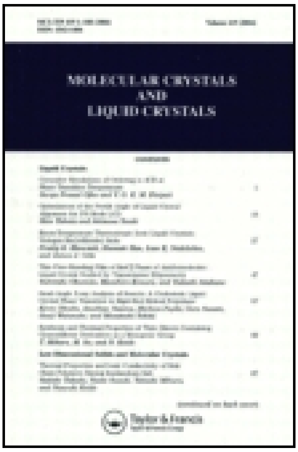

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The Solid State Chemistry and Polymorphism of Aquomagnesium Hydrogen Phthalates

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THE ATTEMPTED SIMULATION OF LAYERED DOUBLE HYDROXIDE INTERCALATES THROUGH LATTICE ENERGY MINIMISATION

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Abstract An attempt was made, using lattice energy minimisation, to model guest orientation within layered double hydroxide intercalates, without explicit consideration of interlayer water. This was found to be unsuccessful, for which an explanation is advanced.

Keywords: lattice energy minimisation, layered double hyroxides, intercalates

INTRODUCTION

A widely studied class of materials, which find application in a number of fields discussed by Reichle[1], are the layered double hydroxide intercalates. A number of these materials occur naturally, in which case the charge balancing anion is generally carbonate, but of more interest in this context are those members of this family in which the charge balancing anion is an organic species introduced synthetically.[2]

The structure of these materials consists of a stack of brucite-like layers (see below), given a positive charge by the substitution of a proportion of the divalent metal cations by trivalent ions, with an equivalent number of anions, generally accompanied by water, sandwiched between the layers to render the structure electrically neutral.

Brucite: The Basic Layer Structure

This structure is of the CdI_2 type, and is shown schematically in figure 1. It consists of magnesium ions surrounded approximately octahedrally by six oxygens in the form of hydroxide. These octahedral units then, by edge sharing, form infinite layers, with the hydroxide ions sitting perpendicular to the plane of these layers. The layers then stack on top of each other to form the 3-dimensional structure.

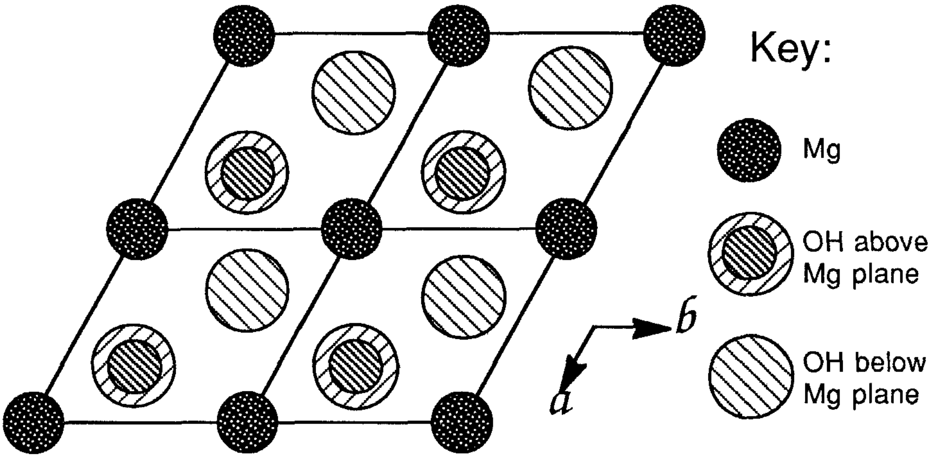


FIGURE 1 Structure of a brucite layer; a=b=3.125Å , $\gamma=120^{o}$

Intercalation

On account of the very weak interactions between separate layers of these materials, they exhibit the property, alluded to above, of accommodating foreign, or "guest", species within the interlayer regions, or "galleries". This process is known as intercalation.

Synthetic specimens of such intercalates do not form crystals of a suitable size for single crystal analysis, and so deductions about guest orientations must be made from evidence such as PXRD, MAS-NMR and IR-spectroscopy. It was hoped that the computer modelling described below might provide information complementary to such experimental data.

