A study of the electronic, magnetic, structural and dynamic properties of low-dimensional NiO on MgO(100) surfaces

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Recent developments in the growth of ultra-thin epitaxial layers of oxides and the fabrication of a diversity of nanostructures has led to current interest in, and much speculation about, the properties of low dimensional systems. In this paper we report recent calculations for low dimensional NiO on MgO(100) surfaces both from first principles electronic structure calculations and free energy calculations based on surface lattice dynamics. The results include surface structures and dynamics at a range of temperatures and electronic structures of ground, excited, ionised, $d \rightarrow d$ and charge–transfer excitonic states in different spin alignments.

1. Introduction

Over the past few years, important advances have been made in the fabrication of ultra-thin crystalline oxide layers grown epitaxially on a variety of substrates.^{1,2} The methods commonly used are direct oxidation of a metallic surface or deposition of metal atoms followed by controlled oxidation. In this way, films a few Angströms thick may be grown, the crystallinity and perfection of which depend strongly on the ratio of the lattice parameter of the oxide to that of the substrate and details of the preparative conditions such as deposition rate, oxidising temperature, *etc.* These ultra-thin films exhibit several unusual properties which are of interest both from a fundamental point of view³⁻⁵ and with regard to potential technological application. First, as a result of their small thickness, they do not charge when exposed to electron or electromagnetic radiation and can thus be submitted to detailed spectroscopic investigation. They may also exhibit surfaces that are not usually obtained by direct cleavage of the bulk, which is the case for high energy surface orientations such as polar surfaces. The constraint imposed by the substrate may also lead these epitaxial oxide layers to adopt lattice symmetries which differ from those of the thermodynamically stable bulk, and, where structural phase transitions occur, transition temperatures can depend strongly on the thickness of the epitaxial layer.

The system NiO(100)–MgO(100) is prototypical of multilayered oxide films, largely because the lattice mismatch between the two components is less than 1%. It has been shown that MgO grows on NiO(100) epitaxially and in a layer-by-layer mode, $^{6-8}$ and that the same is true for NiO on MgO(100). $^{5,6,9-13}$ Intermixing occurs only if films are prepared at high temperature. Several types of experiment indicate a strong dependence of the electronic and magnetic properties of these ultra-thin films on their thickness. EELS (electron energy loss spectroscopy) experiments^{6,10} have

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revealed excitations at energies less than the bulk band gap, which have been attributed to $d \rightarrow d$ transitions. For coverages of NiO on MgO(100) greater than 2.8 monolayers (ML) these excitations are identical to semi-infinite NiO(100), whereas for NiO thicknesses less than 2.8 ML, a new transition at 2.18 eV appears, which has been assigned to surface or interface states and appears to show that the electronic structure of thin NiO films is modified by the presence of the MgO substrate. Other bulk and surface transitions have been reported to shift in energy with coverage.

Two explanations have been suggested to account for these changes. The first is the loss of octahedral symmetry at a surface Ni, associated, not only with the reduced nearest neighbour coordination, but also with a lateral elongation of the NiO lattice and contraction of the interplanar separation. The second is a putative loss of octahedral symmetry at a Ni at the NiO/MgO interface resulting from the difference in covalency between NiO and MgO. With regard to the existence, or otherwise, of NiO/MgO interface states, it is of note that no such states have been detected by EELS⁸ for MgO layers grown on NiO. XPS experiments^{9,13} have shown that Ni and O core level spectra depend on film thickness, which has been interpreted in terms of the number of Ni second neighbours. Such spectra are also consistent with a negative charge transfer from MgO to NiO at large thicknesses. A detailed Hartree–Fock interpretation of core level shifts in NiO/MgO layered systems in terms of surface lattice relaxation and other effects has been given previously.¹⁴ While magnetic data are generally more difficult to obtain, Alders *et al.*⁵ have recently reported some very elegant linear polarised X-ray absorption experiments, from which they obtain values of the Néel temperature, T_N , of NiO overlayers as a function of thickness and show that even for 20 ML films T_N has not recovered the bulk value.

It is within this context that we have initiated a theoretical study of ultra-thin films and surface properties of NiO. NiO is a paradigm magnetic insulator whose bulk and surface properties have been the subject of extensive experimental and theoretical investigation.¹⁵ It has long been considered as highly ionic and early first principles calculations based on the local spin density approximation (LSD) described it as a Mott-Hubbard system in the AF₂ spin arrangement with a narrow gap spanned by Ni d-states.¹⁶ However, seminal work by Sawatzky et al.^{17–19} showed that hole states in Li: NiO were largely of O(p) character, which suggested that the first ionised state of NiO is essentially $d^{8}L$ and the ground state of $p \rightarrow d$ charge-transfer type. Subsequent first principles calculations confirmed the majority weight of the valence band edge to be O(p), including spin unrestricted *periodic* Hartree–Fock (UHF) calculations.^{20–22} The latter have shown that the insulating and (high spin) magnetic properties are the result of large on-site Coulomb and exchange interactions between essentially localised electrons with strong orbital polarisation resulting from the orbital dependence of the one-electron potential. This is determined principally by the non-local exchange interaction which is evaluated exactly within the Hartree-Fock approximation and implemented, again exactly, in the CRYSTAL code.²³ UHF calculations have also provided direct evidence of O(p) holes in Li:NiO and NiO^{24,25} and Fe(d) holes in NiO,²⁵ in agreement with experiment.²⁶ Thus, despite its approximate nature and inherent limitations, the periodic UHF method would seem to be well suited to describing the electronic and magnetic properties of NiO in lower dimensions. Extending a recent UHF study²⁷ of an unsupported NiO(100) monolayer, which included both ground and $d \rightarrow d$ and charge-transfer excited states, here we report similar calculations of several NiO/MgO slab configurations, including NiO(100) monolayers on MgO(100) or sandwiched between two MgO(100) monolayers. While there appear to be no other calculations based on *extended/periodic* systems for comparison, there have been high level *cluster* calculations of magnetic interactions²⁸ and $d \rightarrow d^{29-31}$ and charge-transfer excitations,³¹ which provide a guide as to the influence of both electron correlation and non-local/ extensive effects.

In view of the growing body of experimental data on the high-temperature properties of ultrathin films, we also report quasi-harmonic lattice dynamics and free energies calculations of more extended NiO/MgO slab configurations at elevated temperatures using recently developed atomistic lattice methods based on pair potentials.³² Few calculations have included dynamic effects, such as *temperature*, largely because the full dynamical treatment of surfaces and extended defects, even within the quasi-harmonic approximation, presents severe computational demands if reasonably high precision is required. There are three main simulation techniques available for the calculation of surface lattice properties: Monte Carlo simulation, molecular dynamics and quasi-harmonic lattice dynamics. Of these only the last is capable of giving free energies (as well as

derived properties such as the entropy and the heat capacity) *directly* and to high precision. This method is consequently not only the most suitable for structure optimisation as a function of temperature, but in many applications it has also been shown to be a valid approximation up to two-thirds of the bulk melting temperature.^{33,34}

Accordingly, the paper is organised as follows. In Section 2 we review briefly the theoretical methods used and in Section 3 present the main body of our results, which we discuss in Section 4.

