Vibrational energies and thermal expansion of layered compounds: MgCl₂

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Abstract

Full dynamic free energy minimisation is used to study the stability of different polymorphs of $MgCl_2$, with a new set of interionic potentials derived from ab initio calculations using density functional theory. The calculated difference in free energies between the α- and β-phases is extremely small: the vibrational contribution reverses the relative ordering of these two structures obtained in the static limit. We predict the thermal expansion of both forms is highly anisotropic and that, unusually, above ≈ 60 K the expansion is larger parallel than perpendicular to the layers. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Magnesium chloride is an important catalytic support for titanium halides in the Ziegler–Natta polymerisation of stereoregular polyolefins and its behaviour depends in part on a ready interconversion between a range of structural forms. When the cation–anion radius ratio is less than 0.41, as in $MgCl_2$, layered structures are preferred for crystals with stoichiometry AB_2 and generally these are less ionic than the fluorite or rutile structures. The most common crystalline form of $MgCl_2$ is α-$MgCl_2$ [1], in which close-packed planes of chlorines are stacked ...ABCABC... along the *c*-axis. In β-$MgCl_2$ [2] the chlorines are hexagonally close-packed, ...ABABAB..., and in the δ-form [2] there is a random sequence of cubic- and hexagonal-close packed layers along the *c*-axis. Mg atoms always lie in alternate layers of octahedral sites sandwiched between layers of Cl atoms. All of these layered structures consist of series of Cl–Mg–Cl 'sandwiches' stacked along the *c*-axis.

We have previously carried out a periodic ab initio study of the stability of polymorphs of $MgCl_2$ [3] using both Hartree–Fock (HF) and density-functional theory (DFT). At the HF level, the neglect of correlation leads to a large overestimate of the Cl–Cl interlayer separation. In contrast DFT optimised geometries were in good agreement with experiment, although DFT methods do not include dispersive interactions. The α- and β-forms are sufficiently close in energy at

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the HF and DFT levels that vibrational effects are possibly important in determining the relative stability of the two phases. $MgCl_2$ is the first example in our studies [4] of the stability of the structures of ionic and semi-ionic compounds where vibrational contributions may play a crucial rôle under ambient conditions.

Although temperature effects and properties such as thermal expansion can, in principle, be calculated from ab initio calculations, the high computational requirements of such work makes this currently unfeasible. A convenient alternative is the use of lattice statics and quasiharmonic lattice dynamics using pair-potentials to represent the non-Coulombic interactions between the ions. However, the generation of suitable potentials is notoriously difficult for layered compounds such as $MgCl_2$ where polarisation appears to play an important rôle [5]. Earlier simulations of $MgCl_2$ have been confined to the static limit [6–9]. All the potentials presented in those works are unsuitable to study vibrational contribution to the free energies of α- and β-$MgCl_2$ for different reasons. The potential set proposed by Busing [6] predicts, contrary to observation, that the most stable form of $MgCl_2$ is a distorted rutile structure which is as much as 17.6 kJ mol^{-1} lower in energy than the α-form. Vibrational contributions are unlikely to change this relative ordering in free energies and stabilise the α-structure further. Unfortunately we have been unable to calculate explicitly vibrational contributions to the free energy using this potential because full details of the potential have not been given. The potential set in [7] performs well in modelling bulk and surface structures of the β-phase but it also predicts the rutile phase to be the most stable, both in the static limit and when vibrational contributions to the free energy are included.

Harrison and Leslie [8] proposes two further potential sets, generated by fitting the potentials to reproduce energies obtained from ab initio HF calculations. At the HF level, using the basis sets of [8], β-$MgCl_2$ is predicted to be unstable with respect to interlayer separation, and so the authors introduced an additional empirical dispersion interaction between the Cl atoms of the form: $V_{ij} = Cr_{ij}^{-6}$, with the parameter C adjusted to yield

