

The stability of polymorphs of MgCl_2 – an ab initio study

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Abstract

Periodic Hartree–Fock calculations show that the layered structures of α - and β - MgCl_2 are stable at the HF level; earlier work has suggested this was not so for β - MgCl_2 . The neglect of correlation leads to a large overestimate of the Cl–Cl interlayer separation and hence of the c lattice parameter. Structures optimised using density functional theory and the same basis set are in better agreement with experiment. α - and β - MgCl_2 are close in energy at HF and DFT levels, and vibrational effects are likely to be important in determining their relative stability. Neglecting possible distorted variants of the more ionic rutile and fluorite structures, we estimate transition pressures of ~ 17 GPa for β - $\text{MgCl}_2 \rightarrow$ rutile and ~ 77 GPa for rutile \rightarrow fluorite. © 1997 Elsevier Science B.V.

1. Introduction

Magnesium chloride exists in several structural modifications and the interconversion between these by milling is important in its action as a catalytic support for titanium halides in the Ziegler–Natta polymerization of stereoregular polyolefins. The most common crystalline form is α - MgCl_2 [1] in which the chlorines form a cubic-close-packed array, with close-packed planes stacked ...ABCABC... along the c -axis. In the β -modification [2] the chlorines are hexagonally close-packed (...ABABAB... along the c -axis), and there is a random sequence of cubic and hexagonal close-packed layers in the δ -form [2]. In

all of these structures Mg atoms are in alternate layers of octahedral sites sandwiched between layers of Cl atoms; a series of Cl–Mg–Cl “sandwiches” is stacked along the z -axis.

MgCl_2 occupies an interesting position in the series of crystal structures with stoichiometry AB_2 . The fluorite structure is usually adopted when the radius ratio $r_A/r_B > 0.73$, and compounds with this structure are generally highly ionic (e.g., CaF_2). When $0.73 > r_A/r_B > 0.41$, the rutile structure is expected, as with MgF_2 . When $r_A/r_B < 0.41$, such as for MgCl_2 , layered compounds are preferred, and in general these are less ionic and covalency much more important.

A major theoretical investigation of the stability of ionic and polar solids over wide ranges of pressure and temperature is currently underway in our laboratory, using both classical simulation and ab initio techniques. Most attention has been paid to the B1 and B2 structures of the alkali halides and alka-

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line-earth oxides [3–7], including the dynamics of the transition between these [8]. We have recently extended these studies to anisotropic systems and used both lattice dynamics and periodic Hartree–Fock theory to examine the pressure induced phase transition from rutile to fluorite in MgF_2 [9]. The agreement with experiment was excellent.

We now extend these studies to MgCl_2 , which represents a further step forward in complexity. Since this is less ionic than the compounds we have studied previously, it is problematic to generate reliable interionic potentials for this system and we concentrate on ab initio methods. The only such study of MgCl_2 of which we are aware is that of Harrison and Saunders [10], hereafter referred to as HS, who carried out periodic Hartree–Fock calculations for $\beta\text{-MgCl}_2$ using 8-5-11G* and 8-6-311G* basis sets [11] for Mg and Cl respectively. Somewhat surprisingly the structure was found to be unstable with respect to the inter-layer separation along the *c*-axis. It is not clear whether this failure is an inherent limitation of the Hartree–Fock approximation, which neglects correlation, or due to the limitations of the basis set. Accordingly, in this paper we carry out a series of Hartree–Fock (HF) and density-functional (DFT) calculations using more extended basis sets than those used previously [10], and examine the relative stability of the different polymorphs of MgCl_2 .

The behaviour of ionic and semi-ionic solids at high pressures is a key aspect of condensed matter chemical physics. For a compound with stoichiometry AB_2 , we would expect to observe with increasing pressure a sequence of structures of increasing coordination number including the rutile and subsequently the fluorite structure. Hence we also examine the energetics of the rutile and fluorite phases of MgCl_2 , and estimate the transition pressures between these structures.

2. Computational methods

The calculations reported here were carried out using the all electron ab initio LCAO periodic Hartree–Fock method as described in detail previously [12] and implemented in the CRYSTAL computer code [13]. As pointed out by HS, there are

three main limitations with this approach. The first is due to the accuracy with which the self-consistent field (SCF) equations are solved as well as with the approximations made in calculating reciprocal space integrals and evaluating the Coulomb and exchange series. We have used the default tolerances provided in the program CRYSTAL95 and verified that more strict conditions gave essentially the same results; in particular the truncation criteria for the evaluation of bielectronic integrals provides better accuracy than that used previously [10]. For the SCF iterations the convergence tolerance was 10^{-8} Hartree for both the eigenvalues and total energy. For the reciprocal space integration the Monkhorst–Pack sampling scheme was used with a shrinking factor of 8 (eg. 65 points in the irreducible part of the first Brillouin zone for $\beta\text{-MgCl}_2$). Results of test runs using more stringent convergence criteria and more *k*-vectors were virtually identical.

