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# A theory of the relative stabilities of the cubic phases of magnesium and calcium oxides

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**Abstract.** The B2 and B3 phases of solid magnesium and calcium oxides are studied non-empirically with a fully ionic model in which the major portion of the cohesion, that not originating from electron correlation effects, is computed *ab initio* using the relativistic integrals program. Electron correlation is incorporated by adding the short-range contributions derived from density functional theory to the inter-ionic dispersive attractions evaluated with the inclusion of their damping caused by overlap of the ion wavefunctions. The two-body inter-ionic interactions and rearrangement energies needed to convert a free  $O^-$  ion into an in-crystal  $O^{2-}$  ion are reported.

Improved predictions are reported for the energy differences separating the B2 and B3 phases from the B1 structure. Previous calculations overestimated each energy difference between the B1 and B2 phases because either the electron correlation contributions were not fully considered or the model for the in-crystal environment failed to produce sufficiently compressed  $O^{2-}$  wavefunctions. The inadequacies of the environmental model in which two units of positive charge are distributed over the surface of a sphere also explain the previous underestimation of each energy difference between the B1 and the B3 phases. The present calculations avoid these difficulties by using a much more realistic model for computing the in-crystal  $O^{2-}$  wavefunctions.

## 1. Introduction

Magnesium and calcium oxides are the simplest solid oxides which have electronic charge distributions of sufficiently high ionic character that it is reasonable to try to understand their properties using a suitably defined fully ionic model [1]. This observation coupled with two further reasons motivated intense theoretical study of these materials. The first of these reasons is that they are the simplest members of a wide range of solid oxides of technological importance. Thus  $CeO_2$  and  $ZrO_2$  are ceramics like  $MgO$  and  $CaO$  [2–4],  $ThO_2$  is both a nuclear material [5] and used in fluorescent tubes whilst  $UO_2$  and  $PuO_2$  are reactor fuels [6, 7]. The second reason for the interest in  $MgO$  and  $CaO$  is that they are both major constituents of the mantle of the Earth and thus of geological importance [8–12]. The development of useful geophysical models requires accurate predictions of the pressure–volume equation of state in the experimentally inaccessible high-pressure regions for the B1 (sixfold-coordinated rock-salt structured) phases of both these solids. Furthermore the construction of such models requires knowledge of whether the high pressures in the interior of the earth induce the phase transition which transforms either of these solids from its lowest-energy B1 structure into the eightfold coordinated B2 structure. Although this information is available from experiment [13–15] for  $CaO$ , theoretical predictions are still required for  $MgO$ .

The numerous theoretical studies of magnesium and calcium oxides can be divided into two broad types depending on whether these solids are assumed to be fully ionic. In calculations of the first type, such as the crystal Hartree–Fock method [16–18] or various forms of the local-density-functional linearized augmented-plane-wave method [19, 20], no *a-priori* assumptions are made concerning the ionicity. The absence of any such assumption renders these methods especially suitable for solids that are partially or wholly bound by covalent forces. In contrast all the calculations [9–12, 21–23] of the second broad type are distinguished by resting on the fundamental assumption of a suitably defined fully ionic model. Although the greater generality of calculations of the first type, manifested by their avoidance of any ionicity assumption, might at first suggest that they are in all cases preferable to those of the second type, such a conclusion would not be correct. Thus this very generality of the former type of calculation necessitates introducing various approximations such as the local-density-functional description of either exchange or correlation. Since a local correlation functional misses entirely the dispersive attraction between two ions of non-overlapping electron density, such attractions, which have been shown [22] to contribute significantly to the cohesion of many polar solids, are not correctly treated in calculations of the first type. Such difficulties can be eliminated from calculations of the second type which also have two additional advantages. The first is the ability to compute exactly, given wavefunctions of the interacting ions, the major portions of each inter-ionic interaction, those not arising from electron correlation. The second advantage of calculations based on the ionic model is that they yield a transparent breakdown of the cohesive energy into inter-ionic pair potentials plus rearrangement energies needed to convert an isolated ion into its in-crystal form. Such decomposition is valuable because it provides the basis for constructing a simple, transparent and yet physically highly realistic model [24], called the compressible ion model, which can be used to predict the energetic properties of the ionic assembly for nuclear positions other than those occurring in the cubic crystal structure for which the original *ab-initio* computation was performed. This model thereby not only allows the elastic constants, which are implicitly governed by the crystal properties in nuclear geometries of lower than cubic symmetry, to be studied using such *ab-initio* results but also enables these to be introduced [24] into molecular dynamics simulations used to study ionic melts.

Use of a fully ionic model with its attendant advantages is justified by the evidence that many solid oxides are essentially fully ionic. Thus analysis [25] of the electron densities yielded by local-density-functional band-structure computations suggests full ionicity for both MgO and CaO which is also indicated [16] for MgO by a similar analysis of the crystal Hartree–Fock wavefunction. Furthermore there is strong evidence that UO<sub>2</sub>, which would be expected *a priori* to be less ionic than the alkaline earth oxides, is also essentially fully ionic. Thus its magnetic properties indicate a uranium 5f<sup>2</sup> electronic configuration [26] whilst analysis of the experimental phonon dispersion curves, treating the uranium charge as an adjustable parameter, predicts this charge to be four [27].

The advantages of a fully ionic model were exploited in a study [22] of the B1 phase of MgO, with the relativistic integrals program (RIP) [28, 29] being used to compute exactly all the inter-ionic potentials that resulted from the model used to describe the in-crystal O<sup>2-</sup> ion. The theoretical methods used [22] were subsequently refined [23] to meet the more severe challenges of not only significantly improving on the description [22] of MgO but also providing a good description of the cohesion of the B1 phases of both CaO as well as ThO<sub>2</sub> [30] and UO<sub>2</sub> [31, 32]. Here the previous study [23] is extended to investigate with the same methods the cohesive properties of MgO and CaO both in the B2 phase as well

as in the fourfold-coordinated B3 phase having the zincblende structure. This extension achieves three objectives. The first of these is to study the relation between the electronic and structural properties of the B1, B2 and B3 phases, examining in particular the phase dependence of the rearrangement and two-body inter-ionic potential contributions to the cohesive energy. New and improved predictions for the experimentally unknown cohesive properties of the B2 and B3 phases are obtained as a byproduct of this investigation. The second objective of this paper is to present a critical comparison of the different predictions of the cohesive properties of these two phases emphasizing especially the energy needed to convert the B1 structure into either the B2 or the B3 phase. The third objective is to present all the *ab-initio* results that were both used to parametrize the compressible ion model description [24] of MgO and CaO and invoked as independent data to test its predictive power. This model was used derive from the present *ab-initio* results both the pressure–volume equations of state and the pressures needed to induce the B1-to-B2 transitions [24].

## 2. Theory and computational methods

The methodology is merely summarized, being the same as that introduced [23] to study the B1 phases of MgO and CaO. The basic assumption is that both oxides are ionic, containing  $O^{2-}$  ions. Although the discussion [33] might suggest ambiguity for this concept, arguments [34] justify the definition used in studies [22, 23, 28–30, 35, 36] with the RIP program [28, 29]. A solid is taken as ionic provided that, with neglect of inter-ionic electron correlation, the electronic wavefunction of the crystal can be written as an anti-symmetrized product of wavefunctions for individual ions each of which contains an integral number of electrons and is spherically symmetric. The cations were taken to be unaffected by their in-crystal environment [37–40].