2. Theoretical methods

2a. Electronic structure calculations

The all-electron *ab initio* LCAO Hartree–Fock method for periodic systems and its computational implementation in the CRYSTAL 95 computer $code^{23}$ have been described in detail previously.³⁵ The calculations reported here use extended Gaussian basis sets and are based on the spin unrestricted (UHF) procedure³⁶ to describe open-shell electronic configurations. The numerical values of the tolerance parameters involved in the evaluation of the (infinite) Coulomb and exchange series were identical to those used in recent studies:^{24,25,27} a detailed account of the effect of these tolerances is discussed elsewhere.³⁷ The reciprocal space integration utilised the Monkhorst–Pack sampling,³⁸ with shrinking factors that gave 15–36 k-points in the IBZ, depending on the overall symmetry of the calculation, and the SCF convergence criterion based on differences in the total energy of the unit cell of less than 10⁻⁶ Ha. *A posteriori* corrections for electron correlation based on three generalised gradient approximations are included in the present study: they are due to Perdew,³⁹ Perdew and Wang⁴⁰ and Perdew, Burke and Ernzerhof⁴¹ and are referred to P, PW and PBE, respectively. As in previous calculations,^{20–22,24,25,27} the localised crystal orbitals consisted of 25 atomic orbitals for Ni, 15 for Mg and 14 for O of the type

Ni: 1s(8)2sp(6)3sp(4)4sp(1)5sp(1)3d(4)4d(1)

Mg: 1s(8)2sp(5)3sp(1)4sp(1)

O: 1s(8)2sp(4)3sp(1)4sp(1)

where the numbers in brackets are the numbers of Gaussian functions used to describe the corresponding shell, *e.g.*, 1s, 2sp, 3d, *etc.* The exponents and contraction coefficients were identical to those used for the bulk.²⁰⁻²²

In this study we consider various slabs of NiO and MgO, for which we use the notation, $(type)_{nlm}^N$, where N refers to the number of layers and nlm to the orientation. Thus, NiO(100) monolayer is $(NiO_{100}^1$, the bi-layer NiO/MgO $(NiO/MgO)_{100}^2$ and the three tri-layers we consider here $(NiO/MgO/MgO)_{100}^3$, $(NiO/MgO/NiO)_{100}^3$ and $(MgO/NiO/MgO)_{100}^3$. Furthermore, all our calculations are based on a constant cation–anion distance of 2.1 Å fixed by the MgO substrate, while our axis system equates the xy-plane with (100), so the p_z and d_{z^2} orbitals are perpendicular to the slab planes.

As in a previous study,²⁷ to investigate the magnetic properties of these slabs we have considered four spin arrangements of a 2] 2 surface unit cell shown below,

$$\mathbf{F} : \ \mathsf{C} \ \underset{\mathsf{C}}{\overset{\mathsf{C}}{\mathsf{O}}} \ \mathsf{C} \quad \mathbf{A_1} : \ \mathsf{C} \ \underset{\mathsf{B}}{\overset{\mathsf{C}}{\mathsf{O}}} \ \mathsf{B} \quad \mathbf{A_2} : \ \mathsf{C} \ \underset{\mathsf{B}}{\overset{\mathsf{B}}{\mathsf{O}}} \ \mathsf{C} \quad \mathbf{A_3} : \ \mathsf{C} \ \underset{\mathsf{B}}{\overset{\mathsf{C}}{\mathsf{O}}} \ \mathsf{C}$$

where C and B represent high spin Ni²⁺ ions and F, A₁, A₂ and A₃ the ferromagnetic, antiferromagnetic, fully-frustrated and ferrimagnetic spin alignments, respectively.²⁷ In the case of (NiO/MgO/NiO)³₁₀₀ we consider slabs in which two ferromagnetic NiO layers are aligned both ferromagnetically and antiferromagnetically. In this way we have been able to distinguish superexchange coupling within and between NiO planes as a first step towards understanding the recent results reported by Alders *et al.*⁹ As described in detail below, we have obtained converged UHF solutions for a number of excited states involving both single and quadruple, *i.e.*, complete, local d \rightarrow d excitations, which we designate as e₁ and e₄, respectively.²⁷ Thus, by an 'e₄ d_{xy} \rightarrow d_{z2} excited state' we mean a state in which all four Ni ions of the unit cell have undergone a d_{xy} \rightarrow d_{z2}

Our treatment of hole states follows that previously used for NiO bulk²⁴ and (100) monolaver,²⁷ wherein a renormalisation of the (infinite) inter-cell Coulombic interaction is effected by adding a uniform background charge of opposite sign and equal magnitude to the crystal potential in the plane of the monolayer. As our results indicate, this has no effect on the densities of states, other than a rigid shift in energy of the single particle spectrum. Furthermore, we confine our attention to differences in total energy only, as between various electronic and spin states of the hole and small lattice distortions, which, again, are invariant to the uniform background charge.

2b. Lattice simulations

The methods we have used to carry out lattice simulations at finite temperatures based on lattice statics and quasi-harmonic lattice dynamics have been described in full recently.^{31,42} For a slab of sufficient thickness to provide what, in effect, is a bulk-like region in the interior and two noninteracting, free surfaces, the Helmholtz free energy of the system, F, at a temperature, T, is minimised with respect to the collection of structural parameters, $\{E_A\}$, that define the slab. In the quasi-harmonic approximation it is assumed that $F(\{E_A\}, T)$ can be written as the sum of static and vibrational contributions,

$$F(\{\mathbb{E}_{A}\}, T) = \mathsf{U}_{\mathsf{stat}}(\{\mathbb{E}_{A}\}) + F_{\mathsf{vib}}(\{\mathbb{E}_{A}\}, T)$$

 $U_{\text{stat}}(\{E_A\})$ is the potential energy of the static lattice in a given state of strain $\{E_A\}$ and is evaluated from interatomic pair potentials, while $F_{\rm vib}$ is the sum of harmonic vibrational contributions from all the normal modes. For a periodic structure, the frequencies $v_i(q)$ of modes with wavevector q are obtained by diagonalisation of the dynamical matrix D(q). F_{vib} is given by,

$$F_{\rm vib} = \sum_{q,j} \left\{ \frac{1}{2} h v_j(q) + k_{\rm B} T \ln[1 - \exp(-h v_j(q)/k_{\rm B} T)] \right\}$$

in which the first term is the zero-point energy and the associated vibrational entropy, S,

$$S = \sum_{\boldsymbol{q},j} \frac{(hv_j(\boldsymbol{q})/T)}{\exp(hv_j(\boldsymbol{q})/k_{\rm B}T) - 1} - k_{\rm B} \ln[1 - \exp(-hv_j(\boldsymbol{q})/k_{\rm B}T)]$$

For a macroscopic crystal the sum over q becomes an integral over a cell in reciprocal space, which can be evaluated by taking successively finer uniform grids until convergence is achieved. Since the reciprocal space is two-dimensional the Brillouin zone summation requires a two dimensional mesh of wavevectors.