The second limitation is associated with the finite size of the basis set used, and is discussed in the next section. Thirdly, correlation is ignored and so we have also performed self-consistent calculations with the DFT package also implemented in CRYSTAL95 [14]. For the correlation contribution we used the Vosko–Wilk–Nusair parameterization of the Ceperley–Alder free electron gas correlation results [15] and for the exchange the LSD potential of Dirac–Slater [16].

3. Results

3.1. Basis sets

We start with $\beta\text{-MgCl}_2$. The space group is $\text{P}\bar{3}\text{m}1$. The hexagonal unit cell can be described by the structural parameters *a* ($=b$) and *c*, and one internal degree of freedom *u* (~ 0.25) such that in

Table 1
Exponents α (bohr^{-2}) of the Mg valence Gaussian-type functions and polarization d functions used

Shell type	1	2	3
3sp	0.6500	0.6697	0.6696
4sp	0.1100	0.1846	0.1886
3d	0.4000	0.3350	0.3329

Table 2
Exponents α (bohr⁻²) of the Cl valence Gaussian-type functions and polarization d functions used

Shell type	1	2	3
4sp	0.3250	0.3231	0.3122
5sp	0.1500	0.1451	0.1453
3d	0.5000	0.2898	0.3042
4d	–	–	0.1173

fractional coordinates an Mg atom is at the origin and the chlorines at $\pm(\frac{1}{3}, -\frac{1}{3}, u)$.

Our first calculations used the same basis sets for Mg and Cl as HS [10]. The exponents of the (uncontracted) Gaussian-type functions of the valence shells are given in Tables 1 and 2. This is our basis set (1). As reported by HS, this predicts a structure unstable with respect to the inter-layer separation along the *c*-axis. In order to test whether this failure is a inherent limitation of the HF method or a problem associated with the basis set, we re-optimised the exponents of the Gaussian functions of the outer shells of both ions at the experimental structure. The resulting basis set (2) is also listed in Tables 1 and 2. The lattice parameters subsequently obtained using this basis set are given in Table 3. Though the lattice parameter *c* is overestimated by $\sim 17\%$, the crystal structure is now stable. This clearly indicates the need to use properly optimised basis sets in studies of layered compounds such as these. To investigate further the importance of d-orbitals in the basis to describe accurately the structural parameters, we added a second d-function to the chlorine atoms basis and re-optimised the exponents of the outer orbitals of both ions (basis set number 3). With basis set (3), the lattice parameter *a* hardly changes but the lattice parameter *c* is now only $\sim 10\%$ larger than the experimental value. The addition of a second d-orbital to the magnesium ions (basis set 4, not

given) results in only a very slight improvement in *a*, *c* and *u* (Table 3). The use of s- and p-orbitals with different exponents further increases the agreement with experiment, giving *c* = 6.463 Å. The overestimation of *a* ($\sim 3\%$) and *c* ($\sim 10\%$) is larger than that observed for alkali-metal halides and alkali-line-earth oxides.

The most common form of MgCl₂ is α -MgCl₂ which adopts the CdCl₂ structure. This is a layered structure similar to that of β -MgCl₂ but the Cl atoms are cubic- rather than hexagonal-close packed. The space group is $R\bar{3}m$; in rhombohedral coordinates Mg lies at the origin and Cl atoms at $\pm(u, u, u)$ (with *u* ~ 0.25). At the HF level the agreement between calculations and experiment for α -MgCl₂ (Table 5) is very similar to that for β -MgCl₂.

The main reason for the discrepancy at the HF level between the experimental and calculated value of the lattice parameter *c* is the interlayer Cl–Cl distance and not the Mg–Cl separation, which is in very good agreement with experiment.

3.2. DFT calculations

In order to take electron correlation into account we have carried out SCF-DFT calculations as explained above, using basis set 3. The resulting optimised lattice parameters of β -MgCl₂ (Table 4) are in better agreement with experiment. Both *a* and *c* are now underestimated rather than overestimated; an explicit inclusion of zero point energy would increase these values [9]. The correlation contribution is evidently important for the interlayer Cl–Cl interaction.

