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A computer simulation study of domain walls in NH_4Cl

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Abstract. The effect of antiphase domain walls in NH_4Cl was studied by quantum mechanical calculations using a plane-wave pseudopotential code. The calculated structural parameters for the low-temperature ferro-phase are in good agreement with experimental data. Calculations based on a supercell approach show that, to a first approximation, a model with non-interacting infinitesimally thin domain walls is applicable to ammonium chloride.

1. Introduction

The structure, energetics, and interactions of structural domain walls are of great interest both in basic and applied research, as they determine many properties of twinned crystals, such as the switching behaviour in ferroelectric crystals. The formation of structural domains and domain walls has therefore been studied extensively, both theoretically and experimentally. Atomistic models can only be used to elucidate the energies and structural distortions associated with the formation of domain walls if they are very accurate and precise. This generally excludes the use of models based on empirical potentials (force fields) and semi-empirical models. While this implies that quantum mechanical models have to be used, these are computationally very demanding, and hence studies are restricted to rather small structures. However, if quantum mechanical calculations can be used, such as for studying the stacking of polytypes, antiphase boundaries, and stacking faults, which are related to domain crystals, they can be employed very successfully [1, 2]. Here we present a computer simulation study aimed at determining the energies associated with domain walls and quantifying the distance over which domain walls interact with each other in a ‘soft’ compound. The model system chosen for this study is ammonium chloride, NH_4Cl .

The high-temperature structure of ammonium chloride, NH_4Cl , can be described as being isostructural to the CsCl-type structure, as the NH_4^+ tetrahedra are disordered over the two possible orientations shown in figure 1. Down to a temperature of $T_c = 242$ K the tetrahedra are dynamically disordered. Below this transition temperature, a parallel alignment of the tetrahedra is energetically more stable. In analogy to magnetic spin systems with two orientations, here the ordered phase will be called the ferro-phase, and the two possible orientations of the tetrahedra will be referred to as ‘up’ and ‘down’, respectively. That an Ising model is a good approximation to the pseudo-spin system of NH_4Cl has been pointed out by Garland and Renard [3]. Although the phase transition is strongly first order at ambient pressure, it has already become continuous at 0.15 GPa [4]. As the high symmetry of the lattice allows an analytic description of the interionic interactions and therefore offers the possibility of understanding the complex pressure and temperature dependence of the phase diagram, the

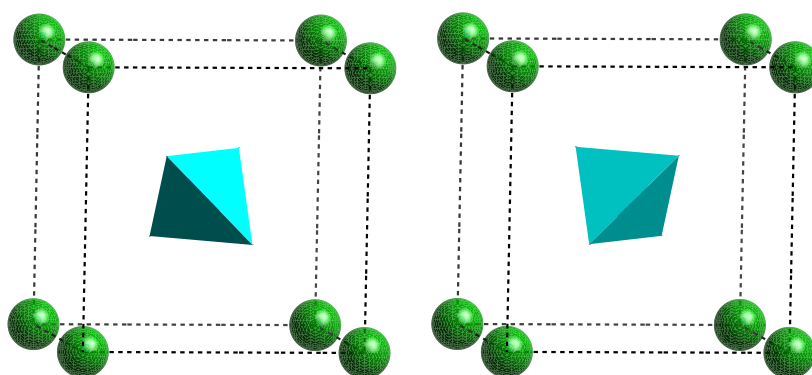


Figure 1. The two possible orientations of the NH_4^- -tetrahedra in NH_4Cl . Domain structures consist of coherent regions in which all tetrahedra point in the same direction.

(This figure can be viewed in colour in the electronic version of the article; see www.iop.org)

order–disorder transition in NH_4Cl has been studied extensively [5–10]. However, to the best of our knowledge, the domain structure of NH_4Cl below the transition has not been investigated by parameter-free quantum mechanical methods.

