LAYER RIGIDITY IN INTERCALATION COMPOUNDS

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INTRODUCTION

During the past several years there have been extensive experimental and theoretical advances in the understanding of the effect of microscopic layer rigidity on the macroscopic properties of pristine and intercalated layered solids. In this review we bring these experimental and theoretical developments together in a concise description which highlights the interplay between them. Since we and our students and colleagues were heavily involved in first defining and then elucidating the concepts of layer rigidity, we have drawn freely from our previous work to formulate the review presented here.

Solin has classified layered solids into three qualitatively distinct subgroups on the basis of the rigidity of the layer units with respect to transverse distortions in which the constituent atoms are displaced in directions normal to the layer planes. According to this classification scheme, solids with monatomically thin host layers belong to Class I, the members of which are graphite and boron nitride and their intercalation compounds. The layers of these solids are floppy with respect to transverse distortions. Class II contains solids, the layers of which are typically constructed from three planes of interconnected atoms. Materials such as the layer dichalcogenides, iron oxchloride and a number of metal halides belong to this group, whose layers are more rigid than those of the Class I solids. Class III solids, which include the layered alumino silicate clays and layered perovskites, are among the most rigid known in nature. These solids typically consist of five or more interconnected planes of atoms and are much more rigid than those in Classes I or II. The above classification can of course serve only as a rough guide. Thus it has recently been shown that some layer double hydroxides, though they exhibit Class II - like structures actually exhibit rigidities which span those of Class II and Class III.

By definition, layered solids are those for which the intralayer interatomic forces binding the layers together are much stronger than the forces between layers. The resultant anisotropy gives rise to the phenomenon of intercalation whereby guest species can occupy the gallery spaces between the host layers. To first order the only perturbation of the host layers upon intercalation is their increased separation. In Class I and II materials, intercalation is mitigated by charge exchange between the guest species and the host layer.
Thus graphite, which is amphoteric, can accommodate either donor or acceptor guest species into its galleries.\footnote{3} In contrast, layered silicate-clays and layer double-hydroxides possess a fixed negative or positive layer charge, respectively and intercalation into these materials typically constitutes ion exchange of one guest cation or anion for another.\footnote{4}

To establish a quantitative measure of layer rigidity, and thus justify the above qualitative classification scheme, Solin and Thorpe and coworkers developed experimental methods and supporting theoretical models which are based on the variation of the c-axis repeat distance or basal spacing with the composition of a 2D disordered solid solution intercalated into the galleries of the host solid.\footnote{2,5,6} The generic formula for such a system is $A_xB_{1-x}L$ where $0 < x < 1$, $B$ is the smaller guest ion or a vacancy, $A$ is the larger guest ion and $L$ represents the host layer. The basal spacing, or equivalently, the spacing between the layers,\footnote{2} can be obtained from the spacing between the Bragg peaks in a diffraction experiment, using x-rays or neutrons, where the scattering wave vector is perpendicular to the layers.\footnote{1} In most layer rigidity studies carried out to date,\footnote{5,7} the composition of the host layer was independent of the composition of the intercalated 2D solid solution. More recently, solids in which the host layer and guest layer compositions are interdependent have been studied.\footnote{2}

**THEORY**

In this section we review the theory of the catchment area model which has been remarkably successful in quantitatively accounting for the composition dependence of the basal spacing of intercalated layered solids. We also address two refinements of this model; one with a soft catchment area, and one with terraces, around the large intercalant ion. Two general conditions will be addressed: (1) the composition of the host layer is independent of the composition of the guest layer so $L \neq f(x)$ and (2) the composition of the host layer depends on the guest layer composition so $L = f(x)$, where $f(x)$ is some function of the composition.