The minimisation of F, and subsequent thermodynamic manipulation, can, of course, be carried out by brute force from numerical values of F. However, for the slabs of any complexity, such as those considered here, there are large numbers of internal strains, E_A , and it is much more efficient to use analytic expressions for the derivatives of F with respect to strain. The strain derivatives are given by,

$$\left(\frac{\partial F_{\text{vib}}}{\partial \mathbb{E}_{\mathbf{A}}}\right)_{\mathbf{E}', T} = \sum_{\boldsymbol{q}, j} \left\{\frac{h}{2\nu_{j}(\boldsymbol{q})} \left(\frac{1}{2} + \frac{1}{\exp(h\nu_{j}(\boldsymbol{q})/k_{\mathrm{B}}T) - 1}\right) \left(\frac{\partial\nu_{j}^{2}(\boldsymbol{q})}{\partial \mathbb{E}_{\mathbf{A}}}\right)_{\mathbf{E}'}\right\}$$

where the subscript E' denotes that all the E are kept constant except for the differentiation variable. In a recently developed code⁴⁰ the derivatives, $(\partial v_j^2(q)/\partial \mathbb{E}_A)_{\mathbb{F}'}$, are obtained from analytic expressions for the derivatives, $(\partial D(q)/\partial \mathbb{E}_A)_{\mathbb{R}'}$, by first-order perturbation theory.^{42,43} Full details of the particular derivatives of the Parry summation needed for the Coulombic interactions in ionic slabs are given by Taylor et al.;³² the derivatives required for pairwise short-range potentials are collected together in ref. 42. Since the perturbation is infinitesimal, the procedure is exact. In addition, for thermodynamic properties no special consideration needs to be given to degeneracies in first-order perturbation theory, for the trace of $(\partial D(q)/\partial \mathbb{E}_A)_{r'}$ is invariant for any complete normal set of eigenvectors of D. To obtain the equilibrium structure a variable metric method is used for the minimisation of F with respect to the E_A . In the initial configuration the *static* energy Hessian, $(\partial^2 U_{\text{stat}}/\partial E_A \partial E_B)$, which is a good approximation to $(\partial^2 F/\partial E_A \partial E_B)$, is calculated from its analytic expression, and its inverse together with the $(\partial F/\partial E_A)$ are used to obtain an improved

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configuration. In subsequent iterations the $(\partial F/\partial E_A)$ are calculated in the new configuration and the inverse Hessian updated by the BFGS formula.⁴⁴ An optimisation therefore requires one static Hessian calculation, and a small number of dynamic gradient calculations. In practice it has been found that this is much more efficient than methods involving repeated evaluation of the Hessian, or frequent line minimisations, or methods in which the derivatives are determined numerically.

3. Results

3a. Electronic ground states

We begin with a brief resumé of NiO bulk²⁰ and (100) monolayer,²⁷ which, despite their different dimensionality and consequent nearest-neighbour coordination, and different ligand-field splitting, exhibit several common features. Both are predicted to be highly ionic, high spin insulators with lattice constants of ≈ 4.3 Å and ≈ 4.0 Å, respectively. Moreover, for both systems the d⁸ ground state configuration is

$$[(d_{xz})^2 (d_{yz})^2 (d_{xy})^2 (d_{z^2})^1 (d_{x^2-y^2})^1]$$

with

$$\varepsilon(e_g)_{\alpha} < \varepsilon(t_{2g})_{\alpha} < \varepsilon(t_{2g})_{\beta} < \varepsilon(e_g)_{\beta}$$

for the bulk and

$$\varepsilon(\mathbf{d}_{z^2})_{\alpha}/\varepsilon(\mathbf{d}_{x^2-y^2})_{\alpha} < \varepsilon(\mathbf{d}_{xz})_{\alpha}/\varepsilon(\mathbf{d}_{yz})_{\alpha} \varepsilon(\mathbf{d}_{xy})_{\alpha} < \varepsilon(\mathbf{d}_{xz})_{\beta}/\varepsilon(\mathbf{d}_{yz})_{\beta} \varepsilon(\mathbf{d}_{xy})_{\beta}$$

for (NiO)¹₁₀₀ where ε are the single particle eigen values and the subscripts α and β refer to spin up (C) and spin down (B) electrons, respectively. The local Ni spin magnetic moment is calculated to be $\approx 1.9 \ \mu_{\rm B}$ for both systems and the stability of low index spin alignments,

$$AF_2 > F > AF_1$$
 (bulk)

and

$$A_1 > A_3 > F > A_2$$
 ((NiO)¹₁₀₀)

below the Néel temperature. If, to a first approximation, it is assumed that the differences in energy between the spin alignments for each system separately can be written simply in terms of direct spin-spin (E_d) and indirect superexchange (E_{se}) interactions, UHF total energies lead to values for E_d and E_{se} of -1.6 meV and -8.2 meV, respectively, for NiO bulk at a lattice constant of 4.2 Å, and -1.0 meV and -6.9 meV for $(NiO)_{100}^1$ at the same lattice constant. Another major difference between the two systems is that from an analysis of the unoccupied O(p) density of states (DOS) of the self-trapped hole, the band gap is estimated to be $\approx 4 \text{ eV}$ for the bulk^{24,25} and $\approx 5 \text{ eV}$ for $(NiO)_{100}^{1}$.²⁷

Turning now to the various NiO/MgO(100) slabs, we have obtained converged UHF solutions of the ground electronic states of the *F*, A₁, A₂ and A₃ spin alignments. As before,^{20,27} Mulliken analyses⁴⁵ yield effective atomic charges of $\approx 1.9 \ e$, 3d populations of ≈ 8.1 and local spin moments of $\approx 1.9 \ \mu_B$, all of which indicate that the highly ionic, high spin character previously found for the bulk²⁰ and (NiO)¹₁₀₀²⁷ is retained in multi-layered NiO/MgO systems. Furthermore, the d⁸ ground state configuration, $[(d_{xz})^2(d_{yz})^2(d_{xy})^2(d_{zz})^{1}]$, of (NiO)¹₁₀₀ is found to remain unchanged in all four spin alignments, the stabilities of which are in the order,

$$A_1 > A_3 > F > A_2$$

as shown in Table 1. As before,²⁷ the relative energies of A_1 , A_2 , A_3 and F can be written to a first approximation in terms of direct and superexchange interactions as,

$$E(F) = B + 2E_{d}$$
$$E(A_{1}) = B + E_{d} + 2E_{se}$$
$$E(A_{2}) = B$$
$$E(A_{3}) = B + E_{d} + E_{se}$$

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Table 1 Comparison of the energies (meV/Ni) of the F, A₂ and A₃ spin alignments (F and AF₁ in the case of the bulk) relative to A₁ (AF₂) for NiO bulk and various (100) NiO/MgO slabs all at $a_0 = 4.2$ Å

System	A ₃	F	$A_2(AF_1)$
$\begin{array}{c} Bulk \\ (NiO)^{1}_{100} \\ (NiO/MgO)^{2}_{100} \\ (NiO/MgO/MgO)^{3}_{100} \\ (NiO/MgO/NiO)^{3}_{100} \\ (MgO/NiO/MgO)^{3}_{100} \end{array}$	6.9 7.4 7.4 7.4 8.5	19.7 12.8 13.6 13.5 13.6 15.4	26.2 14.8 16.0 15.9 16.1 18.6

from which E_d and E_{se} can be obtained. These are given in Table 2, where E_d and E_{se} , corresponding to direct and superexchange interactions within a single NiO(100) layer, are seen to increase monotonically with Ni coordination to broadly that of the bulk in (MgO/NiO/MgO)³₁₀₀. In addition, our results for (NiO/MgO/NiO)³₁₀₀, in which the two ferromagnetic NiO layers are coupled antiferromagnetically, suggest stronger superexchange between NiO(100) layers than within the layers, at least for the simple tri-layer we have examined.

