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Computer Simulation of Polytypes*

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Abstract

Polytypes have been simulated, treating them as analogues of a one-dimensional spin-half Ising chain with competing short-range and infinite-range interactions. Short-range interactions are treated as random variables to approximate conditions of growth from melt as well as from vapour. Besides ordered polytypes up to $12R$, short stretches of long-period polytypes (up to $33R$) have been observed. Such long-period sequences could be of significance in the context of Frank's theory of polytypism. The form of short-range interactions employed in the study has been justified by carrying out model potential calculations.

I. Introduction

In an earlier paper (Ramasesha & Rao, 1977, referred to as R & R from here on), we discussed our attempts at computer simulation of polytypes treating them as analogues of a one-dimensional spin-half Ising chain with competing short- and infinite-range interactions. The growth conditions simulated were akin to the conditions of growth of polytypes from melt, but the interaction parameters were considered as constant during any given simulation. However, during the growth of a polytype (whether it be from melt or vapour), it is reasonable to assume that the atoms in the layers are jostling about leading to fluctuations in interlayer interaction strength. A proper simulation of polytypes should take into account such fluctuations.

This becomes possible if we treat the interaction parameters in the simulation as random variables (varying with time) during any given simulation. We have, therefore, carried out a computer simulation of polytype growth from vapour employing both constant and fluctuating short-range interaction parameters. Finally, we have carried out model potential calculations aimed at justifying the form of short-range interaction parameters employed in the present study.

II. Model employed

Since any layer in a close-packed structure can either be in a hexagonal (h) or a cubic (k) configuration, each layer can be represented by any of the two spin states of an Ising spin with $S = \frac{1}{2}$. In this representation, a polytype corresponds to an ordered (equilibrium or metastable† state of a chain of such spins. To obtain such an ordered state, it is necessary to invoke infinite-range interactions between the spins, the system of interest being essentially one-dimensional. As already discussed by R & R, such an interaction term can arise due to elastic interactions between the layers. This interaction favours a completely cubic or a completely hexagonal close-packed arrangement. In spin terminology, this is equivalent to the two possible states of magnetization of a ferromagnetic Ising chain. The elastic interaction, being infinite ranged, would in

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† It is not possible to say definitely whether a given polytypic form is an equilibrium or a metastable phase under given temperature and pressure conditions because many polytypic forms exist with no discernible differences in stability at ordinary temperatures and pressures.

this terminology imply an equivalent-neighbour ferro-magnetic interaction. To obtain a wide variety of equilibrium or metastable spin arrangements of the chain (corresponding to different stable polytypic forms), it is necessary that a short-range interaction term, which opposes the infinite-range interaction term, be introduced. Such an Ising chain with nearest-neighbour and next-nearest-neighbour antiferro-magnetic interactions and infinite-range ferromagnetic interactions has already been studied by Theumann & Høye (1971). Monte Carlo simulation studies of this Ising chain (Ramasesha, 1978) showed that the properties of the Ising chain are akin to those of polytypes. Simulation studies of polytypes by R & R were, therefore, based on the Theumann–Høye Hamiltonian. The same basic Hamiltonian is employed in the present study and is given by

$$H = -J \sum_i S_i^z S_{i+1}^z - K \sum_i S_i^z S_{i+2}^z - L \sum_{i,j} S_i^z S_j^z$$
$$- H^{\text{ext}} \sum_i S_i^z, \qquad (1)$$

where S_i^z can take the values $\pm\frac{1}{2}$, J, K, L are the interaction parameters and H^{ext} is the applied field, which in polytype terminology is responsible for a difference in the energy between isolated layers in h and k configurations. The results of R & R are summarized in Table 1.