The nuclear geometry of a cubic crystal is defined by the closest cation–anion separation  $R$ . For a bound crystal, the negative binding energy  $U_L(R)$  is defined as the difference between the crystal energy and the sum of the energies of free doubly charged cations, free singly charged  $O^-$  ions and free electrons. Neglecting the small nuclear zero-point motions, the equilibrium closest cation–anion separation  $R_e$  is the value of  $R$  minimizing  $U_L(R)$ . The lattice energy  $D_e$ , the energy required to convert the crystal at its equilibrium geometry into free cations, free  $O^-$  ions and free electrons, then equals  $-U_L(R_e)$  and can be determined [9] experimentally from a Born–Haber cycle.

The cohesive energy  $U_L(R)$  yielded by the present fully ionic model is [22, 41]

$$U_L(R) = N_f \{ E_{re}(R) - M/R + n_{CA} V_{sCA}(R) + (1/2)[n_{AA} V_{sAA}(x_{AA}R) + n_{CC} V_{sCC}(x_{CC}R)] \} + U_{disp}(R) \quad (1)$$

after neglecting explicitly three-body and higher-order multi-body terms expected to be small [34]. All terms inside the curly brackets are in atomic units with stationary isolated electrons having zero energy. The constant  $N_f$  ( $= 2625.5$ ) converts an energy per ion in atomic units into an energy per mole of crystal. In (1),  $E_{re}(R)$  is the rearrangement energy required to convert one free  $O^-$  ion of energy  $E_{O^-}$  plus an electron into an  $O^{2-}$  ion in the crystal with geometry defined by  $R$ . Thus

$$E_{re}(R) = E_A(R) - E_{O^-} \quad (2)$$

where  $E_A(R)$  is the energy that an  $O^{2-}$  ion with wavefunction optimal for the crystal would have when isolated if it retained its in-crystal wavefunction. Each  $V_{sXY}(x_{XY}R)$  ( $X$  or  $Y =$  cation C or anion A) is the short-range energy of interaction between ions X and Y separated by the distance  $x_{XY}R$  with  $x_{XY}$  being an  $R$ -independent geometrical constant

depending on the crystal type. Each  $V_{sXY}(x_{XY}R)$  arises from overlap of the wavefunctions of ions X and Y and vanishes for separations sufficiently large that this overlap is negligible. Each such term excludes both the point Coulomb interaction  $q_X q_Y / (x_{XY}R)$  where  $q_X$  is the net charge ion of X as well as the dispersive attraction. The only non-negligible short-range terms are those  $V_{sCA}(R)$  between one cation and its  $n_{CA}$  closest anions plus those  $V_{sXX}(x_{XX}R)$  between one ion of type X and the  $n_{XX}$  closest ions of the same type. The sum of all point Coulomb interactions enters (1) as  $-M/R$  where  $M$  is the Madelung constant whilst  $U_{disp}(R)$  is the sum of all the two-body dispersive attractions [42–44].

Both  $E_{re}(R)$  and  $V_{sXY}(x_{XY}R)$  are the sum of uncorrelated contributions denoted by a zero superscript plus correlation corrections denoted *corr*. The latter were evaluated using the best of the previously presented [23] density functional methods [45, 46] from relativistic ion wavefunctions optimizing the uncorrelated description of the crystal. Thus the  $E_{re}^{corr}(R)$  were calculated through (4.6) of [23] using  $A_{corr}(\zeta)$ -values in table 8 of [23].  $U_{disp}(R)$  was evaluated [23, 47] using the damping parameters of table 9 of [23] which are correct for the present  $O^{2-}$  wavefunctions.

Each in-crystal  $O^{2-}$  wavefunction was computed using the Oxford Dirac–Fock program [48] by adding to the intra-ionic potential acting on an electron at position  $r_a$  relative to the  $O^{2-}$  nucleus the spherical average  $F_{env}^{(0)}(r_a; R)$  of the potential generated by the remaining ions in the crystal. Only this average is needed when the orbitals have the standard central field form [49] and either are completely filled with electrons or are empty.  $F_{env}^{(0)}(r_a; R)$  is composed of the point lattice term arising if the ion overlapped only negligibly with its neighbours plus corrections introduced by overlap. The first contribution, which acts to contract the anion [22, 23, 34, 37–39, 50], is a constant stabilizing potential equal to  $-\phi_{env}/R$  between  $r_a$ -values of zero and  $R$  after which it rises towards zero after several smaller oscillations. This is represented by the Fermi-smoothed function  $F_{MFS}(r_a; R)$  [23]. The overlap contribution, which also acts to contract an anion, is a repulsive potential arising in spatial regions where the electron density of other ions is not negligible, the  $n_{CA}$  closest cation neighbours yielding the dominant terms. The optimized-with-eigenvalues Madelung–Fermi smoothed (OEMFS) model ( $F_{OEMFS}(r_a; R)$ ) for  $F_{env}^{(0)}(r_a; R)$ , which is one of the two most equally satisfactory descriptions [23], results as a local approximation for the overlap term derived from Phillips–Kleinman pseudopotential theory. Thus

$$F_{OEMFS}(r_a; R) = F_{MFS}(r_a; R) - n_{CAA} \sum_{i \in c} (\epsilon_i - \epsilon_0) \{[\rho_{iC}(\mathbf{r}_C)]^k\}^{(0)}. \quad (3)$$

Here the sum over  $i$  is over all filled orbitals of one neighbouring cation  $C$ ,  $\rho_{iC}(\mathbf{r}_C)$  is the density generated by an electron in orbital  $i$  of ion  $C$ ,  $\{[\rho_{iC}(\mathbf{r}_C)]^k\}^{(0)}$  is the spherically symmetric quantity resulting when  $[\rho_{iC}(\mathbf{r}_C)]^k$  is expanded about the anion nucleus,  $\epsilon_i$  ( $< 0$ ) is the binding energy of the free-cation orbital  $i$  and  $\epsilon_0$  is the energy of a stationary electron in just the constant part of  $F_{env}^{(0)}(r_a; R)$ .  $A$  and  $k$  are determined by optimizing the cohesive energy  $U_L^0(R)$  predicted without including the electron correlation terms but using the RIP program to compute the uncorrelated short-range interactions  $V_{sXY}^0(x_{XY}R)$ . This avoids the previously discussed [51] uncertainties that would arise if the  $V_{sXY}^0(x_{XY}R)$  were evaluated using density functional theory.

The potential  $F_{OEMFS}(r_a; R)$  and hence the in-crystal  $O^{2-}$  wavefunctions depend on both  $R$  and the crystal structure. The constant  $\phi_{env}$  introduces structural dependence into the point lattice term  $F_{MFS}(r_a; R)$  whilst the overlap term depends on structure through the explicit factor of  $n_{CAA}$ .

