

## Localized electron behaviour within band theory: a Hartree–Fock description of $M_xMg_{1-x}O$ ( $M = Mn, Ni$ )

M D Towler†|| N L Allan†, N M Harrison‡, V R Saunders‡ and W C Mackrodt§

† School of Chemistry, University of Bristol, Cantocks Close, Bristol BS8 1TS, UK

‡ CCL Laboratory, Daresbury, Warrington, Cheshire WA4 4AD, UK

§ School of Chemistry, University of St Andrews, St Andrews, Fife KY16 9ST, UK

Received 5 May 1995

**Abstract.** Results are presented of *ab initio* periodic unrestricted Hartree–Fock calculations which show the density of states for  $M_xMg_{1-x}O$  ( $M = Mn, Ni$ ) to be essentially independent of dopant ( $M$ ) concentration  $x$ . The small variations of the projected densities of states with dopant concentration are of the same magnitude as those resulting from changes in magnetic order. This is consistent with the marked similarity of the low-energy optical spectra of  $NiO$ ,  $Ni_xMg_{1-x}O$  and aqueous solutions of  $Ni(II)$  salts, which suggests ‘independent ion’ behaviour in these systems. It is thus argued that the unrestricted Hartree–Fock approach correctly reproduces the qualitative features of the ground state of magnetic insulators such as  $MnO$  and  $NiO$  which result from strong on-site Coulomb interactions between essentially localized electrons.

### 1. Introduction

There has been considerable discussion as to whether single-particle theories can give a qualitatively correct description of the ground state of magnetic insulators such as  $MnO$  and  $NiO$ . A commonly expressed view is that the strong Coulomb interaction between the  $d$  electrons in these materials is large enough to render an independent electron approach of limited value. Nevertheless, numerous band theory calculations have been reported, most often using the local spin density approximation (LSDA) to treat the effects of exchange and correlation (see, for example, [1] and [2]). In general, the results of most of these studies have been qualitatively incorrect in that calculations within the LSDA tend to predict metallic behaviour or to underestimate band gaps by an order of magnitude, whereas inverse photoemission spectroscopy has shown unequivocally this class of materials to be large-band-gap insulators. However, these results are not a failure of the independent electron approach *per se* but arise from the use of particular Hamiltonians. A useful discussion of the approximations made in local spin density theory, and of the kinds of modification which need to be made to render the one-electron theory *qualitatively* correct, has been given by Brandow [3].

Recent studies [4, 5] based on spin-unrestricted Hartree–Fock theory have shown that the insulating and magnetic properties of materials such as  $MnO$  and  $NiO$  are the result of large on-site Coulomb and exchange interactions between essentially localized electrons. These have an important effect on the single-particle spectrum and open a large band gap.

|| Present address: Theoretical Chemistry Group, Department CIFM, University of Torino, via P Giuria 5, I-10125 Torino, Italy.

Localization relates to the real space nature of the one-electron orbitals, in that it depends crucially on strong 'orbital polarization', i.e. a marked departure from near-uniform d orbital occupancies. A qualitatively correct one-electron band theory thus needs to incorporate correctly the orbital dependence of the one-electron potential, which is the main driving force for this polarization [3]. The orbital dependence is determined principally by the *non-local* exchange interaction, and this is evaluated exactly within the Hartree–Fock approximation. Calculation of the exchange through a local approximation such as the LSDA is equivalent to the assumption of an orbitally unpolarized solution.

