements on  $\text{La}_2\text{CuO}_4$  by Rossi *et al.*,<sup>37</sup> where the Cu  $3d^{10}$  peak is at lower energy ( $\approx 530.2$  eV), and also in the close coincidence with the position of the  $3d^9$  peak of NiO (Fig. 3).

Going back to the  $\text{La}_{1.85}\text{Sr}_{0.15}\text{NiO}_4$  spectra, the absorption at 528 eV is due to holes induced by Sr doping, as is clear from the stoichiometry dependence described below. Contrary to what has been observed in  $\text{Bi}_2\text{Ca}_2\text{SrCu}_2\text{O}_8$ ,<sup>38,39</sup> the intensity of this absorption peak is not polarized solely in the  $MO_2$  plane (where  $M$  is the transition-metal element), but is almost polarization independent. There seems to be a polarization-dependent shift in the position of this peak which could indicate symmetry-dependent final-state energies. The observed shifts, however, could also be due to sampling different parts of the light beam from the monochromator upon rotating the sample so any speculation must be done with this in mind.

Results of the scrapped polycrystalline samples are shown in Fig. 2. A linear background was subtracted from the spectra and they were scaled by a rather arbitrary

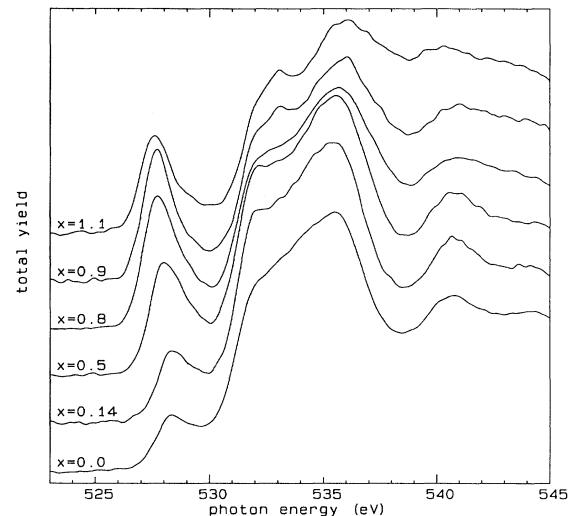


FIG. 2. O 1s XAS of a series of ceramic  $\text{La}_{2-x}\text{Sr}_x\text{NiO}_{4+\delta}$  samples.

factor. The oscillations in the absorption above 538 eV, which reflect the local atomic environment of the oxygen atoms, again are in agreement with data on  $\text{La}_2\text{CuO}_4$ .<sup>40</sup> The absorption peak at 536 eV is reduced by replacing lanthanum by strontium which has no low-lying  $4f$  states. Strontium doping also causes a small shift of this peak to higher energy. If the peak at 532 eV is due to Ni  $3d^9$  final states, its reduction can be explained in the same way as in the case of  $\text{Li}_x\text{Ni}_{1-x}\text{O}$ , by transfer of the intensity of this peak to the doping-induced peak at lower energy.<sup>30</sup>

The obvious effect of Sr doping is the growth of the absorption at about 528 eV. This peak is caused by transitions to the induced holes in the oxygen  $2p$  band. This intensity is not proportional to the doping as it is in  $\text{La}_2\text{CuO}_4$  (Refs. 31 and 35) and  $\text{Li}_x\text{Ni}_{1-x}\text{O}$ .<sup>30</sup> The solution can be found in the oxygen stoichiometry. According to a neutron-diffraction investigation by Jorgensen *et al.*,<sup>5</sup> oxygen annealed  $\text{La}_2\text{NiO}_{4+\delta}$  had  $\delta=0.18$  while nitrogen annealed  $\text{La}_2\text{NiO}_4$  had  $\delta=0.07$ . If our pure single crystal has the composition  $\text{La}_2\text{NiO}_{4.07}$  it can be understood why single crystalline  $\text{La}_{1.85}\text{Sr}_{0.15}\text{NiO}_4$  has a very similar prepeak intensity. If we plot the prepeak height as a function of the hole concentration calculated as  $h=(x+2\delta)/(4+\delta)$ , we find reasonable agreement with a straight line (not shown).

