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Quantum-mechanical calculation of the solid-state equilibrium $MgO+\alpha\text{-}Al_2O_3 \rightleftarrows MgAl_2O_4$ (spinel) versus pressure

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The ground-state crystal energies of cubic $MgAl_2O_4$ (spinel) and MgO (periclase) and of rhombohedral α-Al_2O_3 (corundum) have been calculated at different volumes, relaxing the corresponding structures, by all-electron periodic Hartree-Fock methods (CRYSTAL program). Basis sets of contracted Gaussian-type functions are employed for the 18 atomic (including *d*) orbitals representing each of the Mg, Al, and O atoms. Mulliken net atomic charges $z_{Mg}=1.86|e|$ (MgO), $z_{Al}=2.30|e|$ (α-Al_2O_3), $z_{Mg}=1.74|e|$, and $z_{Al}=2.24|e|$ (spinel) are obtained. The elastic bulk modulus, the Murnaghan equation of state $p(V)$ at the athermal limit, the Mg-O and Al-O bond compressibilities, and the binding energy have been derived for each phase (and the elastic constants C_{11} and C_{12} for spinel only). Comparison with existing experimental data is discussed. The enthalpy change for spinel decomposition into the simple oxides has been computed as a function of pressure, including a correction for the electron correlation energy based on local-density-functional theory. A decomposition pressure of 11 GPa at $T=0$ K is predicted, against values of 8 and 13 GPa derived from experimental thermodynamic data and from direct compression experiments, respectively.

INTRODUCTION

The crystalline phases of the Mg-Al-O system play a well-known role in solid-state chemistry and physics and in the geosciences. In particular, MgO (periclase, cubic $Fm\bar{3}m$, $Z=4$), α-Al_2O_3 (α-alumina or corundum, rhombohedral $R\bar{3}c$, $Z=6$ in the hexagonal setting), and $MgAl_2O_4$ (spinel, cubic $Fd3m$, $Z=8$) are important materials for heterogeneous chemical catalysis, for optics and laser technology, and in the ceramic industry. Further, as simple high-density oxides of very abundant chemical elements on earth, they are believed to be present in large quantities in the deep regions of our planet (earth's mantle).[1]

Several theoretical investigations of MgO are reported in the literature,[2-6] dealing with the electronic structure and relative stabilities of its NaCl-, CsCl-, and NiAs-type phases. The modified electron-gas (MEG) model,[2] the local-density-functional approach with pseudopotentials,[3,4] and the *ab initio* all-electron periodic Hartree-Fock method[5,6] have been employed. Much less studied is α-alumina, for which *ab initio* work is given by cluster models[7-9] and by a periodic Hartree-Fock (HF) study[10] using a very simple electron basis set of 6-21G molecular type. Spinel, on the other hand, was investigated by the HF approach with pseudopotentials.[11] All three compounds were dealt with recently[12] using an all-electron local-density-approximation (LDA) scheme, with emphasis on band structures and optical-absorption spectra.

The main aim of this work is to reconsider the $MgAl_2O_4$, α-Al_2O_3, and MgO systems with the all-electron HF method, supplemented by *a posteriori* corrections for the electron correlation energy[13-15] based on the local-density-functional formalism. The stress is here on total energy and related volume-dependent behavior, rather than on optical features. An expanded basis set is developed and used consistently for all three phases, so that the relative energies and equation-of-state properties can be calculated and assessed reliably. This approach has already proved successful for studying ternary systems with similar chemical compositions.[16,17] Further, an *ab initio* calculation of the chemical equilibrium $MgAl_2O_4 \rightleftarrows MgO+\alpha\text{-}Al_2O_3$ at variable pressure and $T=0$ K is attempted, with the aim of checking the experimental results concerning spinel decomposition at high pressure.[1] This can lead to promising applications of quantum-mechanical theoretical methods in the assessment of chemical behavior of solid systems.

ELECTRON BASIS SET AND CHEMICAL BONDING

All quantum-mechanical calculations were performed with the CRYSTAL program,[18] based on the all-electron *ab initio* periodic Hartree-Fock method within the linear combination of atomic orbitals formalism. Every atomic orbital is expressed as the product of an angular real solid harmonic function by a linear combination of radial Gaussian-type functions. Each of the Mg, Al, and O atoms is represented by 18 atomic orbitals, and the corresponding basis sets (Table I) can be denoted[19] as 8-511G*, 8-511G*, and 8-411G*, respectively. As far as the inner shells 1*s*, 2*sp*, and 3*sp* are concerned, the basis sets of Mg and O correspond to those reported in Ref. 6 and therein used for MgO, while for Al all exponents and coefficients

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TABLE I. Exponents (bohr^{-2}) and contraction coefficients of the Gaussian functions adopted for the present study. The contraction coefficients multiply individually normalized Gaussians. $y[\pm z]$ stands for $y \times 10^{\pm z}$. (a), (b), and (c) correspond to MgO, α-Al_2O_3, and $MgAl_2O_4$, respectively.