**Catchment Area Model for $A_xB_{1-x}L$ Layered Solids**

(1) $x$ – Independent Host Layer

**Catchment Area Model**

We assume that because the host layer composition is independent of the guest layer composition; the thickness of the host layer is fixed. In systems such as the graphite intercalation compounds for which the charge exchange to the host layer is dependent on the guest layer composition, this assumption is only an approximation, but changes in host layer thickness are known to be negligibly small. We define the layer spacing in the 2D solid solution $A_xB_{1-x}L$ as $h_2$ if all the intercalant ions are $A$ ($x = 1$) and $h_1$ if all the ions are $B$ ($x = 0$) where $h_2 > h_1$. For the alloy, this spacing will vary with position within the layer depending on the local configuration. The average spacing is $h$, which can be obtained from the diffraction pattern of the alloy. In this paper we neglect any layer–layer interaction effects; to date no evidence has been found from experimental results that suggests that such effects have any influence on the mean spacing $h$ between the layers. The catchment area model could probably be generalized to include such layer–layer effects if necessary.

Each intercalant ion lies between the layers. The precise geometry of the centers is not relevant. The centers of the intercalant ions can lie on some of the sites of a regular lattice (lattice gas model) or at random positions. The catchment area model is not sensitive to this. This is both a weakness (the precise in-plane structure of the intercalant ions has little effect on the c-axis spacing) and a strength (it is not necessary to know the in-plane
structure to predict the c-axis spacing). For convenience in the following discussion of the catchment area model, we will place the intercalant ions in the centers of cells between the layers, so that the ion sites form a triangular lattice between the layers. This lattice is shown in Fig. 1(a) with a few B ions replaced by larger A ions. The ideas developed in this review are quite general to 2D intercalated alloys and A and B are used here as convenient labels for the large and small ions, respectively.

Suppose the A ion has a catchment area associated with it such that the height, or spacing of the layers, is raised to \(h_2\) over the ion A and its catchment area and remains at \(h_1\) elsewhere. The catchment area is characterized by a parameter \(p\) which is a dimensionless area. The parameter \(p\) is also reflective of the rigidity of the host layer with respect to gallery induced distortions. It has therefore been referred to as the interlayer rigidity parameter. In Fig. 1(a), \(p = 7\). Other possible catchment areas with different values of \(p\) are shown in Fig. 2. The parameter \(p\) is a measure of the dimensionless size of the catchment area. The assumption that the height is raised to \(h_2\) over the catchment areas and discontinuously drops to \(h_1\) elsewhere is obviously not correct, but hopefully captures the essence of layer rigidity in a simple and tractable way. In reality the changeover from \(h_2\) to \(h_1\) is more gradual, relaxing as a power law or as an exponential away from a single large intercalant ion. This more gradual change is discussed in the slightly more refined models in the next two subsections. The parameter \(p\) can range from 1 up to a large value as illustrated in Fig. 2. The model is best solved by going to the limit \(x = 1\) (all A) and replacing a few A ions with B ions as shown in Fig. 1(b).

In order for a particular B ion to have a height \(h_1\) associated with it, the neighboring A ions must be sufficiently far away that their catchment areas do not cover the B ion. This defines a reciprocal catchment area around the B ion which also has a size \(p\). What happens outside that area is irrelevant for this particular B ion. The probability of a site having such a B ion on it is \(1 - x^p\) so that

\[
h = h_1(1-x)^p + h_2[1-(1-x)^p]
\]

(1)

where \(h_1\) is associated with the probability \((1-x)^p\) and \(h_2\) with the remaining probability \(1 - (1-x)^p\). Rearranging (1) gives a normalized spacing

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Figure 1. (a) The solid hexagons contain A ions and the unshaded triangles contain B ions. The partially shaded hexagons contain B ions but are in the catchment area of A ions, (b) A single A ion is replaced by B, and the A ions in its catchment area are also replaced by B ions to define the reciprocal catchment area of the central B.
\[ d_s(x) = \frac{h - h_1}{h_2 - h_1} = 1 - (1 - x)^p. \] (2)

This result is derived for a particular intercalation geometry but is very robust. It is independent of the lattice and the shape of the catchment area and depends only on a concentration \( x \) and the size of the catchment area through the rigidity parameter \( p \).

\[ \text{Figure 2. Showing how the catchment area around the large } A \text{ ion increases as } p \text{ increases.} \]