SIMULATION METHOD

The method used was that of lattice energy minimisation, which takes a starting structure and a set of interatomic potentials, and produces a structure corresponding to a lattice energy minimum. This procedure has been fully described in several reviews.[3,4]

It was hoped that a reasonable prediction of the structure could be obtained without the necessity of considering the presence of water in the interlayer; this will be the case if the structure is determined primarily by the interactions between the layers and the relatively large anions, and the water molecules merely fill the empty space thus created. If this proved not to be the case, then the number of variable parameters would be increased enormously, with a concomitant decrease, quite probably to a negligible level, in the likelihood of finding a relaxed structure close to the global minimum.

Single crystal work by Allmann,[5] on a natural specimen of pyroaurite, indicated a disordered interlayer with identifiable guest sites, but this could not be modelled using the software available[6], which operates on a perfect lattice; therefore, a unit cell of sufficient size to contain one guest was chosen.

The procedure followed was to treat both the $M(OH)_2$ layers and the guests as rigid bodies, and model interactions between separate rigid bodies using a potential set due to Oie et al.[7]

Two guests were considered- carbonate, since this is the most common guest in minerals and has received extensive study, and terepthalate, an example of the type of organic anion which may be of interest.

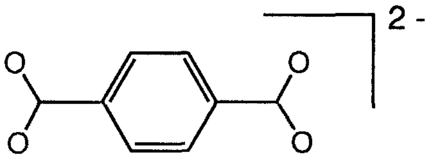
Coulombic interactions between non-bonded atoms were also included, using the charges shown in table I.

TABLE I Atomic charges used in the simulation.

Molecule	Atom	Charge / e
$M(OH)_2$ layer	M	See text
	O	-1.426
	H	+0.426
Carbonate	C	+0.94
	O	-0.98
Terephthalate	C(carboxyl)	+0.3667
	O	-0.6292
	C(ring)	-0.0712
	H	+0.0527

The layer geometry was taken from that observed in brucite, and the layer-atom charges were assigned by assuming random M^{2+}/M^{3+} substitution, and by giving the hydroxide ion the same charge partitioning that Saul & Catlow had derived from an *ab initio* study of crystalline sodium hydroxide.[8]

Carbonate geometry and charges were taken from a study by Pui Sum Yuen et al.[9], whilst the terephthalate geometry was taken, with small modification to permit easier coding (see figure 2), from the crystal structure of calcium terephthalate dihydrate,[10] and its atomic charges calculated using the MNDO method.



Anion planar.
All C - H bonds =1.08Å
All C - O bonds = 1.27Å
All C - C ring bonds = 1.40Å
Both C - C exocyclic bonds = 1.50Å
All bond angles = 120 degrees

FIGURE 2 Geometry of terephthalate anion adopted.

RESULTS

Carbonate Guest

Most minerals with carbonate as the interlayer anion ideally have a $M^{2+}:M^{3+}$ ratio of 3:1, and so this layer charge density was adopted, giving each metal a charge of +2.25e, and necessitating an enlarged unit-cell with {2**a**,4**b**} compared to brucite, in order to accommodate one carbonate ion. Initially, the layers were constrained to lie so that hydroxyl groups on the lower surface of one layer were directly above those on the upper surface of the one below, this being the arrangement seen by single crystal work on natural pyroaurite.[4]

The carbonate ion was started in the orientation observed in pyroaurite, and allowed to find its minimum energy orientation for a series of layer spacings. The results are graphed in figure 3