Shell		Magnesium Coefficients			Aluminum Coefficients			Oxygen Coefficients	
type	Exponents	*s*	*p,d*	Exponents	*s*	*p,d*	Exponents	*s*	*p,d*
1*s*	6.837[+4]	2.226[−4]		7.051[+4]	2.226[−4]		8.020[+3]	1.080[−3]	
	9.699[+3]	1.898[−3]		1.008[+4]	1.900[−3]		1.338[+3]	8.040[−3]	
	2.041[+3]	1.105[−2]		2.131[+3]	1.110[−2]		2.554[+2]	5.324[−2]	
	5.299[+2]	5.006[−2]		5.475[+2]	5.090[−2]		6.922[+1]	1.681[−1]	
	1.592[+2]	1.691[−1]		1.631[+2]	1.697[−1]		2.390[+1]	3.581[−1]	
	5.468[+1]	3.670[−1]		5.448[+1]	3.688[−1]		9.264	3.855[−1]	
	2.124[+1]	4.004[−1]		1.905[+1]	3.546[−1]		3.851	1.468[−1]	
	8.746	1.499[−1]		5.402	4.430[−2]		1.212	7.280[−2]	
2*sp*	1.568[+2]	−6.240[−3]	7.720[−3]	1.396[+2]	−1.120[−2]	8.900[−3]	4.943[+1]	−8.830[−3]	9.580[−3]
	3.103[+1]	−7.882[−2]	6.427[−2]	3.253[+1]	−1.136[−1]	6.060[−2]	1.047[+1]	−9.150[−2]	6.960[−2]
	9.645	−7.992[−2]	2.104[−1]	1.023[+1]	−7.110[−2]	1.974[−1]	3.235	−4.020[−2]	2.065[−1]
	3.711	2.906[−1]	3.431[−1]	3.810	5.269[−1]	3.186[−1]	1.217	3.790[−1]	3.470[−1]
	1.611	5.716[−1]	3.735[−1]	1.517	7.675[−1]	2.995[−1]			
3*sp*	0.680	1.0	1.0	0.59	1.0	1.0	0.479	1.0	1.0
4*sp*	0.280	1.0	1.0(a)				0.195	1.0	1.0 (a)
				0.350	1.0	1.0 (b)	0.200	1.0	1.0 (b)
	0.280	1.0	1.0 (c)	0.280	1.0	1.0 (c)	0.206	1.0	1.0 (c)
d	0.650		1.0 (a)				0.450		1.0 (a)
				0.510		1.0 (b)	0.570		1.0 (b)
	0.540		1.0 (c)	0.470		1.0 (c)	0.470		1.0 (c)

of the Gaussian functions were optimized in this work by minimizing the energy of the isolated atom. The exponents of the outer $4sp$ and of the d shells of all three atoms, on the other hand, were optimized individually for each of the three phases MgO, α-$\mathrm{Al_2O_3}$, and $\mathrm{MgAl_2O_4}$ by minimization of the corresponding total crystal energies. Small differences are obtained (Table I), corresponding to minor variations of chemical bonding in each substance. In particular, MgO and α-alumina seem to have slightly more diffuse and contracted atomic electron clouds, respectively, with spinel in an intermediate position. Including d orbitals in the atomic basis sets (especially for Al and O) proved to be effective in lowering the energy, and influenced also the calculated equation-of-state behavior, particularly for α-alumina and spinel.

Mulliken population analyses were performed on the Hartree-Fock wave functions of the three compounds, in order to compare the respective electron-distribution features. The results of this type of analysis are well known to be affected by some degree of arbitrariness, related to basis-set dependencies; however, this drawback is overcome where trends in related compounds with consistently designed basis sets are investigated, as in the present case. Mulliken net atomic charges, d-shell atomic populations, and bond populations for atomic pairs are reported in Table II. The importance of d orbitals on Al (less on Mg and O) is confirmed by the corresponding values of electron population. A strong electron transfer in the Al-O bond is shown clearly by the significant corresponding population and by the deviation of z(Al) from its ideal ionic value $+3$. These effects are observed both for spinel and for α-alumina, and show a considerable covalent contribution to Al-O bonding. On the other hand, the Mg-O bond features are quite different in MgO and spinel, where Mg shows octahedral and tetrahedral coordination, respectively. The Mg net charge is substantially smaller and the Mg-O bond population larger in the latter than in the former compound, indicating a more covalent bonding (consistent with the lower coordination number). Negative bond-population parameters for O-O are observed in all cases and are related to strong repulsion of close-packed oxygen atoms. These results compare reasonably with those obtained in the local-density-approximation study[12] ($\mathrm{Mg}^{1.83+}\mathrm{O}^{1.83-}$, $\mathrm{Al}_2^{2.63+}\mathrm{O}_3^{1.75-}$, $\mathrm{Mg}^{1.79+}\mathrm{Al}_2^{2.63+}\mathrm{O}_4^{1.76-}$), where, however, the charges were derived by numerical integration of the electron density around the atoms, and the atomic basis sets were not optimized variationally as in our case. Such computational features can explain the slightly more ionic character of the Al-O bond resulting from the LDA calculation.

