Character of Holes in $Li_x Ni_{1-x}O$ and Their Magnetic Behavior

P. Kuiper, G. Kruizinga, J. Ghijsen, and G. A. Sawatzky

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

H. Verweij

Philips Research Laboratories, P.O. Box 80000, 5600 JA Eindhoven, The Netherlands (Received 3 October 1988)

Using oxygen K-edge x-ray-absorption spectroscopy we show that the holes compensating the Li^{1+} impurity charge in $Li_x Ni_{1-x}O$ are located primarily in the O 2p states rather than in the conventionally assumed Ni 3d states. These holes are bound to the Li^{1+} impurities forming states in the NiO band gap. We also argue that these O 2p holes have a very large antiferromagnetic exchange interaction with neighboring Ni²⁺ (d⁸) spins, which makes them appear like low-spin Ni³⁺ states in macroscopic magnetic measurements. This is similar to what could be happening in the Cu-based high- T_c superconductors.

PACS numbers: 78.70.Dm, 75.30.Et

The late 3d transition-metal (TM) oxides, up to quite recently, have been thought to be Mott-Hubbard systems, 1-5 with states of primarily 3d character spanning the Fermi level and gaps caused by strong d-d Coulomb interactions. In this picture substitutions like, for example, monovalent Li for divalent cations in the monoxides would be charge compensated by the presence of trivalent cations, which leads to mixed-valent systems.⁶ The magnetic and electrical properties of an extremely wide class of such substituted oxides have generally been discussed in these terms. For example, for $Li_x Ni_{1-x}O$ one assumed the presence of Ni³⁺ which would have to be in a low-spin d^7 (Ref. 7) configuration to explain the magnetic properties. This was quite surprising because, as van Houten⁸ argued, the ligand field in oxides is not expected to be sufficiently strong to overcome the Hund's-rule stabilization of the high-spin state. More recently, the interpretation of high-energy electron spectroscopy data of Cu⁹ and Ni¹⁰ dihalides and oxides,¹¹⁻¹⁴ as well as the high- T_c superconductors, ¹⁵ led to the conclusion that these systems are not conventional Mott-Hubbard systems, but rather that the gap in the insulators is of the charge-transfer type¹⁶ and that the first ionization states are of primarily anion p character rather than of TM d character. This relatively new suggestion for the oxides has had the most impact in the high- T_c field of research. Although it may be difficult in a time of high- T_c craze to rekindle the interest in magnetic properties of substituted and nonstoichiometric TM oxides, we will in this Letter present new experimental and theoretical information on $Li_x Ni_{1-x}O$ that should change our way of thinking about the magnetic properties of substituted and nonstoichiometric compounds with especially the 3d, 4d, and, to some extent, rareearth elements.

The suggestion that the first ionization states in sys-

tems like MnO, FeO, CoO, NiO, and CuO are of primarily O 2p character would lead directly to the conclusion that the holes compensating the lithium charge in our example of $Li_x Ni_{1-x}O$ would be in O 2p bands. Having said this, one is confronted with the question concerning the exchange coupling of the O holes with the localized TM unpaired spins. For localized O 2p holes we could expect the O-2p-TM-3d exchange interaction to be an order of magnitude larger¹⁷ than the superexchange interaction,¹⁸ which couples the TM spins via virtual excitations involving the O 2p states. Of even more general interest are the possibilities such systems provide for studying Kondo or Anderson lattice systems in which the charge carriers move in narrow bands with a relatively low Fermi energy as compared to the exchange interaction between the charge carriers and the localized spins on the transition-metal ions.