It was suggested in [3] that, because of the mathematical difficulties associated with the non-locality of the full Hartree–Fock potential, the LSDA might be used as far as possible, but supplemented by a tight-binding parametrization of the d–d interactions. However, the computational implementation of exact non-local exchange within periodic LCAO Hartree–Fock theory has now been carried out [6–8]. The resulting computer code [7] provides fully self-consistent solutions in both restricted and spin-unrestricted modes and is capable of treating both open and closed shell systems to high numerical accuracy. It has now been applied by numerous authors to a range of transition metal oxides and fluorides, including NiO and MnO [4, 5], Fe<sub>2</sub>O<sub>3</sub> [10], KNiF<sub>3</sub> [11], K<sub>2</sub>NiF<sub>4</sub> [12], KCuF<sub>3</sub> [13], LiM<sub>1-x</sub>O (M = Mn, Ni) [14] and layered MgO–NiO thin films [15]. In each case, the known features of the ground state electronic and magnetic properties are reproduced semiquantitatively, including, where appropriate, their wide-band-gap insulating nature, magnetic ordering and exchange striction, Jahn–Teller distortion, orbital ordering and the geometry dependence of exchange constants.

The purpose of this paper is to provide quantitative support for the Mott–Hubbard interpretation of the low-energy optical spectra of mixed MgO/transition metal oxide systems by means of Hartree–Fock calculations for M<sub>x</sub>Mg<sub>1-x</sub>O (M = Mn, Ni). The physical model under investigation is one of *independent ion* character, in which Mn and Ni ions in the parent oxides and M<sub>x</sub>Mg<sub>1-x</sub>O (M = Mn, Ni) behave essentially as free M<sup>2+</sup> ions, modified by crystal field effects, as traditionally assumed in solid state chemistry. In the low-energy optical absorption spectrum of MgO lightly doped with Ni ions, Frenkel exciton spectra result from transitions of the Ni 3d electrons into excited states of the 3d<sup>8</sup> configuration [16]. Crystal field effects alter this spectrum compared to that of the free ion, but a good fit can be obtained [16] using crystal field multiplet theory. Significantly, the shape of the Frenkel exciton spectra is virtually unchanged as the Ni<sup>2+</sup> concentration in MgO is increased even as far as NiO itself [16]. Similar spectra may be observed for aqueous solutions of Ni(II) salts [17]. Equivalent patterns have been observed in the low-energy optical spectra of MnO, Mn<sub>x</sub>Mg<sub>1-x</sub>O and Mn<sub>x</sub>Ca<sub>1-x</sub>O [21]. The existence of these spectra thus provides strong evidence for independent ion or localized electron behaviour in doped and undoped NiO and MnO.

## 2. Theoretical method

To examine the electronic structure of these putative localized states, we have performed *ab initio* LCAO periodic Hartree–Fock calculations for M<sub>x</sub>Mg<sub>1-x</sub>O, where M = Mn, Ni and  $x = 0.125, 0.25, 0.5, 1.0$ , based on a supercell approach, as implemented in the program CRYSTAL 95 [9]. The theoretical methods are discussed in full in [6–8], while the computational details are similar to those described in [4] and [5]. The exponents and contraction coefficients of the atomic orbital basis sets were the same as those used in recent studies of the bulk properties of MgO [19] and of MnO and NiO [5]. A detailed

study of the supercell method has been given by Freyria-Fava *et al.*, who examined Ca and Be substitution in bulk MgO [18].

The calculations were performed using supercells containing two, four and eight formula units of the host oxide MgO. These were obtained by multiplication of the fcc primitive unit cell vectors by the following expansion matrices:

$$M_2O_2 \begin{pmatrix} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{pmatrix} \quad M_4O_4 \begin{pmatrix} 1 & 1 & -1 \\ 1 & -1 & 1 \\ -1 & 1 & 1 \end{pmatrix} \quad M_8O_8 \begin{pmatrix} 2 & 0 & 0 \\ 0 & 2 & 0 \\ 0 & 0 & 2 \end{pmatrix}.$$