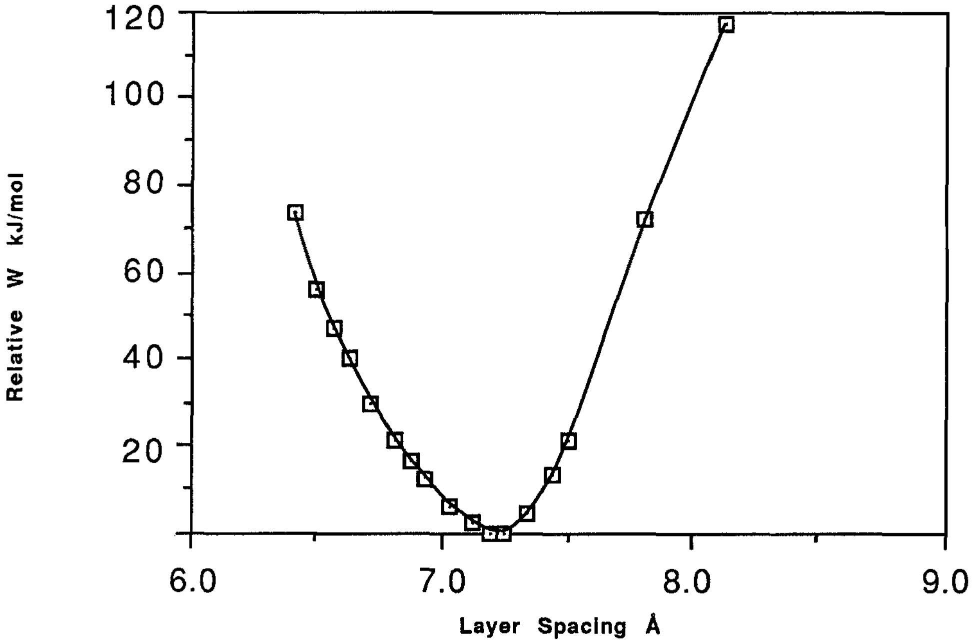


FIGURE 3 Graph of relative energy as a function of layer spacing for the carbonate intercalate.

At the predicted minimum energy spacing, with a layer spacing of 7.25Å, the carbonate is found to be oriented in good agreement with the X-ray structure, but with a layer spacing underestimated by 7%. This predicted orientation is shown in figure 4.

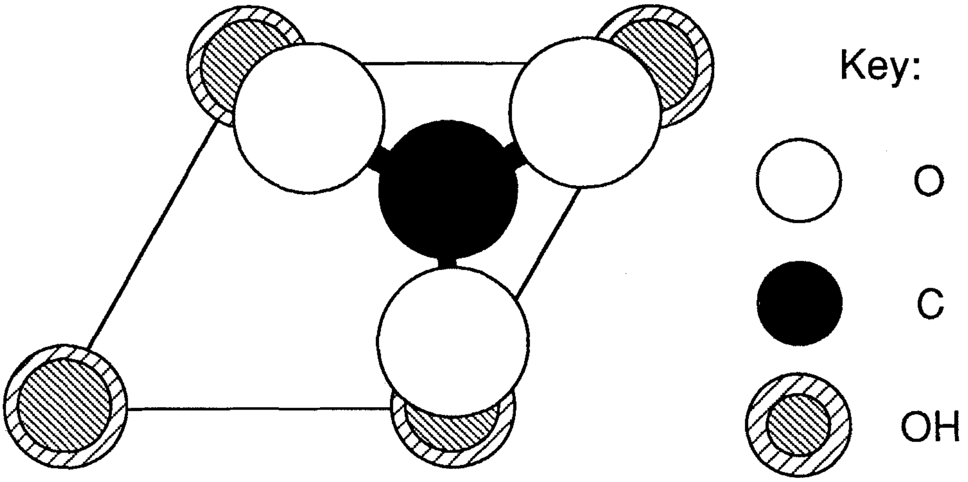


FIGURE 4 Orientation of carbonate viewed normal to the layers

Upon removing the constraint of fixed layers, it was found that adjacent layers slipped over each other by approximately 0.2Å, in a direction normal to the a-axis, but the carbonate retained, as far as possible, the orientation seen with fixed layers.

In a number of cases, relaxations from other starting positions yielded different structures to this, but all were of higher lattice energy, and so were discarded.

Hence, since the aim of the study was to make a prediction of the true structure, without considering the presence of water, this appeared a promising result.

