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Composition-Driven *c*-Axis Expansion of Intercalated Layered Solids: 1D Non-Vegard's-Law Behavior in a 2D Solid Solution

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We show that a layer rigidity model which includes the effects of elastic deformations of the host layers can account for the composition dependence of the *c*-axis lattice expansion of a variety of layered intercalation compounds. Rigidity parameters deduced from this model for each of the three classes of layered solids are reflective of structurally derived rigidity as are the healing lengths computed on the basis of discrete and continuum analyses. The layer rigidity model provides the first quantitative explanation for the 1D non-Vegard's-law behavior of a 2D solid solution.

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All crystalline solid solutions exhibit a composition-dependent unit-cell volume which generally increases with the concentration of the largest constituent.¹ When this variation is linear the system is said to obey Vegard's law.² Most solid solutions exhibit a more complex nonlinear behavior³ which has been accounted for empirically by augmenting Vegard's law with a polynomial that represents a composition-dependent mixing volume.³ In order to gain a more fundamental understanding of the origin of non-Vegard's-law behavior several authors⁴⁻⁶ have found it advantageous to address systems which contain crystalline solid solutions of reduced dimensionality. For instance, there are a variety of ternary layered intercalation compounds (hereinafter called ternaries) of the form $A_{1-x_g}B_{x_g}L$, $0 \leq x_g \leq 1$, where B is the larger ion and x_g defines the composition of the ions which actually reside in the gallery and contribute to *c*-axis expansion. The guest species, A and B , form a 2D commensurate but compositionally disordered solid solution between the host layers, L .⁷⁻⁹ [Note that A can represent a vacancy (i.e., $A=V$).] Because of the highly anisotropic structural and physical properties of ternaries,⁷⁻⁹ the dominant change in their cell volume with intercalate composition results from *c*-axis expansion. The one-dimensional (1D) form of Vegard's law is then

$$c(x_g) = (1-x_g)c_A + x_gc_B, \quad (1)$$

where c , c_A , and c_B are the *c*-axis repeat distances of the mixed and end-member compounds. But most ternaries exhibit a superlinear (concave downward) $c(x_g)$.⁴⁻⁹ Even though ternaries represent the most basic and simplified (e.g., 1D) systems for studying composition-driven lattice expansion, attempts to account for their nonlinear response have to date been markedly unsuccessful. In this Letter we rectify this deficiency and present a one-parameter model which accounts for the *c*-axis expansion of a broad range of ternaries.

Layered solids have been classified into three subgroups on the basis of their rigidity with respect to out-

of-plane distortions.¹⁰ Thus graphite is the prototypical class-I layered solid whose monatomically thin layers¹¹ are "floppy." The three-atom-thick layers of the dichalcogenides¹² such as TiS_2 are more "rigid" and render them class-II status.¹⁰ Finally, the 2:1 layered-silicate clays such as vermiculite (Vm) whose host layers are constructed from seven interconnected planes of atoms¹³ are extremely "rigid" and belong in the class-III grouping.¹⁰ All of the above-mentioned host systems can be intercalated to form solid solution ternaries. Although the three resultant classes of ternaries exhibit a broad range of physical properties, the graphite, TiS_2 , and Vm hosts possess a common structural feature: Their guest sites can form a 2D triangular lattice. We will show that the *c*-axis lattice expansions of these "triangular" ternaries are amenable to an analysis which spans their physical diversity.

In Fig. 1, we show the measured composition dependence of the normalized basal spacing, $d_n(x_g)$, for $V_{1-x_g}\text{Li}_{x_g}\text{C}_6$,⁶ $V_{1-x_g}\text{Li}_{x_g}\text{TiS}_2$,⁴ and $\text{Rb}_{1-x_g}\text{Cs}_{x_g}\text{Vm}$,¹⁴ which represent, respectively, the class-I, -II, and -III triangular host systems. Here

$$d_n(x_g) \equiv [c(x_g) - c(0)]/[c(1) - c(0)].$$

All three ternaries exhibit a superlinear non-Vegard's-law behavior.

