Direct evidence of O(p) holes in Li-doped NiO from Hartree-Fock Calculations

W.C.Mackrodt
School of Chemistry, St.Andrews University, Fife, Scotland

N.M.Harrison and V.R.Saunders
CCL Daresbury Laboratory, Daresbury, Warrington, Cheshire WA4 4AD, England

N.L.Allan
School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, England

M.D.Towler
Theoretical Chemistry Group, Department CIFM, University of Torino, via P. Giuria 5, I-10125 Torino, Italy

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Abstract

First principles periodic Hartree-Fock calculations of the ground state electron distribution and empty oxygen p states in $Li_{0.125}Ni_{0.875}O$ and $Li_{0.25}Ni_{0.75}O$ are reported which provide direct evidence of oxygen p holes in Li-doped NiO. Calculated changes in the densities of empty oxygen p states are in good agreement with oxygen K-edge spectra. The empty states of the Li-doped materials provide a theoretical value of the band gap in NiO which, unlike previous estimates, is reasonably close to the observed value of 3.7 eV.

The electronic structure of NiO has continued to receive considerable attention, both theoretically and experimentally, for reasons of fundamental interest and technological application. Following years of controversy as to the reasons for the high-spin insulating behaviour not only of NiO but of the first row (3d) transition-metal oxides more generally [1-5] , Zaanen, Sawatzky and Allen [6] suggested that the early members of the series are Mott-Hubbard systems, whereas the latter members are p→d charge-transfer insulators. This has now been verified by experiment [7-11] and by first principles computations [12-20], which include spin-unrestricted Hartree-Fock studies [19-20] which found the majority weight of the valence band upper edge of both MnO and NiO to be O(p) in the AF_I, AF_{II} and ferromagnetic states and from an analysis of the type suggested by Brandow [4], confirmed that the gap is the result of large on-site d-d Coulomb interactions. This picture implies, though does not prove, that the first ionised state of NiO is essentially $d^8\underline{L}$, for which there is resonant photoemission evidence [21] and support from parameterised configuration-interaction cluster model calculations [8]. It also implies that in Li-doped NiO the charge compensating holes are essentially empty O(p) states at the valence band edge. This view concurs with the theoretical interpretation of the oxygen K-edge x-ray absorption spectra (XAS) by Kuiper et al [22] and the nickel 2p XAS edges by van Elp et al [23] of $Li_xNi_{1-x}O$ (x = 0 to 0.5) and a subsequent cluster calculation analysis of XPS and BIS spectroscopic data in approximately the same doping regime by van Elp et al[24].

In this Letter we present what we believe to be the first direct evidence of O(p) holes in Li-doped NiO from *fully periodic first principles* calculations. They are based on the spin-unrestricted Hartree-Fock method of the type recently used to calculate the ground state electronic structure, magnetism and elastic properties of MnO and NiO [19-20]. The computational approach used here embraces the all electron first principles LCAO periodic Hartree-Fock method, embodied in the CRYSTAL 95 computer code [25]. The calculations use extended Gaussian basis sets and are based on the spin unrestricted (UHF) procedure of Pople and Nesbet [26] to describe the

high-spin open-shell electronic structures. Full details of the numerical accuracy of the direct space summations and reciprocal space integrations have been reported recently [20]. We have considered two levels of Li doping within the range examined experimentally by Kuiper et al [22] and van Elp et al [23,24], $Li_{0.125}Ni_{0.875}O$ and $Li_{0.25}Ni_{0.75}O$, which we have represented by periodic super-cells of composition $LiNi_7O_8$ and $LiNi_3O_4$ respectively, in keeping with the finding that $Li_xNi_{1-x}O$ retains the NaCl structure up to x ~ 0.25 [23] . The two structures are shown in Figure 1. For simplicity we have used the same value of the cation-anion nearest-neighbour distance of 2.1323 Å for NiO, $LiNi_7O_8$ and $LiNi_3O_4$. It has been shown previously [19-20] that the spin-unrestricted Hartree-Fock method correctly predicts the low temperature ground state of NiO to be AF_{II}. In addition, the electron distribution and projected density of states (DOS) were found to be nearly independent of the magnetic state [20]. We have used, therefore, the computationally more convenient ferromagnetic state to study the electronic structure even though $Li_xNi_{1-x}O$ remains antiferromagnetic for $x < 0.5$ below the Neèl temperature.