The densities of occupied states of the A_1 alignment of $(NiO/MgO)_{100}^2$ over the first 12 eV, shown in Figs. 1a and 1c, indicate further close similarities with 2D and 3D NiO. The upper valence band, ≈ 5 eV wide, is essentially O(p) with only a minor contribution from d_{xy} states at lower energies and negligible Ni weight at the upper edge. The local O(p) DOS of the two planes, shown in Fig. 1b, are similar, both in terms of band width and overall profile. The major difference is the weight of states at the upper edge, shown in Fig. 1b, which derives predominantly from the NiO layer. This suggests, though by no means guarantees, that the low energy holes states will be associated with the NiO lattice. The Ni d states occur ≈ 1 eV below the O(p) band and are dispersed over ≈ 4.5 eV in three distinct sub-bands, with

$$\varepsilon(d_{z^2})_{\alpha}/\varepsilon(d_{x^2-v^2})_{\alpha} < \varepsilon(d_{xz})_{\alpha}/\varepsilon(d_{vz})_{\alpha}\varepsilon(d_{xv})_{\alpha} < \varepsilon(d_{xz})_{\beta}/\varepsilon(d_{vz})_{\beta}\varepsilon(d_{xv})_{\beta}$$

as in the bulk. This is in marked contrast to the crystal-field splitting,

$$\tilde{\epsilon}(\mathbf{d}_{xz})/\tilde{\epsilon}(\mathbf{d}_{yz}) < \tilde{\epsilon}(\mathbf{d}_{z^2}) < \tilde{\epsilon}(\mathbf{d}_{xy}) < \tilde{\epsilon}(\mathbf{d}_{x^2-y^2})$$

which suggests that, as in the bulk, the single particle spectrum is determined to a large extent by the on-site Coulomb and exchange terms.

3b. $d \rightarrow d$ excited states

The lowest energy electronic excitations from the ground state in NiO correspond to orbitally forbidden ($\Delta l = 0$) local d \rightarrow d transitions, or Frenkel excitons, which have been observed in both

Table 2 Comparison of E_d and E_{se} (meV) for NiO bulk and various (100) NiO/MgO slabs all at $a_0 = 4.2$ Å

System	$-E_{d}$	$-E_{\rm se}$
Bulk	1.6	8.2
$(NiO)^{1}_{100}$	1.0	6.9
$(NiO/MgO)^2_{100}$	1.2	7.4
$(NiO/MgO/MgO)_{100}^3$	1.2	7.4
$(NiO/MgO/NiO)^{3}_{100}$ a	1.3	7.4
$(NiO/MgO/NiO)^{3}_{100}$	_	10.5^{b}
$(MgO/NiO/MgO)^3_{100}$	1.6	8.5
		NCO 1

^{*a*} No superexchange coupling between NiO layers. ^{*b*} Superexchange interaction between two ferromagnetic NiO layers antiferromagnetically aligned.

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Fig. 1 a, Valence band DOS of $A_1(NiO/MgO)^2_{100}$. b, Comparison of $O(p)_{MgO}$ and $O(p)_{NiO}$ valence band DOS of $A_1(NiO/MgO)^2_{100}$. c, Comparison of the valence band DOS of AF_{II} bulk NiO, $A_1(NiO/MgO)^2_{100}$, and $A_1(NiO)^1_{100}$.

the optical^{46,47} and EEL^{29,48–51} spectra of the pure material and in EEL spectra of NiO/MgO(100) layered systems.^{6,10} We have obtained variationally minimised solutions corresponding to the complete range of one-electron (e₁) excitations of the type, $d_{xy} \rightarrow d_{z^2}$, $d_{xy} \rightarrow d_{x^2-y^2}$, etc., to the spin-forbidden $d_{x^2-y^2} \rightarrow d_{z^2}$ and $d_{z^2} \rightarrow d_{x^2-y^2}$ states and the two electron $d_{xy}/d_{yz} \rightarrow d_{z^2}/d_{x^2-y^2}$

excited state for $F(NiO/MgO)_{100}^2$. These states remain highly ionic, high spin, insulating with changes in the ionic charges, 3d populations and local spin moments of $\leq 1\%$. The corresponding excitation energies derived from direct total energy differences with respect to the ground state are listed in Table 3, where we include UHF values and those derived from post-Hartree–Fock corrected energies. We have also obtained converged e_4 solutions for a number of these excited states for the F alignment. As found previously for $(NiO)_{100}^{1}$,²⁷ the differences between e_1 and e_4 energies are substantially less than 0.1 eV, so that we have not attempted to obtain excitation energies extrapolated to zero concentration. We have calculated excitation energies of the spin-allowed transitions for the A_1 alignment of $(NiO/MgO)_{100}^2$ to confirm that they are essentially independent of the magnetic state of the lattice, and excitation energies for $F(MgO/NiO/MgO)_{100}^3$ to examine the effect of nearest neighbour coordination. These, together with results for $F(NiO)_{100}^1$ are collected in Table 4, from which the excitation energies for $(NiO)_{100}^1$ (b), $(NiO/MgO)_{100}^2$ (c) and $(MgO/NiO/MgO)_{100}^3$ (e) are plotted as a function of Ni coordination in Fig. 2.

3c. First ionised state

The removal of an electron from fully symmetric NiO/MgO multilayers in whatever spin alignment leads to conducting states of essentially $d^{8}L$ character, exactly as suggested by the ground state DOS, where the unpaired electron/hole is delocalised over the O sites, no matter what starting electronic configuration is chosen. As reported previously for NiO bulk^{24,25} and (100) monolayer,²⁷ the removal of this symmetry constraint allows the electronic configuration to relax to non-degenerate *insulating* states of *lower* energy in which the unpaired electron/hole is localised in a p_{π} orbital at a *single* O site. We have obtained converged solutions for states in which the hole is localised (separately) in both layers of (NiO/MgO)²₁₀₀, and in different spin configurations. The relative energies of the states are collected in Table 5, in which the nomenclature, XO : S⁺ and XO : S⁺(x), correspond to localised holes in the XO layer of (NiO/MgO)²₁₀₀ where S is the spin configuration of the NiO layer and x the alignment (f-ferromagnetic, a-antiferromagnetic) of the unpaired p_{π} electron relative to S. As suggested by the valence band DOS of the ground state (Fig.

Table 3 Comparison of UHF, PBE, PW and P91 $d \to d$ excitation energies (eV) in $F(NiO/MgO)^2_{100}$

Excitation	UHF	PBE	PW	P91
$\begin{aligned} xy \rightarrow z^2 \\ xz \rightarrow z^2 \\ xy \rightarrow x^2 - y^2 \\ xz \rightarrow x^2 - y^2 \\ x^2 - y^2 \rightarrow z^2 a \\ z^2 \rightarrow x^2 - y^2 a \\ xz/yz \rightarrow z^2/x^2 - y^2 \end{aligned}$	1.98 0.83 0.83 1.16 2.97 4.24 1.87	1.94 0.82 0.83 1.17 2.94 4.14 1.85	1.95 0.82 0.83 1.17 2.93 4.13 1.85	1.95 0.83 0.83 1.17 2.88 4.08 1.85
" Spin forbidden				

Table 4 Comparison of $d \rightarrow d$ excitation energies (eV) in (a) $F(NiO)_{100}^1 (a_0 = 4.0 \text{ Å})$, (b) $F(NiO)_{100}^1 (a_0 = 4.2 \text{ Å})$, (c) $F(NiO/MgO)_{100}^2$, (d) $A_1(NiO/MgO)_{100}^2$, and (e) $F(MgO/NiO/MgO)_{100}^3$

Excitation	(a)	(b)	(c)	(d)	(e)
$xy \rightarrow z^2$	1.18	1.27	1.98	1.99	2.66
$xz \rightarrow z^2$	_	0.31	0.83	0.84	_
$xy \rightarrow x^2 - y^2$	1.11	0.85	0.83	0.86	0.81
$xz \rightarrow x^2 - y^2$	_		1.16	1.20	_
$x^2 - y^2 \rightarrow z^2 a$	1.86	2.24	2.97	_	3.68
$z^2 \rightarrow x^2 - y^2 a$	_	5.00	4.24	_	3.54
$xz/yz \rightarrow z^2/x^2 - y^2$	1.81	1.57	1.87	1.90	2.14
^{<i>a</i>} Spin forbidden.					



