The structural properties of beta -MgCl$_2$; an ab initio study

The structural properties of β-MgCl$_2$; an *ab initio* study

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Abstract. We have investigated the electronic and structural properties of the layered compound β-MgCl$_2$ within an LCAO SCF–Hartree–Fock approximation. An examination of the electronic states in k, E space and the charge distribution in real space reveals the partial covalent character of the bonding in this compound. The experimental structural parameters a and u are reproduced faithfully but the calculations predict an unstable structure with respect to layer separations in the c-direction. An estimated Cl–Cl dispersion interaction is found to be sufficient to stabilize the compound at the correct c/a ratio.

1. Introduction

MgCl$_2$ is frequently used as a support for the active titanium halide centre in the Ziegler–Natta polymerization of olefins. Use is usually made of the crystalline α-modification [1, 2] but the important β-modification has been the subject of much recent research on catalyst performance [3–6]. As a preliminary step in an investigation of this catalyst we have calculated the electronic structure and stability of crystalline β-MgCl$_2$ within the Hartree–Fock (HF) approximation.

MgCl$_2$ also occupies an interesting position in the sequence of crystal structures formed by combining group II and group VII elements with the AB$_2$ stoichiometry. Fluorite packing, where the A-coordination is eight, is usually preferred if the radius ratio (r_A/r_B) is greater than 0.73 (CaF$_2$ and SrCl$_2$). Such compounds are usually highly ionic both because at such ionic radius ratios the electronegativity difference of the atoms involved tends to be large, and also because the Madelung constants associated with the fluorite structure strongly favour ionicity. For smaller ionic radius ratios the A-coordination falls to six and firstly rutile (and slightly distorted rutile) structures (MgF$_2$, CaCl$_2$, CaBr$_2$) and then layered structures (MgCl$_2$, MgBr$_2$, CaI$_2$) are adopted [7]. Naturally the ionicity found in such rutile or layered structures is considerably less than in the fluorite case, both because Madelung effects are less favourable, and because the electronegativity difference is smaller.

β-MgCl$_2$ is a layered system with the trigonal P$\bar{3}$m1 space group [4]. The primitive cell is hexagonal and the structure is described by the three structural parameters a, c and u as follows,

$$a = 3.641 \qquad c = 5.927 \qquad u = 0.23$$

$$\text{Mg}(0,0,0) \qquad \text{Cl}\left(\tfrac{1}{3}, \tfrac{2}{3}, u\right) \qquad \text{Cl}\left(\tfrac{2}{3}, \tfrac{1}{3}, -u\right)$$

where lengths are expressed in Ångstroms. This structure corresponds to an almost ideal close packing of the Cl atoms with the coordination of the Mg atoms being consequently close to a regular octahedron. The Mg and Cl atoms are arranged in hexagonal layers which pack in the sequence $\cdots$–Cl–Mg–Cl–Cl–Mg–Cl$\cdots$ along the *c*-direction. The Mg–Cl bond length is 2.5 Å, with each Cl atom sited symmetrically above three Mg atoms (figure 1).
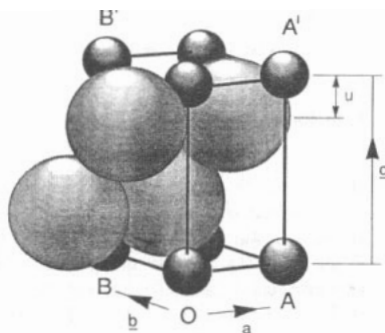

Figure 1. A unit cell of the β-MgCl$_2$. The atoms are drawn as spheres with the (ionic) radii 0.65 and 1.8 Å for Mg and Cl respectively.

2. Computational method and basis set

Calculations were performed within the all electron *ab initio* self-consistent field (SCF) HF-LCAO framework, as implemented in CRYSTAL [8]. There are three sources of error associated with this approach.