The nature of the hole state wavefunction is strongly influenced by symmetry. If a fully symmetric system is assumed, the unpaired electron is forced to delocalise over the six oxygen ions neighbouring the lithium site. The removal of this constraint *allows*, not forces, the electronic configuration to relax to a non-degenerate state in which the unpaired electron/hole is localised on a *single* oxygen site, with stabilisation energies of 3.36 eV and 2.56 eV for $LiNi_7O_8$ and $LiNi_3O_4$ respectively. It is, of course, possible to construct a fully symmetric wavefunction from a linear combination of such localised determinants [24]: however, as discussed below, we find a substantial distortion of the lattice associated with the defect pair, Li^+ - O^-, in $LiNi_7O_8$ leading to a further stabilisation of 0.27 eV, which indicates strongly that the symmetry of the hole state is C_{4v}, not O_h. We conclude, therefore, that the state described by the UHF single determinant is a major component of the many-body wavefunction and that the qualitative picture of the ground state reported here is correct.

To examine the ground state of Li-doped NiO, we have carried out a Mulliken population analysis and computed the spin density and DOS of NiO, $LiNi_7O_8$ and $LiNi_3O_4$. While the Mulliken charge is defined in terms of the basis set and is only a rough guide to the total electron density at an atomic site, differences in the Mulliken charge at a particular site resulting from structural changes such as the addition or removal of a neighbouring atom or substitution by an impurity, are a reasonable measure of the *change* in the electron density, and it precisely this change that is of interest here. Table 1 lists the Hartree-Fock Mulliken charges for the ground states of NiO, $LiNi_7O_8$ and $LiNi_3O_4$, in which the labels of the Ni and O atoms correspond to those in Figure 1. In undoped NiO the atomic charges are $\pm$ 1.9 $|e|$ which, as noted previously [19-20], is indicative of a largely ionic material. As shown in Table 1, Hartree-Fock calculations, in which the spatial symmetry of the lattice is removed, predict that the ionicity remains unchanged in $LiNi_7O_8$ and $LiNi_3O_4$ with Li in its +1 state and the charge compensating hole localised on a *single* neighbouring oxygen ion giving a non-degenerate ground state in each case. Furthermore, a detailed orbital analysis shows that the hole is confined to a $p\sigma$ orbital with respect to Li^+ in both $LiNi_7O_8$ and $LiNi_3O_4$, with the spin of the unpaired $p\sigma$ electron on the neighbouring O^- ion ferromagnetically aligned with the e_g spins of the Ni^{2+} (d^8) lattice.

Unpaired spin density maps in the {100} basal plane of Ni_8O_8 and $LiNi_7O_8$ are displayed in Figure 2. The nickel density corresponds to the open shell $[e_g]^2$ configuration and, as Figure 2a confirms, there is practically no dispersion of net spin on the oxygen sites for undoped NiO (Ni_8O_8). For $LiNi_7O_8$, on the otherhand, Figure 2b shows quite clearly the localisation of unpaired spin density on the central oxygen and its $p\sigma$ character in complete accord with the Mulliken population analysis.

The oxygen K-edge spectrum is a signature of the empty O(p) states, and it was essentially on the differences between the spectra of NiO and $Li_xNi_{1-x}O$, in particular