### 3. Fundamental results

#### 3.1. The oxide ion properties and two-body inter-ionic potentials

For the  $R$ -values in tables 1–6,  $U_L(R)$  has been computed for the B1, B2 and B3 phases using the OEMFS model. The resulting oxide ion rearrangement energies and the short-range interactions within both the closest cation–anion and anion–anion pairs predicted both without and with the inclusion of the contributions from electron correlation are reported. The results for the B1 structure are those of [23] reported to the six decimal places used to predict the crystal cohesion.

**Table 1.** Oxide ion rearrangement energies for the B1, B2 and B3 phases of MgO  $E_{re}(R) = E_{re}^0(R) + E_{re}^{corr}(R)$ .

$R$	$E_{re}^0(R)$ (au)			$E_{re}(R)$ (au)		
	B3 (4:4)	B1 (6:6)	B2 (8:8)	B3 (4:4)	B1 (6:6)	B2 (8:8)
3.25	0.706 314	0.816 522	0.901 348	0.598 857	0.703 242	0.784 280
3.5	0.568 477	0.643 373	0.701 748	0.471 412	0.541 097	0.595 958
3.75	0.488 098	0.538 466	0.578 538	0.399 225	0.445 066	0.481 978
3.981	0.442 032	0.477 418	0.505 826	0.359 232	0.390 688	0.416 283
4.25	0.407 395	0.431 355	0.450 502	0.330 368	0.351 038	0.367 768
4.5	0.388 251	0.406 228	0.420 441	0.315 151	0.330 271	0.342 353
5.0	0.361 923	0.372 198	0.379 970	0.295 563	0.303 752	0.309 928
5.5	0.346 989	0.353 605	0.358 364	0.285 560	0.290 613	0.294 153

**Table 2.** Oxide ion rearrangement energies for the B1, B2 and B3 phases of CaO.

$R$	$E_{re}^0(R)$ (au)			$E_{re}(R)$ (au)		
	B3 (4:4)	B1 (6:6)	B2 (8:8)	B3 (4:4)	B1 (6:6)	B2 (8:8)
3.5	0.892 158	0.945 913	0.985 504	0.734 293	0.784 577	0.821 272
3.75	0.758 065	0.794 198	0.820 473	0.611 432	0.644 847	0.668 823
4.0	0.666 279	0.692 394	0.711 651	0.528 304	0.552 084	0.569 308
4.25	0.585 187	0.609 756	0.628 110	0.454 729	0.476 625	0.492 680
4.544	0.492 503	0.519 933	0.540 201	0.371 960	0.395 630	0.412 922
4.75	0.448 868	0.474 091	0.492 824	0.335 037	0.356 176	0.371 780
5.0	0.417 281	0.438 164	0.453 717	0.309 919	0.326 850	0.339 405
5.5	0.380 600	0.394 326	0.404 968	0.283 462	0.293 973	0.302 000
6.0	0.359 113	0.368 715	0.375 708	0.269 700	0.276 606	0.281 566

The results in tables 1 and 2 show, as would be expected, that for a given  $R$  the rearrangement energies increase on passing from the B3 through the B1 to the B2 structure corresponding to an increasingly compressed  $O^{2-}$  ion. This is confirmed by both the mean radii and the mean square radii (tables 7 and 8) of the anion 2p orbitals which, for a given  $R$ , are smallest in the B2 structure whilst being least reduced in the B3 materials. On passing from the B3 through the B1 to the B2 structure for a given  $R$ , there is only a slight change in  $F_{env}^{(0)}(r_a; R)$  at small  $r_a$  where it is essentially constant and, originating from the point lattice contribution, is equal to  $-M/2R$  [52] (i.e.  $\phi_{env} = M/2$ ). Thus the value  $-3.525\ 34/R$  of  $F_{env}^{(0)}(r_a; R)$  at small  $r_a$  in the B2 structure is almost the same as that of  $-3.495\ 13/R$  in the B1 material whilst neither of these values differs greatly from that

**Table 3.** Short-range cation–anion interactions for the B1, B2 and B3 phases of MgO:  $V_{sCA}(R) = V_{sCA}^0(R) + V_{sCA}^{corr}(R)$ .

$R$	$V_{sCA}^0(R)$ (au)			$V_{sCA}(R)$ (au)		
	B3 (4:4)	B1 (6:6)	B2 (8:8)	B3 (4:4)	B1 (6:6)	B2 (8:8)
3.25	0.102 011	0.085 279	0.074 829	0.099 805	0.083 331	0.073 045
3.5	0.075 029	0.062 258	0.054 311	0.073 185	0.060 626	0.052 820
3.75	0.056 241	0.046 614	0.040 546	0.054 700	0.045 243	0.039 292
3.981	0.043 713	0.036 275	0.031 557	0.042 405	0.035 105	0.030 484
4.25	0.033 264	0.027 716	0.024 193	0.032 179	0.026 738	0.023 292
4.5	0.025 858	0.021 496	0.018 735	0.024 956	0.020 680	0.017 982
5.0	0.016 664	0.013 938	0.012 243	0.016 015	0.013 344	0.011 690
5.5	0.011 215	0.009 399	0.008 304	0.010 740	0.008 961	0.007 894

**Table 4.** Short-range cation–anion interactions for the B1, B2 and B3 phases of CaO.

$R$	$V_{sCA}^0(R)$ (au)			$V_{sCA}(R)$ (au)		
	B3 (4:4)	B1 (6:6)	B2 (8:8)	B3 (4:4)	B1 (6:6)	B2 (8:8)
3.5	0.141 064	0.132 550	0.126 986	0.137 036	0.128 685	0.123 244
3.75	0.093 853	0.088 065	0.084 334	0.090 625	0.084 956	0.081 317
4.0	0.062 920	0.058 660	0.055 861	0.060 351	0.056 185	0.053 460
4.25	0.044 962	0.040 972	0.038 295	0.042 891	0.038 998	0.036 396
4.544	0.034 956	0.030 479	0.027 569	0.033 234	0.028 886	0.026 065
4.75	0.029 662	0.025 344	0.022 593	0.028 123	0.023 940	0.021 280
5.0	0.023 540	0.019 824	0.017 494	0.022 220	0.018 629	0.016 383
5.5	0.014 927	0.012 369	0.010 720	0.013 957	0.011 494	0.009 912
6.0	0.010 060	0.008 179	0.007 045	0.009 334	0.007 527	0.006 442

**Table 5.** Short-range anion–anion interactions in the B1, B2 and B3 phases of MgO:  $V_{sAA}(R') = V_{sAA}^0(R') + V_{sAA}^{corr}(R')$ .