In Fig. 3 the quantity \( d_s(x) \) is plotted against \( x \). The model has no meaning for \( p < 1 \). For \( p = 1 \), Vegard’s law is recovered,

\[ d_s(x) = x \] (3)

and as \( p \) increases the curves lie increasingly above Vegard’s law. This is clear physically. Adding a single \( A \) ion with its catchment area increases the spacing between the layers much more effectively than if there was no catchment area as assumed in Vegard’s law. This leads to an initial slope

\[ d_s(x) = px + O(x^3) \] (4)

for small \( x \) that increases as \( p \) increases. For small \((1 - x)\) at least \( p A \) ions must be removed before the spacing between layers starts to decrease. Thus the curves are always above Vegard’s law and never below. This is one important feature of the catchment area model. As \( p \) becomes very large, expression (2) approaches

\[ d_s(x) = 1 - \exp(-px), \] (5)

a form that is similar to one used by Xia and Thorpe to describe the statistics of elliptical disks that are randomly-positioned and oriented on a plane. More generally as \( p \) approaches unity, the approach to the limit is controlled by the parameter \( p \) as shown in Eq. (2).

Note that the thickness of the layers themselves has been ignored but they are assumed to have a constant thickness \( t \). Then, clearly,
\[ h = t + h_t + d_n(x)(h_2 - h_t). \] (6)

Many generalizations of (2) are possible and some of them can be solved in a straightforward way. Two of these generalizations are considered in the next two subsections.

![Graph](image.png)

**Figure 3.** The spacing between layers \( h = h_t + d_n(x)(h_2 - h_t) \) is determined by the parameter \( d_n(x) \) shown here as a function of the composition \( x \) from Eq. (2). The values of \( p \) correspond to those sketched in Fig. 2.

**Soft Catchment Area Model**

Suppose that the catchment area of the \( A \) ion has a height \( h_c \) rather than \( h_2 \), where \( h_t < h_c < h_2 \). Then it is clear that (1) should be replaced with

\[ h = h_t(1-x)^p + h_c \left[ 1 - (1-x)^p \right] + (h_2 - h_c)x \] (7)

which can be rearranged to give

\[ d_n(x) = \frac{h - h_t}{h_2 - h_t} = \alpha \left[ 1 - (1-x)^p \right] + (1 - \alpha)x, \] (8)

where

\[ \alpha = \frac{h_2 - h_t}{h_2 - h_t}. \] (9)

It should be noted that Eq. (8) is a weighted averaged of the previous result (2) for the catchment area, and Vegard's law. In the limit \( h_c = h_t \), the parameter \( \alpha = 0 \) and Vegard's law \( d_n(x) = x \) is recovered. Note that there is no catchment area in either the limit \( \alpha \to 0 \) or \( p \to 1 \) and Vegard's law is again recovered. In the limit \( h_c = h_2 \), the parameter \( \alpha = 1 \) and (2) is recovered. The form (8) has \( 0 \leq \alpha \leq 1 \) and also always gives a \( d_n(x) \) that lies above Vegard's law.
**Terraced Structures**

In the previous two models, the whole catchment area of an $A$ ion was assigned the same height no matter how many other $A$ ions were in the vicinity. This constraint will now be relaxed. For example, suppose that the effect of the catchment area is cumulative. Focusing attention on Fig. 1(b), a height $h_1$ is associated with the central $B$ ion if the reciprocal catchment area contains no $A$ ions. If the reciprocal catchment area contains $r$ $A$ ions, then the height associated with the central $B$ site might be reasonably written as

$$h_i = \frac{r(h_i - h_1)}{p - 1}.$$  \hspace{1cm} (10)

When $r = p - 1$, this reaches the single height $h_1$ used in the previous section in the discussion of the soft catchment area model. If the central site is $A$, the height is still $h_2$ as before, of course. Thus the effects of the catchment areas are additive, leading to many different heights and a terraced structure. Adding these heights together, weighted with their appropriate probabilities, gives

$$h = \sum_{r=0}^{p-1} \frac{r}{p-1} C_r [h_1 + r(h_i - h_1)/(p-1)](1-x)^{p-r} x^r + h_2 x \hspace{1cm} (11)$$