agreement with the experimental lattice parameter c. This procedure is not fully self-consistent. For this reason we have calculated the elastic moduli $C_a = \partial^2 E / \partial (\ln a)^2$ and $C_c = \partial^2 E / \partial (\ln c)^2$ which give a measure of the curvature of the crystal energy as a function of the lattice parameters a and c. Using the potential set from [8] obtained by fitting energies of different configurations of β-$MgCl_2$ and including the empirical dispersion term, C_a and C_c are 85 and 11 GPa, respectively for β-$MgCl_2$. For the potential set generated by fitting energies of α- and β-$MgCl_2$ simultaneously, the corresponding values are 128 and 9.9 GPa, respectively. Using potentials generated from the ab initio DFT calculations in [3] (as described later), we obtain $C_a = 216$ and $C_c = 63$ GPa. The elastic moduli predicted from the two potential sets in [8] therefore do not agree even qualitatively with those obtained from our ab initio DFT calculations, which, in turn, are expected to reproduce fairly well the elastic behaviour of these solids. As is well known (see, for instance [10, p. 80]) there is a strong dependence between elastic moduli and thermodynamic properties, particularly at low temperatures. Anisotropic thermal expansion, for instance, can be calculated at low temperatures solely from elastic data. Consequently we do not consider further the potentials of [8].

Colbourn et al. [9] have used electron-gas theory [11] to generate two-body potentials. In order to reproduce the experimental lattice parameters it was necessary to 'shift' the potential parallel to the distance axis by different amounts for the α- and β-structures. The resulting potentials are not transferable and consequently not suitable for the study of other polymorphs of $MgCl_2$. Accordingly in this Letter we show how to obtain suitable shell-model [12] potentials for simulations of $MgCl_2$ by extracting them directly from periodic ab initio DFT calculations. The proposed methodology is general and similar to that used previously for MgF_2 [13] (for related work, see also [14] and [15]). As before, there is no empirical input into the potentials, which are constructed by sampling relevant parts of the (DFT) energy hypersurface. They lead to dynamically stable structures and hence can be used, as in later sections of this Letter, to investigate properties of $MgCl_2$ such as the relative

stability of the possible polymorphs and behaviour at high temperatures.

2. Theoretical methods

As in our previous work we have performed self-consistent field calculations with the DFT package implemented in the CRYSTAL 98 computer code [16]. We have not carried out any further HF calculations due to the poor optimised geometries at the HF level [3,17]. We use the basis set and polarisation functions derived in our earlier work (basis set 3). For the correlation contribution we use the Vosko–Wilk–Nusair [18] parameterisation of the Ceperley–Alder free electron-gas correlation results and for the exchange the LSD potential of Dirac–Slater [19].

For the lattice statics and quasiharmonic lattice dynamics we use the fully dynamic free energy minimisation code SHELL [20]. In the quasiharmonic approximation it is assumed that the Helmholtz free energy of a crystal, F, at a temperature T can be written as the sum of static and vibrational contributions,

$$F(\mathscr{E}, T) = \Phi_{\text{stat}}(\mathscr{E}) + F_{\text{vib}}(\mathscr{E}, T), \tag{1}$$

where Φ_{stat} is the potential energy of the static lattice in a given state of strain $\mathscr{E}$, and F_{vib} the sum of harmonic vibrational contributions from all the normal modes. For periodic structures the frequencies $v_j(\mathbf{q})$ of modes with wavevector $\mathbf{q}$ are obtained by diagonalisation of the dynamical matrix $D(\mathbf{q})$. F_{vib} is given by

$$F_{\text{vib}} = \sum_{\mathbf{q},j} \left\{ \frac{1}{2} h v_j(\mathbf{q}) + k_{\text{B}} T \ln \left[1 - \exp\left(- h v_j(\mathbf{q})/k_{\text{B}}T \right) \right] \right\} \tag{2}$$

in which the first term is the zero-point energy. For a macroscopic crystal the sum over $\mathbf{q}$ becomes an integral over a cell in reciprocal space, which can be evaluated by taking successively finer uniform grids [21] until convergence in F_{vib} is achieved. The free energy thus obtained is a function of both macroscopic (η_λ) and internal strains (ε_k), and it is simplest to treat the ε_k as thermodynamic variables

on the same footing as the η_λ, comprising a total set of strain variables [22] denoted by $\mathscr{E}_{\text{A}}$. The equilibrium structure at an applied pressure P_0 is then that which minimises the availability $F + P_0 V$ with respect to all strains.