III. Simulation procedure

In the simulation of polytypes from melt with random short-range interactions, a random configuration of 1000 layers is stored in the computer. Any one of the 1000 layers is picked at random by use of a random integer between 1 and 1000; a general double-layer mechanism discussed by R & R is used for the rearrangement of this layer and one of its neighbours. The change in energy, ΔE, for this rearrangement process has to be calculated at this stage. Since the interaction strengths J and K are assumed to be random variables, to calculate ΔE for the rearrangement process we have to provide the value of J and K to be used at each step. This is done as follows. We assume that J and K are distributed according to a Gaussian with means J_0 and K_0 and standard deviations σ_J and σ_K respectively. The probabilities that the interaction parameters chosen for the process are J_n and K_n are then given by

$$P(J_n) = \frac{1}{\sigma_J \sqrt{2\pi}} \exp\left[\frac{(J_n - J_0)^2}{2\sigma_J^2}\right], \qquad (2a)$$

$$P(K_n) = \frac{1}{\sigma_K \sqrt{2\pi}} \exp\left[\frac{(K_n - K_0)^2}{2\sigma_K^2}\right]. \qquad (2b)$$

We also assume that the interaction parameters take discrete values and limit their number to eleven lying uniformly in the interval $J_0 \pm 3\sigma_J$ and $K_0 \pm 3\sigma_K$. This interval encloses ~99% of the area under the Gaussian. The probability that a given discrete value, say J_n, is taken up for a rearrangement step is given by

$$\varphi(J_n) \propto \int_{J_{n-1}}^{J_n} P(J) \, dJ. \qquad (3)$$

To make the actual selection, the interval (0,1) is subdivided into eleven subintervals each of length proportional to $\varphi(J_n)$. A random number between 0 and 1 is called and the interaction parameter J_n is picked for the process if this random number lies in the nth subinterval. Similarly, K_n for the process is picked with the help of another random number. The values of J_0 and K_0 as well as the standard deviations used for each simulation are given in Table 2. The choice of J_0 and K_0 were on the basis of the Theumann–Høye Ising-chain studies of Ramasesha (1978). The standard deviations were usually taken to be one quarter of the mean values. After selecting the values of J_n and K_n, ΔE for the process is calculated from (1) with a cyclic boundary condition. If ΔE is negative, the rearrangement is affected and if ΔE is positive, the rearrangement is affected with a probability $\exp(-\Delta E/T)$, where T is the temperature of growth. Generally, about 150 rearrangements/layer are carried out and the order in the resulting layer configuration is deciphered with a display program described by R & R.

Table 1. *Results of polytype simulation from melt with fixed short-range interactions (from R & R)*

No.	Interaction* strengths J	K	Polytype formed (layer sequence in ABC notation in parentheses)	Expected thermo-dynamic behaviour (Ramasesha, 1978)
1	6·0	6·0	3C (ABC) or 2H (AB) exclusively	One first-order transition
2	6·0	12·0	12R ($BABACBCBACAC$)	Two higher-order transitions
3	12·5	12·5	Syntactic coalescence of 12R and 6H ($BACBCA$)	Four higher-order transitions
4	15·0	9·0	Syntactic coalescence of 6H and 9R ($ABCBCACAB$)	Three higher-order transitions
5	18·0	7·0	Syntactic coalescence of 6H and 9R with considerable stacking faults	Four higher-order transitions
6	15·0	3·0	4H ($ABAC$) with stacking faults	Two higher-order transitions

* $H^{\text{ext}} = 0$ and $L = 30/1000$ in all the simulations. The parameters are in arbitrary units with growth temperature fixed at 5.

Crystal growth from vapour involves the formation of a substrate or seed over which there is subsequent condensation or evaporation of layers. For growth to occur, the probability of condensation must be greater than the probability of evaporation. This probability as well as the temperature of crystallization is usually critical if the crystallization is to occur without the introduction of too many stacking faults. Under favourable conditions of growth, the seed propagates to give a macroscopic crystal.

The computer simulation of this process involves specifying the initial length and type (*i.e.* the configuration of layers) of the seed, the temperature, T, of crystallization and the interaction parameters. The interaction parameters employed were the same as those in Table 1. The probability of condensation was fixed at 0·6 and that of evaporation at 0·4 after trial and error. At the beginning of each step, the type of process, *i.e.* whether the process is one of evaporation or condensation, is ascertained with the help of a random number. If the process is one of evaporation, the energy change, ΔE, for the process of removing the outermost layer is calculated from (1) employing free boundary conditions. If ΔE is negative, the outermost layer is removed. If ΔE is positive, the outermost layer is removed with a probability $\exp(-\Delta E/T)$. If the process happens to be condensation, a layer (A, B or C) is chosen at random and the energy change, ΔE, for condensing this layer on the seed is calculated. If ΔE is negative, the layer is condensed onto the seed with a probability $\exp(-\Delta E/T)$. The whole process of evaporation and condensation is continued until the seed propagates to 1000 layers. The order in the resultant polytype is deciphered once again with the display program.