Fig. 2 Comparison of calculated $d \rightarrow d$ excitation energies in $F(NiO)_{100}^1$, $(NiO/MgO)_{100}^2$ and $(MgO/NiO/MgO)_{100}^3$ as a function of Ni coordination.

1b), the lower energy states correspond to the hole localised in the NiO layer. Mulliken population analyses indicate that in all these states $\approx 90\%$ of the hole density is localised at a single O site with a moment of $\approx 0.9 \,\mu_B$ but with no significant change in local moments at the cation sites. Localisation of a hole at a single O site leads to the creation of a narrow band of unoccupied O(p) states at the top of the valence band, with only minimum changes at the conduction band edge, as shown in Fig. 3 for A_1^+ (NiO/MgO)²₁₀₀, and reported previously for NiO bulk^{24,25} and (100) monolayer.²⁷ This is the exactly equivalent to the changes in the oxgygen k-edge spectra obtained originally by Kuiper *et al.*¹⁷ for Li_xNi_{1-x}O, where the energy between the extrinsically controlled unoccupied O(p) states and the conduction band edge approximates the band gap in NiO. We have estimated the band gap, E_g , corresponding to the various holes states given in Table 5 and for the NiO : F⁺(f) state in (NiO/MgO/MgO)³₁₀₀ and (MgO/NiO/MgO)³₁₀₀. The later are given in Table 6 together with that for (NiO)¹₁₀₀, from which the variation of E_g in NiO as a function of Ni coordination can be obtained. This is shown in Fig. 4 where the increase in E_g is seen to be close to linear.

3d. Charge transfer states

In a recent study of NiO(100) monolayer²⁷ we have calculated the energy of the $p_z \rightarrow d_{z^2}$ charge transfer excitonic states as an independent check on estimates of the band gap, E_g , from the unoccupied DOS of the first ionised states. Here we report similar calculations for (NiO/MgO)²₁₀₀. As before,²⁷ we have confined our attention to the computationally more convenient F alignment and obtained variationally minimised solutions for the $e_4 p_z \rightarrow d_{z^2}$ charge transfer state, (Ni⁺O⁻),

Table 5 Relative energies, ΔE (eV), and associated gaps E_g (eV) of the first ionised states of (NiO/MgO)²₁₀₀ and V_{Ni} in F(NiO/MgO)²₁₀₀

State	ΔE	E_{g}
	0.0 0.028 0.161 0.642 0.268	5.7 5.9 6.0 6.0 6.0 3.6

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Fig. 3 Empty gap states of A_1^+ (NiO/MgO)²₁₀₀.

in both triplet and singlet spin states, that is to say, configurations of the type,

 $Ni(d^9)_{\alpha}O(p^5)_{\alpha}$ and $Ni(d^9)_{\alpha}O(p^5)_{\beta}$

These can be viewed as fully-condensed, Mott–Wannier (M–W) exciton states, so that in $Ni(d^9)_{\alpha}O(p^5)_{\alpha}$ the excited electron is β -spin (which it must be) and the hole β -spin giving a triplet

System	E_{g}
$(NiO)_{100}^{1}$	5.1
$(NiO/MgO)_{100}^2$	5.7
$(NiO/MgO/MgO)_{100}^3$	5.7
$(MgO/NiO/MgO)_{100}^{3}$	6.6



Fig. 4 $E_{\rm g}$ in (NiO)¹₁₀₀, (NiO/MgO)²₁₀₀ and (MgO/NiO/MgO)³₁₀₀ as a function of Ni coordination.

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Table 7 Energies (eV/Ni) of the e_4 charge–transfer states of $F(NiO/MgO)^2_{100}$

State	Energy
Triplet $p_{\pi} \rightarrow d_{z^2}$	5.175
Singlet $p_{\pi} \rightarrow d_{z^2}$	5.412
Triplet $p_{\pi} \rightarrow d_{x^2-y^2}$	5.874

exciton. The corresponding formation energies are obtained from *direct energy differences* between the ground and charge transfer states and are *lower bounds* to the optical band gap, thereby providing an alternative estimate of E_g to that from the single-particle eigen values. They are given



Table 8 Electron re-distributions (*e*/atom or *e*/MgO) associated with $V_{Ni}^{(2-)}$ and $V_{Ni}^{(0)}$ and their differences, δq , in (NiO/MgO)²₁₀₀

Vacancy	Mg	O_{MgO}	MgO	Ni	O _{NiO}
$\begin{array}{c} V_{\mathrm{Ni}}^{\ (2-)} \\ V_{\mathrm{Ni}}^{(0)} \\ \delta q \end{array}$	+0.023 +0.020 -0.003	$+0.044 \\ -0.018 \\ -0.063$	+0.067 +0.002 -0.066	-0.019 + 0.031 + 0.050	-0.048 -0.911; -0.075 -0.863; -0.027

3f. Cation vacancy states

The principal oxidative disorder in (bulk) NiO consists of Ni vacancies, V_{Ni} , in different charge states, and (free) holes,⁵⁴ with the reasonable likelihood that similar disorder will prevail in NiO/MgO ultra-thin films, principally at high temperature. We have considered two charged states of the Ni vacancy in a $(NiO/MgO)_{100}^2$ bilayer. They are doubly charged, $V_{Ni}^{(2+)}$, which corresponds to the removal of an Ni²⁺ ion, and neutral, $V_{Ni}^{(0)}$, which corresponds to the removal of an Ni^{2+} ion plus two electrons. As above, our computational resources have limited us to a concentration of 25% vacancies in the NiO layer. Furthermore, we have not considered any lattice relaxation associated with either defect state. Mulliken analysis of the $V_{Ni}^{(2+)}$ state, which is insulating, indicates that the electron distribution in both layers remains largely unchanged from a non-defective $(NiO/MgO)_{100}^2$ bilayer, with a transfer of $\approx 0.07 \ e$ from NiO to MgO, as shown in Table 8. The removal of two electrons from this state results in the formation of the neutral, $V_{Ni}^{(0)}$ state, which is also insulating, with the unpaired electrons/holes localised in p₋ orbitals at two next-nearest-neighbour O sites adjacent to the vacancy. Once again, Mulliken analyses collected in Table 8 indicate that there is very little re-distribution of electron density between the two layers, and that $\approx 91\%$ of the hole density is localised in the NiO layer with local moments close to 1 μ_B at the two O sites. In both vacancy states there is complete retention of the local Ni moments.

As Figs. 6 and 7 show, despite the minimal re-distribution of electron density within and between the two layers, there are substantial changes in the valence band DOS of both vacancy states. In the doubly charged state the Ni sub-bands retain largely the same profile as in the non-defective state, but are shifted to lower energy relative to the top of the valence band by \approx





Fig. 7 Comparison of the valence band DOS of $F(NiO/MgO)_{100}^2$ and V_{Ni} in $F(NiO/MgO)_{100}^2$.

upper edge. In the neutral state the re-distribution of states is even more dramatic with the three Ni sub-bands now further split as a result of the reduced symmetry of the neutral vacancy and shifted to lower energy, again by $\approx 1 \text{ eV}$. The profile of the O^{2-} p DOS is changed to a more even distribution of states across the main part of the band width which remains close to 6 eV in width, with the p states associated with the two O^{-} oxygens, indicated as 'hole' in Fig. 7, shifted to lower energy. As in the case of the free hole, the bound holes of the neutral vacancy give rise to a narrow band of unoccupied states below the conduction band edge. However, as shown in Fig. 8, these states are shifted to higher energy by $\approx 2 \text{ eV}$ compared with the free-hole state, leading to a gap of $\approx 3.6 \text{ eV}$ between the hole and conduction bands.