the emergence of a peak below the NiO edge at an energy close to the band gap, that Kuiper et al [22] concluded that the charge compensating holes were predominantly of oxygen character. Figure 3 shows the calculated Hartree-Fock empty O(p) DOS of $LiNi_7O_8$ and $LiNi_3O_4$, normalised to $Li_{0.125}Ni_{0.875}O$ and $Li_{0.25}Ni_{0.75}O$, compared with that of NiO. Above the conduction band edge of NiO there is practically no change in the DOS, indicating that the existing empty O(p) states of NiO remain essentially unaltered on Li doping. However, *below* the band edge, at energies of approximately 3.5 eV and 2.5 eV for $Li_{0.125}Ni_{0.875}O$ and $Li_{0.25}Ni_{0.75}O$ respectively, we find *additional* empty O(p) states, the intensities of which increase with increasing Li concentration. This corresponds closely to the differences in the oxygen K-edge spectra of NiO and $Li_xNi_{1-x}O$ reported by Kuiper et al [22] and interpreted by them as indicating holes of O(p) character. Thus taken together with the changes in the corresponding Mulliken charges, which are a simple measure of the ground state electron densities, the present calculations provide unambiguous evidence for O(p) holes in Li-doped NiO. Furthermore, since the additional empty states must have originated at the upper edge of the valence band, the gap between these states and the conduction band edge is an estimate of the band gap in NiO. The gap in the more dilute case, 3.5 eV, is close to the observed value of 3.7 eV [27]. The reason why the Hartree-Fock estimates of the band gap of NiO arising from the the Li-doped materials are much more sensible than that arising from NiO itself is that in the Li-doped case we are comparing energies of orbitals of *equal* (zero) occupation. In undoped NiO, on the otherhand, we are comparing the orbital energies of singly occupied and unoccupied otrbitals, so that the former are stabilised by a self-interaction exchange term, leading to a considerable over-estimate of the gap.

We have made a preliminary study of the local geometry of the defect pair, $Li^+ - O^-$, in $LiNi_7O_8$, while retaining the fcc symmetry of the super-lattice, and find that the minimum energy configuration is that in which Li^+ relaxes *away* from the hole towards the opposite O^{2-}. Evidently the O^{2-} exerts a considerably stronger attractive force on

the Li^+ ion compared with the O^- hole site. The lowering in energy from the unrelaxed position is 0.27 eV at the minimum and the displacement 0.27 A. However, as shown in Figure 3c, there is no discernable change in the density of empty O(p) states arising from such relaxation, nor is there in the valence band DOS.

In conclusion, the results of spin-unrestricted Hartree-Fock calculations of NiO, $Li_{0.125}Ni_{0.875}O$ and $Li_{0.25}Ni_{0.75}O$ presented here show unambiguously that the charge-compensating hole states are essentially O(p). Our calculations also indicate strongly that the hole is localised on a single oxygen, forming a Li^+ - O^-, dipolar defect of C_{4v} symmetry, in agreement with a a previous UHF calculation for the $[Li^+Ni2^+(O^{2-})_6]$ cluster by Meng et al [28] and supportive dielectric loss measurements [29]. The positions of the empty oxygen p states below the conduction band edge lead to an estimate of the band gap in NiO which is close to the observed value.

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Table 1. Hartree-Fock Mulliken charges (|e|) in NiO, $LiNi_7O_8$ and $LiNi_3O_4$

Atoms	NiO	$LiNi_3O_4$	$LiNi_7O_8$
Ni_1/O_1	1.88/1.88	1.88 / 1.00	1.85 / 1.89
Ni_2/O_2	-	1.87 / 1.84	1.88 / 1.05
Ni_3/O_3	-	1.87 / 1.84	1.87 / 1.85
Ni_4/O_4	-	- / 1.91	1.87 / 1.85
Ni_5/O_5	-	-	1.87 / 1.85
Ni_6/O_6	-	-	1.87 / 1.85
Ni_7/O_7	-	-	1.88 / 1.84
Ni_8/O_8	-	-	- / 1.89