   The first source of error is concerned with the numerical accuracy with which the SCF equations are solved. Approximations are introduced while calculating reciprocal space integrals (to reconstruct the electronic charge distribution) and in summing the Coulomb and exchange series which contribute to the Fock matrix. The reciprocal space integrals are performed by sampling at a discrete set of *k*-points (N_k) and expanding in Legendre polynomials (to order N_{pol}). In the Coulomb and exchange series the Gaussian integrals are classified according to overlap and penetration criteria. Integrals of sufficiently low overlap or penetration may be neglected, the 'cutoff' being controlled using five overlap cutoffs (T1–T5). The control of these approximations using the computational parameters input to CRYSTAL is described elsewhere [8]. For the results presented in this paper the numerical error is estimated as 1 mHartree in the binding energy and 0.01 mHartree in the relative energy of different structures. This estimate was obtained by performing calculations with tolerances just above and below those actually used. The parameters used are reported in table 1.

Table 1. The computational tolerances used, see [8] for details.

Parameter	T1	T2	T3	T4	T5	N_k	N_{pol}
Value	10^{-5}	10^{-5}	10^{-5}	10^{-5}	10^{-12}	65	25

The second source of error is related to the finite size of the variational basis set. Twenty-two 'atomic orbitals' were used for chlorine and eighteen for magnesium. Each orbital is a linear combination (contraction) of Gaussian-type functions (GTF), which are the product of a radial function and a real solid harmonic function. The details of the basis set adopted in the present calculation are reported in table 2. In the notation of Hehre *et al* [9] the basis sets used were 8-5-11G* and 8-6-311G* for magnesium and chlorine respectively. Here the digits refer to the number of GTFs combined in a contraction and the star indicates the presence of d-polarization functions. The exponents and contraction coefficients for the sp-part of these basis sets had been optimized in parallel studies of MgO and NaCl. The exponents of the outermost sp-shell of both Mg and Cl were reoptimized with respect to the total energy at the experimental structure. An important feature of the basis set choice is the need to include d-orbitals, the effects of which are discussed below.

The third source of error is due to the inherent limitations of the HF approximation. The tendency of HF to underestimate binding energies (by about 30%) and to overestimate the bond lengths of covalent systems (by 0.5–1.5%) is well documented for molecules [9]. This trend has also been observed in recent studies of bulk semiconductors [10]. Attempts have been made to take into account the correlation contribution to the total energy using density functionals of the HF density. In section 3 we report a feature in the energy surface of $MgCl_2$ which requires non-local dispersion forces to be considered. This is inaccessible to local density functionals and thus its effects are estimated using an empirically derived interaction potential.

3. Results and discussion

3.1. The electronic structure of β-MgCl₂

In our initial investigation of the electronic structure of $β$-$MgCl_2$ we performed SCF calculations at the experimentally determined structure. In the following discussion all orbitals energies are measured relative to the Fermi energy (−0.405 Hartree).

The band structure, shown in figure 2, has two major features. The narrow Cl^{3s} states between −0.69 and −0.63 Hartree, and the broader Cl^{3p} $Mg^{3s,3p,3d}$ hybridized states between −0.14 Hartree and the Fermi energy. The width and dispersion of the hybridized bands is indicative of the partially covalent character of the bonding.

The site and orbital decomposed densities of states are shown in figure 3. The lower energy states are confirmed as the Cl^{3s} orbitals. The decomposition is more informative in the bonding region where the hybridized states split into three peaks. The lower peak is seen to be derived from the mixing of $Mg^{3s,3p}$ with Cl^{3p} orbitals while the middle peak is predominantly Mg^{3p}, Cl^{3p} and the upper peak is due to the mixing of Mg^d and Cl^{3p}. As the Cl is coordinated to three Mg atoms (see figure 1) it is essentially 'hyper-valent' and shares one covalent bond amongst three contacts. In table 3 we compare the distribution of charge amongst the atomic orbitals for calculations with and without d-states. The charge distribution is consistent with a partially covalent picture of the bonding. An interpretation of $Cl^{0.5-}$ Mg^{1+} is more in keeping with these calculations than the formal ionic assignment of Cl^{1-} Mg^{2+}. Although the d-orbitals on the Mg site are considerably more occupied than those on the Cl site the overall effect of the d-states is a migration of charge (0.1 electrons) from Cl to Mg. The inclusion of d-orbitals on the Cl site produces a stabilization energy of 18 mHartree per cell; the further addition of Mg d-orbitals produces an

Table 2. The Mg and Cl basis sets.