3g. {100} Surface free energies

Fig. 9 shows the dynamically relaxed $\{100\}$ surface free energy of MgO at 700 K as a function of slab thickness, which indicates that approximately ten layers are required for convergence to 0.001



Fig. 8 Comparison of the empty gap states of $F^+(f)(NiO/MgO)_{100}^2$ and V_{Ni} in $F(NiO/MgO)_{100}^2$.

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Fig. 9 Variation of the MgO {100} surface free energy at 700 K with slab thickness.

J m⁻². This is more than twice the number of layers (4) required to converge the static energy. All the calculations reported here are for slabs comprising twelve layers and 1728 q-vectors used in the Brillouin zone summation.⁵⁵ The {100} surface free energy decreases slightly with temperature, by 0.05 J m⁻² over the temperature range 0–2600 K. Above this temperature, the quasiharmonic approximation breaks down, with the appearance of imaginary frequencies: for the bulk, on the otherhand, imaginary frequencies appear at ≈ 2900 K. Thus the quasiharmonic approximation fails at somewhat lower temperatures for the {100} surface than for the bulk due to the presence of modes with large vibrational amplitudes, which raises the possibility that surface melting occurs at temperatures below that for the bulk.

For NiO our results can be compared directly with those obtained by Mulheran⁵⁶ using an Einstein approximation. Fig. 10 shows the calculated temperature dependence of the unrelaxed and fully dynamically relaxed {100} surface energies. Here it is interesting to note that our value of the surface energy in the static limit, 1.18 Jm^{-2} , compares favourably with that of 1.23 Jm^{-2} from *ab initio* Hartree–Fock calculations.⁵⁷ As shown in Fig. 10, both the relaxed and unrelaxed {100} surface energies decrease by $\approx 0.1 \text{ Jm}^{-2}$ over the temperature range 0–2000 K. The change in the dynamically relaxed surface energy with temperature over this range is only one-third of



Fig. 10 Calculated temperature variation of the dynamically relaxed and unrelaxed free energy of the $\{100\}$ surface of NiO.

that reported by Mulheran⁵⁶ for the same surface, which indicates of the limitations of the Einstein approximation. There are no experimental data for direct comparison, although the temperature variation appears to be consistent with that noted by Benson and Yun⁵⁸ for rocksalt {100} surfaces. The calculated relaxations are also in good agreement with *ab initio* Hartree–Fock calculations.⁵⁷ These found a contraction of the first inter-layer spacing of 0.53%, which provides additional support for our use of two-body potentials in free energy simulations. We note, also, that the reported theoretical relaxations are well within the upper bound of $\approx 2\%$ suggested by LEED measurements.⁵⁹

3h. Surface vibrational densities of states

Bulk and surface vibrational densities of states (VDOS) at 300 K for the {100} surface of NiO are shown in Fig. 11, together with the excess VDOS (surface minus bulk) which is responsible for the dynamic contribution to the surface free energies. The form of the bulk VDOS is in good agreement with that reported by Coy *et al.*⁶⁰ Once again, there does not appear to be any experimental data for direct comparison. The form of the excess VDOS, with a decrease in intensity at ≈ 6 THz, differs significantly from that presented previously for the {100} surface of MgO, due essentially to the different atomic masses of Ni and Mg.

3i. Free energies of Ni2' segregation

We have calculated heats of segregation, Δh , of Ni²⁺ to the surface of an MgO slab, assuming the formation of ordered, fully relaxed structures. At a given temperature, Δh is obtained from the free energies of fully relaxed twelve-layer slabs with two or four cation surface sites, which may be occupied by Mg or Ni ions, and the free energy of a bulk supercell containing one Ni²⁺ ion, which is an excellent approximation to an isolated impurity ion in the bulk. The top and bottom halves of slabs are the same in any calculation. The heat of segregation is therefore not determined as a continuous function of coverage, but at specific coverages, here 25%, 50%, 75% and 100%. The calculated heats of segregation at a range of temperatures are shown in Fig. 12, where for convenience individual points are connected by straight lines. The negative values of the segregation energy denote the segregation of Ni²⁺ ions from bulk to surface sites. The magnitudes of Δh , ≈ 0.15 eV, reflect the small difference in size between Ni²⁺ and Mg²⁺ ions, and at each temperature the variation of segregation energy with coverage, $\approx 4\%$, is considerably less than that noted previously for larger cations such as Ca²⁺ at the {001} surface of MgO in the static limit.⁶¹ The variation of the segregation energy with temperature over the range studied is somewhat



Fig. 11 Calculated bulk, surface and excess (surface minus bulk) vibrational densities of states at 300 K for the $\{100\}$ surface of NiO.



Fig. 12 Calculated heat of segregation, Δh , of Ni²⁺ at the {001} surface of MgO at a range of coverages and temperatures.

greater than the variation with coverage, decreasing, as it does, by $\approx 10\%$ from 100 K to 1900 K. Segregation energies to layers other than the surface layer are found to be negligible. As in the case of the surface energy and lattice relaxation, comparisons with Hartree–Fock calculations are instructive. Differences in energy between the unrelaxed structures (NiO/MgO/MgO)_{100}^3 and (MgO/NiO/MgO)_{100}^3 range from -0.113 eV, for the A₂ alignment, to -0.103 eV for A₁, which compare with a value of ≈ -0.15 eV deduced for the segregation energy from atomistic simulations.

3j. Vibrational densities of states of defective surfaces

It is straightforward within a lattice dynamics approach to evaluate the vibrational densities of states of defective surfaces at finite temperatures, again, based on fully relaxed structures at the



Fig. 13 Vibrational densities of states at 700 K for the $\{100\}$ surface of NiO with 50% Mg²⁺ coverage. The densities of states of the undefective $\{100\}$ surface and the excess DOS (defective–undefective) are also plotted.



Fig. 14 Vibrational densities of states at 700 K for the $\{100\}$ surface of NiO with 50% Ni vacancies compensated by oxygen holes. The densities of states of the undefective $\{100\}$ surface and the excess DOS (defective–undefective) are also plotted.

temperature of interest. Fig. 13 presents two examples, both at 700 K: the first, (Fig. 5) corresponds to a 50% surface coverage of NiO by MgO, the second, (Fig. 6) to a 50% surface coverage by neutral Ni vacancies, $V_{Ni}^{(0)}$, *i.e.*, half the Ni surface sites vacant, with each vacancy charge compensated by two oxygen holes in the surface layer. The difference between the densities of states of non-defective and defective slabs in Fig. 13 indicates the depletion of most low frequency modes (<10 THz) on the introduction of the lighter Mg ions with marked decreases in intensity at \approx 9 THz and \approx 11 THz. These are accompanied by a pronounced shift of density to higher frequencies. Fig. 14, which admittedly relates to a somewhat unrealistic surface vacancy concentration, shows a pronounced decrease in intensity for modes around 12 THz with increases at <5 THz, \approx 10 THz and \approx 17 THz.