The distribution of electron eigenstates was determined by computing the density of states (DOS) for all three crystals for the energy range (including the valence-conduction band gap) shown in Fig. 1. By projecting the total DOS onto contributions of specific atomic orbitals, using a Mulliken partition scheme, the upper and lower valence subbands of each compound in Fig. 1 can be assigned to p and s states of oxygen, respectively. It is interesting to remark that the energy width of the p(O) band decreases from α-alumina to spinel to MgO, consistently with the increasing ionicity due to replacement of Al by Mg. The conduction bands of all phases are contributed by both s metal and p oxygen states. LDA results[12] are substantially confirmed, apart from the band gaps, which are as usual overestimated by the Hartree-Fock calculation.

TABLE II. Mulliken net charges (z) and d-shell populations for individual atoms, and bond populations for atomic pair overlap in MgO, α-$\mathrm{Al_2O_3}$, and $\mathrm{MgAl_2O_4}$ (in units of $|e|$). The multiplicity of O-O pairs is shown in parentheses.

	MgO	α-$\mathrm{Al_2O_3}$	$\mathrm{MgAl_2O_4}$
z(Mg)	1.856		1.742
z(Al)		2.297	2.235
z(O)	-1.856	-1.531	-1.553
$q(d_{\mathrm{Mg}})$	0.033		0.058
$q(d_{\mathrm{Al}})$		0.180	0.198
$q(d_{\mathrm{O}})$	0.008	0.010	0.012
q(Mg-O)	0.006		0.034
q(Al-O)		0.098	0.091
q(O-O)	-0.014 (12)	-0.061 (2)	-0.057 (3)
		-0.030 (2)	-0.010 (6)
		-0.028 (4)	0.000 (3)
		-0.011 (4)	

EQUATIONS OF STATE AT 0 K

For each crystal phase, the dependence of the lattice constants and atomic positions on volume or pressure was calculated by the following procedure. Eight values of the unit-cell volume were selected, corresponding to relative changes between -10% and $+4\%$ with respect to the experimental volume. The total HF ground-state energy was computed for all of them, obtaining the unrelaxed energy $E_u(V)$. For each of the volume values of

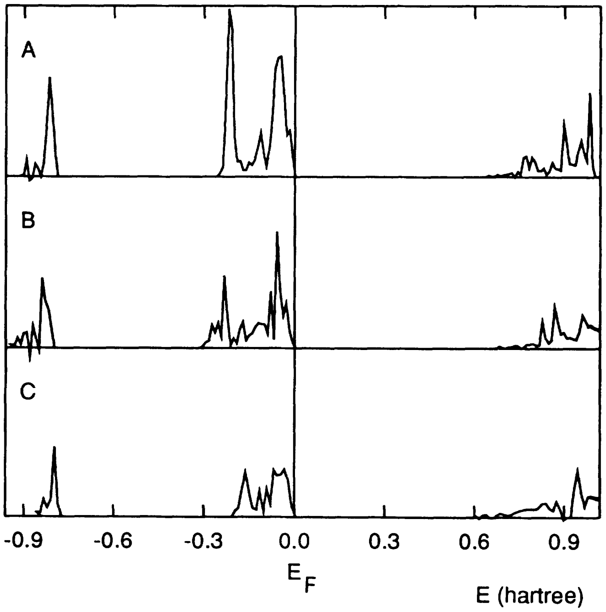

FIG. 1. Total densities of electronic states (DOS's) of $\mathrm{MgAl_2O_4}$ (A), α-$\mathrm{Al_2O_3}$ (B), and MgO (C).

TABLE III. Unit-cell edges (Å), volume per formula unit (Å^3), atomic fractional coordinates, bond distances (Å), bulk modulus (GPa) and its pressure derivative for periclase, corundum, and spinel, and elastic constants (GPa) of spinel. Computed (least-energy) values, experimental values extrapolated to 0 K from literature data (see the text for references), and percentage errors are reported on the first, second (in parentheses), and third lines, respectively, for each quantity.

	MgO	α-Al_2O_3	$MgAl_2O_4$
a_0	4.191	4.742	8.056
	(4.195)	(4.750)	(8.060)
	−0.1%	−0.2%	−0.1%
c_0		12.936	
		(12.96)	
		−0.2%	
V_0	18.40	42.00	65.34
	(18.5)	(42.2)	(65.5)
	−0.5%	−0.5%	−0.2%
x(O)		0.305 71	0.263 78
		(0.306 24)	(0.262 4)
		−0.2%	+0.5%
z(Al)		0.353 38	
		(0.352 16)	
		+0.3%	
$r^0_{\text{Mg-O}}$	2.095		1.939
	(2.098)		(1.918)
	−0.1%		+1.1%
$r^0_{\text{Al-O}}$		1.842	1.908
		(1.851)	(1.920)
		−0.5%	−0.6%
		1.973	
		(1.967)	
		+0.3%	
K_0	180	287	227
	(168)	(261)	(206)
	+7%	+10%	+10%
K'	2.8	3.8	3.4
	(4.1)	(4.3)	(4)
	−32%	−12%	−15%
C_{11}	326		332
	(314)		(296)
	+4%		+12%
C_{12}	111		174
	(94)		(161)
	+18%		+8%