Using the previous definition for $\alpha$ in Eq. (9), the result (11) becomes

$$d_\alpha(x) = \frac{h - h_1}{h_2 - h_1} = x + \alpha x(1-x).$$ \hspace{1cm} (12)

This result is interesting because it is independent of $p$, the size of the catchment area. For $\alpha = 1$, it can be rewritten as

$$d_\alpha(x) = 1 - (1-x)^2$$ \hspace{1cm} (13)

which corresponds to $p = 2$ in Eq. (2). Indeed it is likely that many different and diverse geometrical arrangements can be found that lead to the result (2) even when $p \neq 2$.

**Comments**

The theoretical models discussed above give the mean separation between layers as a function of the composition $x$. They are very different in spirit from spring models that have also been developed theoretically.\cite{11,12} Spring models give quite different functional forms which fail to give such good agreement with experiment.\cite{11} Our discussion has focused on the overall layer spacing, but these catchment area models can be extended to give the mean layer spacing at either $A$ type or $B$ type sites. In general we can write by definition,

$$d_\alpha(x) = xd_\alpha(x) + (1-x)d_\beta(x)$$ \hspace{1cm} (14)

where $d_\alpha(x)$ is the mean gallery spacing at the $A$ site and $d_\beta(x)$ is the mean gallery spacing at the $B$ site. For all three models discussed here, we have $d_\alpha(x) = 1$, so that from Eq. (14), we have for the catchment area model
\[ d_x(x) = 1 - (1 - x)^{p-1} \]  \hspace{1cm} (15)

while for the soft catchment area model

\[ d_x(x) = \alpha \left[ 1 - (1 - x)^{p-1} \right] \]  \hspace{1cm} (16)

and for the terraced structures

\[ d_x(x) = \alpha x. \]  \hspace{1cm} (17)

Note that (15) and (16) have the same form as the respective overall mean spacing \( d_x(x) \), but with a reduced rigidity parameter \( p \to p - 1 \). It would be very desirable to have measurements of \( d_x(x) \) and \( d_y(x) \) using say XAFS, or diffraction experiments with different isotopes, or using the anomalous dispersion at the x-ray edge.

Although XAFS only measure mean distances, other experiments can also measure the widths of the distributions associated with the gallery heights at the \( A \) and \( B \) ions. An example of such an experiment would be the pair distribution function as obtained using neutron or x-ray diffraction. These widths, and indeed the complete distribution function, can be worked out for the models above. In the catchment area model, the \( A \) site always has a reduced height of 1 which therefor occurs with probability \( x \). The \( B \) site can have either a reduced height of 0 with probability \( (1 - x)^p \) or a height 1 with probability \( 1 - x - (1 - x)^p \). Therefor we have

\[ \langle d_x^2 \rangle - \langle d_x \rangle^2 = 0 \]  \hspace{1cm} (18)

and

\[ \langle d_y^2 \rangle - \langle d_y \rangle^2 = [1 - (1 - x)^{p-1}](1 - x)^{p-1}. \]  \hspace{1cm} (19)

Similar arguments can be given for the soft catchment area model and the terraced model. Both these models also have no fluctuations in the \( A \) gallery height which is again given by (18). For the soft catchment area model, Eq. (19) is modified to give

\[ \langle d_y^2 \rangle - \langle d_y \rangle^2 = \alpha^2 \left[ 1 - (1 - x)^{p-1} \right](1 - x)^{p-1}. \]  \hspace{1cm} (20)

which reduces to the expression (19) when \( \alpha = 1 \), while for the terraced model we have

\[ \langle d_y^2 \rangle - \langle d_y \rangle^2 = \frac{\alpha^2 x(1-x)}{p-1}. \]  \hspace{1cm} (21)