For large unit cells with many internal strains, the minimisation of $F + P_0 V$ can be carried out much more efficiently by using analytic expressions for the derivatives of F with respect to strain. These are given by

$$\left(\frac{\partial F_{\text{vib}}}{\partial \mathscr{E}_{\text{A}}} \right)_{\mathscr{E}',T} = \sum_{\mathbf{q},j} \left\{ \frac{h}{2 v_j(\mathbf{q})} \right.$$
$$\times \left(\frac{1}{2} + \frac{1}{\exp\left(h v_j(\mathbf{q})/k_{\text{B}}T \right) - 1} \right)$$
$$\left. \times \left(\frac{\partial v_j^2(\mathbf{q})}{\partial \mathscr{E}_{\text{A}}} \right)_{\mathscr{E}'} \right\}, \tag{3}$$

where the subscript $\mathscr{E}'$ denotes that all the $\mathscr{E}$ are kept constant except for the differentiation variable. We thus require derivatives of the frequencies. The derivatives $(\partial v_j^2(\mathbf{q})/\partial \mathscr{E}_{\text{A}})_{\mathscr{E}'}$ are obtained from the analytic expressions for the derivatives $(\partial D/\partial \mathscr{E}_{\text{A}})_{\mathscr{E}'}$ by first-order perturbation theory [23].

3. Results

3.1. Potentials

All the potential parameters were fitted simultaneously to the energies of a set of 180 different configurations. DFT energies were calculated solely for the β-structure (space group P3̄m1), the hexagonal cell of which can be described by the structural parameters $a(= b), c$, and one internal degree of freedom u (≈ 0.25) such that in fractional coordinates a Mg atom lies at the origin and Cl atoms are at $\pm(\frac{1}{3}, \frac{-1}{3}, u)$. Configurations were generated as follows: (i) the lattice parameter a was varied from 3.25 to 4.5 Å in steps of 0.25 Å, keeping c and the internal degree of freedom u constant at their equilibrium values, c_0 and u_0; (ii) next, the lattice parameter c was varied from 4.21 to 6.71 Å in steps of 0.5 Å, keeping $a = a_0$ and $u = u_0$; (iii) lastly, u varied from 0.20 to 0.28 in steps of 0.02, keeping $a = a_0$ and $c = c_0$. The

short-range interionic potentials fitted simultaneously to all these energies were assumed to be of the Buckingham form, giving total pair potentials

$$Z_a Z_b/r + V_{ab}(r) = Z_a Z_b/r + A_{ab} \exp(-r/\rho_{ab})$$
$$- C_{ab} r^{-6}. \tag{4}$$

Table 1
The potential parameter set for MgCl$_2$ derived in this work

Interaction	A (eV)	ρ (Å)	C (eV Å^6)
Mg^{2+}/Cl$^-$	398476	0.15810	–
Cl$^-$/Cl$^-$	2287.76	0.37568	399.9

For each pairwise interaction $V(r) = A \exp(-r/\rho) - C r^{-6}$, with a cut-off of 10 Å. The charge on Mg is 1.2042e, the Mg ions are unpolarisable, the shell charge of Cl is −3.4937e and the associated spring constant 108.5 eV Å^{-2}.