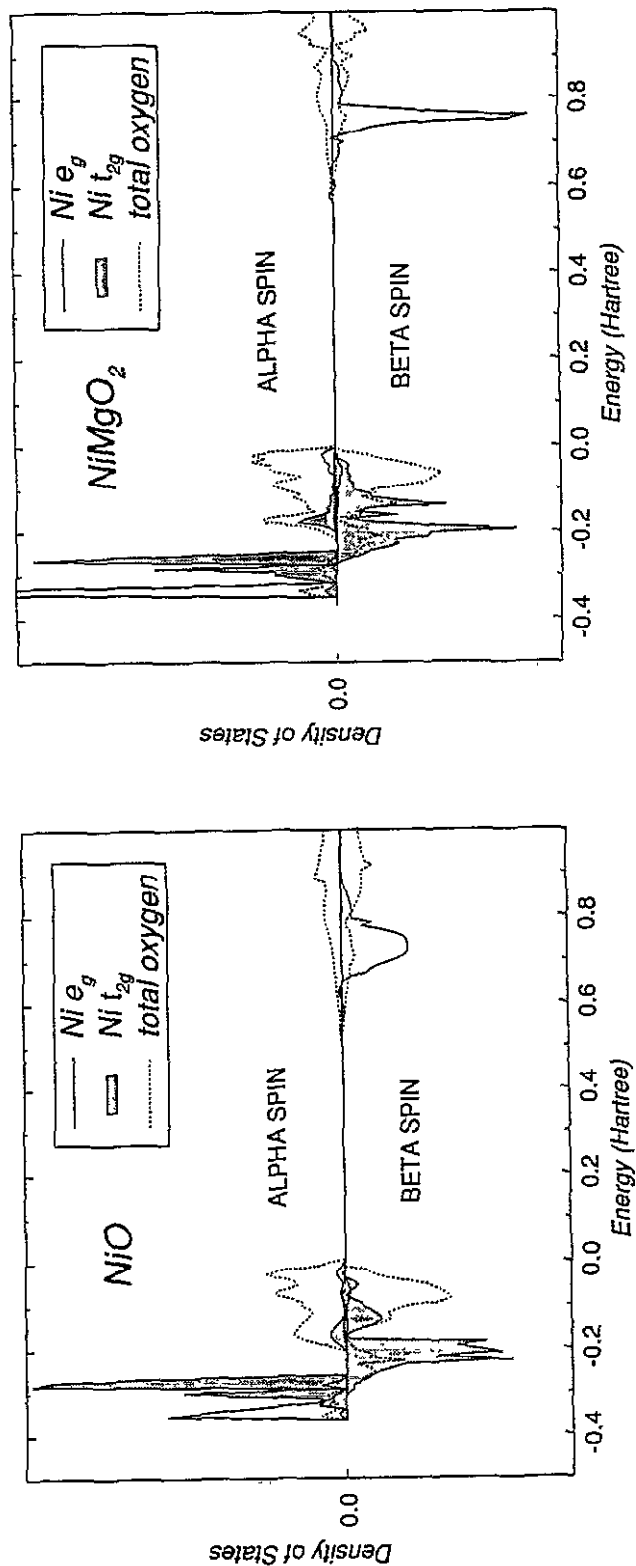
Dopant transition metal ions were introduced by direct substitution of a single Mg ion in each case. Vegard's law was assumed in that the lattice parameter was fixed at the average of the equilibrium Hartree–Fock lattice parameters of MgO and the pure transition metal monoxide MO, weighted by the relative numbers of Mg and M in the doped system. Since the present work is not concerned with the energetics of substitution, no account was taken of the relaxation of the ions surrounding the dopant. However, it is most unlikely that such relaxation would affect the conclusions presented below concerning the density of states and, in any event, the relaxations in Ni-doped MgO will be minimal since the two cation radii are nearly identical.

Our concern here is not the calculation of the optical spectra which involve changes in the d electron configuration such as  $(t_{2g})^6(e_g)^2 \rightarrow (t_{2g})^5(e_g)^3$  and  $(t_{2g})^6(e_g)^2 \rightarrow (t_{2g})^4(e_g)^4$  for  $Ni^{2+}$ . For our purposes, it is sufficient to demonstrate the qualitative behaviour of the theoretical densities of states as a function of dopant concentration. Indeed, it is inappropriate to use Hartree–Fock one-electron eigenvalues for calculating excitation energies involving the promotion of an electron from an occupied to a virtual level. Hartree–Fock band gaps in insulators and semiconductors are usually about twice those given by experiment, although it is possible to modify these to give closer agreement with the optical spectra using corrections such as the GW approximation [20].