$R$	B3 ( $R' = 2\sqrt{2/3}R$ )		B1 ( $R' = \sqrt{2}R$ )		B2 ( $R' = (2/\sqrt{3})R$ )	
	$V_{sAA}^0(R')$ (au)	$V_{sAA}(R')$ (au)	$V_{sAA}^0(R')$ (au)	$V_{sAA}(R')$ (au)	$V_{sAA}^0(R')$ (au)	$V_{sAA}(R')$ (au)
3.25	0.006 432	0.005 801	0.017 285	0.016 230	0.068 066	0.064 909
3.5	0.004 367	0.003 695	0.011 886	0.010 753	0.043 889	0.040 727
3.75	0.002 714	0.002 035	0.007 547	0.006 378	0.026 214	0.023 091
3.981	0.001 628	0.000 961	0.004 541	0.003 368	0.014 640	0.011 588
4.25	0.000 788	0.000 149	0.002 113	0.000 959	0.005 430	0.002 482
4.5	0.000 350	−0.000 235	0.000 805	−0.000 275	0.000 541	−0.002 217
5.0	−0.000 105	−0.000 613	−0.000 632	−0.001 613	−0.004 917	−0.007 412
5.5	−0.000 240	−0.000 672	−0.001 063	−0.001 931	−0.006 506	−0.008 731

of  $-3.27611/R$  in the B3 structure. Hence the overwhelming majority of the increasing anion compression on the passing from the B3 through the B1 to the B2 structure cannot be attributed to the changes in the depth of  $F_{env}^{(0)}(r_a; R)$  at small  $r_a$ . On traversing this sequence, the changes in  $F_{env}^{(0)}(r_a; R)$  are dominated by those of the overlap contribution because the linear dependence on  $n_{CA}$  of the latter (3) causes its variation (at fixed  $R$ ) to outweigh

**Table 6.** Short-range anion–anion interactions in the B1 and B2 phases of CaO.

$R$	B1 (6:6)		B2 (8:8)	
	$V_{sAA}^0(\sqrt{2}R)$ (au)	$V_{sAA}(\sqrt{2}R)$ (au)	$V_{sAA}^0(2/\sqrt{3}R)$ (au)	$V_{sAA}(2/\sqrt{3}R)$ (au)
3.5	0.003 397	0.003 077	0.029 940	0.028 136
3.75	0.002 260	0.001 965	0.019 352	0.017 677
4.0	0.001 445	0.001 186	0.012 417	0.010 921
4.25	0.001 065	0.000 830	0.008 450	0.007 132
4.544	0.001 053	0.000 787	0.005 901	0.004 660
4.75	0.000 953	0.000 653	0.004 307	0.003 067
5.0	0.000 720	0.000 406	0.002 594	0.001 381
5.5	0.000 327	0.000 012	0.000 247	−0.000 894
6.0	0.000 091	−0.000 213	−0.000 916	−0.001 992

greatly the small changes in the point lattice term. This shows that it is the changes in the overlap term which are responsible for the vast majority of the structural dependence of the anion properties at fixed  $R$ .

**Table 7.** Mean radii and mean square radii of outermost anion orbitals in MgO phases. The mean radius  $\langle r \rangle_{2p}$  and mean square radius  $\langle r^2 \rangle_{2p}$  are averages with weights of one third and two thirds of those for the relativistic orbitals  $2p_{1/2}$  and  $2p_{3/2}$  [49] having  $j = \frac{1}{2}$  and  $j = \frac{3}{2}$ , respectively.

$R$	$\langle r \rangle_{2p}$ (au)			$\langle r^2 \rangle_{2p}$ (au)		
	B3	B1	B2	B3	B1	B2
3.75	1.476	1.440	1.417	2.827	2.645	2.536
3.981	1.526	1.492	1.470	3.071	2.887	2.773
4.25	1.578	1.547	1.526	3.342	3.161	3.045

**Table 8.** Mean radii and mean square radii of outermost anion orbitals in CaO phases. The mean radius  $\langle r \rangle_{2p}$  and mean square radius  $\langle r^2 \rangle_{2p}$  are averages with weights of one third and two thirds of those for the relativistic orbitals  $2p_{1/2}$  and  $2p_{3/2}$  [49] having  $j = \frac{1}{2}$  and  $j = \frac{3}{2}$ , respectively.

$R$	$\langle r \rangle_{2p}$ (au)			$\langle r^2 \rangle_{2p}$ (au)		
	B3	B1	B2	B3	B1	B2
4.25	1.435	1.421	1.409	2.599	2.538	2.488
4.544	1.490	1.469	1.452	2.866	2.761	2.686
4.75	1.531	1.506	1.488	3.075	2.942	2.854

Both the  $O^{2-}$  orbital properties (tables 7 and 8) and the rearrangement energies (tables 1 and 2) not only show the obvious result that, in each structure, the anion becomes more compressed with decreasing  $R$  but also demonstrate the much more significant point [53] that the  $R$  dependence of  $E_{re}(R)$  is at least as large as that of the  $V_{sCA}(R)$  (tables 3 and 4). This shows that each quantity regarded as a two-body cation–anion interaction in standard theories of the Born–Mayer type is actually an effective two-body interaction composed of the true two-body potential  $V_{sCA}(R)$  plus a fraction of  $E_{re}(R)$ . The dependence of



this fraction on the crystal type prevents such effective potentials from being transferable between different crystal structures [35]. Furthermore the strong  $R$  dependence of  $E_{re}(R)$  explains [53] the discrepancies between the  $E_{re}(R_e)$ -values predicted using the OEMFS model and the electron affinities of the  $O^-$  ion presented in standard references.

The results in tables 3 and 4 show, for a given  $R$ , that  $V_{sCA}^0(R)$  and  $V_{sCA}(R)$  decrease on passing from the B3 through the B1 to the B2 structure. Since such repulsions originate from the overlap of the wavefunctions of the two interacting ions, they decrease because the anion becomes increasingly compressed on traversing through these structures. These reductions in  $V_{sCA}^0(R)$  more than offset the increases in  $E_{re}^0(R)$  with increasing  $n_{CA}$  and hence the crystal cohesion predicted using anion wavefunctions optimal for a phase is greater than that predicted using  $O^{2-}$  wavefunctions determined for a structure of smaller  $n_{CA}$ . Indeed use of a wavefunction determined for any structure other than that for which  $U_L^0(R)$  is being evaluated always produces a less negative value for  $U_L^0(R)$ . This is a consequence of the variation principle since the use of the environmental potential correct for the structure and  $R$ -value under consideration yields the anion orbitals which minimize the total energy evaluated as the expectation value of the crystal electronic Hamiltonian using the single determinant crystal wavefunction built from these anion orbitals. However, a variation principle does not exactly hold for  $U_L(R)$  evaluated with the inclusion of electron correlation if the latter is calculated, as here, by adding to  $U_{disp}(R)$  density functional correlation predictions derived from anion orbitals computed by minimizing  $U_L^0(R)$ .

### 3.2. The crystal cohesions

The fully optimal predictions (tables 9 and 10) were derived using, at each  $R$ , the  $O^{2-}$  wavefunction derived from the  $F_{env}^{(0)}(r_a; R)$  correct for that structure and  $R$ . The B1 optimal results were derived by using, at each  $R$ , the  $O^{2-}$  wavefunction optimal for the B1 structure at that  $R$ . The calculations agree with experiment, predicting that the B1 structure, adopted under ambient conditions, has the lowest energy. The reliability of these computations for the B1 phase, demonstrated by their excellent agreement [23] with experiment, shows that there is no reason to prefer any previous predictions (table 11) for the experimentally unknown  $R_e$  of the B2 phase over the present results.