The space group symmetry of the high-temperature phase is $P\frac{4}{m}\bar{3}\frac{2}{m}$. The symmetry of the low-temperature phase is $P\bar{4}3m$. The space group of the low-symmetry structure is a subgroup of the space group of the high-symmetry phase. It follows from group-theoretical considerations that two different domains can be formed in the low-symmetry polymorph. Experimentally, single-domain crystals of the low-temperature form of NH_4Cl can be obtained by applying simultaneously a d.c. electric field and uniaxial stress [11].

There are two major approaches for the simulation of solids, where one approach uses periodic boundary conditions, while in the other ‘clusters’, i.e. crystal fragments, are employed. Clusters have the advantage that there is no ‘artificial’ periodicity, and that two individual crystallites can be joined to form a twin crystal, even if there are re-entrant or salient angles. This is generally not possible with studies based on periodic boundary conditions. However, calculations with clusters generally suffer from the limited number of atoms which can be treated and are often not representative of the behaviour of bulk material. Hence, here we choose a method based on periodic boundary conditions to model a domain crystal of NH_4Cl , which was constructed by using a supercell. Different kinds of domain can be constructed by changing the orientation of some of the NH_4 tetrahedra in the supercell. For solids with large unit cells the currently most often used technique is that of calculations based on density functional theory (DFT) [12–15], which we have also used here.

The conceptually easiest cases are shown in figure 2, where layers of NH_4Cl_6 -cubes with differently oriented ammonium ions have been stacked next to each other. This model then allows studies similar to those which have been performed for polytypes with different stacking sequences. Of course, more complex domain structures can be built, where the complexity of the domain structure is only restricted by the available computing power.

2. Calculations

The calculations were performed with academic and commercial versions of the total-energy code CASTEP (‘CAMbridge Serial Total Energy Package’) which is described elsewhere

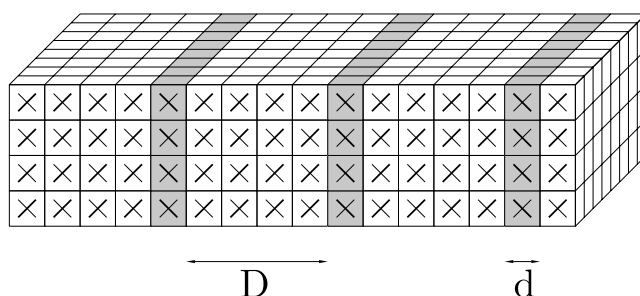


Figure 2. A schematic representation of a simple ‘layer’ domain crystal; D and d are the ‘thicknesses’ of domains in units of the unit-cell edge lengths. Here, $D = 4$ and $d = 1$. For the simulations the smallest building block from which the domain crystal is generated by periodic boundary conditions is chosen.

[16–18]. CASTEP is a pseudopotential plane-wave code, which allows the use of state-of-the-art ‘ultrasoft’ pseudopotentials [19, 20]. Here, the cut-off energy was 380 eV. A generalized gradient approximation was used for the exchange and correlation [21, 22]. For efficient k -space sampling the Monkhorst–Pack scheme was used [23]. Monkhorst–Pack parameters were chosen such that the distance between k -points was $<0.065 \text{ \AA}^{-1}$, which is sufficient for insulators. In the overwhelming majority of the calculations the sampling was even better. After achieving self-consistency, the remaining forces on the atoms were always less than 0.05 eV \AA^{-1} . Residual stresses were always smaller than 0.1 GPa.