In an attempt to explain the *c*-axis expansion of $V_{1-x_g}\text{Li}_{x_g}\text{TiS}_2$, Dahn, Dahn, and Haering⁴ employed a rigid-layer model in which the undeformable layers are coupled by springs of spring constants k and K representing, respectively, the guest-host interaction and the vacancy- or host-host interaction. Safran modified the original rigid-layer model to account for anharmonic softening of the vacancy springs in the presence of the guest springs.⁵ Then the rigid-layer model yields $d_n(x_g) = x_g/[1 - (1-x_g)\alpha + x_g]$ which satisfies the boundary conditions $d_n(0) = 0$, $d_n(1) = 1$ and gives Vegard's-law behavior when $\alpha = 1$. Plots of the modified rigid-layer model for several values of α are shown in Fig. 1. It is evident from these plots that the rigid-layer model

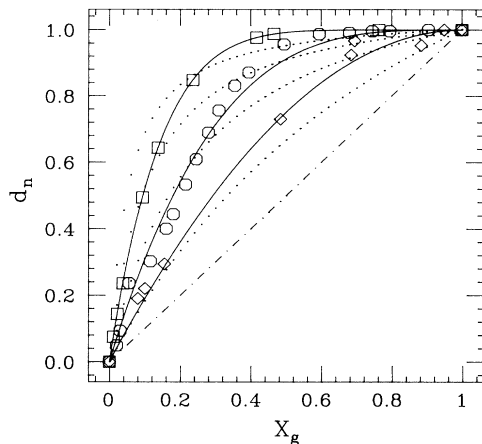


FIG. 1. The normalized basal spacing vs expanding-site gallery composition for $\text{Rb}_{1-x}\text{Cs}_x\text{Vm}$ (squares) (Ref. 14), $\text{V}_{1-x}\text{Li}_x\text{TiS}_2$ (circles) (Ref. 4), and $\text{V}_{1-x}\text{Li}_x\text{C}_6$ (diamonds) (Ref. 6). The solid lines are fits to the data using the layer rigidity model (see text) and yield the rigidity parameters, P , given in Table I. The dotted lines are fits to the data using the rigid-layer model (see text) with $\alpha=0.5, 0.2, 0.1$, and 0.05 , bottom to top, respectively. The straight dash-dotted line represents Vegard's law and corresponds to $P=1$ or $\alpha=1$.

fails to fit the measured $d_n(x_g)$ for any of the ternaries. This is not surprising for graphite or even for TiS_2 since their host layers are far from rigid. But the model also fails for the $\text{Rb}_{1-x}\text{Cs}_x\text{Vm}$ system to which it should be most applicable given its high host-layer rigidity.¹⁰

In an effort to improve upon the rigid-layer model, Jin and Mahanti¹⁵ (JM) introduced a model with nondeformable layers but with "additional" springs which represented the finite compressibility of the guest species. Their model also addressed interlayer correlations. Nevertheless, even though this model employed several parameters, its success was marginal when it was applied to the dual-alkali graphite intercalation compounds (GIC's) of the type $M_{1-x}M'_x\text{C}_8$ for which interlayer correlations should be most pronounced in $d_n(x)$. [We do not address the dual-alkali GIC's because the gallery composition of these materials has not yet been estab-

lished and the actual form of $d_n(x_g)$ is therefore unknown.] Moreover, the multiparameter JM model does not provide an acceptable fit to the data of Fig. 1.

We now describe our layer rigidity model which unlike all previous models accounts for the data of Fig. 1 and does so with the introduction of only one parameter. The essential feature of the layer rigidity model is the deformability of the host layers which in its discrete version is characterized by a rigidity parameter, P . Here we also introduce a continuum version which is characterized by a healing length, λ , and we derive a relation between P and λ which provides an independent test of the model when the host elastic constants or phonon dispersions are known.