**Table 9.** Predicted cohesion of the B1, B2 and B3 phases of MgO. The form (1) is used and thus all electron correlation contributions are included.  $V_m$  is the volume occupied by 1 mol of crystal at its equilibrium geometry  $R = R_e$ .

	B3 (4:4) for the following $O^{2-}$ wavefunctions		B1 (6:6) for the following $O^{2-}$ wavefunctions		B2 (8:8) for the following $O^{2-}$ wavefunctions	
	B1 optimal	Fully optimal	Fully optimal	Experimental	B1 optimal	Fully optimal
$D_e$ (kJ mol <sup>-1</sup> )	2983	2975	3038 [23]	3038 [9]	2861	2951
$R_e$ (au)	3.825	3.769	3.994 [23]	3.974 [61]	4.097	4.195
$V_m$ (10 <sup>-7</sup> m <sup>3</sup> )	153.8	147.1	113.7	112.0	94.5	101.4
$B$ (10 <sup>10</sup> N m <sup>-2</sup> )	16.1	15.1	19.9 [23]	17.5 <sup>a</sup> [62]	19.9	23.1

<sup>a</sup> Average of three different results.

For both MgO and CaO, an increase in  $n_{CA}$ , although predicting  $R_e$  to increase (tables 9 and 10), yields smaller  $V_m$  because the more compact nature of the structures of higher  $n_{CA}$  more than offsets the  $R_e$  increases. For the MgO phases at their equilibrium geometries, the

**Table 10.** Predicted cohesion of the B1, B2 and B3 phases of CaO. The form (1) is used and thus all electron correlation contributions are included.  $V_m$  is the volume occupied by 1 mol of crystals at its equilibrium geometry  $R = R_e$ .

	B3 (4:4) for the following O <sup>2-</sup> wavefunctions		B1 (6:6) for the following O <sup>2-</sup> wavefunctions		B2 (8:8) for the following O <sup>2-</sup> wavefunctions	
	B1 optimal	Fully optimal	Fully optimal	Experimental	B1 optimal	Fully optimal
$D_e$ (kJ mol <sup>-1</sup> )	2505	2522	2645 [23]	2644 [9]	2581	2581
$R_e$ (au)	4.525	4.513	4.536 [23]	4.537 [61]	4.628	4.714
$V_m$ (10 <sup>-7</sup> m <sup>3</sup> )	254.6	252.6	166.6	166.7	136.2	143.9
$B$ (10 <sup>10</sup> N m <sup>-2</sup> )	7.71	8.83	11.7 [23]	11.3 [63]	11.7	11.4

**Table 11.** Comparison of  $R_e$ -values predicted for the B2 phases: Crystal HF, crystal Hartree–Fock [18]; LAPW, linearized augmented-plane-wave method derived from figure 1 of [20]; APW, augmented plane-wave method [64], results referenced in [12]; local density, pseudopotential local-density method [19]; KKR, Korringa–Kohn–Rostoker [54] method.

	$R_e$ (au)					
	Fully optimal, present	Crystal HF	LAPW	APW	Pseudopotential	
					Local density	KKR
MgO	4.195	4.211		4.272	4.301	4.244
CaO	4.714	4.83	4.674	4.692		

anion becomes less compact with increasing  $n_{CA}$  as shown by the simultaneous decrease in  $E_{re}(R_e)$  and increase in both the 2p orbital mean radius and mean square radius as well as in the total mean square anion radius  $\langle r^2 \rangle_{tot}$  (table 12). This trend arises because the influence on the anion of the increase of around 0.2 au in  $R_e$  in passing from both the B3 to the B1 and from the B1 to the B2 phases more than outweighs the tendency of the environments of higher  $n_{CA}$  to produce more confining  $F_{env}^{(0)}(r_a; R)$ . The latter effect is shown by the increases in  $E_{re}(R)$  and decrease in  $\langle r \rangle_{2p}$  and  $\langle r^2 \rangle_{2p}$  occurring when  $n_{CA}$  is increased at constant  $R$  (tables 1, 2, 7 and 8). On passing from the B1 to the B2 phase of CaO, the 0.178 au enhancement of  $R_e$  is comparable with the coordination-number-induced  $R_e$  increases of about 0.2 au in MgO and hence the O<sup>2-</sup> ion in the B2 phase of CaO at its equilibrium geometry is similarly less compact than in the equilibrium structure of the B1 phase. However, the 0.023 au difference between the  $R_e$ -values predicted for the B3 and B1 phases of CaO is so small that differences between the O<sup>2-</sup> ion properties in their equilibrium geometries are dominated by the tendency of environments of higher  $n_{CA}$  to produce more confining  $F_{env}^{(0)}(r_a; R)$ . The O<sup>2-</sup> ion in the B1 phase of CaO is thus more compressed than in the B3 phase as shown by the  $E_{re}(R_e)$  and  $\langle r^n \rangle_{2p}$  in table 12.

Comparison (tables 9 and 10) of the B1 optimal and fully optimal results shows that, with the exception of the B3 phase of MgO, increased crystal cohesion is predicted if wavefunctions optimal for the phase under consideration are used rather than those optimal for the B1 structure at the same  $R$ -values. This is consistent with the variation principle [23] even though this is only rigorously applicable here to the predictions derived from  $U_L^0(R)$ . It is shown in the appendix that electron correlation is responsible for the apparently non-variational results in table 9 for the MgO B3 phase.

**Table 12.** Anion properties for the equilibrium geometries of the B1, B2 and B3 phases. The mean radius  $\langle r \rangle_{2p}$  and mean square radius  $\langle r^2 \rangle_{2p}$  are averages with weights of one third and two thirds of those for the relativistic orbitals  $2p_{1/2}$  and  $2p_{3/2}$  [49] having  $j = \frac{1}{2}$  and  $j = \frac{3}{2}$ , respectively.  $\langle r^2 \rangle_{tot}$  is the sum of contributions from all the anion electrons.

	MgO			CaO		
	B3 (4:4)	B1 (6:6)	B2 (8:8)	B3 (4:4)	B1 (6:6)	B2 (8:8)
$E_{re}(R_e)$ (au)	0.395 405	0.387 926	0.375 238	0.379 019	0.397 450	0.378 094
$V_{sCA}(R_e)$ (au)	0.053 566	0.034 653	0.024 494	0.034 121	0.029 114	0.021 970
$\langle r \rangle_{2p}$ (au)	1.480	1.495	1.515	1.484	1.468	1.481
$\langle r^2 \rangle_{2p}$ (au)	2.847	2.899	2.990	2.836	2.754	2.823
$\langle r^2 \rangle_{tot}$ (au)	20.917	21.260	21.814	20.875	20.372	20.788

#### 4. The differences between the lattice energies of the phases

##### 4.1. Comparison of results

The positive differences  $\Delta U_4$  and  $\Delta U_8$  between the energy of the B1 phase and those of the B3 and B2 phases, respectively, are defined through

$$\Delta U_4 = U_L^{B3}(R_e) - U_L^{B1}(R_e) = D_e^{B1} - D_e^{B3} \quad (4a)$$

$$\Delta U_8 = U_L^{B2}(R_e) - U_L^{B1}(R_e) = D_e^{B1} - D_e^{B2}. \quad (4b)$$

The additional superscript denotes the phase for which  $U_L(R_e)$  has been evaluated. The predictions for  $\Delta U_4$  and  $\Delta U_8$  derived through (1) using both the B1 optimal and the fully optimal methods are presented in table 13. The best of the present results for  $\Delta U_8$ , those of the fully optimal method, are compared in table 14 with previous predictions. The pseudopotential local density [19] and KKR [54] methods are approximations, introduced to reduce computational demands, to LAPW theory [20]. Although the crystal Hartree–Fock [18] and LAPW methods differ in principle from the present approach in making no ionicity assumption, the evidence that these materials are ionic shows the main difference between these two methods and the present approach lies in their treatment of electron correlation.