4. Discussion

4a. Ground state properties

As expected, the ground states of the NiO/MgO multi-layers we have considered here are all ionic, high spin and insulating, with electronic configurations, Mulliken populations and valence band DOS that are very close to those of the bulk²⁰ and {100} monolayer.²⁷ While there is some evidence from XPS^{5,13} of charge transfer from MgO to NiO for sufficiently thick NiO layers, our results are inconclusive in this respect, as shown in Table 9, due mainly to the limited sizes of slab we have examined. The order of the spin alignments is also identical to that reported for the monolayer. However, there are differences in the direct and superexchange coupling energies within an NiO layer, both of which increase with Ni coordination, as shown in Table 2, leading to values for $(MgO/NiO/MgO)_{100}^3$ that are similar to that for the bulk. We note, in particular, our decrease of $\approx 13\%$ in superexchange coupling from $(MgO/NiO/MgO)_{100}^3$ to $(NiO/MgO)_{100}^3$ and $(NiO/MgO/MgO)_{100}^3$, which compares with a decrease of $\approx 20\%$ reported by de Graaf et al.²⁸ based on cluster calculations. The difference in superexchange coupling within (-8.5 meV) and between (-10.5 meV) NiO layers is particularly interesting in relation to the recent report by Alders et al.⁵ that somewhere in excess of 20 ML of NiO on $\{100\}$ MgO are required before the bulk value of the Néel temperature is recovered. As the number of layers increases there is a competition between the A_1 spin alignment of the {100} layered structure and the AF_{II} alignment of the bulk, which the present results suggest might be tilted in favour of the bulk by the interlayer superexchange, since E_{se} for $(MgO/NiO/MgO)_{100}^3$ is calculated to be $\approx 4\%$ greater than that for

the bulk. An important point worth noting here is that our interest here is primarily in the *changes* in the direct and superexchange coupling energies as the local Ni coordination changes and not their absolute values, the reliability of which is the subject of continuing investigation.^{62,63}

4b. $d \rightarrow d$ excitations

Turning now to $d \rightarrow d$ excitation energies, Table 3 shows that corrections derived from correlation only functionals³⁹⁻⁴¹ based on Hartree–Fock densities are negligible. We emphasise that this does not indicate that electron correlation is unimportant or that the use of more sophisticated treatments of electron correlation within the framework of periodic calculations will come to similar conclusions. A comparison of columns (c) and (d) of Table 4, indicates that the spin alignment also appears to have a negligible effect on $d \rightarrow d$ excitation energies, which is reasonable, since the differences in energy between the various spin alignments are at least two orders of magnitude less than those between different electron configurations. What Table 4 and Fig. 2 do show quite clearly, however, is that the local Ni coordination can be an important factor, depending on the initial and final states of the excitation. Thus the energy of the $d_{xy} \rightarrow d_{x^2-y^2}$ excitation is more or less independent of the local Ni coordination, while that of the two-electron excitation $d_{xz}/d_{yz} \rightarrow d_{z^2}/d_{x^2-y^2}$ increases by $\approx 36\%$ from (NiO)¹₁₀₀ to (MgO/NiO/MgO)³₁₀₀. On the otherhand, the energies of the $d_{xy} \rightarrow d_{z^2}$ and spin-forbidden $d_{x^2-y^2} \rightarrow d_{z^2}$ excitations increase by $\approx 109\%$ and $\approx 64\%$, respectively, while that of the spin-forbidden $d_{z^2} \rightarrow d_{x^2-y^2}$ decreases by $\approx 29\%$. This pattern is readly explained in terms of steric hindrance effects. Since a $d_{xy} \rightarrow d_{x^2-y^2}$ excitation involves a transition entirely within a $\{100\}$ layer, it might reasonably be expected that the presence of planes above and below would influence the energy only to a very minor extent, and this is what UHF calculations predict. On the other hand, the $d_{xy} \rightarrow d_{z^2}$ and $d_{x^2-y^2} \rightarrow d_{z^2}$ excitations, which increase by 1.39 eV and 1.44 eV, respectively, from 4 to 6 coordination, involve 'out-ofplane' transitions, which might reasonably be expected to be restricted by planes above and below leading to increases in energy, and, again, this is what we find.

While individual points of detail await further clarification, there is general agreement^{29,30,51} as to the assignment of the reported optical absorption and EEL spectra below $\approx 3 \text{ eV}$ to specific bulk and {100} surface $d \rightarrow d$ excitations. These can be compared with our values for $(\text{NiO/MgO})_{100}^2$ and $(\text{MgO/NiO/MgO})_{100}^2$, which we take to be representative of the 5-fold coordination of the {100} surface and 6-fold coordination of the bulk. With reference to Table 10, absorptions at $\approx 1.0 \text{ eV}$, $\approx 1.9 \text{ eV}$ and $\approx 2.8 \text{ eV}$ have been assigned to spin-allowed ${}^{3}\text{A}_{2g} \rightarrow {}^{3}\text{T}_{2g}$ [($t_{2g}^{6}e_{g}^{2}$) \rightarrow ($t_{2g}^{5}e_{g}^{3}$)], ${}^{3}\text{A}_{2g} \rightarrow {}^{3}\text{T}_{1g}$ [($t_{2g}^{6}e_{g}^{2}$) \rightarrow ($t_{2g}^{4}e_{g}^{4}$)] and ${}^{3}\text{A}_{2g} \rightarrow {}^{3}\text{T}_{1g}$ [($t_{2g}^{6}e_{g}^{2}$) \rightarrow ($t_{2g}^{5}e_{g}^{3}$)] excitations in bulk NiO. In our calculations the D_{4h} symmetry of (MgO/NiO/MgO)_{100}^{2} removes part of the degeneracy of the ${}^{3}\text{T}_{2g}$ and ${}^{3}\text{T}_{1g}$ states, from which we obtain energies of 0.81 eV, 2.14 eV and 2.66 eV corresponding to the bulk excitations. We have not obtained a converged solution for the $d_{xz} \rightarrow d_{z^2}$ excitation, but, with reference to Fig. 2, note that were this transition to follow the linear relationship between energy and coordination number the energy for the trilayer would be 1.30 eV. These compare with values of 0.79 eV, 1.40 eV and 3.40 eV reported by de Graaf *et al.*³⁰ and energies of (0.86–1.04) eV and (1.50–1.81) eV reported by Freitag *et al.*²⁹ for the first two excitations, based on cluster calculations which included electron correlation effects.

As shown in Table 10, EEL excitations at $\approx 0.6 \text{ eV}$, $\approx 1.0 \text{ eV}$, $\approx 1.3 \text{ eV}$, $\approx 1.6 \text{ eV}$ have been assigned to the {100} surface of NiO,^{29,50,51} and that at $\approx 2.2 \text{ eV}$ to a possible transition at a {100} NiO/MgO interface.^{6,10} These compare with our calculated values for (NiO/MgO)²₁₀₀ of

Table 9 Comparison of interlayer electron transfer, δq (*e*/NiO), in various NiO/MgO (100) multi-layers

System	δq
(NiO/MgO) ² ₁₀₀ (NiO/MgO/MgO) ³ ₁₀₀ (NiO/MgO/NiO) ³ ₁₀₀ (MgO/NiO/MgO) ² ₁₀₀	+0.006 -0.007 -0.005 +0.032

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Table 10 Comparison of EELS and theoretical $d \rightarrow d$ transition energies (eV)