From these results the total fluctuation in the gallery height can be found from the general expression

\[ \langle d^2 \rangle - \langle d \rangle^2 = x\langle d_x^2 \rangle - \langle d_x \rangle^2 + (1-x)\langle d_y^2 \rangle - \langle d_y \rangle^2 + x(1-x)[(d_x) - \langle d_x \rangle]^2. \]  \hspace{1cm} (22)

For the catchment area model, this gives

\[ \langle d^2 \rangle - \langle d \rangle^2 = (1-x)^p \left[ 1 - (1 - x)^p \right] \]  \hspace{1cm} (23)
while for the soft catchment area model, we have

$$\langle d^2 \rangle - \langle d \rangle^2 = \alpha^2 (1-x)^p \left[ 1 - (1-x)^p \right] + 2(1-\alpha)\alpha x(1-x)^p + (1-\alpha)^2 x(1-x)$$  \hspace{1cm} (24)

and for the terraced model

$$\langle d^2 \rangle - \langle d \rangle^2 = x(1-x) \left[ (1-\alpha)^2 + \alpha^2 \frac{1-x}{p-1} \right]$$  \hspace{1cm} (25)

Of course all three of these expressions (23) – (25) have the property that the fluctuations go to zero in the limits $x \to 0$ and $x \to 1$. These expressions describe the **corrugations** or **undulations** in the gallery heights and so far have not been measured in any experiment.

### (2) $x$ – Dependent Host Layer

For intercalated layered solids in which the host and guest layer compositions are **interdependent**, both the gallery height and the host layer thickness will vary with $x$. This complication can be readily incorporated into the catchment area model as follows. Assume that the host layer can also be represented as a 2D solid solution. The generalized chemical form of the solid can then be written as $[A_{x}B_{1-x}][C_{y}D_{z}R]$ where the first (second) bracketed term represents the guest (host) layer and $R$ represents the residual constituent atoms of the host layer. An example of such a solid would be one of the layer double hydroxides such as $[Cl,V_{1.3}]-[Ni_{1.5}Al_{0.5}(OH)_{2}]$ where $V$ represents a vacancy in the guest layer.

In the spirit of the catchment area model we write the composition–dependent thickness of the host layer as

$$t(x) = t(0) - (h_x - h_y)x^q,$$  \hspace{1cm} (26)

where $h_x$ and $h_y$ are the respective heights of the $C$ and $D$ ions ($h_x > h_y$) and $q$ is an **intralayer** rigidity parameter which measures the rigidity against puckering due to substitutions within the host layer itself. Now we redefine $h(x)$ as

$$h(x) = t(x) + h_x(1-x)^p + h_y[1-(1-x)^p]$$  \hspace{1cm} (27)

Upon insertion of Eqs. (26) and (27) into Eq. (2), we obtain the normalized basal spacing for the $[A_{x}B_{1-x}][C_{y}D_{z}R]$ solid and

$$d_n(x) = \frac{(h_x - h_y)[1-(1-x)^p] - (h_x - h_y)x^q}{(h_x - h_y) + (h_x - h_y)}.$$  \hspace{1cm} (28)

### EXPERIMENTAL RESULTS

In this section we describe the experiments to which the theory developed above has been applied. To date it has not been necessary to go beyond the catchment area model and
its dimensionless parameters $p$ and $q$. It is quite remarkable that so much can be done with a model that usually contains only one and at most two adjustable parameters.

**Intercalated Graphite**

To date of the two Class 1 materials, graphite and boron–nitride, only the former has been the subject of layer rigidity studies. Graphite, the prototypical lamellar solid consists of layers of carbon atoms in a 3-fold coordinated honeycomb structure. The hexagonal form, with which all the graphite intercalation compounds have been prepared, contains two staggered layers in the 3D primitive unit cell. Fischer and Kim prepared a series of $Li_xV_{1/2}C_6$ graphite intercalation compounds and studied the composition dependence of their basal spacing using neutron diffraction. Graphite intercalation compounds have a well known propensity to form staged structures in which only every $n^{th}$ gallery contains guest species in a stage–$n$ compound. The presence of stages higher than 1 adds unnecessary complications to the interpretation of the composition dependence of the basal spacing. To avoid these complications, Fischer and Kim carried out their neutron studies of $Li_xV_{1/2}C_6$ at sufficiently high temperatures ($T = 700K$) to ensure a stage 1 structure for each compound studied. [They did not publish their diffraction patterns so we cannot present them here.]