3. Results

3.1. Ferro-phase

Firstly, calculations for the fully ordered ferro-phase were performed, to establish the attainable accuracy and precision. The results are shown in figures 3 and 4. The zero-pressure structural data are given in table 1, from which it is obvious that the agreement between experimental data and the model calculations is as good as can be expected from modern DFT-based calculations. The adiabatic bulk modulus B in table 1 and its pressure derivative B' were obtained by fitting a third-order Birch–Murnaghan equation of state to the data. The experimental value has been derived from the room temperature elastic constants $c_{11} = 37.9 \text{ GPa}$ and $c_{12} = 0.97 \text{ GPa}$ [24]. The similarity of the experimental results for the disordered phase and the calculated values for the ordered phase implies that the compressibility is not strongly affected by the ordering. Increasing pressure leads to a small shortening of the N–H bond, from 1.044 \AA at zero pressure to 1.031 \AA at 50 GPa. There was no indication of a pressure-induced strengthening of the hydrogen bonding between the H and the Cl atoms. The main effect of the compression is a shortening of the Cl–H distance from 2.30 \AA at 0 GPa to 1.75 \AA at 50 GPa and a concomitant decrease of the cell edge length from 3.86 to 3.21 \AA .

The symmetric N–H stretching frequency has been obtained by using a frozen-phonon approach, i.e. by calculating the total energy as a function of the N–H distance and fitting the resultant curve (figure 4) with a quadratic function. This expansion was used to evaluate the frequency of the totally symmetric stretching vibration, giving a frequency of 3235 cm^{-1} . It is worthwhile to note that even for very small displacements of a few hundredths of an ångström the potential in which the hydrogen moves is best described by expanding the energy with a quadratic and cubic term. When the cubic term is introduced, the quadratic term does

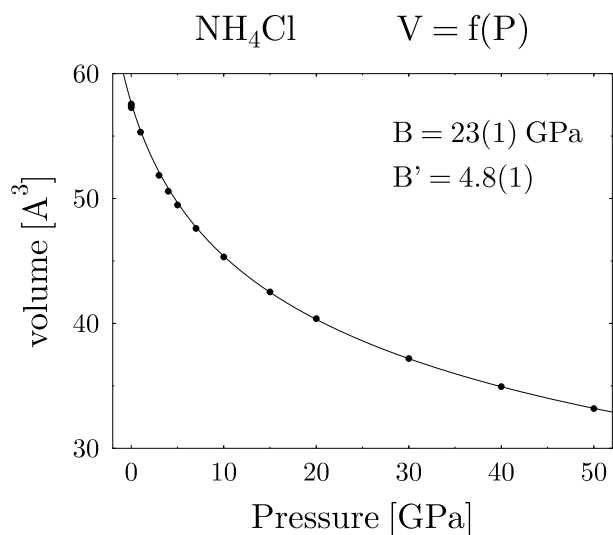


Figure 3. The computed pressure dependence of the unit-cell volume of NH_4Cl . The line represents a third-order Birch–Murnaghan equation of state.

Table 1. Comparison of experimental and calculated data for NH_4Cl .

		Experimental	Calculated	Difference (%)
a	(Å)	3.82631 ^a	3.8613	+0.9
$d(\text{N–H})$	(Å)	1.03 ^b	1.044	+1.5
$d(\text{H–Cl})$	(Å)	2.28	2.300	+0.8
ν_{NH_4}	(cm^{-1})	3043 ^c	3235	+6.5
B	(GPa)	15–23 ^d	23(1)	
B'		4–5.5 ^e	4.8(1)	

^a Reference [27]; measurement at 79 K.

^b References [28, 29].

^c Reference [30].

^d References [24, 31, 32].

^e References [31, 32].

not change significantly, but the associated error decreases drastically. A quartic term does not improve the fit. The $\approx 7\%$ discrepancy between the calculated stretching frequency and the experimentally determined one is larger than is usually encountered in frozen-phonon calculations.