$MgAl_2O_4$ (and for −8%, −4%, 0%, and +4% only of α-Al_2O_3) an explicit structure relaxation was allowed. The independent atomic fractional coordinates x_i not fixed by symmetry [x(O) in the spinel case, and x(O),z(Al) for α-alumina] and, in the α-Al_2O_3 case, the $q=c/a$ lattice ratio as well, were let change according to an appropriate grid of points, keeping V constant and computing the energy for all points. The numerical minimum of the $E(x(\text{O}))$ or $E(x(\text{O}),z(\text{Al}),q)$ function was searched for with the help of least-squares polynomial approximation techniques, obtaining (i) the relaxation energy $\Delta E_r(V)$ and (ii) the dependence on volume of the least-energy structural variables x_i and q for the two phases. Interpolation over V gave results for the four missing values of α-Al_2O_3 corresponding to −10%, −6%, −2%, and +2%. By summing $\Delta E_r(V)$ to $E_u(V)$, in the case of spinel and α-alumina, the total energy $E(V)$ was obtained for the eight V values; for MgO, $E(V)=E_u(V)$.

The $E(V)$ data for each of the three phases MgO, α-Al_2O_3, and $MgAl_2O_4$ were fitted to the Murnaghan equation of state[20]

$$E(V)=K_0V_0\left[\frac{1}{K'(K'-1)}\left[\frac{V_0}{V}\right]^{K'-1}+\frac{1}{K'}\frac{V}{V_0}-\frac{1}{K'-1}\right]+E_0\ ,$$

obtaining the values of V_0 (volume of minimum energy), K_0 (zero-pressure bulk modulus), and K' (pressure derivative of K at $p=0$) reported in Table III, and of E_0 (minimum energy) in Table IV. By substitution of V_0 for V in the least-squares polynomial approximations of $x_o(V)$ (spinel), and $x_o(V)$, $z_{\text{Al}}(V)$, and $q(V)$ (α-alumina), and into the relationships $a=V^{1/3}$ (MgO and spinel), and $a=(2V/\sqrt{3}q)^{1/3}$ and $c=(2q^2V)^{1/3}$ (α-Al_2O_3), the equilibrium zero-pressure values of lattice constants and atomic coordinates were derived (Table III). Results concerning the $r_{\text{Mg-O}}$ and $r_{\text{Al-O}}$ bond distances in the three phases are therein reported, too.

The structural experimental data, reported for comparison in Table III, were obtained by linear extrapolation to the athermal limit ($T=0$ K) of literature results measured by x-ray or neutron diffraction in the range

TABLE IV. Total energies (hartrees) per formula unit for individual atoms and for oxides, and binding energies of oxides. Hartree-Fock values and electron correlation corrections (Ref. 13) are reported. Δ% are the percentage deviations of calculated with respect to experimental data (obtained from thermochemical cycles and data of Table VI).

	HF	Δ%	Corr.	HF+corr.	Δ%	Expt.
E(Mg)	−199.6042		−0.4649	−200.0691		
E(Al)	−241.8607		−0.5062	−242.3669		
E(O)	−74.8012		−0.2727	−75.0739		
E_0(MgO)	−274.6816		−0.8191	−275.5007		
E_0(α-Al_2O_3)	−708.9940		−2.0838	−711.0778		
E_0($MgAl_2O_4$)	−983.6942		−2.8926	−986.5868		
E_B(MgO)	−0.2762	−28.1	−0.0816	−0.3578	−6.8	−0.3841
E_B(Al_2O_3)	−0.8690	−26.4	−0.2534	−1.1224	−5.0	−1.1810
E_B($MgAl_2O_4$)	−1.1638	−25.8	−0.3246	−1.4884	−5.2	−1.5697

300–1300 K. References 21, 22–24, and 25 and 26 pertain to MgO, α-alumina, and spinel, respectively. For the K_0 bulk modulus, linear extrapolations were performed from elastic properties measured at variable temperature, using data from Refs. 27, 28, and 29 for the three phases, respectively. On the other hand, we obtained the values of K' from results of elastic measurements versus pressure in the case of MgO,[30] while for α-alumina[31] and spinel[32] structural data determined at high pressure by x-ray diffraction were employed; in all these cases temperature effects were neglected.