For  $x \geq 0.5$  we also notice a shift of the O  $2p$  prepeak to lower energy. This may be related to the transition to metallic behavior of the resistivity.<sup>13,14</sup>

It is interesting to compare the spectra of  $\text{Li}_{0.2}\text{Ni}_{0.8}\text{O}$  with  $\text{La}_{1.2}\text{Sr}_{0.8}\text{NiO}_4$  where both have 0.2 hole per oxygen. From Fig. 3 we see strong similarities in the near threshold region although the La  $4f$  and  $5d$  states distort the picture somewhat. In the Li-doped case, the  $d^9$  peak is more strongly suppressed than in Sr-doped  $\text{La}_2\text{NiO}_2$  which is simply because Ni is replaced in NiO by lithium. The prepeak in the Li-doped case comes at higher ener-

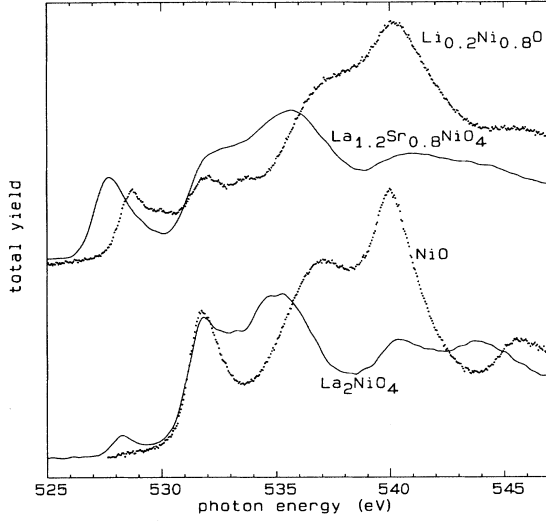


FIG. 3. The XAS of NiO and  $\text{Li}_{0.2}\text{Ni}_{0.8}\text{O}$  compared to  $\text{La}_{1.85}\text{Sr}_{0.15}\text{NiO}_4$  (normal incidence) and  $\text{La}_{1.2}\text{Sr}_{0.8}\text{NiO}_4$ .

gies than in the Sr-doped case, which could indicate that the effect of the impurity potential is considerably larger in the former. This is, in fact, expected purely from geometrical considerations. The O—Sr bond distances are about 2.5 Å, whereas the O—Li bond lengths are 2.08 Å. The comparison with  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  shows that the band gap of intrinsic  $\text{La}_2\text{NiO}_4$  must be as large or even larger than that of NiO, which has a charge-transfer gap of  $\approx 4$  eV.<sup>21</sup> The structure seen optically in  $\text{La}_2\text{NiO}_4$  (Ref. 13) at about 1.5 eV is therefore most probably caused by impurity-induced states due to nonstoichiometry.

## DISCUSSION

Above we assigned the absorption at 532 eV to Ni  $3d^9$  final states because of its polarization dependence. But it is necessary to treat this Ni  $3d^9$  peak in more detail because of its expected splitting in  $D_{4h}$  symmetry, the  $d_{3z^2-r^2}$  hole is at higher energy than the  $d_{x^2-y^2}$  hole. We follow the notation used for  $\text{CuO}_4$  clusters.<sup>41</sup> In the ground state, the Ni  $3d^8$  atom in square plane  $D_{4h}$  symmetry has a hole in the  $d_{x^2-y^2}$  orbital ( $b_1$  symmetry) and a hole in the  $d_{3z^2-r^2}$  orbital ( $a_1$  symmetry), which gives the Hund's-rule  ${}^3B_{1g}$  high-spin state. In  $O_h$  symmetry it would be  ${}^3A_{1g}$  symmetry. For the undoped case, we represent in configuration interaction in  $D_{4h}$  symmetry the ground state by

$$\begin{aligned} \Phi_G({}^3B_{1g}) = & \alpha |d^8({}^3B_{1g})\rangle + \beta |d^9\bar{L}({}^3B_{1g})\rangle \\ & + \gamma |d^{10}\bar{L}^2({}^3B_{1g})\rangle, \end{aligned} \quad (1)$$

where  $\bar{L}$  denotes an oxygen  $2p$  hole with the proper symmetry. Two types of  $d^9\bar{L}$  states are possible, namely,