This vibrational frequency can be compared with the results of QCISD (quadratic configuration interaction with all single and double substitutions) cluster calculations on NH_4^{-1} . These calculations were performed with the Gaussian 92 program [25] using the 6-311 + G* basis set, and the contributions from both MP4 and non-MP4 triples to the energy were evaluated. The calculated N–H bond length is 1.0278 Å, and the frequencies are 1429.6 (T_2), 2122.1 (E), 3246.2 (A_1), and 3250.4 cm^{-1} (T_2). The calculation at the MP2 level with the same basis set gives the N–H bond length of 1.0290 Å, and the frequencies of 1409.9 (T_2), 2135.4 (E), 3222.7 (T_2), and 3223.9 cm^{-1} (A_1). It is interesting that MP2 and QCISD calculations predict different orders of the high-symmetry frequencies. The high-frequency symmetric stretching mode, A_1 , is essentially degenerate with the high-frequency IR-active mode, T_2 .

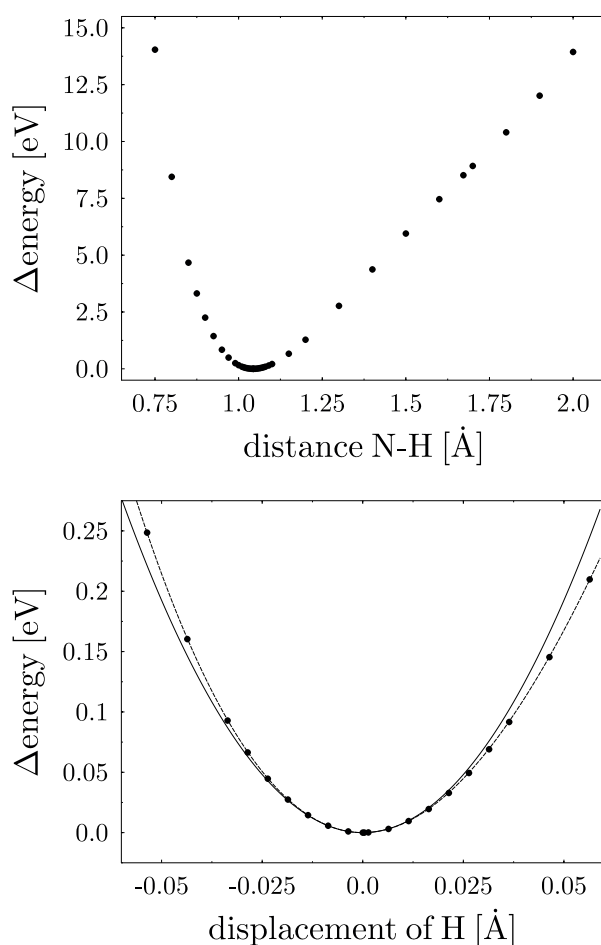


Figure 4. The change of the total energy as a function of the N–H distance. Top panel: the asymmetry of the potential. Bottom panel: a fit with a quadratic function (solid line) gives a frequency of 3235 cm^{-1} . The fit is improved significantly even for small displacements of the H atom if in addition to the quadratic term a cubic term is employed (dashed line).

3.2. ‘Single flip’

For further comparisons, it would be desirable to know the energy cost associated with the flip of a single tetrahedron. To exclude an artificial interaction due to the periodic boundary conditions between ‘flipped’ tetrahedra, the calculations have to be based on a large supercell. However, the limits imposed by the obtainable precision and the necessary computational resources restrict the size of useful supercell calculations.

This became obvious from calculations, where we compared the structure and energy of a $3 \times 3 \times 3$ superstructure with that of a $3 \times 3 \times 3$ superstructure in which the central NH_4 had an opposite orientation. In these calculations the unit-cell volume already exceeded 1500 \AA^3 . The results of the calculations were performed for an orthogonal cell without any symmetry constraints, i.e. for an orthogonal cell with P1 symmetry. The calculations were identical, with the exception of the change in the atomic positions of the four hydrogen atoms, so the accuracy of the calculated energy difference is very high due to the cancellation of errors. However, on

flipping one tetrahedron, the change in the total energy was only 0.1 eV, i.e. the change is less than 0.004 eV per formula unit. The change in the unit-cell volume was a decrease by 1 \AA^3 , i.e. less than 0.06%. Even for a comparison for nearly identical calculations, these changes are too small to be reliable. The small energy difference between the two structures is of course consistent with the very low temperature at which the structural phase transition occurs.