Results reported in Table III show that the computed lattice constants and bond distances of all three phases agree excellently with data from experiment, with relative errors in the range 0.1–1 %. This remarkable success of the periodic Hartree-Fock approximation in reproducing equilibrium structural properties of ionic solids is, however, in a way restricted to compounds of atoms belonging to the first three rows of the periodic system. When heavier atoms are included, errors rise significantly.[17] The elastic bulk modulus at zero pressure K_0 appears to be overestimated by about 10%, as already observed in other similar calculations.[6,16,17] The first pressure derivative of K is an even harder quantity to reproduce, as it is related to third volume derivatives of the energy. We observe in the present cases a systematic underestimate of over 10%; however, the very experimental data of this type are generally subject to a significant uncertainty. On the whole, the solid phases studied here have correct computed volumes, but turn out to be slightly too stiff, yet with a stiffness increasing less than expected with pressure. The amounts of these errors are believed to be very close to the Hartree-Fock limits, in view of the accuracy of the atomic basis sets used.

The present results for α-alumina and spinel can be compared with those of previous HF calculations performed in more approximate ways. For α-Al_2O_3, 6-21G basis sets on Al and O, with comparatively poorer computational conditions, were used, and the structure optimization was carried out independently on each variable in a single step.[10] While the reported unit-cell volume is similar to the present one, slightly larger errors appear for the c/a ratio and for the atomic coordinates. On the other hand, no data were computed for K_0 and K'. In the previous work on spinel,[11] pseudopotentials were employed, instead of all-electron basis sets as in our case. An equilibrium unit-cell edge of 8.01 Å was obtained, significantly shorter than the present value; the error is larger for the bulk modulus (266 GPa), +29% in Ref. 11 against +10% in this study, showing the importance of an all-electron scheme with refined basis sets to reproduce the equation of state satisfactorily. For MgO, our results are very similar to those already found in previous work[5,6] with analogous basis sets.

ELASTIC AND HIGH-PRESSURE BEHAVIOR

The C_{11} elastic constant of spinel was calculated by considering a tetragonal deformation of the lattice (strain along one of the fourfold axes). That requires the symmetry of the crystal structure to be lowered from $Fd3m$ to $I4_1/amd$, so that $x(O)=y(O)\neq z(O)$, and two degrees of freedom instead of one have to be considered for structural relaxation. The relationship $C_{11}=(1/V_0)c^2(\partial^2E/\partial c^2)_{c=a_0}$ was used, and the energy was computed for a number of c values while keeping $a=b$ constant. The two oxygen coordinates were relaxed each time, and the second energy derivative was calculated numerically by polynomial least-squares approximations of the $E(c)$ dependence. A large effect of the structure relaxation on C_{11} is observed; without relaxing the structure, C_{11} would amount to 401 instead of 332 GPa (Table III), with an increase of 21%.

The C_{12} elastic component was derived from the bulk modulus and C_{11} according to $K_0=(C_{11}+2C_{12})/3$, and its value is reported in Table III. On the other hand, C_{44} was not computed because the corresponding deformation would lower the symmetry to rhombohedral, increasing the computational complexity remarkably. The experimental values of C_{11} and C_{12} reported in Table III were obtained by linear extrapolations to 0 K of values measured[29] in the temperature range 300–923 K. A comparison with computed results shows a similar agreement to that obtained for the bulk modulus K_0. For MgO, the computed elastic constants reported in Table III correspond to those already quoted in Ref. 6. For α-alumina, on the other hand, no attempt was made to calculate the elastic constants because of the complexity of structural relaxations involved.

By differentiating the Murnaghan equation $E(V)$, the pressure as a function of volume is obtained,

$$p=-\frac{dE}{dV}=\frac{K_0}{K'}\left[\left(\frac{V_0}{V}\right)^{K'}-1\right].$$

Solving with respect to V, and substituting into all the relations of structural variables versus volume previously obtained, yields the corresponding dependences on pressure. The ratios V/V_0 are shown in Fig. 2 for the three

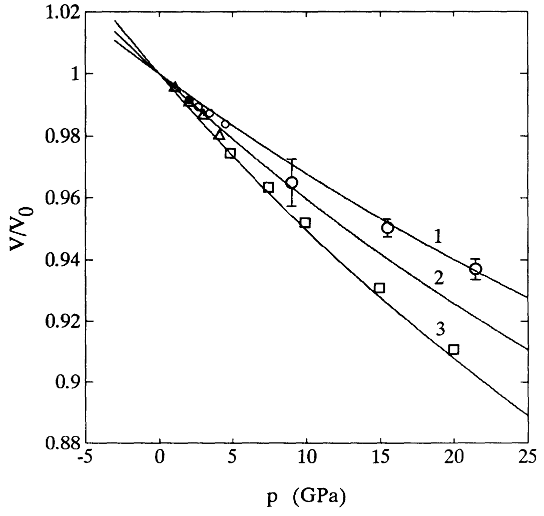

FIG. 2. Calculated V/V_0 ratios against pressure from interpolations of the Murnaghan equation of state for α-alumina (1), spinel (2), and MgO (3). Experimental points [circles (1), triangles (2), and squares (3) for the three phases, respectively] are shown, too; for the references, see the text.