| Shell type	Magnesium			Chlorine		
	Exponent	Coefficient s	Coefficient p or d	Exponent	Coefficient s	Coefficient p or d
1s	6.837×10^4	2.226×10^{-4}		1.353×10^5	2.250×10^{-4}	
	9.661×10^3	1.901×10^{-3}		1.944×10^4	1.910×10^{-3}	
	2.041×10^3	1.104×10^{-2}		4.130×10^3	1.110×10^{-2}	
	5.296×10^2	5.005×10^{-2}		1.074×10^3	4.989×10^{-2}	
	1.592×10^2	1.690×10^{-1}		3.234×10^2	1.703×10^{-1}	
	5.471×10^1	3.670×10^{-1}		1.111×10^2	3.683×10^{-1}	
	2.124×10^1	4.008×10^{-1}		4.340×10^1		
	8.791	1.487×10^{-1}		1.818×10^1	1.459×10^{-1}	
2sp	1.437×10^2	-6.710×10^{-3}	8.070×10^{-3}	3.248×10^2	-7.630×10^{-3}	8.200×10^{-3}
	3.127×10^1	-7.927×10^{-2}	6.401×10^{-2}	7.300×10^1	-8.290×10^{-2}	6.050×10^{-2}
	9.661	-8.088×10^{-2}	2.092×10^{-1}	2.371×10^1	-1.046×10^{-1}	2.115×10^{-1}
	3.726	2.947×10^{-1}	3.460×10^{-1}	9.138	2.540×10^{-1}	3.765×10^{-1}
	1.598	5.714×10^{-1}	3.731×10^{-1}	3.930	6.950×10^{-1}	3.967×10^{-1}
				1.329	3.990×10^{-1}	1.860×10^{-1}
3sp	6.500×10^{-1}	1.0	1.0	4.755	-3.740×10^{-1}	-3.400×10^{-1}
				1.756	-4.754×10^{-1}	1.617×10^{-1}
				7.850×10^{-1}	1.340	9.250×10^{-1}
4sp	1.100×10^{-1}	1.0	1.0	3.250×10^{-1}	1.0	1.0
5sp				1.500×10^{-1}	1.0	1.0
5d	4.000×10^{-1}	0.0	1.0	5.000×10^{-1}	0.0	1.0
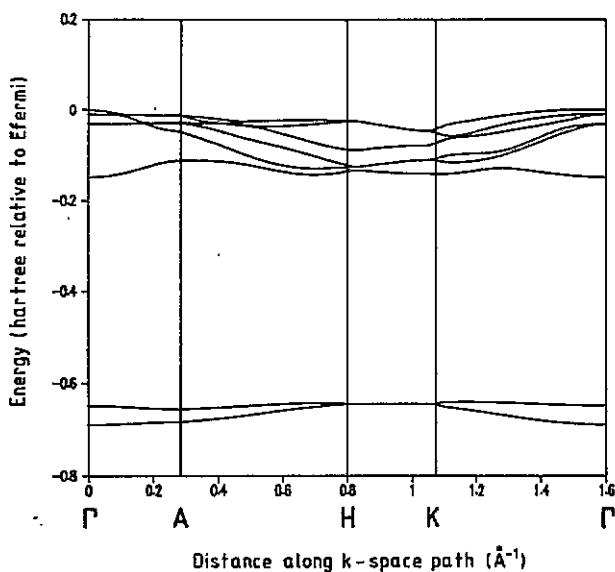
Figure 2. The electronic band structure of MgCl₂ along selected directions of the hexagonal Brillouin zone.

overall stabilization of 32.8 mHartree per cell. The importance of the extra directional flexibility on both sites for the total energy and the distribution of electrons amongst the hybridized states is a further indication of the importance of covalent bonding in this compound. This finding is consistent with the results of parallel studies of partially covalent systems such as magnesium fluoride, III–V semiconductors, aluminates and silicates where the contribution of d-orbitals has been found to be of the order of 30 to 40 mHartree per cell. In similar studies of highly ionic rock-salt structure alkaline halides and oxides, and alkaline earth oxides, d-orbital effects have been found to be quite negligible for elements of the first and second row.