DFT optimised geometries and energies for α -MgCl₂ obtained with basis set 3 are listed in Table 5. The DFT values for *c* and *a* are in particularly good agreement with experiment. The calculated differences in energy between the α and β forms is

Table 3
Optimised lattice parameters and total energies of β -MgCl₂ using different basis sets

	Experiment	Basis set 2	Basis set 3	Basis set 4
<i>a</i> (Å)	3.641	3.743	3.741	3.740
<i>c</i> (Å)	5.927	6.912	6.508	6.502
<i>u</i>	0.23	0.197	0.209	0.209
<i>E</i> (hartree)	–	–1118.823043	–1118.823044	–1118.823576

Table 4

Optimized lattice parameters and energies of β -MgCl₂ (basis set 3)

	Experiment	HF	DFT
a (Å)	3.641	3.741	3.5897
c (Å)	5.927	6.508	5.7068
u	0.23	0.2092	0.2404
V (Å ³)	68.047	78.893	63.685
E (hartree)	–	–1118.823043	–1116.820368

extremely small using either HF or DFT (e.g., only 0.02 eV per formula unit for the latter). With such small energy differences, vibrational contributions may play an important rôle. We have estimated the zero-point energy contribution to both phases using quasiharmonic lattice dynamics and a two-body potential model derived previously [17]. The zero-point energies per formula unit are of the order of 0.1 eV for both layered structures, with differences between the two forms comparable to the difference in the static contributions to the energy.

3.3. Phase transitions

We turn to consider the relative stability of possible structures for MgCl₂. Since the previous sections have shown the importance of the inclusion of correlation to obtain a good description of the structure, we consider only DFT calculations. Correlation has also been shown to play an important rôle in the relative stability of the phases of sulphides such as MgS [18] and MnS [19].

At high pressure phase transitions to the rutile and fluorite structures might be expected. Limited computational resources have restricted us to considering

Table 5

Optimized lattice parameters and energy of α -MgCl₂ (using the basis set 3)

	Experiment	HF	DFT
a (Å)	3.6363	3.745	3.6009
c (Å)	17.6663	19.54	17.7109
u	0.25784	0.26368	0.25651
V (Å ³)	67.433	79.116	66.293
E (hartree)	–	–1118.822937	–1116.819623

Table 6

Optimized lattice parameters and energy of MgCl₂ in the fluorite and rutile structures (basis set 3)

	Fluorite	Rutile
a (Å)	6.252	5.8
c (Å)	–	3.7
u	–	0.31
V (Å ³)	61.107	63.924
E (hartree)	–1116.787505	–1116.816192

these structures undistorted. Thus we have not been able to consider explicitly the CaCl₂ structure, which is a small distortion of the rutile structure. Table 6 gives the zero-pressure lattice parameters and energies of MgCl₂ in these two forms, calculated using DFT and basis set 3.

As expected, at zero pressure, the α - and β -structures are more stable than that of rutile, which in turn is lower in energy than the fluorite structure. As a first approximation, the transition pressure between the different possible phases can be estimated from differences in energies and volumes at $p = 0$ using: $p_t = -(\Delta E / \Delta V)_{p=0}$. Using the results in Tables 4–6 we estimate that β -MgCl₂ will transform to the undistorted rutile structure at $p_t \sim 17$ GPa, and that the rutile structure will then transform to the fluorite structure at $p_t \sim 77$ GPa. β -MgCl₂ would transform directly to the rutile structure at $p_t \sim 56$ GPa. By analogy with MgF₂ [9], vibrational effects on p_t are expected to be very small. Unfortunately we have been unable to find experimental data for comparison.

4. Conclusions

We have established that layered structures such as α -MgCl₂ and β -MgCl₂ are stable at the HF level, contrary to a previous suggestion [10]. However at the HF level the neglect of correlation leads to a large overestimate of the Cl–Cl interlayer separation and hence of the magnitude of c .

The two layered forms of MgCl₂ we have considered, α and β , are close in energy; the difference is of the same magnitude as the estimated difference in the vibrational contribution to the energies of each form.

As expected, the layered structures (α and β) are more stable than the more ionic rutile and fluorite structures. Neglecting possible distorted variants of these structures, the estimated transition pressure for the transition $\beta \rightarrow$ rutile is ~ 17 GPa, while the transition rutile \rightarrow fluorite is estimated to take place at ~ 77 GPa.

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