### 3. Results and discussion

Figure 1 shows the projected density of states (PDOS) for the valence and lower conduction bands of NiO, NiMgO, NiMg<sub>3</sub>O<sub>4</sub> and NiMg<sub>7</sub>O<sub>8</sub>. Although for simplicity we have imposed ferromagnetic spin ordering, the type of magnetic order is immaterial since differences in the energies of magnetic states are very much smaller than the on-site Coulomb interaction. In the plots, only Ni and O bands are seen, since the Mg states lie much lower in energy. It is clear that the position of the Ni  $e_g$  and  $t_{2g}$  bands remains virtually unchanged throughout the series, up to and including NiO itself. As demonstrated previously [5], the relative positions of these bands may be rationalized using a *single-site* Hubbard model along the lines suggested by Brandow [3], in which the Hubbard Hamiltonian ( $U_H$ ) is written in terms of the on-site Coulomb interaction ( $U$ ) and d–d exchange energy ( $J$ ). The separations of the  $e_g$  and  $t_{2g}$  bands are then given in terms of  $U$ ,  $J$  and the crystal field term,  $\Delta_{CF}$ . A Mulliken population analysis indicates virtually the same charge of  $+1.88 \pm 0.02 |e|$  for Ni at all dopant concentrations.

For our particular choice of supercells generated by the expansion matrices given above, the numbers and types of nearest and next-nearest cation neighbours of a given Ni ion change with dopant concentrations as shown in table 1. The minor differences in the densities of states as a function of concentration may be explained in terms of the changes in the intersite hybridization of metal and oxygen orbitals. Changes in the widths of the Ni bands from one



**Figure 1.** Calculated density of states for the valence and lower conduction bands of NiO, NiMgO<sub>2</sub>, NiMg<sub>3</sub>O<sub>4</sub> and NiMg<sub>7</sub>O<sub>8</sub>. The energy scale is defined relative to the highest occupied electron level.

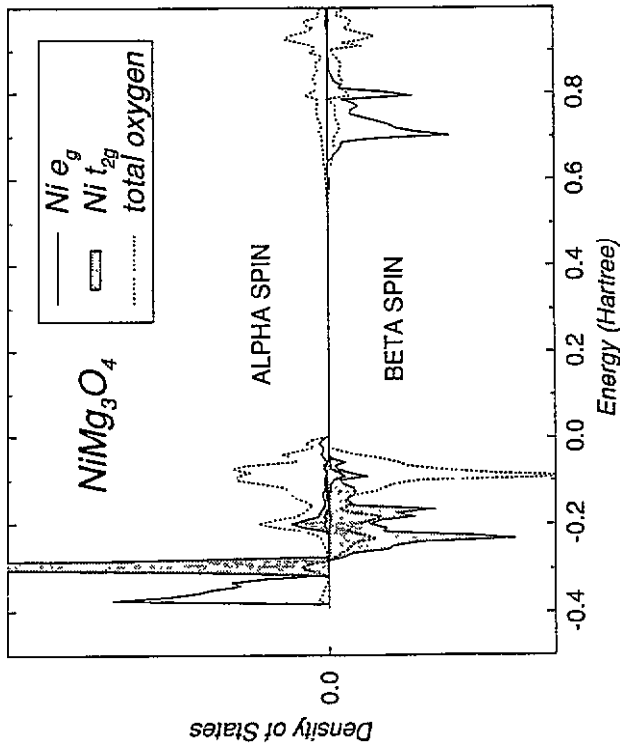
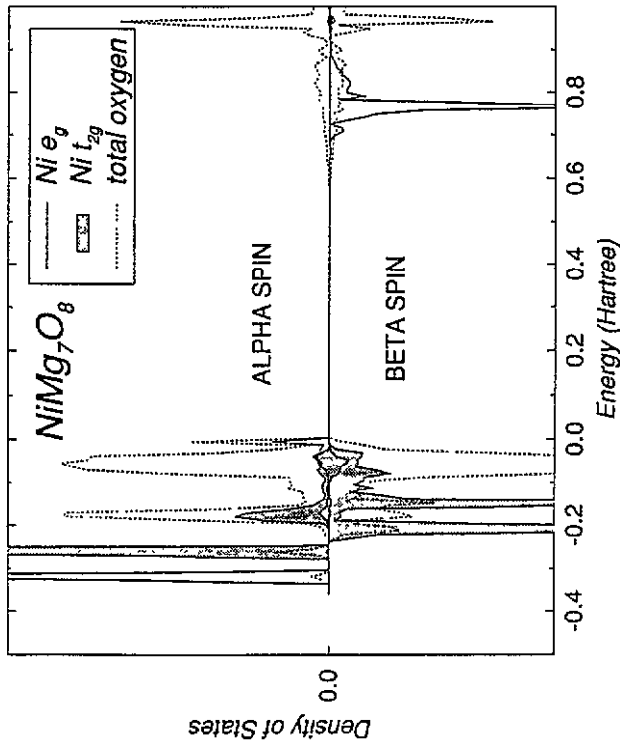