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Figure Captions

Figure 1a. $LiNi_3O_4$ super-cell structure

Figure 1b. $LiNi_7O_8$ super-cell structure

Figure 2a. Ni_8O_8 {100} basal plane unpaired spin density contour

Figure 2b. $LiNi_7O_8$ {100}basal plane unpaired spin density contour

Figure 3. Empty O(p) DOS for $LiNi_7O_8$ and $LiNi_3O_4$

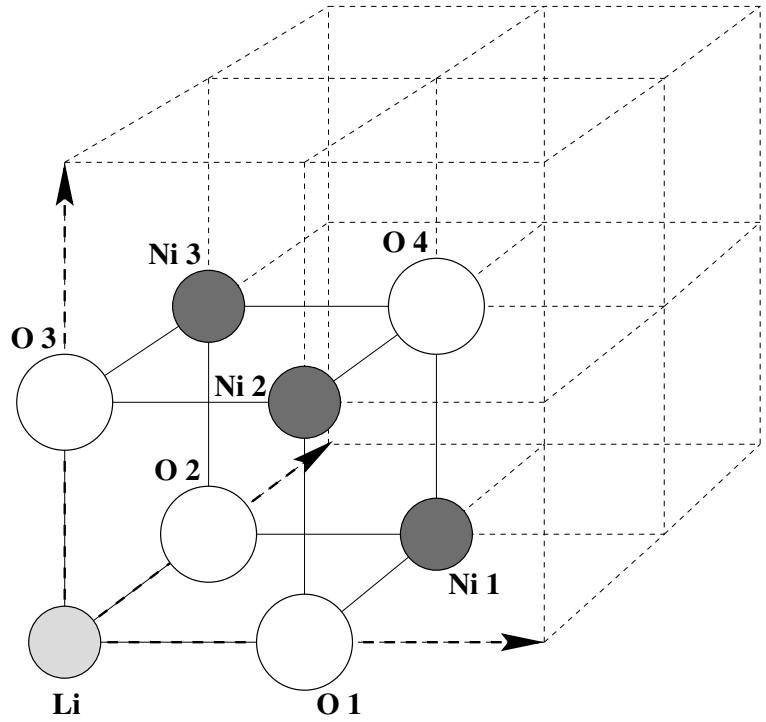

Figure 1a. $LiNi_3O_4$ super-cell structure

