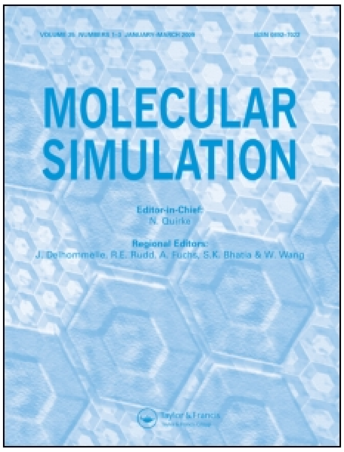

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THE DERIVATION OF SHELL MODEL POTENTIALS FOR $MgCl_2$ FROM *AB INITIO* THEORY

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A dipolar shell model of the interactions in $MgCl_2$ is derived from an extensive *ab initio* investigation of the structural energetics in the α and β phases. A shell model based on the β-phase describes the energy surfaces of this phase accurately and locates the minima in the energy surfaces of the α-phase. A model based on data from both phases gives a better overall description of the energy surfaces but is somewhat less accurate in locating the energy minima. This model also reproduces the experimental high frequency dielectric constants accurately.

KEY WORDS: Shell model, $MgCl_2$

1 INTRODUCTION

The structures adopted by II–VII compounds with the AB_2 stochiometry are strongly influenced by the electrostatic attraction of the ions, packing requirements, and the polarisability of the anion. For compounds with ions of a similar size fluorite packing is favoured with an A-coordination of 8 ($SrCl_2$). For progressively smaller cations first the 6-coordinate rutile structure ($CaCl_2$ has a slightly distorted rutile structure) and then layered structures ($MgCl_2$) are adopted. Clearly the fluorite structure is favoured over the rutile structure from an electrostatic point of view and coordination drops to 6 because the smaller cation is unable to close-pack in a fluorite arrangement. The layered compounds are also characterised by an A-coordination of 6 but with the cations organised in layers rather than distributed evenly throughout the anion lattice. This structure does not appear to optimise the electrostatic energy. In a recent paper [1] (HSI) we investigated the electronic structure and mechanical stability of β-$MgCl_2$ using *ab-initio* methods. The features which contributed to the stability of this structure, relative to the rutile structure, were the strong multipolar distortion of the Cl-ion and the tendancy for co-valent bonds to form.

In Figure 1 we display the structure of the α and β phases of $MgCl_2$. The β phase has the $P\bar{3}m1$ space group, an hexagonal unit cell, and is defined by the structural parameters a, c, u. The α phase has the $R\bar{3}M$ space group, a rhombohedral cell, and is defined by the parameters a, α, u [2]. Each structure consists of close packed layers of ions which are stacked in the sequence . . . Cl–Mg–Cl–Cl–Mg–Cl . . . along the crystallographic c-direction. The structures differ in the relative positioning of the hexagonal close-packed planes. As the stability of these structures, relative to the rutile structure, may largely be attributed to the *dipolar* distortion of the anions we attempt to develop a dipolar *shell model* description of the bonding.

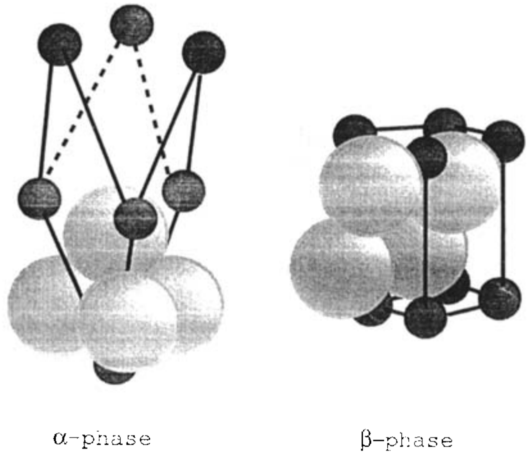

Figure 1 The α- and β-phases of $MgCl_2$.

2 COMPUTATIONAL DETAILS

The *ab-initio* calculations were performed at the Hartree–Fock level using CRYSTAL91 [3–5] Computational tolerances were carefully chosen to confine numerical errors in the total energy in 1 m-hartree and in relative energies to 0.01 m-hartree [1]. The Gaussian basis sets used were[1] 8-5-11G* and 8-6-311G* for the magnesium and chlorine ions respectively. The exponents and contraction coefficients for the *sp*-part of these basis sets had been optimised in parallel studies of MgO and NaCl. The exponents of the outermost *sp*-shell and additional *d*-shell of both Mg and Cl were optimised with respect to the total energy of the β-phase. Further details of our *ab-initio* calculations are provided in HS1.

The shell model parameters were chosen to reproduce, as nearly as possible, the energies of various distortions of the experimental structures. This involves the minimisation of a multivariate function (the "error" in the lattice energy) with respect to the parameters of the model. The position of the shells in each structure was also optimised along with the core-shell spring constant in order to achieve zero net force on the shells. This procedure was performed with the program THBFIT which is part of the CCP5 program library supported by SERC Daresbury Laboratory.