**Table 13.** Energy differences between the ground B1 phase and the B2 and B3 phases, respectively, for MgO and CaO.

	MgO		CaO	
	B1 optimal	Fully optimal	B1 optimal	Fully optimal
$\Delta U_8$ (kJ mol <sup>-1</sup> )	177.3	87.2	64.4	64.1
$\Delta U_4$ (kJ mol <sup>-1</sup> )	55.4	63.3	140.0	123.2

The three types of correlation contribution, the  $V_{sXY}^{corr}(x_{XY}R)$ ,  $E_{re}^{corr}(R)$  and the dispersive attractions, all act to reduce the energies of structures of higher  $n_{CA}$  relative to those of lower coordination for fixed  $R$ . This shows that all these terms contribute positively to  $\Delta U_4$  but negatively to  $\Delta U_8$ . The  $V_{sXY}^{corr}(x_{XY}R)$  contribute negatively to  $U_L^{B2}(R) - U_L^{B1}(R)$  because each of these interactions is attractive; not only are there more cation–anion nearest neighbours in the B2 structure but also the closest anion–anion separation in this structure is much less than in the B1 material at the same  $R$ .  $E_{re}^{corr}(R)$  contributes negatively to  $\Delta U_8$  because the more compact anion charge distribution in the B2 phase causes  $E_{re}^{corr}(R)$

to be more negative than in the B1 structure at the same  $R$ . The total dispersive attraction in the B2 structure is greater at any  $R$  than in the B1 phase as illustrated by values of  $U_{disp}^{B2}(R) - U_{disp}^{B1}(R)$  of  $-34 \text{ kJ mol}^{-1}$  and  $-60 \text{ kJ mol}^{-1}$  for MgO and CaO at  $R = 3.981 \text{ au}$  and  $4.544 \text{ au}$ , respectively. The negative contributions to  $\Delta U_8$  from all three correlation effects show that each crystal Hartree–Fock prediction [18] is an upper bound to  $\Delta U_8$  because electron correlation is not included in this approach.

**Table 14.** Comparison of predictions for energy differences  $\Delta U_8$  between the B1 and B2 phases. The abbreviations are as in table 11.

		$\Delta U_8 \text{ (kJ mol}^{-1}\text{)}$						
		Crystal HF [18]	LAPW [20] local density	Pseudopotential		Density functional		
Fully optimal, present	local density [19]			KKR [54]	[11]	[21]	[12]	
MgO	87.2	170.7	127.4	145.3	70.9	186.0	193.5	195.9
CaO	64.1	111.0	75.3				138.1	138.1

The LAPW computations use a local correlation energy functional, thus implicitly including the contributions  $V_{sXY}^{corr}(x_{XY}R)$ . Although some account of  $E_{re}^{corr}(R)$  is implicit, this is almost certainly underestimated because LAPW computations do not include the scaling factor of roughly two which must be introduced [23] if  $E_{re}^{corr}(R)$  is to be accurately predicted by local-density-functional theory. The use of a local correlation functional causes the LAPW method to predict the total correlation energy of two non-overlapping ions at a finite internuclear separation to be identical with the value of this total when the inter-nuclear separation is infinite. This shows that the LAPW method misses entirely the dispersive attraction between two ions whose inter-nuclear separation is not so short that their electron densities overlap appreciably. Furthermore purely theoretical arguments [34, 55] and computational evidence [22, 56] indicate that use of a local correlation functional misses almost entirely the dispersive attraction between a pair of ions even when their separation is sufficiently small that the overlap of their wavefunctions significantly reduces the standard long-range multi-polar form [57] of this attraction. The inter-ionic dispersive attractions are thus almost completely omitted by LAPW theory at all inter-ionic distances which explains why its predictions for  $\Delta U_8$  are greater than those of the present method.

The results (table 14) headed Density functional were derived using density functional theories [11, 12, 21] which not only were based on the same full ionicity assumption made here but also included the terms  $V_{sXY}^{corr}(x_{XY}R)$  as well as considering in [11, 21] the dispersive attractions. However, despite the inclusion of these correlation terms, all these theories predicted  $\Delta U_8$ -values greater than those of the crystal Hartree–Fock method. This shows, when taken in conjunction with the evidence that MgO and CaO are essentially fully ionic, that these density functional theories must be judged to be inadequate. Since there are significant differences between the computations of [12] and those of [21], the similarity of their predictions is fortuitous.

Electron correlation is not properly considered in either the crystal Hartree–Fock or the LAPW methods whilst the density functional theories [11, 12, 21] are not adequate. It would thus appear that the present fully optimal method currently provides the most trustworthy predictions for  $\Delta U_8$ .

#### 4.2. The role of oxide ion compression in the B1–B3 and B1–B2 energy differences

The density functional theories [11, 12, 21] not only significantly overestimate  $\Delta U_8$  but also almost certainly underestimate  $\Delta U_4$ . Thus, for MgO and CaO, the predictions [21] for  $\Delta U_4$  are much less (table 15) than the present results. In particular the prediction [21] of  $5.3 \text{ kJ mol}^{-1}$  for  $\Delta U_4$  for MgO would appear to be small for an energy difference between the ground state and a phase for which there is no experimental evidence. This suspicion that the  $\Delta U_4$  results of [21] are too small is corroborated by the erroneous prediction [21] that the B3 phase of LiF lies lower in energy than its experimentally observed B1 structure. These difficulties with the density functional predictions of  $\Delta U_4$ , which have been previously recognized and discussed [21], as well as the overestimations of  $\Delta U_8$  uncovered here are different manifestations of the more general problem that the theories [11, 12, 21] consistently underestimate the stability of structures of higher  $n_{CA}$ .

**Table 15.** Comparison of predictions for energy differences  $\Delta U_4$  between the B1 and B3 phases.

	$\Delta U_4$ (kJ mol <sup>-1</sup> )	
	Present fully optimal	Density functional [21]
MgO	63.3	5.3
CaO	123.2	29.1

The theories [11, 12, 21] differ from the present RIP calculations in three respects, firstly in their evaluation of the uncorrelated interactions  $V_{sXY}^0(x_{XY}R)$ , secondly in taking  $E_{re}^{corr}(R)$  to be a constant independent of both  $R$  and phase and thirdly in their description of the in-crystal environment of the  $O^{2-}$  ion. Although evaluation of the  $V_{sXY}^0(x_{XY}R)$ -values by using density functional theory rather than computing them exactly with the RIP program must introduce some inaccuracies [34, 51], there is evidence [22, 58] that the interaction of two ions having a  $p^6$  outermost electronic configuration is described reasonably well by the former. This suggests that the difficulties with the computations [11, 12, 21] do not arise primarily from their mode of evaluating the  $V_{sXY}^0(x_{XY}R)$ .