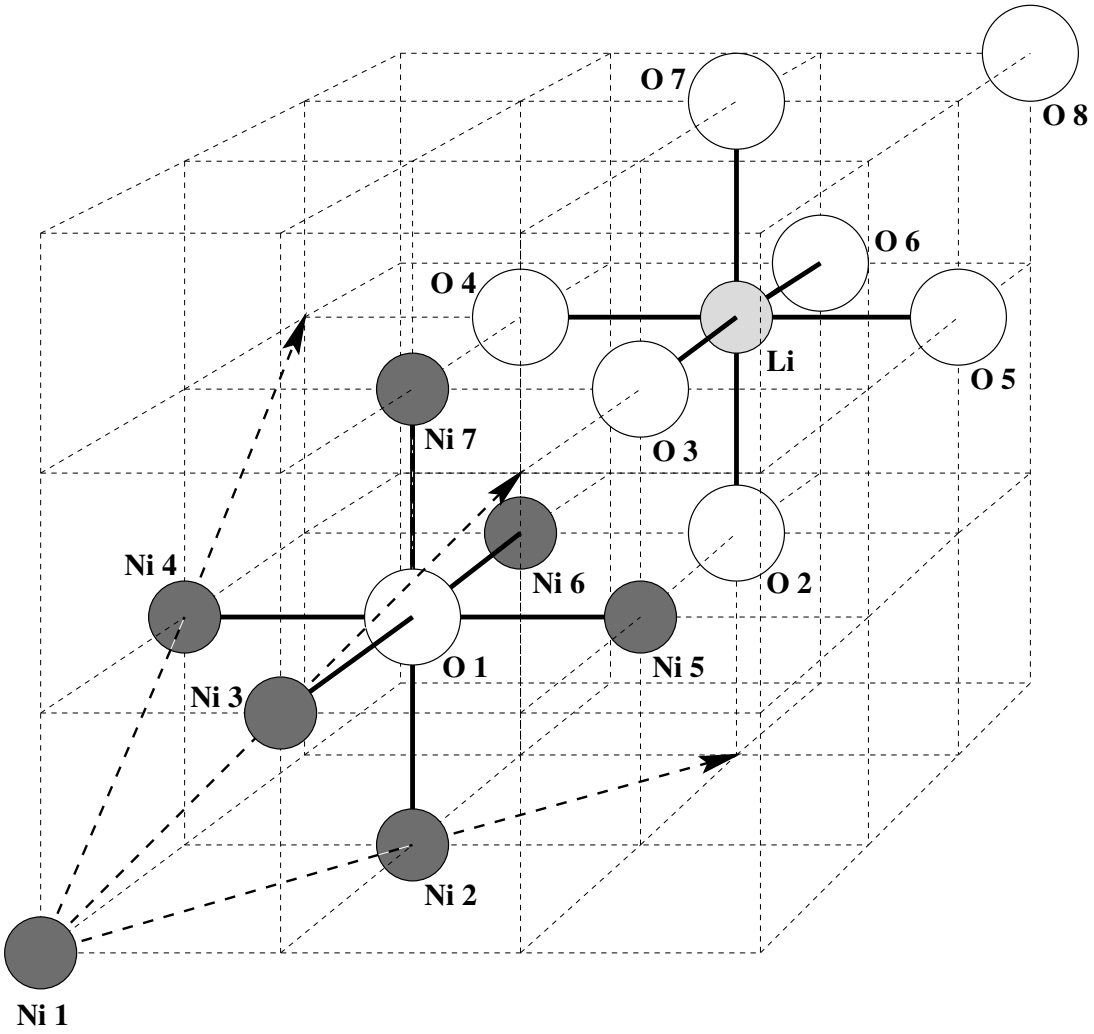

Figure 1b. $LiNi_7O_8$ super-cell structure

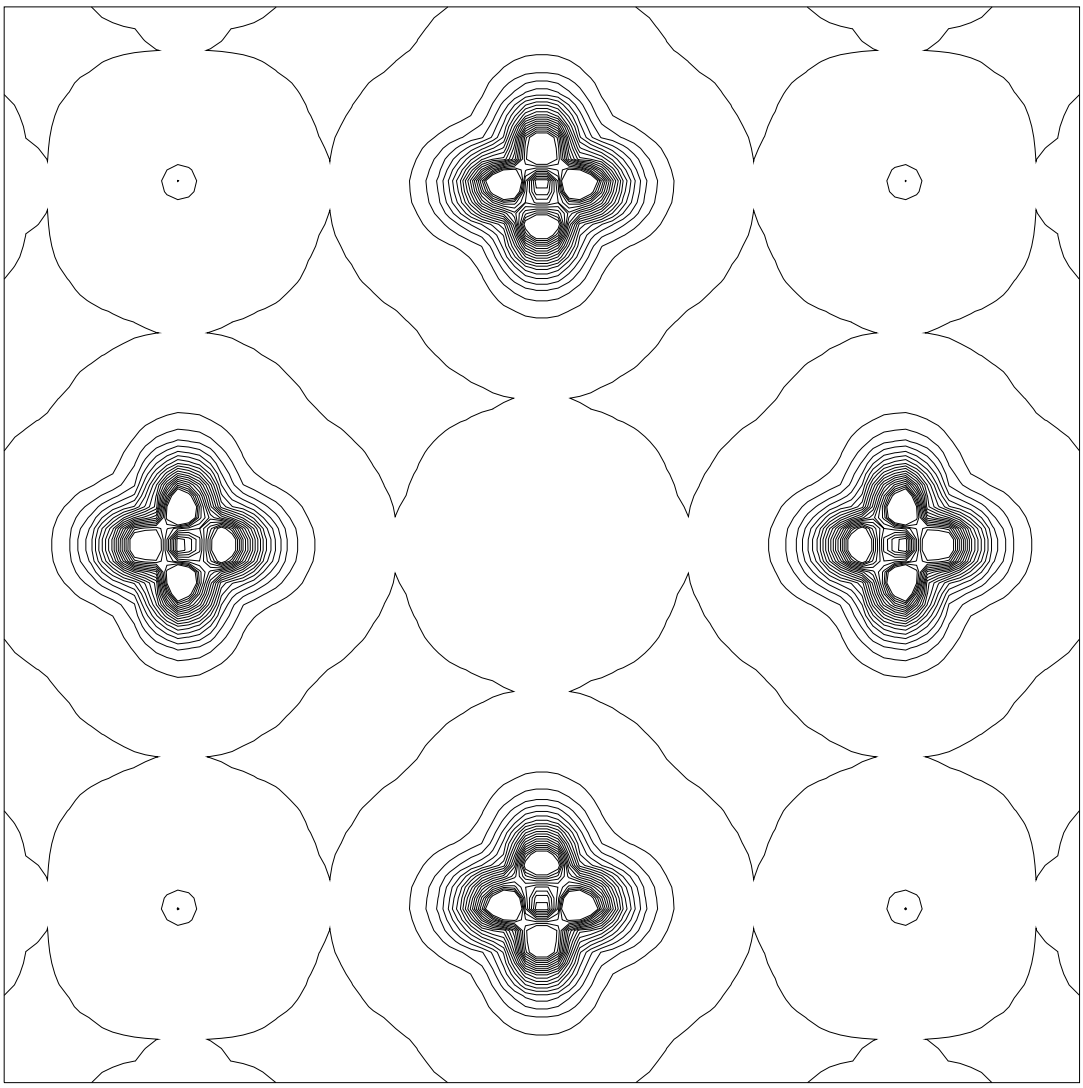

Figure 2a. Ni_8O_8 {100} basal plane unpaired spin density contour