To approximate the growth conditions of polytypes from vapour, we need to use short-range interaction parameters which are random variables. These random variables are distributed according to the distribution parameters given in Table 2. In this case, the simulation procedure is exactly the same as above except that at each step (of condensation or evaporation), the

interaction parameters are chosen randomly as described in the growth from the melt. The results of these simulations are presented in the next section.

IV. Results and discussion

The results of growth from the melt with random short-range interactions are presented in Table 3. We find, by comparison with Table 1, that the results of growth from the melt with and without randomness in short-range interactions are similar. In both cases, given that J_0 and K_0 are the same as J and K (of Table 1), the same polytypic ordering is observed. The longest polytypic ordering observed was 12R, although with varying degrees of stacking faults with or without randomness in short-range interactions. However, the two cases differ in one important respect. The polytypes grown with random short-range interactions show fairly long stretches of longer period polytypes like 14H and 15R, which were absent in a simple growth from melt simulation. Although these periodicities do not repeat a sufficiently large number of times to be considered as polytypes, they could be of significance in the context of Frank's model of polytypism.

One of the objections to Frank's theory has been that the formation of an initial pitch corresponding to a polytype is energetically possible only after the crystal has grown to a sufficient extent. Usually, by the time the crystal has grown to this extent, it is reasonable to expect that the crystal has already adopted a definite polytypic form. The mechanism of formation of this initial pitch or ledge is not explained in the theory. We believe that the longer periodicities repeating over only a few unit cells found in our simulation could indeed

Table 2. *Distribution parameters for random short-range interactions employed in growth from melt and vapour*

The infinite-range interaction parameter was fixed at $L = 30/1000$ and $H^{\text{ext}} = 0$.

No.	J_0	J	K_0	K
1	6·0	1·5	12·0	3·0
2	12·5	3·125	12·5	3·125
3	15·0	3·75	9·0	2·25
4	18·0	4·5	7·0	1·75
5	10·0	2·5	12·0	3·0
6	16·5	4·125	6·0	1·5
7	14·0	3·5	3·0	0·75

Table 3. *Results of the growth of polytypes from melt with random short-range interactions*

No.*	Description of the observed polytyptic ordering
1	Predominantly 12R, short stretches of 6H and a fairly long stretch of 14H ($ABCACABCBACACB$)
2	An interlacing† of 6H and 12R polytypes
3	Predominantly 6H, short stretches of 8H ($ABACBABC$), 12R, 15R ($ABACABCBABCACBC$) and 16H ($ACBCABACABCBACAB$)
4	4H polytype. Can also be viewed as a 6H with large stacking faults. A repeat sequence corresponding to 15R is also observed
5	Syntactic coalescence of 6H and 12R polytypes
6	Same as in no. 4
7	Same as in nos. 4 and 6

* The interaction parameters correspond to the values specified against the same serial number in Table 2.

† This is distinct from syntactic coalescence in the sense that these orderings alternate almost from unit cell to unit cell.

correspond to the initial pitch in Frank's theory. This pitch can then propagate as proposed by Frank to give rise to the polytype. Since the formation of the initial ledge of long periods is due to random short-range interactions and since the random short-range inter-

Table 4. *Results of polytype growth from vapour with fixed short-range interactions*

No.*	Seed type	Seed length	Description of the resulting polytypic ordering
1	$2H$	3 layers	A mixture of $6H$ and $12R$ polytypes
		8 layers	Predominantly $6H$ polytype
	$3C$	3 layers	No descernible polytypic ordering
		9 layers	A mixture of $9R$ and $12R$ polytypic ordering
	$12R$	12 layers	Predominantly $6H$ polytypic ordering
2	$12R$	12 layers	$12R$ polytype
3	$6H$	6 layers	A mixture of $6H$ and $12R$ polytypic ordering
		20 layers	A mixture of $6H$, $12R$ and $9R$ polytypic ordering
4	$6H$	20 layers	4H polytype with very few stacking faults
		6 layers	
	$9R$	20 layers	
		9 layers	Predominantly $4H$ with an admixture of $6H$ polytype
5	$4H$	4 layers	$4H$ polytype
	$9R$	9 layers	$4H$ polytype
6	$4H$	4 layers	$4H$ polytype
	$9R$	9 layers	$4H$ polytype

* Interaction parameters correspond to the values specified against the same serial number in Table 1.

actions are attributed to the growth conditions, we notice that the specific polytype formed depends upon the conditions of growth.