In this Letter we present direct spectroscopic evidence that for the $\text{Li}_x \text{Ni}_{1-x} O$ system the charge-compensating holes reside primarily in the O 2p bands. To do this we use O K-edge x-ray-absorption (XAS) spectroscopy. As has amply been demonstrated core-level x-ray-absorption spectroscopy provides information on the local unoccupied density of states of the symmetry dictated by the core hole and the dipole selection rules.¹⁹ Although one must be aware of core-hole potential effects on the spectral distribution, this does not reduce the capacity of the technique to determine the *presence* of unoccupied states of certain symmetry in the ground state. This technique has been used successfully to show that the holes present in the high- T_c superconductors are primarily of O 2p character.²⁰⁻²²

 $Li_x Ni_{1-x}O$ was prepared as described in Ref. 7 by grinding together the proper proportions of Li_2CO_3 and NiO. The powder was then pelletized under a pressure of 10⁹ Pa. The pellets were calcined at 950 °C for 20 h

under a flow of pure dry oxygen. X-ray diffraction showed a homogeneous material but this method is not sensitive to the presence of lithium oxide. The latticeparameter variation with x (Refs. 7 and 23) as well as wet chemical analysis was used to determine the lithium content. These methods agreed for x < 0.4; in the nominally x = 0.50 sample x-ray diffraction gave x = 0.40 ± 0.02 , indicating the presence of unreacted lithium. The absolute oxygen content of the samples in equilibrium with 1-atm pure O₂ at high temperatures has been determined by equilibration up to 1200 °C, followed by controlled reduction with a final temperature level of 10 h at 800 °C.²⁴ For x < 0.4 the oxygen was found to deviate by less than 2% from that given by the chemical formula above.

For the XAS measurements the samples were scraped in vacuum ($\approx 10^{-9}$ Torr) with an alumina file. The measurements were done at BESSY, the Berlin synchrotron, with an SX700 monochromator²⁵ which operated with an exit slit of 10 μ m, giving a resolution of 400 meV at 500 eV. The absorption was determined by the total-electron-yield method which probes a layer some hundreds of angstroms deep. The total yield was divided by the storage-ring current recorded simultaneously. The energy-dependent photon flux in the O 1s region due to contamination of the optics was found to deviate by only about 2% in the energy range of interest. The absolute energy scale was determined by comparison with data of Nakai *et al.*²⁶ and of Davoli *et al.*²⁷

In Fig. 1 we present the oxygen 1s absorption near edge spectra of $\text{Li}_x \text{Ni}_{1-x} O$ for x between 0 and 0.5. The spectra have been scaled to the area between 530 and 544 eV after subtraction of an energy-independent background. To compare with a material without localized d electrons, we show in the bottom curve the O K-edge of MgO determined by Nakai et al.²⁶ It reflects the structure in the density of states in the O 3p conduction band and its form is explained satisfactorily by a multiple-scattering calculation.²⁸ The next lowest curve shows our data on pure NiO. It agrees with data of Nakai et al.²⁶ and of Davoli et al.²⁷ The most important difference from the MgO spectrum is the peak at 532 eV, which is also present in a multiple-scattering calculation by Vvedensky and Pendry.²⁹

Since the first electron-addition state in NiO is a d^9 state¹¹ the prepeak at 532 eV observed in the O 1s edge is identified as being this state in the presence of an O 1s core hole. The O 1s binding energy in NiO is about 529.5 eV which is 2.5 eV lower than the XAS prepeaks, in rough agreement with a band gap of about 4 eV and a Fermi-level pinning above the valence band.¹¹ We note that this is a good example showing that a prepeak in XAS need not necessarily imply "free" O 2p holes in the ground state. This particular peak gets its transition probability from the hybridization of the ground state.



FIG. 1. Oxygen K-edge absorption spectra of MgO (Ref. 26), NiO, $\text{Li}_x \text{Ni}_{1-x} \text{O}$ for indicated values of x, and $\text{Li}_2 \text{O}$.

with Ni in an octahedron of O ions can be written as ¹¹

$$\Phi_G = \alpha \left| d^8 \right\rangle + \beta \left| d^9 \underline{L} \right\rangle \quad (\alpha^2 + \beta^2 = 1) , \qquad (1)$$

and the first affinity state as

$$\Phi_A \approx |d^{9}\rangle, \qquad (2)$$

neglecting the mixing with the $|d^{10}\underline{L}^2\rangle$ and $|d^{10}\underline{L}\rangle$ states in Eqs. (1) and (2), respectively, because of the large *d*-*d* Coulomb interaction (U_{dd}) .¹¹ Allowing only intra-atomic XAS transition matrix elements we see that the prepeak in the O 1s spectrum has an intensity proportional to β^2 and is a measure of the *covalency* in the ground state.