The assumption of constant  $E_{re}^{corr}(R)$  misses contributions to  $\Delta U_4$  and  $\Delta U_8$  arising from the increases in the magnitude of  $E_{re}^{corr}(R)$  that occur on increasing  $n_{CA}$  at fixed  $R$ , thereby spuriously tending to favour structures of lower  $n_{CA}$ . However, for both  $\Delta U_8$  for MgO and CaO and  $\Delta U_4$  for LiF, the inaccuracies introduced by this assumption are too small to account for the difficulties in the computations [11, 12, 21]. Thus for MgO at  $R = 3.981 \text{ au}$  and for CaO at  $R = 4.544 \text{ au}$ ,  $E_{re}^{B2corr}(R) - E_{re}^{B1corr}(R)$  has values of  $-7.4 \text{ kJ mol}^{-1}$  and  $-7.8 \text{ kJ mol}^{-1}$ , respectively. For a halide, as the total rearrangement energy  $E_{re}(R)$  is defined as the difference between the energy of a singly charged in-crystal anion and that of the free singly charged anion, it is much smaller than for oxides. Consequently the magnitudes of the  $E_{re}^{corr}(R)$  are also greatly diminished as shown both by the ODMFS model prediction of  $-8.6 \text{ kJ mol}^{-1}$  [36] for  $\text{CaF}_2$  at  $R = 4.5 \text{ au}$  near the experimental  $R_e$  of  $4.448 \text{ au}$  [59] and by the OEMFS result of  $-6.7 \text{ kJ mol}^{-1}$  for the B1 phase of LiF at its  $R_e$  of  $3.7965 \text{ au}$  [60]. These values contrast strongly with the  $E_{re}^{corr}(R_e)$  for oxides which are typically some  $-200 \text{ kJ mol}^{-1}$  to  $-300 \text{ kJ mol}^{-1}$ . The differences between the  $E_{re}^{corr}(R)$  in different phases of the same halide are much less than the individual terms and thus too small to account for the erroneous prediction [21] of a ground B3 phase for LiF. For MgO and CaO the present predictions for  $E_{re}^{B3corr}(R) - E_{re}^{B1corr}(R)$  of  $10.3 \text{ kJ mol}^{-1}$  and

9.9 kJ mol<sup>-1</sup> at  $R$ -values of 3.981 au and 4.544 au, respectively, show that the constant- $E_{re}^{corr}(R)$  assumption was not primarily responsible for the previous underestimation [21] of  $\Delta U_4$ . Nevertheless these correlation contributions are comparable with the entire  $\Delta U_4$ -values predicted by the calculations [21], even exceeding the latter for MgO.

The calculations in [11, 12, 21] differ from the present computations in using  $F_{env}^{(0)}(r_a; R)$  constructed by distributing a charge equal to the negative of the anion charge over the surface of a sphere. In the Watson–Madelung (WM) model [23, 34], used in [11], the sphere radius is chosen such that  $F_{env}^{(0)}(r_a; R)$  reduces at small  $r_a$  to the potential generated by the point charge lattice with spacing  $R$ . This potential and the closely related potentials of [12, 21] not only rise much less rapidly from the constant value at small  $r_a$  than the OEMFS potentials (3) do but also are, unlike (3), nowhere positive. Consequently the OEMFS model yields anions more contracted than those produced from the potentials in [11, 12, 21]. Furthermore RIP computations for MgO and CaO [23], UO<sub>2</sub> [31] and CaF<sub>2</sub> [36] have shown that using the less compressed anions produced by the latter type of environmental potential significantly underestimates the crystal cohesion, predicting values of  $D_e$  that are too small and of  $R_e$  that are too large. Computations using insufficiently compressed anions underestimate  $E_{re}(R)$  whilst overestimating  $V_{sCA}(R)$ . For example, for the B1 phase of CaO, use of the WM model predicts an  $E_{re}(4.544)$  smaller by some 300 kJ mol<sup>-1</sup> and a  $V_{sCA}(4.544)$  repulsion 66 kJ mol<sup>-1</sup> greater than the corresponding OEMFS results. The OEMFS prediction for  $V_{sCA}(R)$  is only slightly more than half the WM result. In the approximation in which both  $E_{re}(R)$  and  $V_{sCA}(R)$  are taken to be independent of crystal structure and yet still dependent on  $R$ ,  $E_{re}(R)$  cancels out from an energy difference such as  $U_L^{B2}(R) - U_L^{B1}(R)$  which then depends solely on the interplay between the Madelung terms, the dispersion and the short-range repulsions of which  $V_{sCA}(R)$  is by far the most important. This shows, in the approximation of phase-independent  $E_{re}(R)$  and  $V_{sCA}(R)$ , that the energies of phases of higher  $n_{CA}$  will be overestimated when compared with those of lower coordination if one uses an environmental potential which produces insufficiently compressed anion wavefunctions and hence values of  $V_{sCA}(R)$  that are too large. These excessive repulsions are of exactly the right size to explain why the theories in [11, 12, 21] predict  $\Delta U_8$ -values about 100 kJ mol<sup>-1</sup> greater than those derived from the present computations. Thus, for example, the 66 kJ mol<sup>-1</sup> overestimation of  $V_{sCA}(4.544)$  by the WM model for CaO introduces a spurious extra contribution of 132 kJ mol<sup>-1</sup> into its prediction of  $U_L^{B2}(4.544) - U_L^{B1}(4.544)$ . Even if the approximation of phase-independent  $E_{re}(R)$  and  $V_{sCA}(R)$  is removed, it is clear that structures of higher coordination number will still be spuriously disfavoured if the environmental potential is insufficiently compressive and cannot fully describe the adjustment of the anion to its in-crystal environment.

The report of the density functional theory results [21] examined three possible explanations for the underestimation of  $\Delta U_4$  including the suggestion that the WM environmental model fails to produce sufficiently compressed anion wavefunctions. However, all these three explanations were dismissed, possible inadequacies of the WM model being discounted on the grounds that the density functional computations yielded good predictions for the cohesive properties of the B1 phase. The present results and discussion reverse this latter conclusion because it has been shown that most of the difficulties with the density functional theories [11, 12, 21] do actually originate from using environmental potentials, such as the WM model, which fail to describe fully the confining nature of the in-crystal environment experienced by an anion electron.