$|b_1\uparrow\bar{L}(a_1)\uparrow\rangle$  and  $|a_1\uparrow\bar{L}(b_1)\uparrow\rangle$ , where  $\bar{L}(b_1)$  is an appropriate linear combination of bonding O  $2p_{x,y}$  orbitals and  $\bar{L}(a_1)$  also involves apex oxygen  $p_z$  orbitals. Since these  $\bar{L}$  have quite different hybridizations with the  $d^8$  state, they will have different  $\beta$  coefficients, so that we write

$$\begin{aligned} \Phi_G({}^3B_{1g}) \approx & \alpha |d^8\rangle + \beta(b_1) |d^9\bar{L}(b_1)\rangle \\ & + \beta(a_1) |d^9\bar{L}(a_1)\rangle, \end{aligned} \quad (2)$$

and we will leave out the  $d^{10}\bar{L}^2$  states since these are very high in energy. The effective transfer integral coupling  $|d^8\rangle$  and  $|d^9_{3z^2-r^2}\bar{L}(b_1)\rangle$  is  $T(b_1)$  and that coupling  $|d^8\rangle$  with  $|d^9_{x^2-y^2}\bar{L}(a_1)\rangle$  is  $T(b_1)/\sqrt{3} + T_{\text{apex}}$ , where  $T_{\text{apex}}$  is the transfer integral of  $3d_{3z^2-r^2}$  and the apex  $2p_z$  orbitals.

From the above we see that transitions to O  $p_{x,y}$  orbitals can bring us to either  $d_{x^2-y^2}$ - or  $d_{3z^2-r^2}$ -like final states. For perpendicular incidence the relative intensity of the two final states is given by

$$\frac{I(d^9_{x^2-y^2})}{I(d^9_{3z^2-r^2})} = \frac{\beta^2(a_1)}{\beta^2(b_1)} \approx \frac{T^2(a_1)}{T^2(b_1)} = \frac{1}{3}. \quad (3)$$

For z-polarized light (grazing incidence), transitions to the apex oxygen  $p_z$  orbitals are possible. The intensity will be proportional to the apex  $p_z$  hole occupation in the ground state, which is proportional to  $T_{\text{apex}}^2$  orbital which mixes with  $3d_{3z^2-r^2}$ . A transition to this apex  $2p_z$  brings us to a  $d^9_{x^2-y^2}$  final state. Remembering the ratio of 0.36 from the proportionality of  $T^2$  to  $R^7$  and taking into account a factor  $\frac{2}{3}$ , we see that the  $d^9_{x^2-y^2}$  final state is only slightly polarization dependent, whereas the  $d^9_{3z^2-r^2}$  final state can only be reached in perpendicular incidence.

To compare with the experiment we need an estimate of the energy separation of these peaks. The splitting is caused by the differing hybridization of both  $d^9$  final states with the  $d^{10}\bar{L}$  continuum. But because the  $d^{10}\bar{L}$  states are high ( $U + \Delta$ ) above  $d^9$ ,<sup>25</sup> the hybridization and the differences in hybridization are small. We get

$$E(a_1) - E(b_1) = [T^2(a_1) - T^2(b_1)] / (U + \Delta). \quad (4)$$

Taking  $T(a_1) = 2$  eV,  $\Delta = 6$  eV, and  $U = 8$  eV, and using our estimates of the  $T$  ratio, we get 0.16 eV. So the separation is smaller than the experimental resolution.