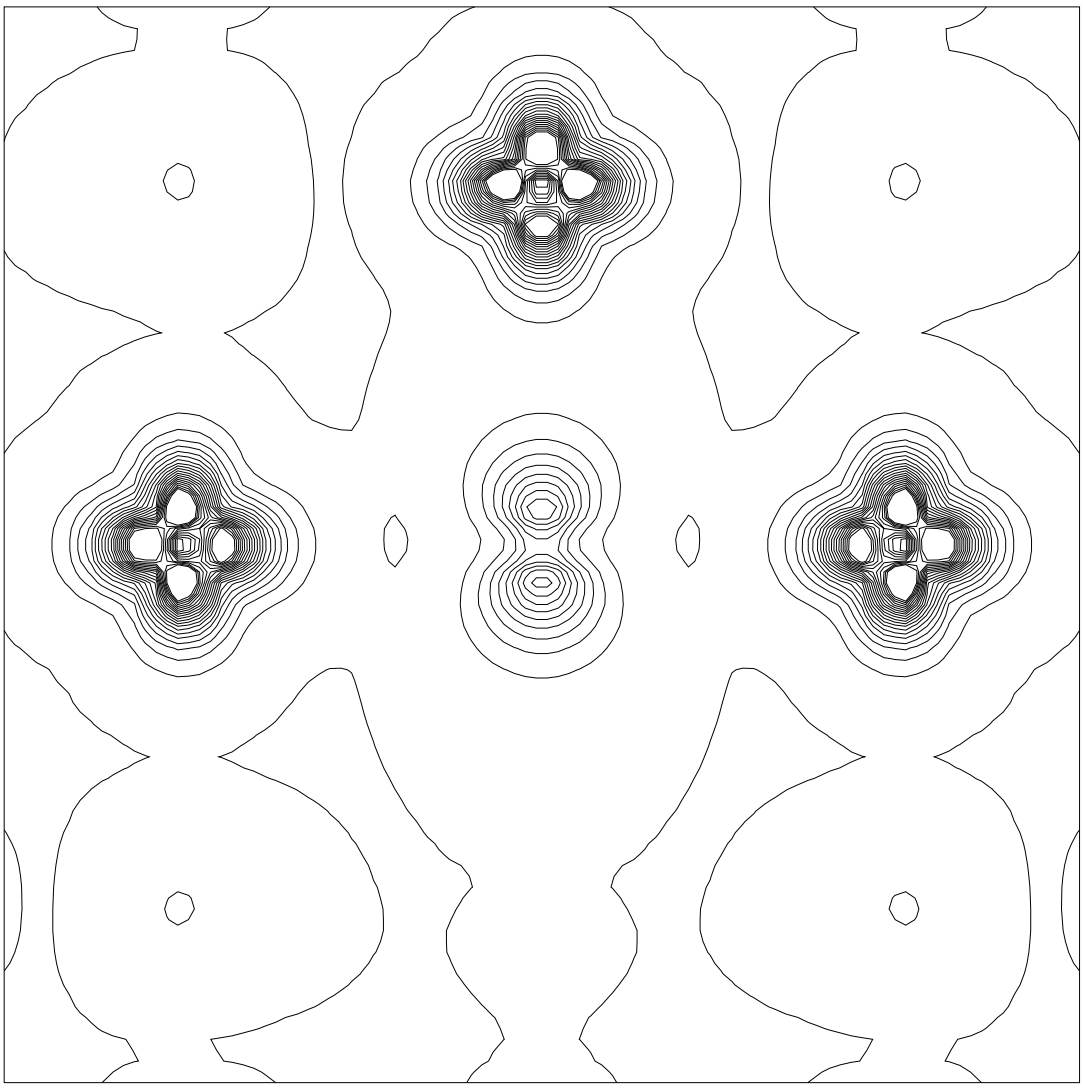

Figure 2b. $LiNi_7O_8$ {100}basal plane unpaired spin density contour

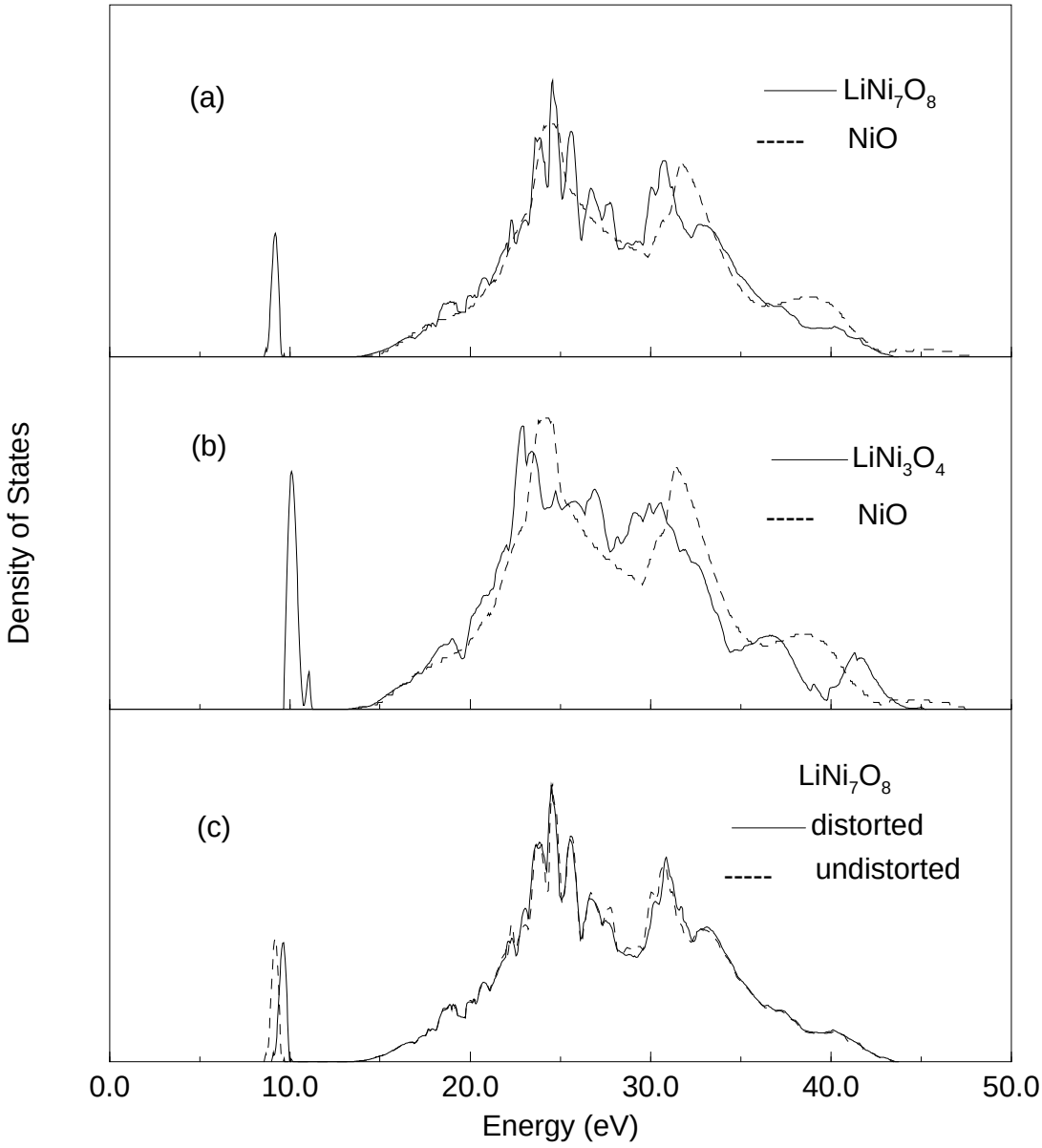

Figure 3. Empty O(p) DOS for $LiNi_7O_8$ and $LiNi_3O_4$