In the discrete embodiment of the model which we introduced¹⁴ to explain the sigmoidal form of $d_n(x)$ for Vm ternaries, one envisions a single gallery bounded by a pair of host layers. Incompressible guest ions whose relative proportions depend on x_g randomly decorate the sites of a 2D triangular lattice. The layers experience a pillboxlike discrete puckering over the larger B ion. The lateral extent of this puckering is specified by P which is equal to the total number of puckered lattice sites for a single B ion. Computer simulations¹⁵ of the average gallery height, $d(x_g)$, yield a normalized basal spacing which obeys Vegard's law for $P=1$ and exhibits super-linear behavior for larger values of P . These simulation results are in excellent agreement with an analytical solution of the form^{14,16}

$$d_n(x_g) = 1 - (1 - x_g)^P, \quad 0 \leq x_g \leq 1. \quad (2)$$

In Fig. 1 the solid lines represent fits to the data using Eq. (2). With the exception of the $\text{V}_{1-x}\text{Li}_x\text{TiS}_2$ system the fits are excellent and far superior to those obtained using the rigid-layer model. The rigidity parameters deduced from the fits to the data in Fig. 1 are given in Table I and as expected increase from class-I to class-III ternaries.

It is desirable to relate P to a healing length which is a measure of the lateral range over which a puckered layer returns to its undistorted form. The healing length, λ_d , for the discrete layer rigidity model can be simply es-

TABLE I. Important parameters for several ternary layered intercalation compounds.

Stage of structure	Class	Sample	Rigidity parameter P	Site ratio α	Intersite distance a_0 (Å)	Healing lengths	
						λ_d (Å)	λ_c (Å)
Stage 1, triangular	I	$\text{V}_{1-x}\text{Li}_x\text{C}_6$	2	3	2.46	3.16	2.45
	II	$\text{V}_{1-x}\text{Li}_x\text{TiS}_2$	3.5	1	3.41	3.35	2.60
	III	$\text{Rb}_{1-x}\text{Cs}_x\text{Vm}$	7	1	5.34	7.42	5.77
Stage 2, unknown	II ^a	$\text{V}_{2-x}(\text{H}_2)_x\text{KC}_{24}$	4.8 {6.9} ^b	...	$\sqrt{12}(2.46)^c$
	II ^a	$\text{V}_{2-x}(\text{D}_2)_x\text{KC}_{24}$	5.0 {24.8} ^b	...	$\sqrt{12}(2.46)^c$

^aThe class designation of this compound is based on the fact that the KC_{24} "host layers" consist of three atomic planes (see text).

^bThe bracketed number is the measured value and the unbracketed number is the actual (corrected) value (see text).

^cThis value is based on a stoichiometric K/C ratio of exactly 1/24.

timated from the relation $P = (\pi\lambda_d^2)/\alpha A_0$, where the numerator is the area of the puckered region and α is the ratio of the area per site of the saturated ($x_g = 1$) superlattice to the area per host site [for $\text{Li}_{x_g}\text{C}_6$ the superlattice is $(\sqrt{3} \times \sqrt{3})R30^\circ$, so $\alpha = 3$]. If a_0 is the host-lattice intersite distance, then $\lambda_d = [1/(3.63)^{1/2}](\alpha P)^{1/2}a_0$ (see Table I).