Experiment		Theory			
Bulk—					
Transition	Energy/eV	Ref. 29	Ref. 30	Present	
$ {}^{3}A_{2g} \rightarrow {}^{3}T_{2g} (t_{2g}^{6}e_{g}^{2}) \rightarrow (t_{2g}^{5}e_{g}^{3}) $	$1.05,^{a}, 1.08,^{b,c}, 1.10,^{d}, 1.13,^{a,e}, 1.16,^{f}, 1.1^{g}$	0.86–1.04	0.79	0.81	
	1.79, ^a 1.86, ^b 1.87, ^d 1.95, ^{a,e}	1.50-1.81	1.40	2.14	
	$2.75,^{f} 2.8,^{g} \approx 3^{a}$	—	3.40	2.66	
{100} Surface—					
Transition	Energy/eV	Ref. 29	Ref. 31	Present	
	$\begin{array}{c} 0.57,^{d} \ 0.60^{g.h} \\ 1.0^{h} \\ 1.3^{h} \\ 1.6,^{g} \ 1.62,^{d} \ 1.63^{f} \\ 2.18^{i} \end{array}$	0.54–0.65 0.86–1.00 1.11–1.30 1.22–1.44	0.46 0.83 1.04 1.17 2.55	0.83 0.83 1.16 1.87 1.98	
^{<i>a</i>} Ref. 48. ^{<i>b</i>} Ref. 47. ^{<i>c</i>} Optical absorption. ^{<i>d</i>} Ref. 29. ^{<i>e</i>} Ref. 46. ^{<i>f</i>} Ref. 49. ^{<i>g</i>} Ref. 50. ^{<i>h</i>} Ref. 51. ^{<i>i</i>} Refs. 6 and 10.					

0.83 eV, 0.83 eV, 1.16 eV, 1.87 eV and 1.98 eV with an average discrepancy of ≈ 0.2 eV. Furthermore, as pointed out by Fromme *et al.*,⁵¹ the energy of the $d_{xy} \rightarrow d_{x^2-y^2}$ excitation would be expected to remain more or less unchanged from 6-fold to 5-fold coordination and that of the $d_{xz} \rightarrow d_{z^2}$ excitation to decrease, which, as Table 4 shows, is exactly what we find. Thus, bearing in mind that unrelaxed (NiO/MgO)²₁₀₀ is only an approximate representation of the non-defective, semi-infinite {100} surface of NiO, the inclusion of which is largely to examine the effects of changing the local Ni coordination, our results would seem to reproduce qualitatively the surface $d \rightarrow d$ excitation energies. Table 10 also shows that, overall, our results are, at least, comparable to those reported by Freitag *et al.*²⁹ and Geleijns *et al.*,³¹ which suggests that for *extended/periodic* systems the neglect of correlation effects beyond Hartree–Fock would seem to be less important than it is for (NiO₆)¹⁰⁻ and (NiO₅)⁸⁻ clusters.

4c. Hole states and band gaps

In view of its p-type properties, the nature of hole states in NiO has continued to attract considerable attention.¹⁵ Previous UHF studies of the bulk^{24,25} and {100} monolayer²⁷ have provided direct evidence for localised holes with strong O(p) character, in complete agreement with Sawatzky and coworkers.^{17–19} They have shown, by analogy with the oxygen k-edge spectra of $Li_xNi_{1-x}O$,¹⁷ that reasonable estimates of the band gap, E_g , in NiO can be obtained from the gap between the polaron band and conduction band edge, as shown in Fig. 3. Here we find that the calculated band gap of the unsupported {100} monolayer, 5.1 eV, which is $\approx 25\%$ greater than that of the bulk, increases in (NiO/MgO)²₁₀₀ to 5.7–6.0 eV for different hole states. As suggested by the ground state valence band DOS, holes within the NiO layer are more stable than those within MgO by 0.27–0.64 eV, with further differences in energy between different spin configurations of 0.03–0.16 eV for the NiO layer and 0.37 eV for the MgO layer. As in the case of other quantities of interest, we have estimated the variation of E_g with Ni coordination. Fig. 4 shows a near linear increase in E_g from 5.1 eV in (NiO)¹₁₀₀ to 6.6 eV in (MgO/NiO/MgO)³₁₀₀, where in each case the hole/unpaired electron is in a p_π orbital in the NiO plane. This trend indicates that the hole is less stable in (MgO/NiO/MgO)³₁₀₀ than it is in (NiO)¹₁₀₀, which reflects the change in Madelung potential. Pauli repulsion between the unpaired electron and the neighbouring Mg²⁺ ions might also contribute to this increase.

As in a previous study of the $\{100\}$ monolayer,²⁷ we have obtained variationally-converged solutions for charge-transfer states of from which the corresponding

variables. Furthermore, since the sizes of slab used are sufficiently thick to provide a bulk-like region in the interior of the slab and two essentially free surfaces, the simulations reported here represent a radical departure from the two-region strategy used by Tasker⁶⁶ and Gay and Rohl,⁶⁷ in which the positions (and polarisations) of the ions in the vicinity of the surface *only* are relaxed explicitly by minimising the *internal* energy of the system, while the remainder are constrained to their bulk lattice positions.

Two important points emerge from our surface free energy calculations. The first is the requirement that many more layers are required for convergence than for static simulations. This is due to the contribution to the free energy of long wavelength phonons perpendicular to the slab, particulary at low temperatures. Similar considerations apply to molecular dynamics simulations where the unit cell size prevents the inclusion of small q vibrations. The second is the limitation of the Einstein approximation which, again, severely restricts the range of phonons that contribute to the free energy. Fundamental to all simulations is the quality of the interatomic potentials, particularly where a paucity of experimental data limits the extent to which the validity of the simulations can be examined. Here, support for the potentials used is provided by the close agreement between the static surface energy and lattice relaxation predicted from UHF calculations and lattice simulations. In the absence of data for direct comparison, it is also re-assuring that the temperature dependence of the surface free energy is consistent with that for other rocksalt systems.

With regard to NiO/MgO multilayers, perhaps the most significant of the simulation results concern the free energies of Ni segregation to the $\{100\}$ surface of MgO, for they appear to confirm the stability of NiO overlayers, even at high temperatures. However, this is clearly a complex issue which involves both thermodynamic and kinetic factors, particulary in view of the reported *negative* deviation from ideality of the enthalpy of mixing of NiO and MgO.⁵²

5. Conclusions

The overall conclusion of this paper is that useful information concerning the electronic, magnetic, structural and dynamic properties of NiO monolayers on MgO {100} surfaces can be obtained from a combination first principles unrestricted *periodic* Hartree–Fock calculations and atomistic lattice simulations based on quasi-harmonic lattice dynamics. From an examination of several *semi-infinite* slab configurations, including an unsupported NiO monolayer, an NiO monolayer deposited on MgO {100} layers and an NiO layer sandwiched between two MgO {100} layers, we have been able to obtain the dependence of physical quantities, such as the magnetic exchange coupling constants and the d \rightarrow d and charge transfer excitation energies, on the Ni coordination number Z, which increases from 4 to 6 in this series. Furthermore, they are all obtained from differences in *total* Hartree–Fock energies and show a remarkably monotonic variation with Z. Further work, currently in progress, compares these results with those of pure bulk NiO and systems with reduced dimensionality.⁶⁸ In addition, information of practical importance has been obtained for Ni/Mg substitutional defects and cation vacancies in the NiO layer, both of which might reasonably be expected to occur in ultra-thin films of NiO on MgO as a result of intermixing and non-stoichiometry.

Finally, free energy calculations based on surface lattice dynamics have been used to estimate the surface contribution to the vibrational density of states of NiO {100} and the heat of segregation of Ni²⁺ to the MgO surface as a function of temperature, which appears to confirm the stability of NiO overlayers, even at high temperature. These show that potential-based approaches are capable of providing detailed dynamic and temperature-dependent information, for which, at present, there is little experimental data for comparison. The results reported here also show that the calculation and subsequent minimisation of the free energy *via* quasiharmonic lattice dynamics is sufficiently rapid that an extension to more complex surface structures with more extensive disorder is perfectly feasible.

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