Table 3. A Mulliken population analysis of the crystal wavefunctions from calculations performed with and without d-orbitals.

|		s	2sp	3sp	4sp	5sp	5d	Total
sp-	Mg	2.000	6.484	1.493	1.272			11.248
basis	Cl	1.999	8.033	1.797	3.593	1.953		17.376
spd-	Mg	2.000	6.482	1.503	1.037		0.088	11.110
basis	Cl	1.999	8.032	1.784	3.648	1.969	0.012	17.445

In figures 4(a) and 4(b) we show charge density difference maps (referred to a superposition of atomic charge densities) for two planes through the unit cell. The plane in figure 4(a) passes through the centre of the Cl atom and bisects the 'bond' between it and the Mg. The general migration of charge from Mg to Cl is apparent. The strong polarization of the charge on the Cl site towards the bonding region confirms the partially covalent picture seen in the hybridization of the orbitals. In figure 4(b) the plane is perpendicular to the c-axis, and thus parallel to the Mg and Cl planes; it is cut between the Mg and Cl layers at a height of 3.81 Å above the plane of Mg atoms. The threefold coordination of the Cl site is apparent as charge

Energy relative to fermi energy (hartrees)
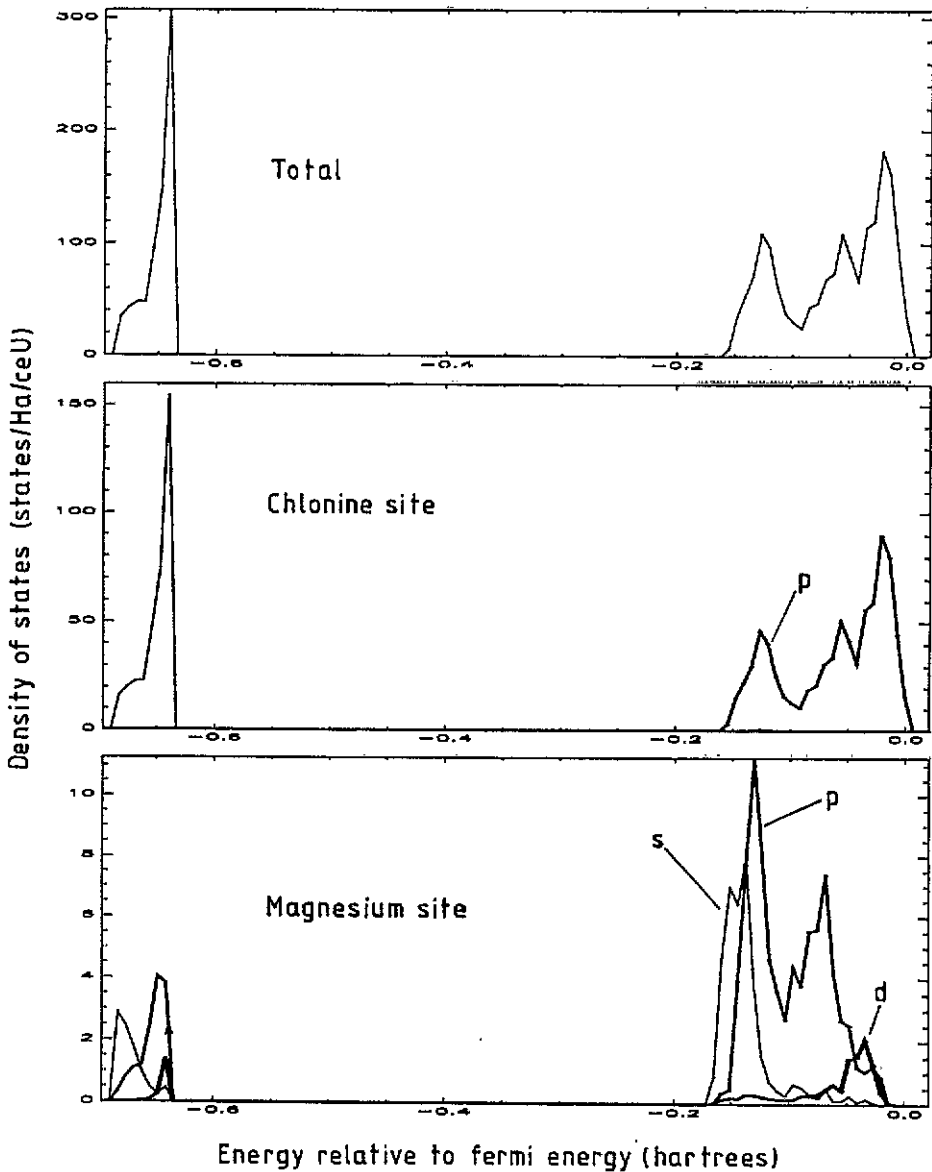
Figure 3. The site and symmetry (s, p, d) projected density of states in $MgCl_2$. The top panel is the total density of states. In the lower panels the components are distinguished as (fine line) s, (medium line) p and (heavy line) d.