Terephthalate Guest

This intercalate, with a Mg:Al ratio of 2:1, has been synthesised by Drezdzon,[11] and is seen to have a layer spacing of 14.4Å, which is rationalised as corresponding to the anion sitting normal to, and in contact with, the sandwiching layers.

The $M^{2+}:M^{3+}$ ratio of 2:1 requires each metal to possess a charge of +2.333e, and necessitates an enlarged unit-cell with {**2a**,**3b**} compared to brucite, in order to accommodate one terephthalate ion.

The starting position for the anion was chosen to be symmetrically between the sandwiching layers, in the orientation proposed by Drezdzon, with the carboxylate groups sited over the layers as shown in figure 5. (This was the lowest energy orientation found in a set of relaxations from arbitrarily chosen starting positions, at the observed layer separation of 14.4Å).

A series of relaxations with constrained layer atom positions, gave the results graphed in figure 6. The minimum energy spacing is predicted to be 13.4Å, which underestimates the true value by 7%. Although the predicted orientation of the terephthalate anion is in agreement with Drezdzon's analysis, this result is rather disappointing in view of the fact that Drezdzon was able to rationalise the observed spacing correct to an accuracy of 0.1Å, using a purely geometrical model; this method used his conclusions as a starting point, and produced a result inaccurate by over 1Å. Furthermore, the relaxations so far have not allowed for the possibility of the layers sliding over each other, nor have they investigated other starting orientations, either of which may yield a lower energy relaxed structure.

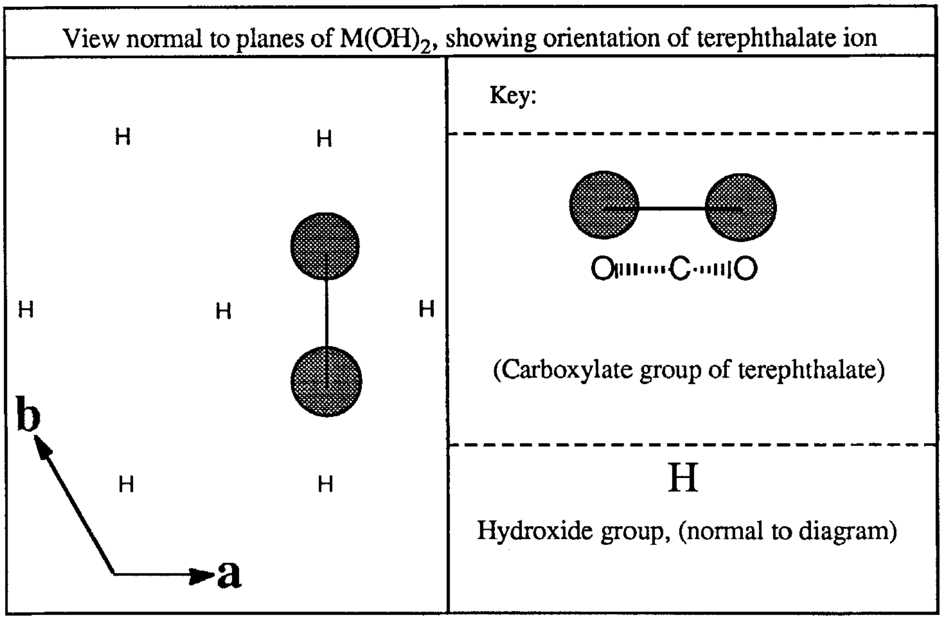


FIGURE 5 Starting position of terephthalate anion.

It was decided to try first a relaxation in which all the layers were allowed to slide over each other The starting configuration for this relaxation was chosen to be the minimium energy structure obtained from the previous series of relaxations.

Upon performing this relaxation, it was found that the structure in which the terephthalate ion sat normal to the layers was only a constrained minimum. When the layers were able to translate relative to each other, the terephthalate ion was found to tilt away from this perpendicular orientation, giving a final structure in which the layer separation was 9.60Å, and the terephthalate ion sat at an angle of approximately 64^{o} to the normal to the planes. This result would seem to spell disaster for the method, since the predicted structure now is not even qualitatively similar to the truth.