To more precisely quantify the influence of layer deformations on c -axis expansion we treat the host layers as a stacked set of elastic continua in the form of deformable plates of finite thickness. For galleries which each contain single pointlike B ions at \mathbf{r}_0 in a sea of vacancies or A ions, the gallery height, $W(\mathbf{r} - \mathbf{r}_0)$, is obtained from^{17,18}

$$\{D\nabla^4 - K\nabla^2 + G\}W(\mathbf{r} - \mathbf{r}_0) = f_0\delta(\mathbf{r} - \mathbf{r}_0), \quad (3)$$

where D and K are, respectively, the flexural rigidity and the transverse rigidity of the individual plates, and G is the c -axis compressibility of the stack while f_0 represents the δ -function-like force from the B ion. Each of the coefficients in the curly brackets in Eq. (3) can be expressed in terms of the effective layer thickness, $2H$, the basal spacing, d , and the host elastic constants, C_{ij} .¹⁸ Thus $D = 2[(C_{11}^2 - C_{12}^2)H^3]/3C_{11}$, $K = dC_{44}$, and $G = 2C_{33}/d$. Equation (3) can be solved to give

$$W(\rho) = \frac{f_0}{2\pi(DG)^{1/2}} \int_0^\infty \frac{qJ_0(q\rho/l_0)}{q^4 + 2\delta q^2 + 1} dq, \quad (4)$$

where $\rho = |\mathbf{r} - \mathbf{r}_0|$, $l_0 = (D/G)^{1/4}$ gives the length scale, and $\delta = K/2(GD)^{1/2} \leq 1$ gives the relative strength of the transverse rigidity.

For a single defect, we can define the healing length λ_c as the distance at which the gallery height relaxes to half its maximum value, i.e., $W(\lambda_c) = \frac{1}{2}W(0)$. From Eq. (4) we obtain $\lambda_c(\delta) = Z(\delta)l_0$, where $Z(\delta)$ is a slowly decreasing function of δ with $Z(0) = 1.302$, $Z(0.5) = 1.276$. One can obtain λ_c from δ and l_0 . These are functions, respectively, of D , K , and G , the first two of which can be determined from the in-plane TA dispersion of layered solids given by $\omega^2(q) \propto Dq^4 + Kq^2$. Alternatively, K and G can be obtained from the stiffness constants as can D if H is known. For graphite $K \approx 0$, so the TA dispersion yields D directly and K and G are found from the known basal spacing and reported C_{ij} 's. Using this approach we find $\lambda_c = 1.88 \text{ \AA}$ in reasonable agreement with the value 2.45 \AA obtained from the experimental value of P (see Table I and the following discussion).

For most layered materials, neither the elastic constants nor the phonon dispersions are available. Therefore, it is useful to derive a relationship between λ_c and P by extending the continuum theory to the case of a dilute distribution of B ions. Using the superposition principle, we can obtain the average gallery height, $\langle W \rangle$, as a function of the concentration of x_g . In the limit $x_g \ll 1$ the result for $\langle W \rangle$ normalized by the maximum gallery

height, $W(\rho=0)$, due to a single B ion yields

$$d_n(x_g) = \alpha g(\delta) [\lambda_c(\delta)/a_0]^2 x_g, \quad (5)$$

where $g(\delta)$ is given by

$$g(\delta) = \frac{16}{\sqrt{13}} \frac{(1 - \delta^2)^{1/2}}{1 - (2/\pi) \tan^{-1}[\delta/(1 - \delta^2)^{1/2}]}. \quad (6)$$

By comparing Eq. (5) with Eq. (2), we have

$$\lambda_c(\delta) = a_0[\alpha P/g(\delta)]^{1/2}. \quad (7)$$

The values of $\lambda_c(\delta)$ thus evaluated for stage-1 ternaries compare reasonably well with those of λ_d (see Table I). Note that λ_c for a defect of finite size should be somewhat larger than of a point object. Here the value of δ is assumed to be the same as for graphite (0.14) in the cases of TiS_2 and Vm . The short healing length found for graphite is consistent with the results of x-ray studies of disordered alkali graphite intercalation compounds¹⁹ which indicate that the host potential is strongly modulated in the vicinity of a guest ion.