![Graph showing composition dependence of basal spacing](image)

**Figure 4.** The composition ($x$) dependence of the normalized basal spacing $d_0$ of several layered solids including $\bullet [CO_3]_xH_2O\{H_2O\}$, $\square Li_xNi_1/3(OH)_2$, $\triangle CsRb_1xVermiculite$, $\triangle Li_xV_{1/2}TiS_2$, and $o Li_xV_{1/2}C_6$, (the error bars are smaller than size of the data points). The solid lines are nonlinear least squares fits to the data using Eq. (29) for the double hydroxide and Eq. (2) for the others. The $p$ and $q$ parameters yielding these solid lines are also shown in the figure. The dashed line is Vegard’s law.

The normalized basal spacing of $Li_xV_{1/2}C_6$ deduced from the data of Fischer and Kim is shown as open circles in Fig. X1. The solid line in the figure is a one–parameter fit to the data using Eq. (2). As can be seen the fit is very good and yields an interlayer rigidity parameter for graphite of $p = 2$. 

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Layer Dichalcogenides

There are many layer dichalcogenides which define a large portion of the Class II layered solids. Among these the most thoroughly studied vis-à-vis the layer rigidity is $Li_xV_{1-x}TiS_2$. The layers of titanium disulfide are composed of face shared $TiO_6$ octahedra and can adopt a number of stacking arrangements (polytypes) in the pristine form. The $Li$ ion intercalates the host material to form a stage 1 compound at all compositions in the range $0 < x \leq 1$.

Dahn and coworkers$^{11}$ used x-ray diffraction to measure the composition dependence of the basal spacing of $Li_xV_{1-x}TiS_2$. Their normalized results are shown as open triangles in Fig. 4. Dahn and coworkers$^{11}$ have attempted to interpret their data using a rigid layer model in which the inflexible host layers are coupled by harmonic Hooke's springs. Two spring constants were employed, one representing the Van der Waals bonds between the host layers and one representing the intercalant. Both Fischer and Kim$^{14}$ and Solin and coworkers$^5$ noted that the rigid layer model did not adequately describe the composition dependence of the basal spacing for either the graphite or layer dichalcogenide intercalation compounds. Solin and coworkers$^5$ also noted the same deficiency with respect to the layered clays (see discussion below). In contrast, the solid line through the $Li_xV_{1-x}TiS_2$ data of Fig. 4, which is based on the one parameter catchment area model [Eq. (2)], provides an excellent account of the data and yields a rigidity parameter of $p = 3.5$.

Clays

Clay intercalation compounds are naturally occurring or synthetic minerals that can be characterized as layered alumino-silicates. Such layered alumino-silicates are formed from the basic chemical building blocks: MO4 tetrahedra and MO6 octahedra where M is usually Si4+ but sometimes Al3+ and M' is usually Al3+ but can also be other metal ions such as Mg2+, Li1+ or Fe3+. The clay layers themselves are composed of sheets of corner connected tetrahedra coupled at a common oxygen interface to sheets of edge shared octahedra. A variety of such couplings is possible. For example when one octahedral sheet is bounded at its oxygen planes by two tetrahedral sheets the resultant structure is that of a 2:1 clay. Because the layers of such a structure are themselves composed of several multiply interconnected atomic layers, they form a very rigid entity. One such compound of this form is magnesium vermiculite the chemical formula of which is $Mg_{6,[Si4Al3]}[Al(OH)]_{3[Si4Al3]}$ where Mg is an exchangeable cation located in the gallery between the host layers which are represented by the bracketed term. Vermiculite is the quintessential member of the Class III group of layered solids.