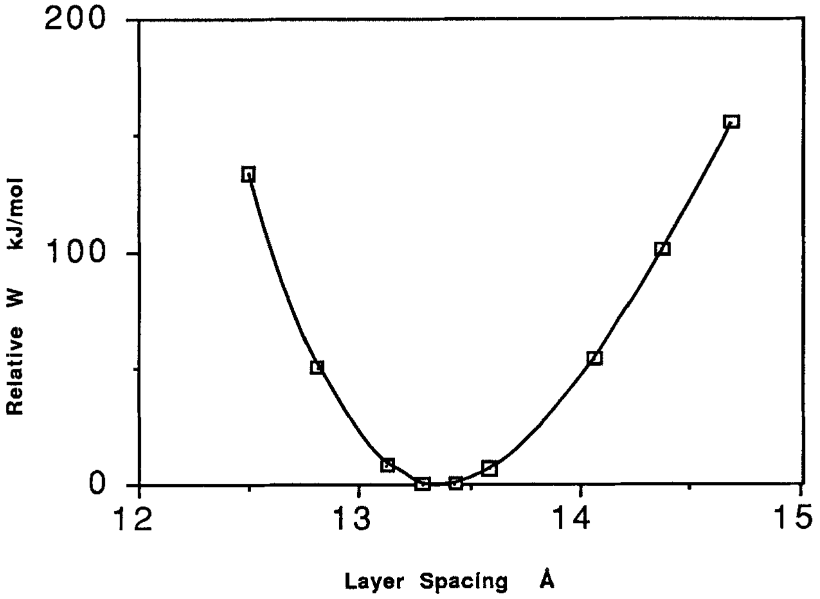


FIGURE 6 Graph of relative energy as a function of layer spacing for the terephthalate intercalate, for terephthalate normal to layers

DISCUSSION

It is interesting to consider why this failure with the terephthalate ion should have occurred. Qualitatively, it may have been thought that the layers, which carry a net positive charge, would electrostatically repel each other, but feel an attraction towards the negatively charged intercalated anion, and the layer separation be determined by this balance of forces, with appropriate contributions from short range interactions. It is reasonable to assume that the carboxylate moieties of the terephthalate, which carry the majority of the negative charge of the anion, should remain in close contact with the surfaces of the $M(OH)_2$ layers, since this will be a very favourable interaction, both electrostatically and through hydrogen bonding. From this argument, it could then be concluded that the layers repel each other, and move as far apart as possible whilst maintaining the required close contact with the carboxylate groups. This would necessitate that the terephthalate ion sit normal to the layers.

At the magnitude of layer separations being considered here, any repulsion between the layers would have to be Coulombic in nature, and so this hypothesis was tested as follows:

The carboxylate groups of the terephthalate ion were both positioned in the sites determined to be the preferred binding locations. For separations lower than the predicted equilibrium separation, adjacent layers were translated by an appropriate distance so that these sites could still be occupied by the carboxylate groups, without altering the geometry of the anion, which then sat at an angle to the normal to the planes, whilst for separations greater than the predicted equilibrium, the terephthalate was positioned normal to the planes, midway bewteen the sandwiching layers, with its carboxylate groups sitting vertically above the preferred sites. Since only electrostatic interactions were to be considered, the terephthalate ion was represented by four oxygen ions, each with charge -0.5, positioned at the correct relative positions found in the anion. Additionally, to try to ensure that interactions between individual terepthalate ions were kept to a minimum, the size of the supercell was quadrupled to {4a,6b}, with appropriate modification of the metal charge, to 2.0833 in order to maintain overall charge neutrality.

The electrostatic energy of the unit cell was then calculated as a function of layer separation, giving the results graphed in figure 7. It can be seen that the energy increases monotonically with layer separation, with a much larger gradient being observed once the layer separation is so great that the anion find itself displaced by any significant distance normal to the layers. Because of this monotonic increase of energy with separation, it can be concluded that the layer separation will collapse to the minimum value possible before short range repulsions become an important factor.