Figure 1. Continued.

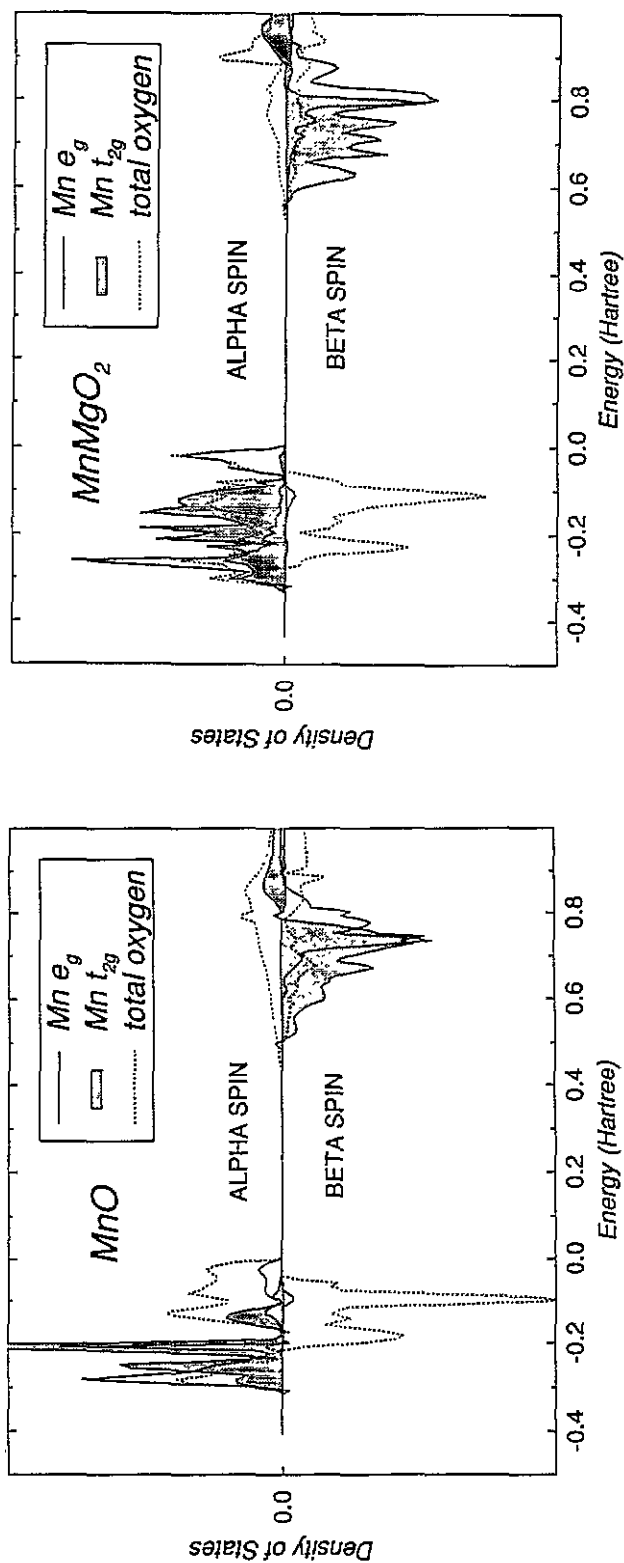


Figure 2. Calculated density of states for the valence bands of MnO, MnMg<sub>3</sub>O<sub>4</sub> and MnMg<sub>7</sub>O<sub>9</sub>. The