Now we look at the polarization dependence expected for the extra holes in a  $\text{NiO}_6$  cluster, where the extra hole is expected to have primarily oxygen character. First we recall that a possible explanation for the pure  $x,y$  polarization of the threshold O  $2p$  states in the Bi cuprates is that the first ionization states in a  $\text{CuO}_2$  layer are singlet states pushed out of the O  $2p$  band due to the strong Cu—O hybridization.<sup>42,43</sup> These states mainly consist of one hole in a Cu  $d_{x^2-y^2}$  orbital ( $b_1$  symmetry) and the other in a linear combination of four oxygen  $\sigma$  bonding orbitals also with  $b_1$  symmetry, producing a  ${}^1A_1$  singlet. In fact, the polarization-dependent XAS is strong support for this picture. In view of this we should ask what the symmetry of the first ionization state of  $\text{La}_2\text{NiO}_4$  is. For Ni

in  $O_h$  symmetry<sup>44</sup> we again find these pushed-out states in the  $\text{NiO}_2$  layers, but now the high-spin  $^4T$  is the lowest-energy state followed very closely by a low-spin  $^2E$  state. These states are much more complicated than for the Cu oxides. The  $^4T_1$  state involves three holes: two in  $e_g$  symmetry ( $d_{x^2-y^2}$  and  $d_{3z^2-r^2}$ ) and one in  $t_{2g}$  symmetry ( $p_{xy}$ ,  $p_{xz}$ , or  $p_{yz}$ ). The lowest-energy wave function has two of these holes primarily on the Ni and one on the oxygen, but that could be any one of the three. A similar situation occurs for  $^2E$ . So, in this case of  $d^8\bar{L}$ , we could have  $p_z$ -like holes mixed in.

The calculation published by Grant and McMahan<sup>28</sup> gives, as the first ionization state, a low-spin state with the added hole having primarily oxygen character and  $b_1$  symmetry. This is in disagreement with the polarization independence of the O  $2p$  hole states, which can probably be attributed to their neglect of the  $t_{2g}$  orbitals.

So far we assumed that the holes are in the first ionization state of the undoped material. However, Fujimori has pointed out<sup>24</sup> that the Li-induced hole in  $\text{Li}_x\text{Ni}_{1-x}\text{O}$  (Ref. 29) is different from the first ionization state of pure NiO (which is a high-spin  $^4T_1$  state), because of the Li impurity potential. For low strontium doping in  $\text{La}_2\text{NiO}_4$ , the charge-compensating hole will be localized near the Sr impurity. This leads to our second possible explanation of the z-polarized part of the 528-eV peak. The Sr-induced crystal will preferentially have the oxygen hole in  $2p$  orbitals oriented towards it. These orbitals would make an angle of  $45^\circ$  with the  $c$  axis and will be hybridized with Ni  $3d$  orbitals of  $e$  ( $p_{xy}, p_{yz}$ ) and  $b_2$  ( $p_{xy}$ ) symmetry. An estimate of this Sr-induced crystal-field splitting can be made using data for O  $2p$  in Li-doped BeO (Ref. 45) and a  $1/R^3$  relation, which yields 0.4 eV. This could be enough to stabilize these states.

In Fig. 4 we compare the bremsstrahlung isochromat spectra<sup>46</sup> (BIS) and XAS spectra by lining them up at the La  $4f$  structure. This requires a shift of 526.5 eV for the XAS spectrum. In a purely one-electron material with negligible core-hole potential, this shift should be equal to the oxygen  $1s$  x-ray photoemission spectroscopy (XPS) binding energy of 528.4 eV. Here we see that it is 1.9 eV less, which is a direct result of the many-body nature of the problem. One should not mistake this extra shift as being only due to the core-hole potential. It is, in fact, a result of different hybridization shifts for the different final states reached.<sup>47</sup>

In the BIS spectra, the intensity of the La  $4f$  peak has been scaled to the La concentration. The shoulder at 5–6 eV mainly has La  $5d$  character and some Ni  $3d^9$  intensity (Ni  $3d^9$  has a much smaller cross section). La replacement will reduce the La  $5d$  part. Doping will also reduce the Ni  $3d^9$  intensity by final-state hybridization with  $d^8\bar{L}$  states, but this effect cannot be observed here as clearly as in BIS of  $\text{Li}_x\text{Ni}_{1-x}\text{O}$ .<sup>48</sup>