Here a and b refer to the ion type and r is the interionic distance. Z_{Mg} $(= 2 Z_{Cl})$ was included in the fitting procedure as an adjustable parameter, though the optimised value of 1.204e is very similar to the Mulliken charge of 1.186e. The Mg ions were treated as unpolarisable. For the Cl atoms the shell charge and spring constant were included as further variables in the fitting procedure. The potential parameters were then obtained by fitting V_{MgMg}, V_{MgCl} and V_{ClCl} simultaneously with a cut-off of 10 Å for each. The final potential parameters are collected together in Table 1. V_{MgMg} is not included in this table since the fitted values indicated the interaction between the ions was entirely Coulombic. Figs. 1a–c shows a selection of ab initio DFT energies as a function of a, c and u compared with those
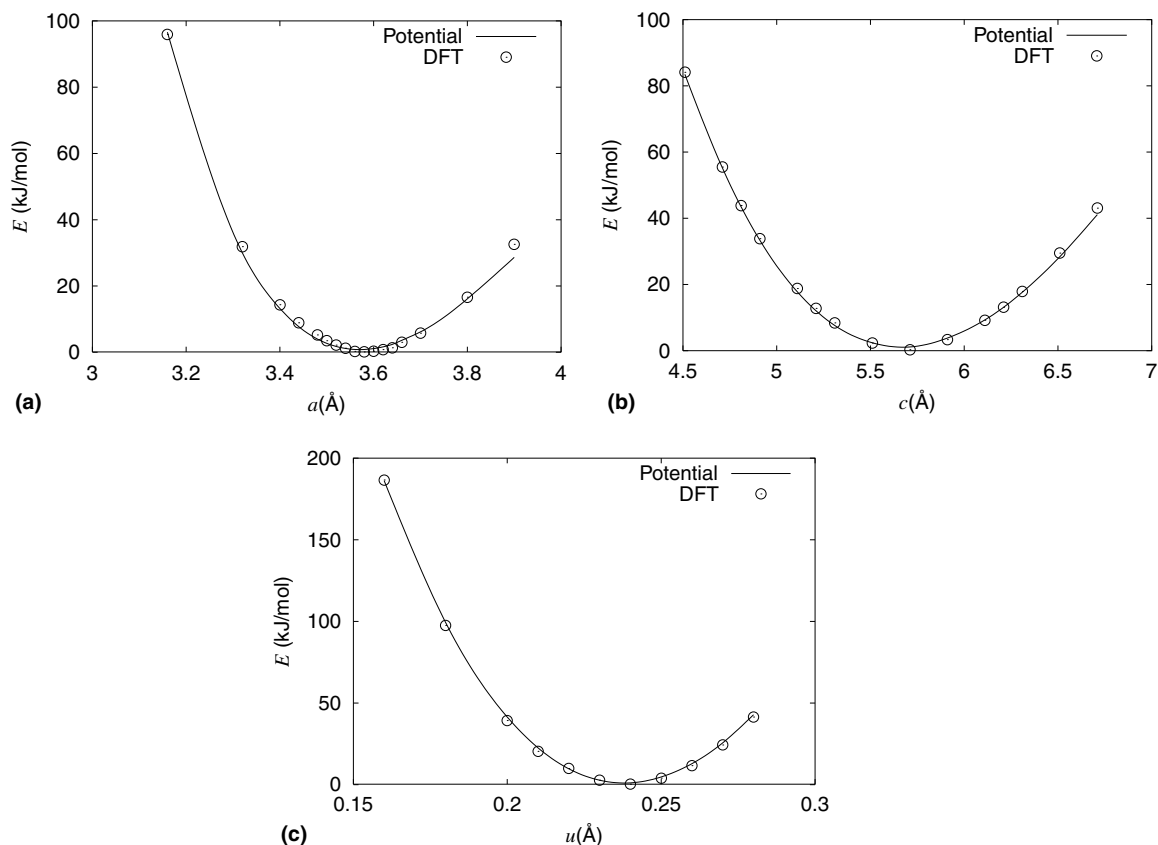

Fig. 1. Ab initio DFT energies for β-MgCl$_2$ as a function of a (a), c (b) and u (c) compared with those obtained using the set of potentials derived in this work (Table 1).

Table 2
Ab initio DFT optimised lattice parameters for β-MgCl$_2$ together, for comparison, with those calculated at 300 K, in the static limit and in the limit $T \to 0$, using the fitted potentials

Parameter	a (Å)	c (Å)	u
Ab initio DFT	3.590	5.707	0.240
Experiment (300 K)	3.641	5.927	0.23
Calculated (300 K)	3.622	5.770	0.226
Calculated (static limit)	3.565	5.711	0.227
Calculated ($T \to 0$)	3.590	5.742	0.227

Experimental values at 300 K [6] are also listed.

obtained using our new potentials. Agreement is excellent.

We also investigated the use of the formal charges for Mg (+2) and Cl (−1) rather than treating them as adjustable parameters (or using the Mulliken charges). Calculations using the resulting set of fitted potentials revealed imaginary frequencies at many **q**-vectors and so we did not pursue this avenue further.

Table 2 lists the ab initio DFT optimised lattice parameters for β-MgCl$_2$ together, for comparison, with those calculated in the static limit using the fitted potentials and the experimental values at 300 K. The accuracy of the potentials away from equilibrium can be assessed from Fig. 1 where we compare the ab initio DFT energies as a function of a, c and u with those obtained using the final set of potentials.

3.2. Phase stability

We turn to consider the relative stability of possible structures for MgCl$_2$ using our potentials, assuming that these potentials are transferable from one polymorph to another. We note first that calculated lattice parameters for α-MgCl$_2$ at 300 K ($a = 3.625$ Å and $c = 17.286$ Å) are in reasonable agreement with experiment ($a = 3.596$ Å and $c = 17.590$ Å) [6]. Our potential set is transferable at least from the β- to the α-phase. The calculated difference in free energy in the static limit between the α- and β-forms is extremely small (≈ 0.065 kJ mol^{-1}), as also found in the static limit in ab initio calculations [3]. With such small energy differences, vibrational contributions can play an important rôle. In the static limit, both periodic DFT