phases, displaying clearly that the compressibility increases along with the ionicity (cf. the discussion of bandwidth above) as Al is replaced by Mg. Experimental points from compression measurements are also reported in Fig. 2 for comparison; data for α-Al_2O_3 come from Refs. 33 (lower pressure) and 34 (higher pressure), while those for spinel and MgO refer to Refs. 32 and 35, respectively. The relevant structural distances versus pressure can be expressed by least-squares parabolic approximations of the type $r/r_0=1+D_1p+D_2p^2$, where r may be a unit-cell edge or a bond length, and r_0 is the corresponding equilibrium ($p=0$) value reported in Table III. The coefficients D_1 and D_2, obtained by least-squares fits, are reported in Table V. $-D_1$ is equal to the bond or cell-edge compressibility. In Figs. 3 and 4 the bond-distance results are plotted against pressure. The Mg-O bonds in octahedral (MgO) and tetrahedral (spinel) coordination, though having substantially different lengths, show the same compressibility. This is larger than that of Al-O bonds in α-alumina and spinel. The compression of the α-Al_2O_3 unit cell is practically isotropic, and corresponds to that of the Al-O bonds. For spinel, the cell-edge compressibility is slightly larger than those of the Mg-O and Al-O bonds, indicating some additional shortening of the O-O contacts, too. The theoretical bond compressibilities reported in Table V could be compared with those derived from x-ray-diffraction structure refinements at variable pressure (up to 4.6 GPa) for spinel[32] and α-alumina.[33] Indeed, such experimental bond distances are affected by fairly large uncertainties (related to those of fractional atomic coordinates); linear regressions vs pressure yield values of 1.6 and 0.9 TPa^{-1} for Al-O in α-alumina and 2.6 and 1.2 TPa^{-1} for Mg-O and Al-O in spinel, respectively. These experimental results seem to be reasonable for spinel, but for α-alumina they show the shorter Al-O bond to be more compressible than the longer one, which does not appear to be realistic.

EQUILIBRIUM OF SPINEL DECOMPOSITION

The binding energies at zero pressure E_B of spinel, α-alumina, and MgO were computed as differences between the total crystal energies per formula unit E_0 and the energies of the constituent isolated atoms. The Hartree-Fock estimates of binding energies are reported in the first column of Table IV. Atomic energies were obtained by using the same basis sets as for the crystal calculations, but supplemented by two more diffuse shells, the exponents of which were optimized. The experimental values of binding energies (last column of Table IV) were derived by appropriate Born-Haber thermochemical cycles, according to the relationship $E_B(\text{expt})=\sum_i [H^0_{a,i}+(H_i^{298}-H_i^0)]+\Delta H_f^{298}-(H^{298}-H^0)-E^0_{\text{vib}}$; the sum is extended to all chemical elements in the formula unit. All values involved are reported in Table VI. Sublima-

TABLE V. Coefficients of the least-squares parabolic approximation $1+D_1p+D_2p^2$ for the pressure dependence of lattice constants and bond lengths of MgO, α-Al_2O_3, and $MgAl_2O_4$.

	D_1 (TPa^{-1})	D_2 (TPa^{-2})
	MgO	
a/a_0	-1.83	12
	α-Al_2O_3	
a/a_0	-1.09	6
c/c_0	-1.29	9
$r_{\text{Al-O}}/r^0_{\text{Al-O}}$	-1.07	5
	-1.26	9
	$MgAl_2O_4$	
a/a_0	-1.45	9
$r_{\text{Mg-O}}/r^0_{\text{Mg-O}}$	-1.81	13
$r_{\text{Al-O}}/r^0_{\text{Al-O}}$	-1.26	7

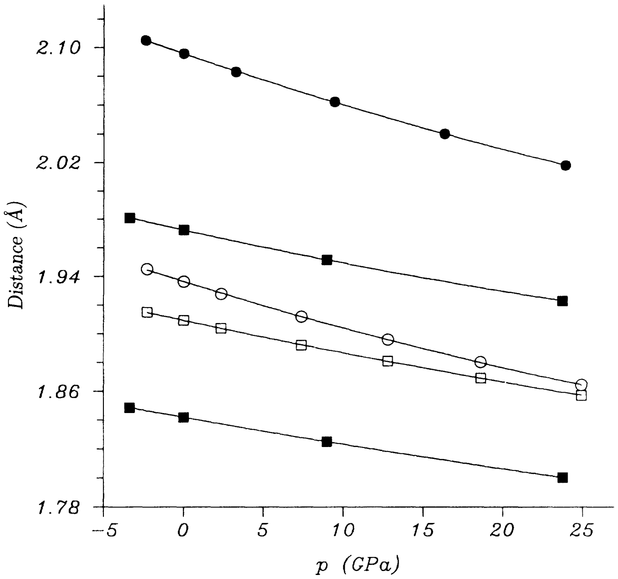

FIG. 3. Calculated Mg-O (circles) and Al-O (squares) distances in spinel (open) and α-Al_2O_3 and MgO (closed symbols) against pressure.