The BIS spectra show that, with La substitution, states are introduced over a large region of the band gap starting from about 1 eV above the Fermi energy (the zero in Fig. 4) and extending all the way to the conduction band edge at about 4 eV above  $E_F$ . This is interesting for two reasons, first of all it shows that the peaking seen in the

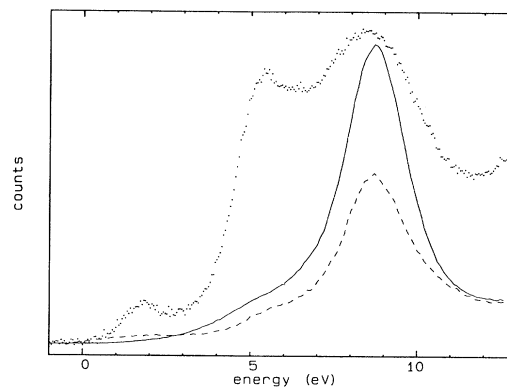


FIG. 4. BIS spectra (1487 eV) of reduced  $\text{La}_2\text{NiO}_4$  (solid line) and of  $\text{La}_{0.85}\text{Sr}_{1.15}\text{NiO}_4$  (dashed) compared to the shifted O  $1s$  absorption spectrum of single crystalline  $\text{La}_2\text{NiO}_{4+\delta}$  at normal incidence (dots). The zero of energy is at the Fermi level which is about 0.5 eV above the top of the valence band.

XAS spectrum at about 2 eV about  $E_F$  in Fig. 4 is most likely an effect of the O  $1s$  core-hole potential and not due to a well-defined impurity state. Secondly, it shows that the simple picture of the Fermi level moving into the O  $2p$  band with doping is probably not correct. What seems to happen instead is that states are pulled out of the valence band to energies above  $E_F$  and are spread across a large portion of the gap. This is similar to findings in the high  $T_c$ 's.<sup>49</sup>

## CONCLUSIONS

We have shown by varying the stoichiometry that the holes compensating for the Sr impurities are primarily on oxygen, as are the holes due to excess oxygen. The polarization-dependent spectra clearly show an in-plane polarized Ni  $3d^9$  final-state peak. The Sr-induced oxygen  $2p$  holes, however, are nearly isotropic. Two possible explanations were offered: the first is that the extra hole in the appropriate  $\text{NiO}_6$  cluster intrinsically has much  $z$  character, and the second that the Sr impurity "pulls the holes out of" the  $\text{NiO}_2$  plane. We concluded that the charge-transfer gap in  $\text{La}_2\text{NiO}_4$  is at least 4 eV, and that parameters like  $U$  and  $\Delta$  are comparable to those of NiO. BIS measurements show that the Sr-induced hole states are, in fact, spread out over a large portion of the band gap and are not concentrated in a narrow energy region.

## ACKNOWLEDGMENTS

We are grateful to J. de Boer for establishing the orientation of the crystals. We benefitted from the  $\text{La}_2\text{CuO}_4$  data G. Rossi had given us before publication. We thank the Berliner Elektronenspeicherring für Synchrotronstrahlung (BESSY) for access to their facilities. This investigation was supported in part by the Netherlands Foundation for Chemical Research (SON) and the Foundation for Fundamental Research on Matter (FOM) with financial support from the Netherlands Organization for the Advancement of Pure Research (ZWO) and the Committee for the European Development of Science and Technology (CODEST) program.