3.3. Domain walls with $d = 1$, $1 \leq D \leq 10$

A study of a domain crystal such as that shown in figure 2 is more straightforward than the calculations mentioned above. Calculations were performed with $d = 1$ and D ranging from 1 to 15. To ensure the highest precision possible, even with respect to small changes in the sampling of reciprocal space, we performed all calculations with and without the flipped ammonium ion. Only supercells of equal size were compared, so that any artificial computational effects could be excluded.

3.3.1. Volume. As in the ‘single-flip’ calculations, the effect on the volume per formula unit was very small and close to the limit of the accuracy of the calculations. The largest effect was observed for $d = D = 1$, where the volume increased by 0.8%. Therefore, the volume does not depend strongly on the concentration of domain walls. However, a more detailed inspection reveals two general trends. Firstly, we observe no change of the lattice parameters parallel to the inserted sheets of unit cells with ammonium ions pointing in the opposite direction; i.e. the two unit-cell vectors within the sheet remain constant in all calculations (figure 5). Secondly, there is a small effect on the unit-cell vector perpendicular to the inserted sheet. This distance increases slightly with the number of domain walls per unit cell. This increase seems to be linear (figure 5).

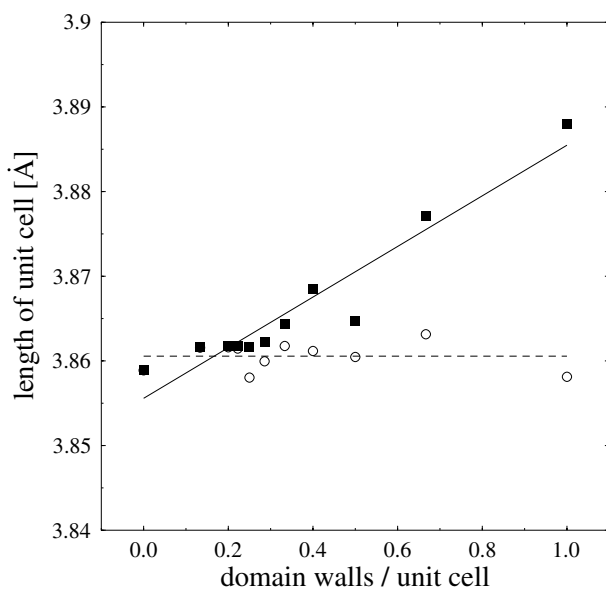


Figure 5. The length of the unit-cell edges parallel (circles) and perpendicular (squares) to the inserted sheets of domains with flipped ammonium ions. Whereas parallel to the sheets no effect is observed, there is a small linear increase of the length of the unit-cell edge perpendicular to them.

3.3.2. *Energy.* In contrast to the case for the volume per formula unit, we observe unambiguously an effect of the domain walls on the total energy. Although the change in energy is small, only of the order of a few meV, our data clearly indicate a linear relationship between the total energy and the number of domain walls per unit cell (figure 6). We observe an additional energy of 23 meV for each wall normalized to one unit-cell face. This is in good agreement with the ‘single-flip’ calculations, where we observed approximately a six-times-larger energy increase, corresponding to six unit-cell faces.