By exchanging the Mg gallery cation in vermiculite with a solid solution of Cs and Rb, Solin and coworkers were able to study the composition dependence of the basal spacing of $Cs_xRb_{1-x}Vm$ ($Vm$ = vermiculite); a 2:1 clay.$^{5,6}$ The normalized basal spacing which they measured is shown as open squares in Fig. 4. Again Eq. (2) yields an excellent one parameter fit to the data (solid line) and the resultant value of the rigidity parameter is 7. To within experimental error, the same rigidity parameter was obtained in a study of the analogous compound $[(CH_3)NH]^+[(CH_3)NH]_{1-x}Vm$.$^5$

Layer Double Hydroxides

Layer double hydroxides are the first layered compounds studied for which both the guest and host layer compositions are interdependent. These compounds can be characterized by the chemical form $[A,B_{1-x}]_{3-D}C_{1-x}D_{x}R$ where A and B represent, respectively, anions and/or vacancies while C and D represent, respectively divalent and trivalent metal...
ions and \( R = (\text{OH})_2 \). For these compounds, homogeneous materials only exist for a narrow range of \( x \). The parent material \( \text{Ni(OH)}_2 \) crystallizes in the cadmium iodide (or equivalently, the brucite) structure. Thus host layers of this structure are composed of pairs of close packed planes of hydroxyl ions which themselves lie on a triangular lattice. The \( \text{Ni} \) ions lie in a plane between alternate pairs of \( \text{OH} \) planes and occupy octahedral sites. They thus form a triangular lattice identical to that adopted by the \( \text{OH} \) ions. Using sol–gel synthesis techniques, \( \text{Ni}^{2+} \) ions in nickel hydroxide can be substitutionally replaced by \( \text{Al}^{3+} \) ions with the concomitant insertion of carbonate ions and water into the gallery to provide overall charge neutrality in the presence of the positively charged host layer.

The resultant layer double hydroxide, \([(\text{CO}_3)_2x\gamma(\text{H}_2\text{O})] - [\text{Ni}_{1-x}\text{Al}_x(\text{OH})_2]\) has been studied extensively by Solin and coworkers\(^2\) with particular emphasis on the composition dependence of the basal spacing which is shown as solid diamonds in Fig. 4. This basal spacing response is unique since it exhibits a distinct maximum in contrast to other 2D solid solutions which exhibit a monotonic increase in the range \( 0 \leq x \leq 1 \). However this novel behavior can be fully accounted for using the catchment area model as embodied in Eq. (28). That equation when recast using parameters relevant to the \( \text{Ni–Al–CO}_3 \) layer double hydroxide becomes

\[
d_n(x) = \frac{2(r_{al} - r_{ni})[1 - (1 - x)^q] + h_{co3}[1 - (1 - x)^p]}{2(r_{al} - r_{ni}) + h_{co3}}
\]  

(29)

where \( h_{co3} \) is the effective height of the carbonate ion, \( r_{ni} = 0.69\text{Å} \) is the ionic radius\(^{16} \) of \( \text{Ni}^{2+} \), \( r_{al} = 0.51\text{Å} \) is the ionic radius\(^{16} \) of \( \text{Al}^{3+} \). The solid line through the solid diamonds in Fig 4 is a fit to the data using Eq. (29) with \( p, q \) and \( h_{co3} \) as adjustable parameters. The fit is quite satisfactory and yields \( h_{co3} = 2.9 \pm 0.1\text{Å}, \ p = 34.8 \pm 2.5 \) and \( q = 2.6 \pm 0.6 \). It is well known that the planar \( \text{CO}_3 \) ion is parallel to the host layer planes in \( \text{Ni–Al–CO}_3 \) layer double hydroxides. The height of the \( \text{CO}_3 \) ion in the gallery should thus be close to the van der Waals diameter of oxygen, 2.80Å. The fact that the value returned for the height of the carbonate from the fit using Eq. (29) is in good agreement with the expected value of lends credence to the validity of the catchment area model.