In the Li-doped samples we see, aside from some broadening at higher energy, an additional peak appearing at about 528.5 eV, while, as expected, the peak at 532 eV decreases as the Ni is replaced by Li. The peak at 534 eV in the x=0.40 and x=0.50 samples is probably due to Li₂O as is evident from comparison with the Li₂O absorption spectrum. At first glance one might expect the 532-eV peak to decrease linearly with the Li concentration to about 50%, at x=0.5, of the intensity for NiO. It is rather surprising then that this peak has all but disappeared at x=0.4. There are two rather interesting reasons for this behavior. First the hybridization in the ground state will decrease with x since if a Ni ion has an O nearest neighbor with a hole, then the charge-transfer state in Eq. (1) will involve two ligand holes which will be higher in energy by the O-2p-O-2pCoulomb interaction U_{pp} . A rough estimate yields a reduction of β^2 for such a case by about 50%. A second effect, however, could be even more important and this has to do with the hybridization in the *final* state. For x=0 the final state is given by Eq. (2) which has no states with lower energy with which it can hybridize. However, for finite x the $d^{9}(\underline{L})$ -like final state [where (\underline{L}) is the Li-induced hole] can hybridize with the lower-energy states in which the Li-induced hole is occupied, i.e., d^8 . As is well known, this kind of final-state hybridization always shifts the spectral weight to the lowest-energy state.^{9,10} A more detailed analysis of this will be published elsewhere.

The separation between the new peak and the prepeak in NiO is about 3.2 to 3.5 eV which is close to but smaller than the band gap of NiO of about 4 eV. The intensity of this prepeak increases linearly with Li content and for $Li_{0.3}Ni_{0.7}O$ is about the same as for the 532 eV prepeak in NiO. Since β^2 for NiO is about 0.2,¹⁰ the extra holes introduced by the Li doping have about 70% O 2p character. This peak in interpreted as being due to the holes corresponding to the first ionization states of NiO. That these holes are of primarily O 2p character is in agreement with the interpretation of the photoemission and inverse photoemission spectra of NiO and the charge-transfer nature suggested for the band gap.³⁰ That the energy separation between this peak and the prepeak in NiO is less than the band gap indicates that these hole states are in fact impurity states in the gap, most likely bound to the effectively negative charged lithium sites. This also explains the absence of metallic conductivity in these systems.³¹

In Fig. 2 we show schematically the physics involved. In Fig. 2(a) we show the states in NiO below and above the Fermi level together with their rough assignment.¹¹ The arrow indicates the state reached by XAS at the O 1s edge. Figure 2(b) shows what would happen in a rigid-band model of $\text{Li}_x \text{Ni}_{1-x}$ O in which the Fermi level is merely shifted to the top of the $d^8\underline{L}$ -like band states. Again the final states reached by O 1s XAS are indicated. In Fig. 2(c) the Li impurity potential is taken into account, causing the hole states to split off from the band and appear as impurity states in the NiO gap.

One of the most interesting questions now concerns the exchange interaction between these holes and the nearest-neighbor Ni ions. We remind the reader that the Ni ions (nominally d^8) are in a high-spin ${}^{3}A_{2g}$ $(t_{2g}^{6}e_{g}^{2})$ electronic configuration. The extra hole could, for example, be in a totally symmetric (A_{1g}) state about the Li impurity with a wave function of the form

$$(p_{z1}+p_{z2}+p_{z3}+p_{z4}+p_{z5}+p_{z6})/\sqrt{6}, \qquad (3)$$



FIG. 2. (a) Sketch of the electron-removal and electronaddition states of NiO. Transitions in Li-doped NiO, (b) assuming a rigid-band model and (c) assuming localization of O 2p holes around lithium.