energy scale is defined relative to the highest occupied electron level.

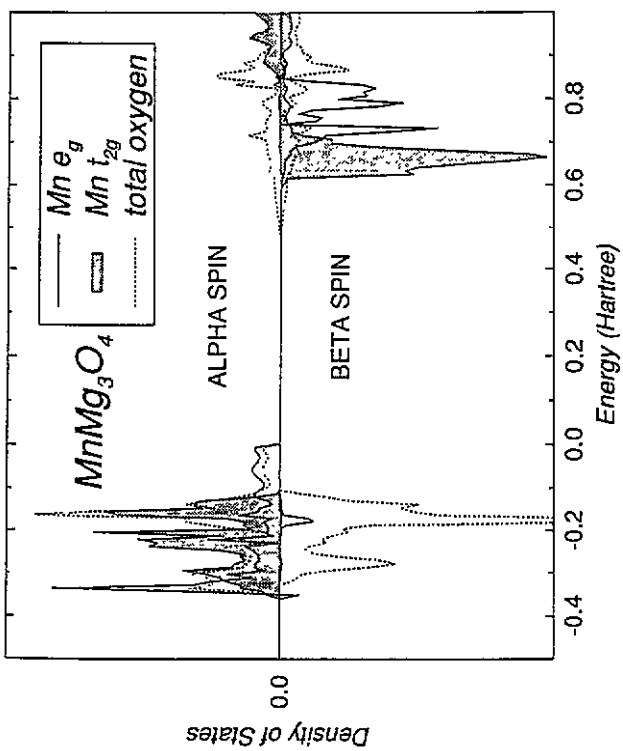
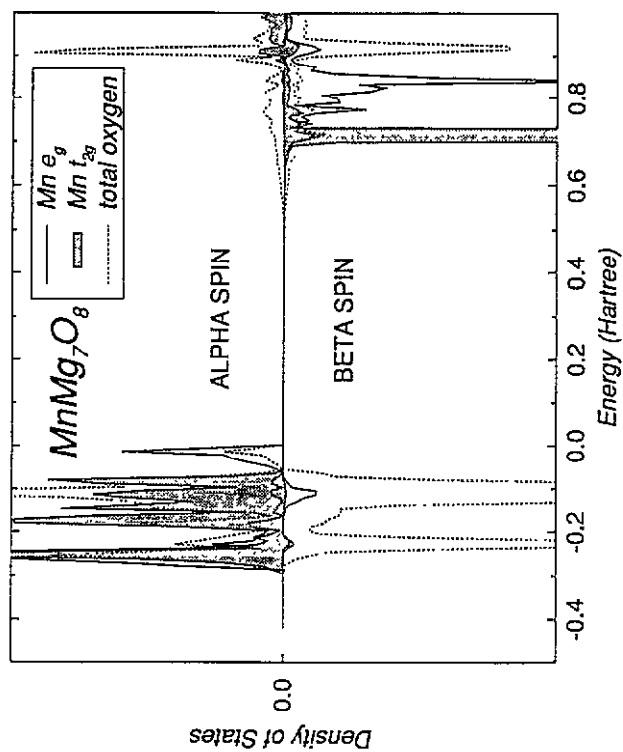


Figure 2. Continued.