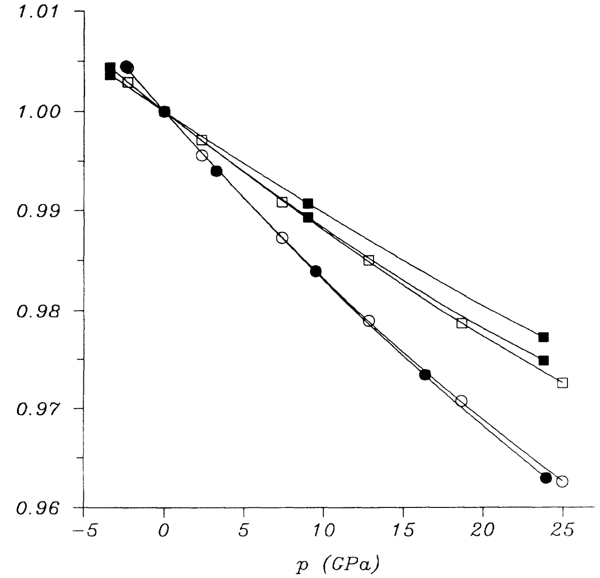

FIG. 4. Calculated bond distances (symbols as in Fig. 3) divided by their equilibrium values (Table III) against pressure.

TABLE VI. Formation (ΔH_f^{298}), heating ($H^{298}-H^0$), and sublimation or dissociation (H_a^0) enthalpies, and zero-point vibrational energies (E_{vib}^0) per formula unit, used in thermochemical cycles yielding the experimental binding energies (Table IV). Units are hartrees. For references, see the text.

	H_a^0	E_{vib}^0	$H^{298}-H^0$	ΔH_f^{298}
Mg	−0.055 79		0.001 90	
Al	−0.123 40		0.001 74	
O	−0.093 99		0.001 65	
MgO		0.006 75	0.001 97	−0.229 16
α-Al_2O_3		0.018 61	0.003 81	−0.638 20
$MgAl_2O_4$		0.021 94	0.005 87	−0.875 71

tion (Mg and Al) and dissociation (O_2) enthalpies H_a^0, heating $H^{298}-H^0$, and formation ΔH_f^{298} enthalpies (except for spinel) were taken from Ref. 36. The heating and formation enthalpies of spinel come from Ref. 37. A particular importance is presented by the vibrational energies E_{vib} at 0 K of all three solids, because they are significant terms in the thermochemical cycles but are not easy to determine with accuracy. An estimate of them was obtained by the Debye model. The Debye temperatures of all three compounds were derived from the elastic constants (extrapolated to 0 K) using Anderson's approximation:[38] 947, 1045, and 880 K were obtained for MgO, α-Al_2O_3, and $MgAl_2O_4$, respectively.

The Hartree-Fock binding energies appear to be underestimated by 26–28 % with respect to experimental values, and this is an expected result. Most of the error, due to neglect of the electron-correlation contribution to energy, can be corrected for by using an *a posteriori* estimate based on density-functional theory.[13,14] The results obtained by the first formula[13] (differing by about 1% from those of the second one[14] for the binding energies) are reported in Table IV. All errors are reduced substantially, from over 0.050–0.012 hartrees/atom, on the average. On the other hand, because of the approximate character of this correction no reliable results can be obtained to account for the correlation contribution to first or second derivatives of the energy with respect to volume. The minimum of the $E(V)$ curve would be shifted toward a too small unit cell, owing to the non-self-consistent nature of the *a posteriori* correction.

A more challenging quantity to compute is the energy of the formation reaction (at 0 K in static conditions) of spinel from the simple Mg and Al oxides, $\Delta E_0 = E_B(MgAl_2O_4) - [E_B(MgO) + E_B(\alpha\text{-}Al_2O_3)]$, as it is a small difference between large numbers. Indeed, the corresponding "experimental" quantity itself is difficult to obtain accurately, also because of the approximations involved in the estimate of the zero-point vibrational energies E_{vib}^0. However, in order to be closer to the experimental situation, we have preferred to do the calculation at 0 K in dynamic conditions, i.e., including the zero-point vibrational contribution $\Delta E_{\text{vib}}^0 = -0.0034$ hartrees (cf. Table VI) in the theoretical ΔE_0 values, which are reported in Table VII. While the HF reaction energy appears to be too large, the correlation-corrected value agrees reasonably with the experimental energy, taking also into account the uncertainty of the ΔE_{vib}^0 quantity included in the theoretical results.

TABLE VII. Volume (Å^3) and energy (hartrees) differences per formula unit at $T=0, p=0$ between $MgAl_2O_4$ and the sum of $MgO + \alpha$-Al_2O_3. The zero-point vibrational contribution $\Delta E_{\text{vib}}^0 = -0.0034$ hartrees has been added to theoretical ΔE_0 values. Pressure (GPa) of the spinel decomposition reaction $MgAl_2O_4 \rightarrow MgO + \alpha$-$Al_2O_3$ at $T=0$ (approximate p_t' and exact p_t values). Theoretical [Hartree-Fock and Hartree-Fock including correlation correction (Ref. 13)] and experimental values are given.