is transferred towards the three surrounding Mg atoms. In figures 4(c) and 4(d) we examine the effects of d-orbitals on this real space distribution of charge. The charge in the 'bonds' is enhanced considerably at the expense of the inter-plane region. It is clear that the function of the d-orbitals is to assist the movement of charge into directional bonds.

The effects of these features on the structural stability of this compound are discussed below.
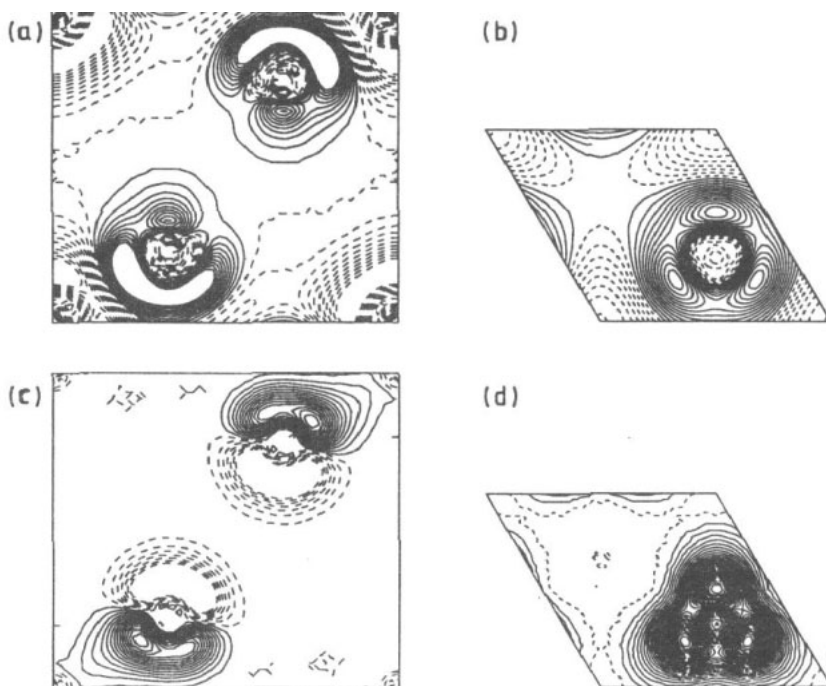
Figure 4. Electronic charge difference isodensity plots, referred to neutral atoms, for the plane AA'B'B (see figure 1) and a plane parallel to the basal plane of the cell (BOA) at a height of 3.81 Å are shown in (a) and (b) respectively. Figures (c) and (d) display the redistribution of charge as d-orbitals are introduced for the same planes. There are 21 contours in each plot which are equally spaced in the range −0.01 to 0.01 Hartree Bohr^{-3} in figures (a), (b), (c) and in the range is −0.0005 to 0.01 Hartree Bohr^{-3} in figure (d). Negative contours are dashed.

3.2. The structural and energetic properties of β-MgCl₂

The variation of the SCF total energy of β-MgCl₂ as a function of the three structural parameters is shown in figure 5.

The calculation reproduces the experimentally measured internal coordinate (u) to within 0.5%. The inclusion of d-orbitals pulls the Cl atoms slightly further down into the plane of Mg atoms. The lattice parameter a is more sensitive to the d-orbitals. It is predicted as 5.2% too large with an sp basis set and 2.5% too large when the d-orbitals are included (figure 5(b)). As, in general, SCF calculations tend to overestimate bond lengths, and the a curve is rather flat, this is a tolerable error.