Structural minimisations within the shell model were performed with the THBREL code which is also part of the CCP5 library. This program minimises the energy of a structure with a given potential model to zero bulk and internal strain using a modified Newton–Raphson method.

3 RESULTS AND DISCUSSION

The energies of the α and β phases of $MgCl_2$ were calculated for 29 different structures; 15 of which were distortions of the β-phase and 14 distortions of the α-phase. Variations from the equilibrium structural parameters of up to 20% were employed.

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[1] We use the notation of Hehre *et al.* [6].

Table 1 Shell model force fields fitted to the *ab-initio* results.

	Charge				*Core–Shell spring constant*	*Short range potentials*			
	Mg		*Cl*			*Mg–Cl*		*Cl–Cl*	
	Core	*Shell*	*Core*	*Shell*		*A*	ρ^*	*A*	ρ^*
β-fit	1.0	0.0	7.0	−7.5	486.40	37462.2	0.1913	4428.6	0.3062
$\alpha\beta$-fit	1.0	0.0	7.0	−7.5	266.92	14651857.	0.1263	2678.7	0.3312

In fitting shell models to this data we chose the charges on the ion-cores and shells to be consistent with the Mulliken population analysis of the *ab initio* wavefunction. An essentially unpolarisable Mg^{1+} ion with a neutral shell and a $Cl^{-1/2}$ ion with a shell charge of -7.5 electrons were used. We did not allow shell charges to vary in the optimisation procedure. Short range repulsive interactions between ion shells were modelled with Buckingham potentials, that is;

$$V_{ij} = A \exp\left(\frac{|\mathbf{r}_i - \mathbf{r}_j|}{\rho}\right) \tag{1}$$

with A and ρ as parameters in the fit. The shell on the magnesium site was held static with a large spring constant whereas the core-shell spring constant on the chlorine site was a free parameter. In HS1 we found the β-phases to be unstable within Hartree–Fock theory with respect to layer separation in the c-direction. The introduction of a dispersion interaction between the ion cores of the form

$$V_{ij} = \frac{C_6}{|\mathbf{r}_i - \mathbf{r}_j|^{-6}} \tag{2}$$

with $C_6 = 75.1\,\mathrm{eV}\,\text{Å}^{-6}$ stabilized the compound at the experimental c-parameter. This dispersion interaction was included in the shell models as a fixed parameter.

Two shell models were developed in this manner; the β-fit, which was fitted to the energies of the 15 β-phase structures and the $\alpha\beta$-fit which was fitted to all 29 structures. The details of thee fits are reported in Table 1. The rather large changes which occur in the details of the shell model when information from the α phase is included indicate the volatile nature of this parameterisation. The fitting procedure found many minima in which apparently diverse shell models fitted the β-phase data rather well. The $\alpha\beta$-fit was to a more clearly defined global minimum.

The root-mean-square residual was 0.02 eV for the β-fit and 0.2 eV for the $\alpha\beta$-fit. Clearly the dipolar shell model is capable of providing a consistent description of the local energy surfaces of the β-phase but has some difficulty with a simultaneous discription of the α and β-phases.

In Table 2 we compare the performance of the two fits in reproducing the static lattice properties of the α and β phases of $MgCl_2$. This data was generated by allowing a full minimisation of the atomic coordinates and unit cell volume and geometry with respect to the total energy. The excellent performance of the β-fit in describing the β-phase is thus a non-trivial result as the model calculations were able to explore far more phase space than that mapped out by the 14 representative structures. The performance of the β-fit in describing the α-phase is also encouraging but the poor quality of the high frequency dielectric constants (HFDC) indicates the incompleteness of this description. The $\alpha\beta$-fit provides a tolerable description of the α- and

Table 2 The static lattice properties of $MgCl_2$. The experimental high frequency dielectric constants are derived from the refractive index [7].

	Expt.	*β-fit*	*αβ-fit*	*Ab-initio*
β-phase				
a	6.88	6.87	6.63	6.91
c	11.20	11.24	12.07	11.20
u	0.23	0.23	0.23	0.23
α-phase				
a	11.75	11.90	12.68	12.33
α	33.6	33.6	30.3	36.8
u	0.273	0.256	0.257	0.272
HFDC	2.81	1.78	2.87	
	2.53	1.77	2.60	

β-phase geometries. The significant improvement in the HFDC reflects the refinement of the chlorine ion core-shell spring constant and thus the polarisability of the chlorine ion.

4 CONCLUSIONS

The derivation of empirical shell-model potentials to *ab initio* energy surfaces is a practical and fairly automatic computational procedure. Some care must be exercised in choosing a suitably diverse set of structures in order to uniquely determine the shell model. In the case of $MgCl_2$ we find that a reasonable shell model may be derived from structures corresponding to distortions of the α and β phases. The *ab-initio* evidence for co-valent bonding and strong non-dipolar distortions of the chlorine ion imply that a more accurate description may be obtained with an extended shell model.

Acknowledgements

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