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Layer Rigidity in Lamellar Solids

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A number of theoretical models have been put forth to account for the layer rigidity of a variety of intercalated layered solids with fixed host structures as revealed by the composition-dependence of the basal spacing. The main features of each model will be reviewed briefly and their strengths and weaknesses will be assessed. It will be shown that no single model proposed to date is sufficiently universal to explain the available data.

Keywords: lamellar solids; layer rigidity; fixed-host; variable-host

INTRODUCTION

One of the most basic properties of a lamellar solid is its layer rigidity with respect to transverse distortions of the host layer in the direction normal to the layer plane. Layer rigidity impacts a number of the novel physical phenomena exhibited by lamellar solids including staging[1], anomalous diffusion[2], and most importantly basal expansion.[3] It is the latter property which is normally used to determine the rigidity. Specifically, one measures $d_n(x) = \{[d(x)-d(0)]/[d(1)-d(0)]\}$, the composition dependence of the normalized basal spacing of a ternary solid solution layered solid of the form $[A_{1-x}B_x]$: [L], $0 \leq x \leq 1$. Here the first (second) bracketed term represents the guest (host) layer, A (B) is the smaller (larger) guest ion (A can also be a vacancy) and d(x) is the observed dependence of the basal spacing on composition. Also note that solids for which the host layer composition does not vary with x are referred to as "fixed-host" materials whereas those whose host structure depends on x are

labeled "variable-host" materials. We address only the former here since there is very little data on the latter.

During the past several years, a number of theoretical models have been put forth to account quantitatively for the function $d_n(x)$ as determined experimentally from x-ray diffraction measurements. [By fitting the model function to the data for a given lamellar solid, the relevant rigidity parameter(s) can be deduced.] Here we briefly describe the rigidity models, assess their relative strengths and weakness and indicate possible directions for further improvements.

DISCUSSION OF THE MODELS

The bulk of layer rigidity studies reported to date have been carried out on fixed-host lamellar solids including graphite, layer dichalcogenides, layer double hydroxides, layer perovskites and clays (layered alumino-silicates). The first rigidity model employed was the Rigid Layer (RL) model[4] in which the host layers are treated as perfectly rigid sheets coupled to deformable guests by two types of spring, one representing the host-host interaction with spring constant K and one representing the guest host interaction with spring constant k. In this model, the normalized basal spacing is given by

$$d_n(x) = \frac{x}{(1-x)\gamma + x} \tag{1}$$

where $\gamma = K/k$. The RL model was applied to $V_{1-x}Li_xTiS_2$ and $V_{1-x}Li_xC_6$ (where V = vacancy) but without much success and has therefore not been further studied.

By far the most successful and popular model developed to date is the Finite Layer Rigidity Model[5] in which all elastic distortions are incorporated into the host layer while the guest ions are treated as rigid spheres. The normalized basal spacing in the FLR model is given by

$$d_n(x) = 1 - (1-x)^p \tag{2}$$

where p is the rigidity parameter. Physically in the discrete version of the FLR, if one introduces a B ion of height h_B into a region of A ions of height h_A, then p is the number of lattice sites around B that acquire the height h_B as a result of the host layer rigidity. In Fig. 1, we show the fits of the FLR model to a wide variety of fixed-host intercalated lamellar solids.

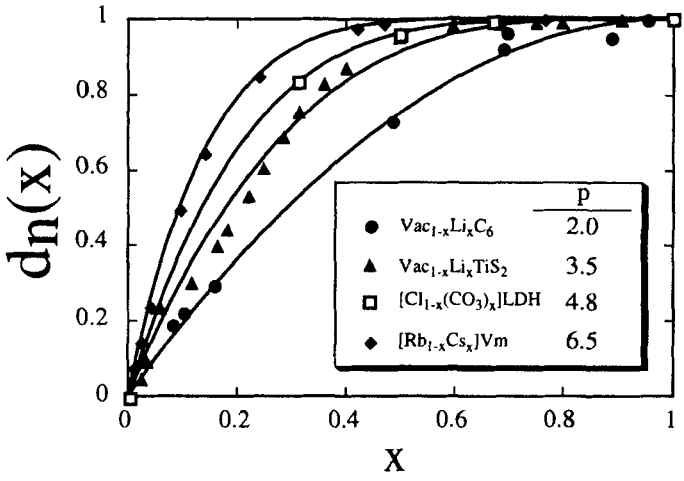

FIGURE 1 The composition-dependence of the basal spacing of a number of fixed-host layered intercalation compounds (Vm=vermiculite, LDH= layer double hydroxide). The solid and open symbols are data from x-ray diffraction measurements. The solid lines are least squares fits to the data using Eq. (2) of the text. The resultant rigidity parameter, p, for each fit is shown in the legend.

As can be seen from Fig. 1, not only does the FLR model provide an excellent fir to the data but it also yields rigidity parameters which are consistent with intuition, e.g. the rigidity increases monotonically from graphite which is "floppy" to clay which is "rigid".

Though the FLR model works well for the solids shown in Fig. 1, it fails dramatically when applied to the fixed-host layer perovskites of the form, $A_xB_{1-x}[C_{n-1}D_nO_{3n+1}]$ where the $[C_{n-1}D_nO_{3n+1}]$ host layers themselves consist of a stack of n sheets of corner connected DO_6 perovskite octahedra.[6]

These fixed-host materials are quite unusual because the thickness and thus the rigidity of the host layer is stepwise variable. The experimentally determined $d_n(x)$ for the bilayer[7] and trilayer[8] perovskites $Cs_xRb_{1-x}[LaNb_2O_7]$ and $Cs_xRb_{1-x}[Ca_2Nb_3O_{10}]$, respectively are shown in Fig. 2.