- \*Present address: Physics Department, Brookhaven National Lab., Bldg. 510B, Upton, Long Island, NY 11973.
- <sup>1</sup>J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64**, 189 (1986).
  - <sup>2</sup>J. M. Tarascon, L. H. Greene, P. Barboux, W. R. McKinnon, G. W. Hull, T. P. Orlando, K. A. Delin, S. Foner, and E. J. McNiff, Jr., *Phys. Rev. B* **36**, 8393 (1987).
  - <sup>3</sup>J. Spálek, Z. Kakol, and J. M. Honig, *Solid State Commun.* **71**, 511 (1989).
  - <sup>4</sup>K. S. Nanjundaswami, A. Lewicki, Z. Kakol, P. Gopalan, P. Metcalf, J. M. Honig, C. N. R. Rao, and J. Spálek, *Physica C* **166**, 361 (1990).
  - <sup>5</sup>J. D. Jorgensen, B. Dabrowski, Shiyong Pei, D. R. Richards, and D. G. Hinks, *Phys. Rev. B* **40**, 2187 (1989).
  - <sup>6</sup>J. Rodríguez-Carvajal, J. L. Martínez, J. Pannetier, and R. Saez-Puche, *Phys. Rev. B* **38**, 7148 (1988).
  - <sup>7</sup>G. Aeppli and D. J. Buttrey, *Phys. Rev. Lett.* **61**, 203 (1988).
  - <sup>8</sup>X. Batlle, J. L. García-Muñoz, M. Medarde, J. Rodríguez-Carvajal, X. Obradors, J. L. Martínez, M. Vallet, J. González-Calbet, M. J. Sayagues, and J. Fontcuberta, *Physica C* **162-164**, 1273 (1989).
  - <sup>9</sup>D. J. Buttrey, P. Ganguly, J. M. Honig, C. N. R. Rao, R. R. Schartman, and G. N. Subanna, *J. Solid State Chem.* **74**, 233 (1988).
  - <sup>10</sup>R. J. Cava (private communication).
  - <sup>11</sup>T. Nitadori, M. Muramatsu, and M. Misono, *Bull. Chem. Soc. Jpn.*, **61**, 3831 (1988).
  - <sup>12</sup>M. Sayer and P. Odier, *J. Solid State Chem.* **67**, 26 (1987).
  - <sup>13</sup>S. Tajima, H. Ishii, T. Nakahashi, T. Takagi, S. Uchida, M. Seki, S. Suga, Y. Hidaka, M. Suzuki, T. Murakami, K. Oka, and H. Unoki, *J. Opt. Soc. Am B* **6**, 475 (1989).
  - <sup>14</sup>M. Khairy, P. Odier, and J. Choisnet, *J. Phys. (Paris) Colloq.* **47**, C1 831 (1986).
  - <sup>15</sup>C. P. J. Soethout, G. P. J. Geelen, and D. M. de Leeuw (unpublished).
  - <sup>16</sup>G. Y. Guo and W. M. Temmerman, *J. Phys. C* **21**, L917 (1988).
  - <sup>17</sup>G. Y. Guo and W. M. Temmerman, *Phys. Rev. B* **40**, 285 (1989).
  - <sup>18</sup>K. Terakura, T. Oguchi, A. R. Williams, and J. Kübler, *Phys. Rev. B* **30**, 4734 (1984).
  - <sup>19</sup>L. F. Mattheiss, *Phys. Rev. Lett.* **58**, 1028 (1987).
  - <sup>20</sup>O. Gunnarsson and K. Schönhammer, *Phys. Rev. Lett.* **56**, 1968 (1986).
  - <sup>21</sup>G. A. Sawatzky and J. W. Allen, *Phys. Rev. Lett.* **53**, 2239 (1984).
  - <sup>22</sup>A. Fujimori, E. Takayama-Muromachi, Y. Uchida, and B. Okai, *Phys. Rev. B* **35**, 8814 (1987).
  - <sup>23</sup>Z.-X. Shen, J. W. Allen, J.-J. Yeh, J.-S. Kang, W. Ellis, W. Spicer, I. Lindau, M. B. Maple, Y. D. Dalichaouch, and M. S. Torikachivili, *Phys. Rev. B* **36**, 8414 (1987).