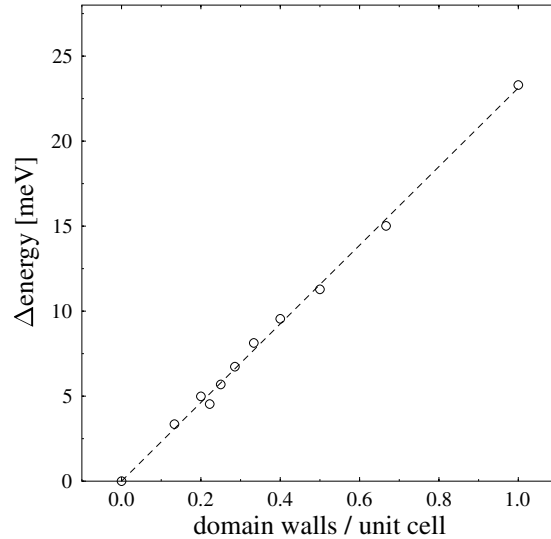


Figure 6. The relative energy per unit cell as a function of the number of domain walls per unit cell. We observe a linear increase of 23 meV per domain wall.

3.3.3. *Ising model.* As has been mentioned in the introduction, the first-order phase transition becomes second order at low pressures and NH_4Cl has been shown to provide a physical realization of a compressible Ising model [3]. The observations described above are consistent with the assumption of non-interacting domain walls. To a first approximation NH_4Cl can therefore be described as a simple spin-1/2 Ising system with $J > 0$, corresponding to the model Hamiltonian

$$E = -J \sum_{\langle ij \rangle} \sigma_i \sigma_j \quad (1)$$

where E denotes the excess energy due to the presence of domain walls, $J = 23$ meV is the interaction parameter, and σ_i represents the orientation of the ammonium ions and takes the values +1 or -1. $\langle ij \rangle$ denotes the summation over all nearest neighbours in the system. As $J > 0$, our calculations correctly predict a ‘ferromagnetic’ ground state with all ammonium ions pointing in the same direction. From the numerical value of J we can estimate the temperature of the transition into a disordered phase. From theory it is known that for a three-dimensional primitive cubic lattice

$$0.75180 = \frac{kT_c}{qJ} \quad (2)$$

where $q = 6$ is the number of nearest neighbours [26]. From equation (2) we find $T_c = 1200$ K. This is larger by a factor of five than the observed phase transition temperature. Better

agreement cannot be expected, as the calculated interaction parameter has been derived in the athermal limit and the applicability of the Ising model can only be confirmed indirectly by noting that the phase transition becomes continuous at 0.15 GPa.

4. Summary and discussion

We have shown that the structure of NH_4Cl can be accurately modelled with the computational approach used here. The lattice parameter, bond lengths, frequency of the N–H stretching mode, and compressibility all are in good agreement with experimental data.

Furthermore, we have demonstrated that the presence of antiphase domain walls leads only to small changes of the structure and total energy. Therefore, only very high-precision calculations can reveal the small changes associated with these domain walls. Hence, a very good convergence with respect to structural parameters has to be ensured. This is a difficult task, as the calculations have to be performed with translational symmetry only, to allow the description of different domain structures within one supercell. This requires a significant computational effort even for very small structures such as the one investigated in this study.

The present results can be compared to experimental and theoretical studies of antiphase boundaries in intermetallic compounds [2]. In these studies, the antiphase boundary energies range from a few tens to a few hundreds mJ m^{-2} . The boundary energy obtained in the present study is 25 mJ m^{-2} and therefore of the same magnitude as those observed for the intermetallic compounds. It is worthwhile to note that in most earlier studies only energies for unrelaxed structures have been computed, and it was often argued that the lattice relaxation will only change the results slightly. This is quantitatively confirmed by the present study.

In the case of NH_4Cl we observe only small long-range effects of the domain walls, which are at the limit of the accuracy of the calculations. However, the current calculations show that the approximation of infinitesimally thin and non-interacting domain walls is a good model for ammonium chloride. Within this model one would expect a linear relation between the domain wall concentration and the total energy per unit cell, but no effect on the size of the supercell. The only deviation from these predictions is the small increase of the length of the cell edges perpendicular to the inserted sheets of antiphase domains. The applicability of this model is consistent with the ‘softness’ of this structure as indicated by the low bulk modulus. We would expect ‘hard’ structures, e.g. silicates, to show more pronounced long-range effects.

Acknowledgments

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