The variation of the energy with the lattice parameter c is more interesting. The mode by which the compound would separate in the c-direction is with the Cl–Mg–Cl 'sandwiches' coming apart. We therefore performed a series of calculations in which c was increased but the nearest-neighbour Mg–Cl distance kept constant. The results are displayed in figure 5(c). No minimum was found and it was concluded that β-MgCl₂ is unstable with respect to layer separation within SCF. The most likely stabilizing influence missing from the SCF calculation is the dynamic dipole–dipole interaction which will be dominated by interactions between the Cl atoms. In order to estimate the effects of such an interaction we consulted the literature for empirical van
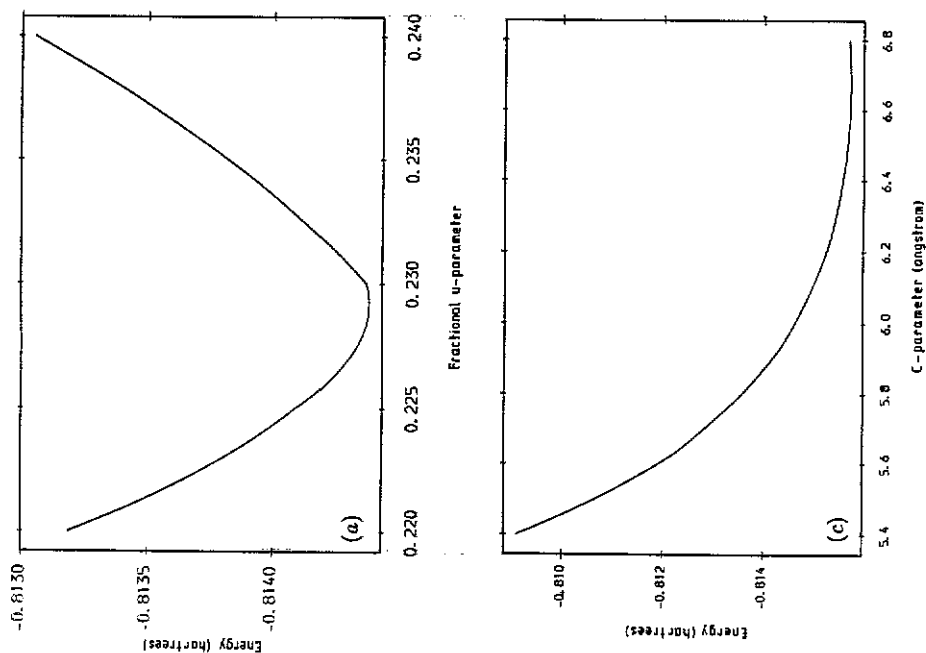
Figure 5. The variation of the HF total energy with respect to the structural parameters. An offset of 1118 Hartree has been added to all energies. The fractional u-parameter (a), the a-parameter (b), the c-parameter (c) and the c-parameter with dispersion effects included in (d).

der Waals pair-potentials which have been fitted to material properties for a variety of local Cl environments [11–16]. The form of this potential for the interaction between the ith and jth atoms is $V_{ij} = -C_6/r_{ij}^6$. The published C_6 coefficients varied from 100 erg cm^6 for atomic Cl to 300 erg cm^6 for highly ionic Cl, and we have therefore taken 200 erg cm^6 as a reasonable estimate for this partially ionic scenario. The dispersion contribution to the total energy was obtained as a real space summation which converged to an accuracy of 0.01 mHartree per cell when the contributions from 25 shells of atoms were included. The variation of the total energy with c including the dispersion contribution is shown in figure 5(d). The estimated dispersion contribution is sufficient to stabilize the layered structure and to produce a lattice parameter c which is 7% less than the experimental value. A C_6 coefficient of 120 erg cm^6 reproduces the experimental lattice parameter. The effect of dispersion interactions on the a and u parameters was also studied. The parameter a was strongly affected and reduced to only +0.2% larger than the experimental value. The parameter u was also reduced to 1.0% less than the experimental value.

4. Conclusions

The Hartree–Fock theory accurately describes the structural parameters of β-MgCl$_2$ after dispersion effects have been accounted for by a simple empirical model. The calculations clearly show the partially covalent nature of the bonding as evidenced by the Mulliken populations, the analysis of the band structure, density of states and distribution of charge in real space. The contribution of the d-orbitals is surprisingly important both for the energetic and structural properties.

Acknowledgments

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