**Table 1.** Numbers of nearest and next-nearest cation neighbours of a transition metal ion in the supercells studied.

	Nearest neighbours	Next-nearest neighbours
NiO	12 Ni	6 Ni
NiMgO <sub>2</sub>	6 Ni, 6 Mg	6 Mg
NiMg <sub>3</sub> O <sub>4</sub>	12 Mg	6 Ni
NiMg <sub>7</sub> O <sub>8</sub>	12 Mg	6 Mg

system to another are determined by the number of superexchange interactions via oxygen with smaller contributions from direct Ni–Ni overlap. The widths of the individual  $e_g$  and  $t_{2g}$  bands thus increase slightly with increasing numbers of Ni neighbours. For example, the occupied ( $\alpha$  spin)  $e_g$  band is narrower in NiMgO<sub>2</sub> than in either NiO or NiMg<sub>3</sub>O<sub>4</sub>, since in NiMgO<sub>2</sub> the Ni has only Mg second neighbours. Figure 2 shows the analogous PDOS for Mn<sub>x</sub>Mg<sub>1-x</sub>O systems. Again it is clear that the relative positions of the 3d bands are virtually unchanged as a function of dopant concentration.

By comparison the LSDA description of magnetic insulators depends explicitly on *reciprocal space* properties, such as changes in the size of the unit cell associated with magnetic ordering or structural distortions. Thus, for particular magnetic states or distorted cells, the LSDA Hamiltonian is capable of opening a small band gap to give a semiconducting ground state [1, 22]. However, despite recent progress in extending the LSDA description (SIC-LDA [23], LDA+U [24]), the method is still applied in its uncorrected form [2]. Although, to our knowledge, calculations for the mixed MgO/TMO systems studied here have not been performed within the LSDA, we suspect that the results would depend explicitly on both the magnetic states and the size and shape of the unit cell, and would be unlikely to reproduce the qualitative features of the ground state as a function of *dopant concentration*.

In summary, then, within the framework of one-electron calculations, the localized electron features of magnetic insulators are essentially a consequence of the correct treatment of non-local exchange interactions. The direct correlation, which is neglected within the Hartree–Fock approximation, is a short-range screening effect which is less crucial to Mott localization. It seems reasonable, therefore, to assume that the latter effect may be taken into account by supplementing an exact description of the exchange with a correlation-only LDA. Such correlation functionals have now been implemented in the CRYSTAL program via a hybrid Hartree–Fock/Kohn–Sham scheme [25]. The effectiveness of these functionals in describing selected magnetic insulators is now under examination.

#### 4. Conclusions

We have shown that the single-particle spectrum of Ni<sub>x</sub>Mg<sub>1-x</sub>O and Mn<sub>x</sub>Mg<sub>1-x</sub>O within the Hartree–Fock approximation is essentially invariant with dopant concentration, a qualitative feature that is in agreement with the low-energy optical spectroscopic data. It is argued that this supports the Mott–Hubbard interpretation of magnetic insulators. The inclusion in a band theory calculation of the exact non-local exchange, or a non-local approximation to this using angular gradient corrections [26], for example, would be essential for a correct description of localized electron behaviour.



## Acknowledgments

MDT wishes to thank SERC and ICI for the award of a CASE studentship, and the Commission of the European Communities for the award of a fellowship under the Human Capital and Mobility Scheme (contract ERBCHBICT941605). The work was also supported by SERC grants GR/J26243, GR/K06389 and EC HC&M contract CHRX-CT930155.