  - <sup>24</sup>A. Fujimori, in *Strong Correlation and Superconductivity*, edited by H. Fukuyama *et al.* (Springer, Berlin, 1989).
  - <sup>25</sup>J. Zaanen, G. A. Sawatzky, and J. W. Allen, *Phys. Rev. Lett.* **55**, 65 (1989).
  - <sup>26</sup>A. K. McMahan, R. M. Martin, and S. Satpathy, *Phys. Rev. B* **38**, 9028 (1988).
  - <sup>27</sup>M. S. Hybertsen, M. Schlüter, and N. E. Christensen, *Phys. Rev. B* **39**, 9028 (1989).
  - <sup>28</sup>J. B. Grant and A. K. McMahan, *Physica C* **162-164**, 1439 (1989).
  - <sup>29</sup>A. K. McMahan (private communication).
  - <sup>30</sup>P. Kuiper, G. Kruijzinga, J. Ghijsen, G. A. Sawatzky, and H. Verweij, *Phys. Rev. Lett.* **62**, 221 (1989).
  - <sup>31</sup>N. Nücker, H. Romberg, X. X. Xi, J. Fink, B. Gegeheimer, and Z. X. Zhao, *Phys. Rev. B* **39**, 6619 (1989).
  - <sup>32</sup>N. Ogita, M. Udagawa, K. Kojima, and K. Ohbayashi, *J. Phys. Soc. Jpn.* **57**, 3932 (1988).
  - <sup>33</sup>T. Kajitani, S. Hosoya, M. Hirabayashi, T. Fukuda, and T. Onuzaka, *J. Phys. Soc. Jpn.* **58**, 3616 (1989).
  - <sup>34</sup>J. Fink, Th. Müller-Heinzerling, B. Scheerer, W. Speier, F. U. Hillebrecht, J. C. Fuggle, J. Zaanen, and G. A. Sawatzky, *Phys. Rev. B* **32**, 4899 (1985).
  - <sup>35</sup>N. Nücker, J. Fink, J. C. Fuggle, P. J. Durham, and W. M. Temmerman, *Phys. Rev. B* **37**, 5158 (1988).
  - <sup>36</sup>W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).
  - <sup>37</sup>G. Rossi *et al.* (unpublished).
  - <sup>38</sup>F. J. Himpsel, G. V. Chandrasekhar, A. B. McLean, and M. W. Shafer, *Phys. Rev. B* **39**, 2926 (1989).
  - <sup>39</sup>P. Kuiper, M. Grioni, G. A. Sawatzky, D. B. Mitzi, A. Kapitulnik, A. Santaniello, P. de Padova, and P. Thiry, *Physica C* **157**, 260 (1989).
  - <sup>40</sup>N. Nücker, J. Fink, B. Renker, D. Ewert, C. Politis, P. J. W. Weijs, and J. C. Fuggle, *Z. Phys. B* **67**, 9 (1987).
  - <sup>41</sup>H. Eskes, L. H. Tjeng, and G. A. Sawatzky, *Phys. Rev. B* **41**, 288 (1990).
  - <sup>42</sup>F. C. Zhang and T. M. Rice, *Phys. Rev. B* **37**, 3759 (1988).
  - <sup>43</sup>H. Eskes and G. A. Sawatzky, *Phys. Rev. Lett.* **61**, 1415 (1988).
  - <sup>44</sup>J. Zaanen, Ph.D. thesis, University of Groningen, 1986.
  - <sup>45</sup>O. F. Schirmer, *J. Phys. C* **11**, L65 (1978).
  - <sup>46</sup>J. van Elp, A. Fujimori, P. Kuiper, and G. A. Sawatzky (unpublished).
  - <sup>47</sup>H. Eskes and G. A. Sawatzky, *Phys. Rev. B* **43**, 119 (1991).
  - <sup>48</sup>J. van Elp, H. Eskes, P. Kuiper, and G. A. Sawatzky (unpublished).
  - <sup>49</sup>J. W. Allen, C. G. Olson, M. B. Maple, J.-S. Kang, L. Z. Liu, J.-H. Park, R. O. Anderson, W. P. Ellis, J. T. Market, Y. Dalichaouch, and R. Liu, *Phys. Rev. Lett.* **64**, 595 (1990).