where in p_{zi} the *i* labels the oxygen ion and on each ion we have defined a local z axis pointing towards the Li impurity.³² Each of these oxygen ions has a Ni nearest neighbor along the local z axis which for $T < T_N$ has its spin opposite to that of the Ni ion replaced by the Li impurity. We consider now the exchange interaction between a hole in an O p_z orbital with the spin $3d^8({}^3A_{2g})$ on a neighboring Ni ion. In analogy to a similar problem treated by Zhang and Rice¹⁷ for the high- T_c compounds, there are two contributions to the exchange involving virtual states: (i) where a majority-spin (e_g symmetry) electron has been transferred from Ni to the O 2p hole involving a d^7 state, which gives an antiferromagnetic contribution and (ii) where an O $2p \sigma$ -bonding electron has been transferred to the Ni involving the state $d^{9}L^{2}$, which also yields an antiferromagnetic contribution. The net antiferromagnetic exchange is then

$$J \approx T_{\text{eff}}^2 \left[\frac{1}{U_{dd}(^2 E) - \Delta} + \frac{1}{\Delta + U_{pp}} \right], \tag{4}$$

where Δ is the charge-transfer energy defined in Fig. 2, U_{pp} is the O 2p Coulomb interaction, ³³ $U_{dd}({}^{2}E)$ is the effective Coulomb interaction of the $d^{7}[{}^{2}E(e_{g}^{3})]$ state, and T_{eff} is the transfer integral for the coupling of an O p_{z} orbital to a Ni $d_{3z^{2}-r^{2}}$ orbital. From detailed analysis of various spectroscopies and the superexchange interaction in NiO we previously found ³⁴ $\Delta = 6.0$ eV, $U_{dd}({}^{2}E) \approx 9.5$ eV, $T_{\text{eff}} \approx 0.9$ eV, and from O Auger spectroscopy in Cu₂O (Ref. 35), $U_{pp} \approx 4.6$ eV. This leads to an O-Ni antiferromagnetic exchange interaction of 0.36 eV, which is about 2 orders of magnitude larger than the superexchange interaction.³⁴

In conclusion, we have shown that the holes compensating the Li⁺ impurity charge in Li_xNi_{1-x}O are of primarily O 2p character. The exchange interaction of these holes with the localized Ni d electrons is antiferromagnetic and estimated to be about 2 orders of magnitude larger than the Ni-Ni superexchange interaction. Such large exchange interactions between O 2p holes and TM spins are expected for late 3d transition-metal oxides in general and could lead to new ideas for materials with interesting magnetic, optical, and electrical properties.

We are grateful to the Berlin Elektronenspeicherring für Synchrotron- strahlung (BESSY) for access to facilities and to H. Petersen for allowing us to use the SX700 monochromator. We thank L. F. Feiner for helpful discussions, P. J. W. Weijs and F. M. F. de Groot for helping with the measurements, and J. Hommes and W. H. M. Bruggink for doing the chemical analysis. We especially thank O. Strebel for doing XAS measurements on the Ni 2p edge which will be published elsewhere. 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 (NWO) and the Committee for the European Development of Science and Technology (CODEST) program.

¹N. F. Mott, Proc. Phys. Soc. London, Sect. A 62, 416 (1949).

²J. Hubbard, Proc. Roy. Soc. London A 277, 237 (1964).

³J. Hubbard, Proc. Roy. Soc. London A **281**, 401 (1964). ⁴N. F. Mott, in *Metal-Insulator Transitions* (Barnes and

Noble, London, 1974). ⁵B. K. Brandow, Adv. Phys. **24**, 651 (1977).

⁶J. B. Goodenough, *Magnetism and the Chemical Bond* (Krieger, New York, London, 1963).

⁷J. B. Goodenough, D. G. Wickham, and W. J. Croft, J. Phys. Chem. Solids **5**, 107 (1958).

⁸S. van Houten, J. Phys. Chem. Solids 17, 7 (1960).