## 5. Conclusion

The B2 and B3 phases of magnesium and calcium oxides have been investigated using a fully ionic model in which the total electronic wavefunction of the crystal is written as an anti-symmetrized product of individual ion wavefunctions each of which is spherically symmetric and contains an integral number of electrons, ten for the  $O^{2-}$  ion. The major and uncorrelated portions of the two-body inter-ionic interactions, computed with the RIP, are exact, once the wavefunctions for the interacting ions are given. The reliability of these results was ensured by using one of the two most sophisticated models currently available, namely the OEMFS model, to describe the in-crystal  $O^{2-}$  ions. The different types of electron correlation contribution to the crystal cohesion are too important to ignore and were therefore considered. The inter-ionic dispersive attractions were evaluated taking account of the damping of these interactions from their standard long-range multi-polar forms when the overlap of the wavefunctions of the interacting ions ceases to be negligible. A local-density approximation to density functional theory was used to evaluate the correlation contributions to both the short-range two-body inter-ionic interactions and the rearrangement energy needed to convert a free  $O^-$  ion into an in-crystal  $O^{2-}$  ion. The excellent agreement between experiment and the cohesive properties of the B1 phases of MgO and CaO predicted [23] from the theory incorporating all these refinements is evidence for the reliability of the present new predictions for the cohesive properties of the B2 and B3 phases. Four main conclusions emerge from the present investigation.

The first conclusion emerges from the finding that, for a fixed cation–anion inter-nuclear separation  $R$ , the  $O^{2-}$  ion becomes increasingly compressed with increasing coordination number. This is manifested by the increase in oxide rearrangement energy  $E_{re}(R)$  and decrease in closest cation–anion short-range two-body interaction  $V_{sCA}(R)$  on passing from the B3 through the B1 to the B2 phase. These structural dependences are appreciable, showing that they cannot be neglected if the energy differences  $\Delta U_4$  and  $\Delta U_8$  between the ground B1 phase and the B2 and B3 phases, respectively, are to be reliably predicted. The present *ab-initio* results for the two-body potentials and rearrangement energies provided the data for the construction and testing of the compressible ion model [24]. After parametrizing from only the results for the B1 phase, this model reproduced the significantly different *ab-initio* predictions for the rearrangement energies and two-body potentials in the B2 and B3 phases of both MgO and CaO without invoking any of the *ab-initio* data for the latter two phases. This provides the evidence for the reliability of the compressible ion model [24] that is required before it can be exploited to study the much wider range of properties of ionic assembles having nuclear geometries of lower than cubic symmetry.

The second conclusion of the present paper is that, in the equilibrium geometries of the three phases, the anion becomes less compressed as the coordination number increases except when passing from the B3 to the B1 phase of CaO. These expansions arise because the equilibrium cation–anion separation  $R_e$  always increases with increasing coordination number. In all the cases, except for the transition from the B3 to the B1 phase of CaO, the tendency of structures of higher coordination number to produce more compressive and confining environmental potentials  $F_{env}^{(0)}(r_a; R)$  and hence more compressed anions is more than outweighed by the reduction in the confining tendencies of  $F_{env}^{(0)}(r_a; R)$  produced by the increase in  $R$ .

The third conclusion from the present work is that previous computations have overestimated the energy differences  $\Delta U_8$  between the B2 and B1 phases whilst underestimating the energy differences  $\Delta U_4$  between the B3 and B1 phases. Predictions for  $\Delta U_8$  that are too high result from the computations [19, 20] based on the LAPW method

principally because these miss almost entirely the inter-ionic dispersive attractions. Even though the density functional computations [11, 21] based on the same ionic model as the present approach also included dispersion, the former computations overestimated  $\Delta U_8$  partly because the structural dependence of  $E_{re}^{corr}(R)$  was ignored but mainly because the model used to describe the environmental potential fails to generate sufficiently compressed in-crystal  $O^{2-}$  wavefunctions. These deficiencies also explain the apparent underestimation of  $\Delta U_4$  by the density functional computations [21].

The fourth conclusion of the present study is that the energy differences between the different crystal phases cannot be reliably predicted unless an accurate model is used for the environmental potential  $F_{env}^{(0)}(r_a; R)$  acting on the in-crystal oxide ion electrons. Whilst the OEMFS model for  $F_{env}^{(0)}(r_a; R)$  used in the present computations is sufficiently realistic, this is not the case for previous environmental potentials generated by distributing two units of positive charge over the surface of a sphere. It has already been shown [23] that models of the latter type fail to produce sufficiently compressed  $O^{2-}$  wavefunctions and hence cannot accurately predict the cohesive properties of individual phases. Here it has been further shown that the use of insufficiently compressed  $O^{2-}$  wavefunctions will spuriously tend to disfavour structures of higher coordination number. The employment of such wavefunctions is at least a major and most probably the principal cause of the difficulties with the density functional computations [11, 12, 21].

## Appendix

The contributions of electron correlation to both the rearrangement energy and the two-body inter-ionic potentials are responsible for the apparently non-variational results in table 9 for the B3 phase of MgO. This is shown by predicting the properties of the B3 phase from the cohesive energy function  $U_L^0(R) + U_{disp}(R)$  which excludes all those correlation contributions which differ between the B1 optimal and the fully optimal approaches. The B1 optimal method then predicts  $D_{e-}$ ,  $R_{e-}$  and  $B$ -values of  $2716 \text{ kJ mol}^{-1}$ ,  $3.890 \text{ au}$  and  $13.8 \times 10^{10} \text{ N m}^{-2}$  compared with those of  $2719 \text{ kJ mol}^{-1}$ ,  $3.832 \text{ au}$  and  $13.4 \times 10^{10} \text{ N m}^{-2}$  in the fully optimal approach which thus predicts greater cohesion in accordance with the variation principle. For the B3 phase at each  $R$ , the fully optimal method produces a less compact  $O^{2-}$  wavefunction than the B1 optimal approach which causes the magnitude of  $E_{re}^{corr}(R)$  in the former to be less than in the latter. This reduction in  $|E_{re}^{corr}(R)|$  therefore tends to increase the cohesion predicted by the B1 optimal approach when compared with the fully optimal method. For any  $R$ , the fully optimal approach yields a negative term  $V_{sCA}^{corr}(R)$  of greater magnitude than the B1 optimal method because the more compact  $O^{2-}$  wavefunction produced by the latter method overlaps less with the cation orbitals than does the anion wavefunction generated by the fully optimal method. Although this effect will tend to increase the cohesion predicted by the fully optimal method, it is more than outweighed by the contrary tendency of the term  $E_{re}^{corr}(R)$  with the result that the introduction of electron correlation will tend to increase the cohesion predicted by the B1 optimal method when compared with the fully optimal approach. Thus, for example at  $R = 3.981 \text{ au}$ , the B1 optimal approach yields an  $E_{re}^{corr}(3.981)$ -value more negative by  $10.3 \text{ kJ mol}^{-1}$  compared with the fully optimal method whilst the former predicts a value for  $4V_{sCA}^{corr}(3.981)$  that is less negative than that produced by the fully optimal approach by just  $1.5 \text{ kJ mol}^{-1}$ . Although the introduction of these correlation terms has only favoured the B1 optimal method by  $8.8 \text{ kJ mol}^{-1}$ , the very small differences between the uncorrelated  $U_L^0(R)$  functions produced by the two methods causes the introduction of these correlation terms to reverse the order of the cohesive energies predicted by these two methods for the case of MgO B3 phase.



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