## References

- [1] Terakura K, Williams A R, Oguchi T and Kübler J 1984 *Phys. Rev. B* **30** 4734
- [2] Eyert V and Hock K H 1993 *J. Phys.: Condens. Matter* **5** 2987
- [3] Brandow B 1992 *J. Alloys Compounds* **181** 377
- [4] Mackrodt W C, Harrison N M, Saunders V R, Allan N L, Towler M D, Aprà E and Dovesi R 1993 *Phil. Mag. A* **68** 653
- [5] Towler M D, Allan N L, Harrison N M, Saunders V R, Mackrodt W C and Aprà E 1994 *Phys. Rev. B* **50** 5041
- [6] Pisani C, Dovesi R and Roetti C 1988 *Hartree-Fock Ab Initio Treatment of Crystalline Systems* (Berlin: Springer)
- [7] Dovesi R, Pisani C, Roetti C, Causà M and Saunders V R 1989 *CRYSTAL 88—An Ab Initio all Electron LCAO Hartree-Fock Program for Periodic Systems* (QCPE Pgm. N. 577, Quantum Chemistry Program Exchange, Indiana University, Bloomington, IN 1989)  
Dovesi R, Saunders V R and Roetti C 1992 *CRYSTAL 92 User Documentation* (University of Torino and SERC Daresbury Laboratory, 1992)
- [8] Causà M, Dovesi R, Orlando R, Pisani C and Saunders V R 1988 *J. Phys. Chem.* **92** 909
- [9] *CRYSTAL 95* University of Torino and CCL Daresbury Laboratory, to be published
- [10] Catti M, Valerio G and Dovesi R 1995 *Phys. Rev. B* **51** 7441
- [11] Ricart J M, Dovesi R, Saunders V R and Roetti C *Phys. Rev. B* at press
- [12] Dovesi R, Ricart J M, Saunders V R and Orlando R 1995 *J. Phys.: Condens. Matter* submitted
- [13] Towler M D, Dovesi R and Saunders V R *Phys. Rev. B* submitted
- [14] Towler M D, Allan N L, Harrison N M, Saunders V R and Mackrodt W C *Phys. Rev. B* to be submitted
- [15] Towler M D, Harrison N M and McCarthy M I 1995 *Phys. Rev. B* at press
- [16] Reinen D 1965 *Bunsenges, Phys. Chem.* **69** 82
- [17] Stephens D R and Drickamer H G 1961 *J. Chem. Phys.* **34** 937
- [18] Freyria-Fava C, Dovesi R, Saunders V R, Leslie M and Roetti C 1993 *J. Phys.: Condens. Matter* **5** 4793
- [19] McCarthy M I and Harrison N M 1994 *Phys. Rev. B* **49** 8574
- [20] Hedin L 1965 *Phys. Rev.* **139** A796  
Baroni S, Pastori Parravicini G and Pezzica G 1985 *Phys. Rev. B* **32** 4077  
Hott R 1991 *Phys. Rev. B* **44** 1057
- [21] Reinen D, Schwab G and Günzler V 1984 *Z. Anorg. (Allg.) Chem.* **516** 140
- [22] Mattheiss L F 1972 *Phys. Rev. B* **5** 290, 306
- [23] Svane A and Gunnarsson O 1988 *Phys. Rev. B* **37** 9919; 1990 *Phys. Rev. Lett.* **65** 1148  
Szotek Z, Temmerman W M and Winter H 1993 *Phys. Rev. B* **47** 4029  
Temmerman W, Szotek Z and Winter H 1993 *Phys. Rev. B* **47** 11533
- [24] Anisimov V I, Zaanen J and Andersen O K 1991 *Phys. Rev. B* **44** 943
- [25] Causà M and Zupan A 1995 *Int. J. Quant. Chem. S* **28** 633
- [26] Dufek P, Blaha P, Sliwko V and Schwarz K 1994 *Phys. Rev. B* **49** 10170