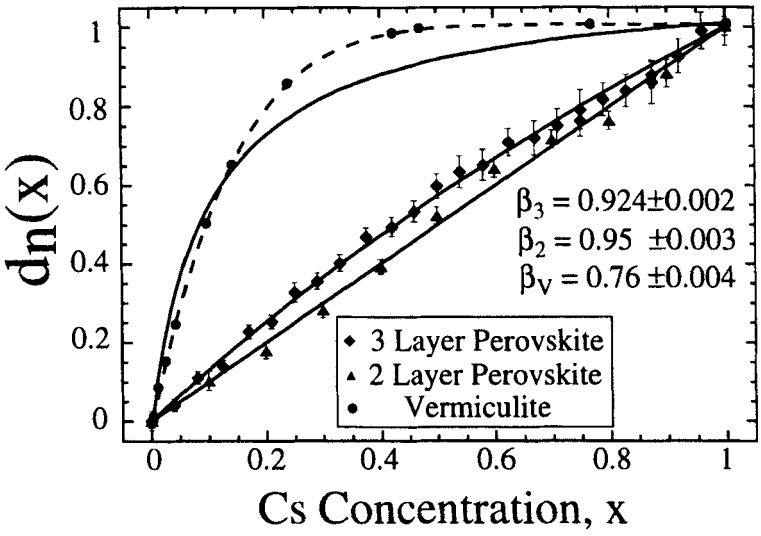

FIGURE 2 The composition-dependence of the basal spacing of the bilayer $Cs_xRb_{1-x}[Ca_2Nb_3O_{10}]$ and trilayer $Cs_xRb_{1-x}[Ca_2Nb_3O_{10}]$ perovskite fixed-host compounds and Cs_xRb_{1-x}Vermiculite. The solid symbols are data from x-ray diffraction measurements. The solid lines are least squares fits to the data using the ALJ model [Eq. (3)]. The resultant β parameter for each fit is shown in the legend. The dashed line is a least squares fit to the data using the FLR model [Eq. (2)].

The perovskite data of Fig. 2 can be fit quite well with the FLR model but yield rigidity parameters p_3=1.2[7] and p_2=1[8] for the trilayer and bilayer compounds, respectively. These results are unphysical because the multi-connected layers of the preovskites are certainly more rigid than those of graphite. One might expect the RL model to work well on such rigid materials but it too yields highly unphysical results. The weakness of the FLR and RL

models is that they are both fully harmonic and both incorporate assumptions (complete rigidity of either the host or guest layers) which are apparently not valid for the perovskites.

The anharmonic Lennard-Jones (ALJ) model that was recently developed by Solin and co-workers[7] cures these deficiencies. While the FLR and RL models require only one adjustable parameter to fit the data, the ALJ model requires two unless one assumes the layers are rigid. With this assumption, the ALJ model yields

$$[d_n(x)]_{LJ} = \frac{\left[\frac{x+\alpha\beta^{14}(1-x)}{x+\alpha\beta^{8}(1-x)}\right]^{1/6} - \beta}{1-\beta} \tag{3}$$

where $\alpha = K_B / K_A$ is the (known) stiffness constant ratio of the gallery ions and $\beta = h_B^0 / h_A^0$ is the ratio of the equilibrium gallery heights. If we define the host layer thickness to be t, then the parameter β can be rewritten as

$$\beta = \frac{h_B^0}{h_A^0} = \frac{d(0)-t}{d(1)-t}. \tag{4}$$

The parameter $\alpha = 1.73$ is deduced from the compressibilities of Rb and Cs. Thus the rigid layer ALJ model, like the RL and FLR models requires only a one-parameter fit to the basal spacing data. But there is a self-consistency check on the ALJ fits because the fitted value of b can be used to compute the host layer thickness using Eq. (4) and the result can be compared with values obtained crystallographically. Following this approach, Solin and co-workers found values of β_3=0.924±0.002 and β_2=0.95±0.003 yielding values of t_3=12.5±0.5Å and t_2=7.7±0.2Å in good agreement with the crystallographic values of 11.96Å and 7.97Å, respectively.

It is informative to test the ALJ model on one of the lamellar solids for which the FLR model was successful. The ideal choice for this comparison is $Rb_{1-x}Cs_x$:Vermiculite since it contains the same pair of guest ions as were employed in the studies of the perovskites. Figure 2 shows the fit to the vermiculite basal spacing data using Eq. (3) of the ALJ model (with rigid layers) together with the fit to the same data (see Fig. 1) using the FLR model.

The ALJ fit, while reasonable, is not as good as that obtained with the FLR model. Nevertheless, the value of β_V= 0.760±0.004 deduced from the fit yields a layer thickness value of t_V = 9.18Å which is in very good agreement with the corresponding crystallographic value of 9.34Å. The fit can be improved by relaxing the rigid layer assumption but this would involve an additional parameter. So the FLR model is more suitable in the case of vermiculites.

CONCLUSION

For most intercalated layered solids studied to date, incorporating the elastic distortions into the host layers while treating the guest as rigid is justified and the FLR model accounts well for $d_n(x)$. In the case of the layer perovskites, the reverse assumptions obtain and the ALJ model is superior. It is likely that any system whose host and guest layers both carry significant elastic distortion energy, will require a more complex multi parameter model.

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