Since the charge on the host layers in class-III ternaries is fixed, their c -axis expansion is purely elastic. However, the success of the layer rigidity model for the class-I and -II ternaries is an indication that charge exchange has a small effect on host layer stiffness. If this were not so, P would be composition dependent and the data in Fig. 1 could not be fitted with a single parameter. As further evidence of the success of the layer rigidity model for systems dominated by elastic forces, we address the case of the physisorption of H_2 and D_2 into stage-2 KC_{24} to form the ternaries $V_{2-x'}(R_2)_{x'}\text{KC}_{24}$, $0 \leq x' \leq 2$, $R = \text{H, D}$.²⁰ (Here we consider KC_{24} to be the host material.) Although the structure of the site superlattice for this has not been definitively clarified,^{7,20} and there appear to be two sets of guest sites,^{20,21} it is well established that the physisorption of H_2 or D_2 into KC_{24} does not result in measurable charge backtransfer from the host layers to the intercalate layer.^{7,20} Therefore the layer rigidity model should account well for the c -axis expansion in these ternaries. That this is indeed the case is evidenced by the data shown in Fig. 2. These data were derived from the work of Doll, Eklund, and Senatore,²⁰ who fitted $d(x')$ with the arbitrary function $d(x') = 1 - \exp(-\gamma x')$. The same function when normalized and rescaled from x' to x with $0 \leq x \leq 1$ gives a reasonable fit to $d_n(x)$ (dotted lines in Fig. 2). However, Eq. (2) of the layer rigidity model gives an equally good fit for both D_2 and H_2 . The reason that the function chosen by Doll, Eklund, and Senatore works so well is that Eq. (2) extrapolates to that function at small x and the two functions are very similar but do not extrapolate for $x \rightarrow 1$.

The rigidity parameters obtained from the fits to the data in Fig. 2 are given in Table I. Since the site superlattice structure is uncertain,^{7,20} we cannot calculate the healing lengths. Nevertheless, the measured rigidity pa-

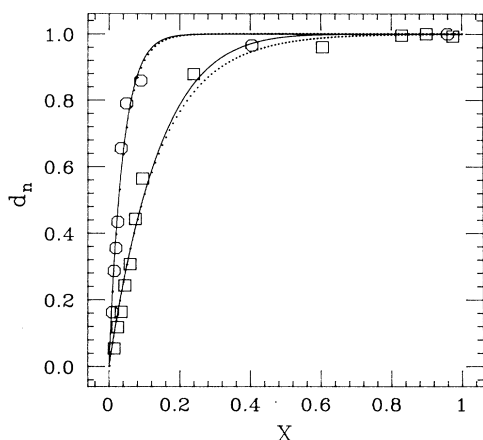


FIG. 2. The normalized basal spacing vs gross composition for $V_{1-x}(R_2)_x\text{KC}_{24}$ (Ref. 20), $R=\text{H}$ (squares), D (circles). The solid lines are fits to the data using Eq. (2) of the text and yield the measured rigidity parameters given in Table I. The dotted lines are fits using the function $d_n(x) = 1 - \exp(-\gamma x)$ with $\gamma = 7.26$ and 25.2 for H_2 and D_2 , respectively.

rameters are large especially in the case of D_2 . We suggest that this apparent enhancement of the rigidity parameter results from the presence of two types of gallery sites^{20,21} of which only one contributes to c -axis expansion.²⁰ The fraction of expanding sites can be estimated from the minimum value of x at which $d_n(x) = 1$ and is estimated from Fig. 2 to be ~ 0.2 and 0.7 for D_2 and H_2 , respectively. Thus the actual rigidity parameters which correspond to a rescaling (stretching) of the abscissa in Fig. 2 are $0.2 \times 24.8 = 5.0$ and $0.7 \times 6.9 = 4.8$ (see Table I). The increased rigidity of the stage-2 KC_{24} "host" relative to that of graphite is a consequence of the fact that the host "layers" in the former contain three interconnected planes of atoms (two C layers and one K layer), whereas those in the latter are single atomic sheets.

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