Table 3
Free energies of the α- and β-phases of MgCl$_2$ (kJ mol^{-1}) calculated in the static limit and at 300 K, using the set of potentials derived in this work (Table 1)

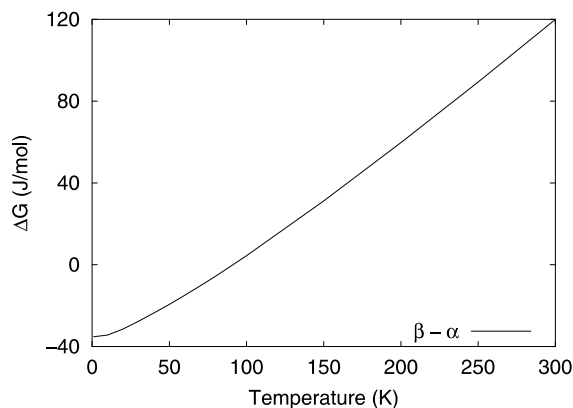|	Static limit	300 K
α-MgCl$_2$	−1008.335	−1012.441
β-MgCl$_2$	−1008.400	−1012.321

Fig. 2. Difference in Gibbs energy between β- and α-MgCl$_2$ as a function of temperature calculated using lattice statics and dynamics and the potential derived in this work (Table 1). A grid of 125 k-points was used in the Brillouin zone summation.

and the potentials derived from these ab initio calculations (Table 3) indicate that the β-phase is lower in energy. Fig. 2 shows the difference in free energies between α- and β-MgCl$_2$ as a function of temperature calculated by using quasiharmonic lattice dynamics and therefore taking vibrational contributions into account. It is clear from Fig. 2 and also the values of the free energies collected together in Table 3 that the inclusion of these

terms *reverses* the relative energy ordering of the α-
and β-phases for temperatures above ≈ 100 K.
The α-phase is then predicted to be the most stable
at room temperature, in agreement with experi-
ment, though at low temperatures the β-phase is
the preferred polymorph. The rutile and fluorite
structures are both predicted to be much higher in
energy, consistent with our ab initio results [3].

We cannot simulate directly the disordered δ-
phase but we have explicitly considered all possible
stackings of the close-packed Cl planes consistent
with the unit cell comprising up to 12 Cl layers.
There are eight possible stackings for a unit cell of
eight layers, 16 for 10 layers and 48 for 12. At 300 K,
the free energies of all of these structures lie in a very
narrow band, confirming the ready-interconversion
between these structures due to the weak interac-
tions between the 'sandwiches'.

3.3. Thermal behaviour

Finally we examine the thermal expansion of
the two layered structures, again using fully dy-
namic free energy minimisation and our new po-
tentials. The calculated thermal expansion
coefficients for the α- and β-phase are shown in
Fig. 3. We have been unable to find any experi-
mental data for comparison. The expansion is
highly anisotropic for both polymorphs. It is small
and negative at very low temperatures for dilations
perpendicular to the main crystal axis (*c*) and
larger and always positive for dilations parallel to
the main crystal axis. At ≈ 60 K there is a cross-
over above which the expansion is considerably
larger along the *a*- (and *b*-) axis, parallel to the
layers, than along the *c*-axis and perpendicular to
the layers. Such thermal behaviour is highly un-
usual [10] (cf. the layered compound InBi [10]).
The general 'rule' is that anisotropic crystals ex-
pand more along the 'softer' axes and less in the
'harder' directions, with graphite the classic ex-
ample of such a layered crystal.

As discussed in detail by Barron and White [10],
thermal expansion in anisotropic systems is deter-
mined by a complex interplay of the elasticity and
the Grüneisen functions. For a hexagonal system
such as β-MgCl$_2$, the thermal expansion coefficients
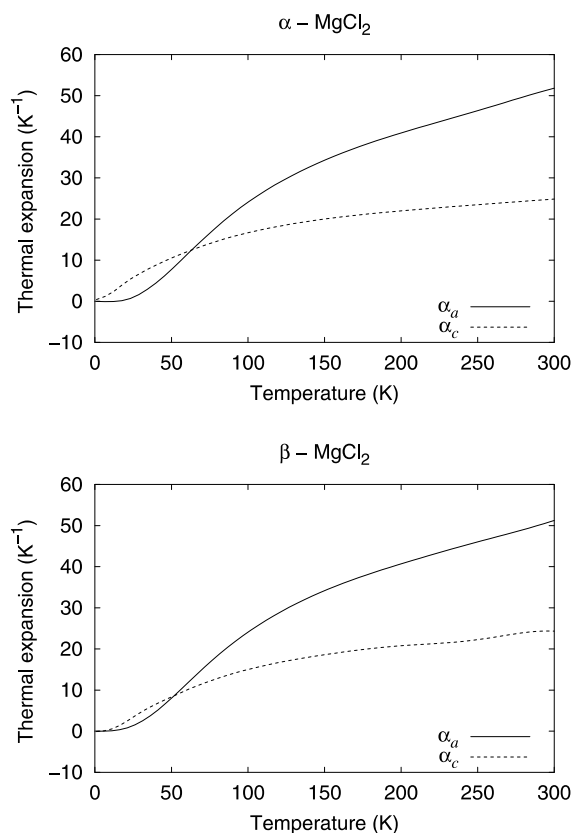along the *a*- and *c*-axes, α$_a$ and α$_c$, are given by