The value of \( p = 34.8 \pm 2.5 \) is much higher than obtained for any other compound studied to date. We believe this large value is due to the water that is associated with the \( \text{CO}_3 \) ion in the galleries.\(^2\) We have shown that between 5 and 6 water molecules are tied to each carbonate ion as a result of intercalation. The precise number depends upon the concentration \( x \) as shown in Fig. 5 of ref. 2. The lateral area of the carbonate ion\(^{16} \) can be estimated as 22.7Å\(^2\), and the lateral area of the water molecule\(^{16} \) is 12.2Å\(^2\). This assumes that the water molecule lies flat with the two protons in the plane. The area quoted is the area of the circumscribing circle. From these values, we deduce that the radii of the carbonate ion and water respectively, are 2.7Å and 2.0Å, and hence the area of the circle that contains a carbonate ion surrounded by 5 or 6 water molecules is 69.4Å\(^2\). This is a factor of 6.21 larger than the area 22.7Å\(^2\) of the bare carbonate ion. Using this as the reference value, the dimensionless rigidity parameter \( p \), which measures the size of the catchment area, is reduced by a factor 6.21, from the value of 34.8 to a renormalized value of 5.6. This value is large, as the layers are very rigid, but not so unreasonably large as the unrenormalized value of 34.8. Note that our discussion of the apparent large value of \( p \) and Eqs. (26)–(29) are different from previously\(^2\), and our current discussion represents further thinking on this matter. The experimental results remain the same of course.
CONCLUDING REMARKS

The rigidity parameters for all of the materials discussed above have been listed in Table I by Class together with the intersite distance between the guest ions and the site ratio. It has been implicitly assumed that the guest ions for all materials studied decorate a lattice defined by the basal surface of the host layers. The intersite distance is then the lattice constant of the decorated lattice.

Table 1. Classification and Relevant Rigidity Parameters for Layered Solids.

<table>
<thead>
<tr>
<th>Host</th>
<th>Class</th>
<th>Intersite Distance $a(\text{Å})$</th>
<th>Interlayer Rigidity $p (\pm 5%)$</th>
<th>Intra layer Rigidity $q (\pm 5%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>I</td>
<td>2.4704±0.0001</td>
<td>2</td>
<td>—</td>
</tr>
<tr>
<td>Titanium Disulfide</td>
<td>II</td>
<td>3.410±0.005</td>
<td>3.5</td>
<td>—</td>
</tr>
<tr>
<td>Nickel Hydroxide</td>
<td>II–III</td>
<td>3.126±0.005</td>
<td>5.6</td>
<td>2.4</td>
</tr>
<tr>
<td>Vermiculite</td>
<td>III</td>
<td>5.344±0.003</td>
<td>7</td>
<td>—</td>
</tr>
</tbody>
</table>

† This is the renormalized value. The measured value is 3.48. See text.

As can be seen from Table I, the interlayer rigidity parameter provides a quantitative measure of the systematic increase of layer rigidity with the thickness and interconnectivity of the host layer as expected on qualitative grounds. Thus the layers of vermiculite are much more rigid with respect to transverse distortions than those of titanium disulfide which in turn are more rigid than those of graphite. The results for $p$ given in Table 1 track our intuition regarding the rigidity of the layers. The case of nickel hydroxide is particularly interesting as the interlayer rigidity parameter is the largest we have measured to date and puts the material in Class III, whereas the intralayer rigidity parameter is smaller, corresponding to a Class II material like titanium disulfide.

The catchment area model works well in a wide variety of layered intercalation compounds. To date all of the compounds to which the model has been applied have been amenable to a description in which the stiffness of the bonds between the guest ions in the gallery and the host layers is much greater than the transverse rigidity of those layers. This is what allows us to associate composition dependent changes in the basal spacing solely with the rigidity of the host layers. However, if the layer rigidity greatly exceeds the guest–host bond stiffness, the catchment area model might yield a very low rigidity parameter for a solid with extremely rigid layers. There is preliminary evidence that the layered perovskite system $Cs_{x}Rb_{1-x}Ca_{2}Nb_{3}O_{10}$, the layers of which consist of three interconnected perovskite–like layers of corner shared $NbO_{6}$ octahedra and are separated by 2D solid solution layers of $Cs/Rb$, has these very characteristics.17

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REFERENCES