	ΔV_0	ΔE_0	p_t'	p_t
HF	4.94	−0.0220	19.4	20.8
HF+corr.		−0.0116	10.2	10.6
Expt.	4.80	−0.0084	7.7	8.0
Expt.[a]				13.3

[a]Data from compression experiment (15 GPa at 1800 K, see Ref. 1) corrected for cooling to 0 K.

It is also feasible to consider the pressure dependence of the chemical equilibrium $MgAl_2O_4 \rightleftharpoons MgO + \alpha$-$Al_2O_3$. From Table III spinel appears to have a larger molar volume than the sum of those of the simple oxides ($\Delta V_0 > 0$), so that from standard thermodynamics a decomposition reaction of spinel at high pressure can be foreseen. That has in fact been observed to occur above 15 GPa at 1800 K by static-compression experiments.[1] The decomposition pressure of spinel at $T = 1800$ K can be corrected for the cooling down to 0 K, according to the expression $\Delta p_t = (\Delta G^{1800\,\text{K}} - \Delta E_0)/\Delta V_0$. By using the experimental value of -27.07 kJ mol^{-1} $= -0.0103$ hartrees for $\Delta G^{1800\,\text{K}}$ (cf. Ref. 37), and assuming that the temperature change of ΔV is negligible, $\Delta p_t = -1.7$ GPa, and $p_t = 13.3$ GPa is obtained (Table VII). If the enthalpies of all phases are known, p_t can be computed by solving for pressure the equation $\Delta H(p) = E_0 + \int_0^p \Delta V\,dp = 0$. An approximate solution is obtained as $p_t' = -\Delta E_0/\Delta V_0$, by neglecting the pressure dependence of ΔV. The equation is solved exactly by first deriving the explicit pressure dependence of the enthalpy of each phase from its Murnaghan relation $E(V)$,

$$H(p) = E_0 + \frac{K_0 V_0}{K' - 1}\left[\left[\frac{K'}{K_0}p + 1\right]^{1-1/K'} - 1\right].$$

The quantity $\Delta H(p)$ is thus readily obtained by use of the V_0, K_0, and K' parameters reported in Table III for each of the three phases, and of the ΔE_0 values in Table VII, both for experimental and for theoretical data. The equation $\Delta H(p) = 0$ was solved numerically for both sets of results, yielding the p_t values reported in Table VII. It should be noticed that the decomposition pressure consistent with experimental thermodynamic data is significantly smaller than that observed in direct compression measurements. The discrepancy could be due either to inaccuracies of the data or to hysteresis effects responsible, at least in part, for an overestimate of p_t in the compression experiment. As for theoretical results, while the Hartree-Fock p_t value is clearly too large,

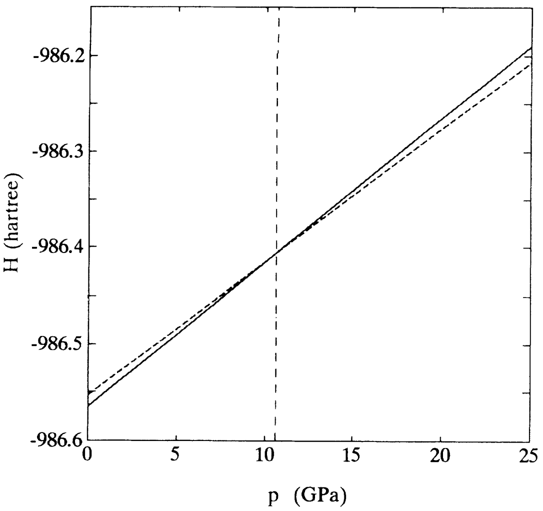

FIG. 5. Calculated enthalpies per formula unit (hartrees) of spinel (full line) and of the assembly MgO+α-Al_2O_3 (dashed line) vs pressure. The electron correlation energy was included.

the decomposition pressure computed with the correlation correction performs surprisingly well, lying just halfway between the two kinds of experimental values. In Fig. 5 the theoretical enthalpies of spinel and of the sum of binary oxides are plotted against pressure, showing clearly that the energy differences involved in the reaction are quite small.

CONCLUSIONS

A full *ab initio* quantum-mechanical treatment has been applied successfully to the study of a solid-state chemical reaction depending on pressure. The equations of state at the athermal limit have been calculated for each of the three compounds involved, $MgAl_2O_4$, α-Al_2O_3, and MgO, including structure relaxations and derivation of the bond-length changes with pressure up to over 20 GPa. In order to reproduce the experimental equilibrium enthalpy change for the decomposition of spinel into the binary oxides, inclusion of an electron-correlation correction and appropriate handling of the zero-point vibrational energies have proved to be very important. The pressure of spinel decomposition is predicted by theoretical results to be 11 GPa at $T=0$ K, in quite reasonable agreement with the 8 (from thermodynamic data) and 13 GPa (from static-compression experiment) observed values.

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