Fig. 3. Calculated thermal expansion coefficients along direc-
tions perpendicular (α$_a$) and parallel (α$_c$) to the main crystal axis
as a function of temperature for α- and β-MgCl$_2$.

$$\alpha_a = \frac{C}{V}\{(s_{11}+s_{12})\gamma_a + s_{13}\gamma_c\},$$

$$\alpha_c = \frac{C}{V}\{2s_{13}\gamma_a + s_{33}\gamma_c\}, \tag{5}$$

where C is the heat capacity at constant strain, V
the volume, the s_{ij} elastic compliances and γ_a and
γ_c dimensionless anisotropic Grüneisen functions.
In graphite low frequency modes are polarised
roughly perpendicular to the layers and the high
frequency modes roughly parallel to the axis; this
is not the case in MgCl$_2$ due to the strong ionic
interactions between each Mg and the top and
bottom layers of its 'sandwich'.

In graphite the Grüneisen functions and elas-
ticity combine to yield large positive expansion
perpendicular to the planes and small negative

expansion in the planes. $MgCl_2$ is broadly similar only at low temperatures < 60 K when only low frequency modes are excited. The low intersandwich frequencies are weakened by stretching along the *c*-axis (which reduces the restoring forces for motion in this direction) and are strengthened by stretching perpendicular to this axis (increasing the restoring force perpendicular to the layers because of the tension between neighbours) so that for these modes γ_a is negative and γ_c positive. The calculated cross-compliance s_{13} is small for $MgCl_2$. Thus at low temperatures there is a relatively large expansion along the *c*-axis and negative or small positive expansion within the layers. At high temperatures the excitation of high frequency modes with large positive γ_a, reverses the relative magnitudes of α_a and α_c.

Comparison of the values of *a* and *c* obtained in the static limit with those obtained by using quasiharmonic lattice dynamics and extrapolated to $T = 0$ (Table 2) shows the effect of zero-point energy contributions; estimated dilations as $T \rightarrow 0$ are $\delta a = 0.025$ Å and $\delta c = 0.031$ Å. Plots of the lattice parameters *a* and *c* as a function of temperature indicate a characteristic divergence of slope at $T \geqslant 600$ K, indicating that the quasiharmonic approximation is beginning to break down, at $\approx 2/3$ of the melting point (≈ 990 K). As we found for MgF_2 [13], lattice dynamics and the quasiharmonic approximation can be remarkably robust at elevated temperatures.

4. Conclusions

We have derived a set of two-body potentials for $MgCl_2$ from ab initio DFT calculations that is transferable from one polymorph to another. As also observed previously [13] quasiharmonic lattice dynamics appears to be remarkably robust at elevated temperatures. Fully dynamic free energy minimisation shows that at low temperatures the vibrational contributions to the free energy differences between the structures are comparable to differences in the static contribution to the energy and can thus determine the relative thermodynamic stability of the phases. α-$MgCl_2$ is predicted to be the most stable polymorph at temperatures

greater than 100 K, in agreement with experiment. At lower temperatures β-$MgCl_2$ is predicted to be the most stable form, though no experimental information to confirm this has been found. We predict unusual thermal expansion behaviour at room temperature – highly anisotropic and larger within than perpendicular to the layers. Correct reproduction or prediction of thermal expansion is a severe test of any computational method and we hope this study may prompt an experimental study of this and other layered materials.

In conclusion we believe that the simple approach to potential generation for ionic and layered compounds outlined here is sufficiently robust to justify its wider use, and in particular its extension to more complex systems.

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