 9 G. van der Laan, C. Westra, C. Haas, and G. A. Sawatzky, Phys. Rev. B **23**, 4369 (1981).

¹⁰G. van der Laan, J. Zaanen, and G. A. Sawatzky, Phys. Rev. B **33**, 4253 (1986).

¹¹G. A. Sawatzky and J. W. Allen, Phys. Rev. Lett. 53, 2339

(1984).

¹²A. Fujimori and F. Minami, Phys. Rev. B **30**, 957 (1984).

¹³S. Hüfner, J. Osterwalder, T. Riesterer, and F. Hulliger, Solid State Commun. **52**, 793 (1984).

¹⁴S. Hüfner, Solid State Commun. **53**, 707 (1985).

¹⁵A. Fujimori, E. Takayama-Muromach, Y. Uchida, and B. Okai, Phys. Rev. B **35**, 8814 (1987).

¹⁶J. Zaanen, G. A. Sawatzky, and J. W. Allen, Phys. Rev. Lett. **55**, 418 (1985).

¹⁷F. C. Zhang and T. M. Rice, Phys. Rev. B **37**, 3759 (1988); see also H. Eskes and G. A. Sawatzky, Phys. Rev. Lett. **61**, 1415 (1988).

¹⁸P. W. Anderson, Phys. Rev. B 115, 2 (1959).

¹⁹Core-level Spectroscopy in Condensed Systems, edited by J. Kanamori and A. Kotani (Springer-Verlag, New York, 1988).

²⁰J. A. Yarmoff, D. R. Clarke, W. Drube, U. O. Karlsson, A. Taleb-Ibrahimi, and F. J. Himpsel, Phys. Rev. B **36**, 3967 (1987).

²¹N. Nücker, J. Fink, J. C. Fuggle, P. J. Durham, and W. M. Timmerman, Phys. Rev. B **37**, 5158 (1988).

²²P. Kuiper, G. Kruizinga, J. Ghijsen, M. Grioni, P. J. W. Weijs, F. M. F. de Groot, G. A. Sawatzky, H. Verweij, L. F. Feiner, and H. Petersen, Phys. Rev. B **37**, 6483 (1983).

 $^{23}W.$ Bronger, H. Bade, and W. Klemm, Z. Anorg. Allg. Chem. **333**, 188 (1964).

²⁴A. H. Verweij and W. H. M. Bruggink, Phys. Chem. Solids **49**, 1063 (1988).

 25 H. Petersen, Nucl. Instrum. Methods Phys. Res., Sect. A **246**, 260 (1986).

²⁶S. Nakai, T. Mitsuishi, H. Sugawara, H. Maezawa, T. Matsukawa, S. Mitani, K. Yamasaki, and T. Fujikawa, Phys. Rev. B **36**, 9241 (1987).

²⁷I. Davoli, A. Marcelli, A. Bianconi, M. Tomellini, and M. Fanfoni, Phys. Rev. B **33**, 2979 (1986).

²⁸Th. Linder, H. Sauer, W. Engel, and K. Kambe, Phys. Rev. B 33, 22 (1986).

²⁹D. D. Vvedensky and J. B. Pendry, Phys. Rev. Lett. **54**, 2725 (1985).

³⁰J. Zaanen and G. A. Sawatzky, to be published.

 31 For a review of the transport data see A. J. Bosman and A. J. van Daal, Adv. Phys. **19**, 1 (1970).

 32 It was pointed out to us by L. F. Feiner that the hole could also be in a much lower symmetry orbital accompanied by a small lattice deformation in such a way as to form an electric dipole with the Li¹⁺ impurity.

³³We note that in the equation of Zhang and Rice they have assumed $U_{pp} = 0$.

³⁴J. Zaanen and G. A. Sawatzky, Can. J. Phys. **65**, 1262 (1987).

³⁵J. Ghijsen, L. H. Tjeng, J. van Elp, H. Eskes, J. Westerink, G. A. Sawatzky, and M. T. Czyzyk, to be published.