Thus, in the full relaxation described in the previous section, the factor which prevented the terephthalate ion from becoming coplanar with the $M(OH)_2$ layers must have been steric repulsions between individual terephthalate ions, rather than any balance between repulsive interactions between the layers and their attraction for the guest. Therefore, it should be the case that performing a full relaxation with the extended supercell used for these electrostatic caclulations should yield a structure in which the terephthalate ion is much more closely coplanar with the $M(OH)_2$ layers.

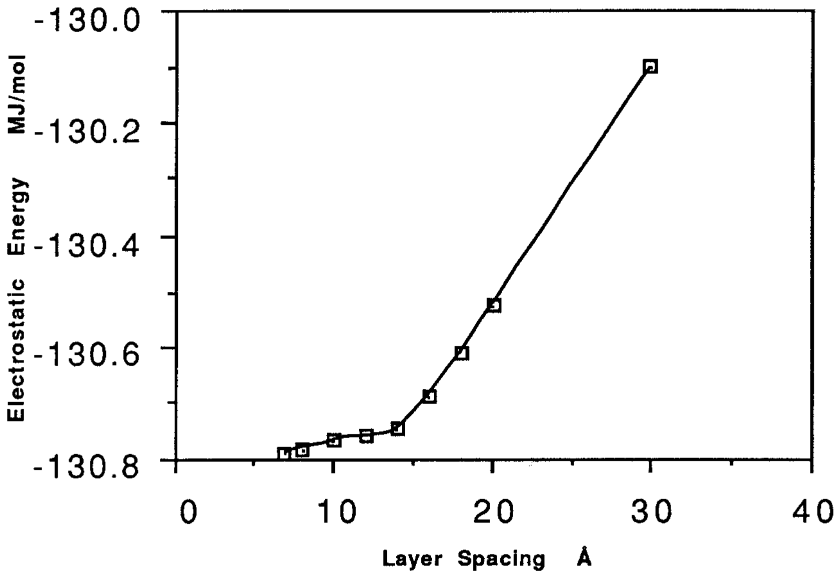


FIGURE 7 Graph of electrostatic energy as a function of layer spacing for the 'pseudo-terephthalate' intercalate.

To investigate whether this was indeed so, a relaxation was performed using the quadrupled cell used in the investigation just described, with initial anion orientation and layer separation taken from the relaxed structure with the terephthalate at 64^{o} to the layers. Upon minimisation, a structure was indeed obtained with a much reduced layer separation of 8.17Å, in which the terephthalate ion is close to coplanarity with the $M(OH)_2$ layers.

This being the case, it can be concluded that it will not be possible to obtain a useful prediction of the true structure of an intercalate by the method described. This is because the layer separation must be determined by a balance between energy gained by intercalating further molecules of water and the energy lost by moving apart the layers as necessary to accommodate these additional water molecules. Therefore, any prediction of the structure cannot divorce itself from an explicit consideration of the presence of water in the interlayer region.

Such consideration would present a formidable problem to the method of lattice energy minimisation, since the number of diverse possible starting configurations for such a system would be large, and the chances of obtaining a relaxed structure close to the global minimum correspondingly small. Furthermore, there would still exist the problem of coping with the possibility of a disordered interlayer, a problem which may be aggravated by the higher density of molecules in the interlayer region.

It can be seen that the reason the method performed rather better in the case of hydrotalcite is that, in this mineral, the carbonate does indeed find itself coplanar with the $M(OH)_2$ layers, which will be precisely the orientation to which the model will relax in the near absence of steric hindrance afforded by the omission of water.

How the method would perform in modelling an intercalate which was in reality free of water is not known, but the results described suggest that, since the synthetic routes to these intercalates allow ample opportunity for the inclusion of water, this method is not of great application, failing to providing any additional information beyond that already ascertained from experimental methods and a simple geometrical analysis.

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