In Table 4, our results on the growth of polytypes from vapour with fixed short-range interactions are shown. When fixed short-range interactions are employed, the lowest periodicity observed is $4H$ in contrast to $2H$ and $3C$ observed in the growth from melt. This can be readily explained since short-range interactions are more dominant in the growth of polytypes from vapour than in the growth from melt. It appears that short-range interactions usually determine the nature of ordering and infinite-range interactions help in propagating this order over macroscopic distances.

Another interesting feature of polytype growth from vapour with fixed short-range interactions is that the polytype formed depends more strongly on interaction strengths than on seed type. That is the interaction strength governs the polytype formed and not the ordering of the layers in the seed, although larger seed sizes always result in polytypes with fewer stacking faults. The display of a $12R$ polytype grown from vapour is shown in Fig. 1.

The introduction of randomness in short-range interactions in the growth of polytypes from vapour has similar effects on the polytype formed, as in the case of growth from melt. Short stretches of fairly long ordered polytypes such as $14H$ and $33R$ were observed (Fig. 2). These short stretches could once again be important in the context of Frank's theory.


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A B A B C A C A B C B . B A C A C B A B A C B C B A C A C B A B A C B C B A C A C B A . C A C A B C
B C A B A B C A . B A B A C B C B A C A C B A B A C B C B A C A C . C B A C A C B A B A C B C B A C
A C B A B A C B C B A C A C B A . C A C A B C B C A B A B C A C A B C B C A B A . A C B C B A C A C
B A B A C B . A B A B C A C A B C B C A B A B C A . . . . . . . . . . B A C B C B A C A C . . . . . .
C B C B A C A C B A B A C B C B A C A C . C B A C A C B A B A C B C B A C A C . C B C A A C B A B A
C B C B A C A C B A B A C B C B A C . B C B C A B A B C A C A B C B C A B A B C A C A B C B C A B A
B C A C A B C B C . C A B C B C A B A B C A . B A B A C B C B A C A C B A B A C B C B A . . . . . . C
A B C B C A B A B C A C A B C B C A B A B . B C A B A B C A C A B C . . . . . . . . . A C B A B A C
B . . B A C B C B A C A C B A B . B C A C A B C B C A B A B C A C A B C B C A B A B C A C A B C B C
A B A B C A C A B C B C A B A B . B C A B A B C A C A B C B C A B A B C A C A B C B C A B A B C A C
A B C B C A B A B C A C A B C B C . C A B C B C A B A B C A . B A B A C B C B A C A C B A B A C B C
. A C A C B A B A C B . A B A B C A C A . A B C A C A B C B C . C A B C B C A B A B C A C A B C B C
. . . . . C B A C A C B A . C A C A B C B C A B A B C A C A B C . A C A C B A B A C B C B A C A C B A
B A C B C B A C A C B A B A C B C B A C A C B A B A C B C B A C A C B A B A C B C B A C A C B A B A
C B C B A C . . . . . . . . . . C B A C A C B A . . . . . . C B A C A C B A B A C B C B A C A C B A B
A C B C B A C A C B A B A C B . A B A B C A C A B C B C B A B . . C A C A B C B C A B . C B C B A
C A C B A B A C B C B A C . . C B A C A C B A B A C B . A C A B C B C A B A B C A C A B C B C . C A
B C B C A B A B C A C A B C B C A B A B C A C A B C B C A B A B . . C A C A B C B C A B A B C A C A
B C B C A B A B C A C A B C B C . C A B C B C A B A B . . . . . . . . . B A B A C B C B A C A C . . .
. C A B C B C A B A B C A C A B C B C A B A B C A C A B C B C A B A B C A C A B C B C A B A B C A C
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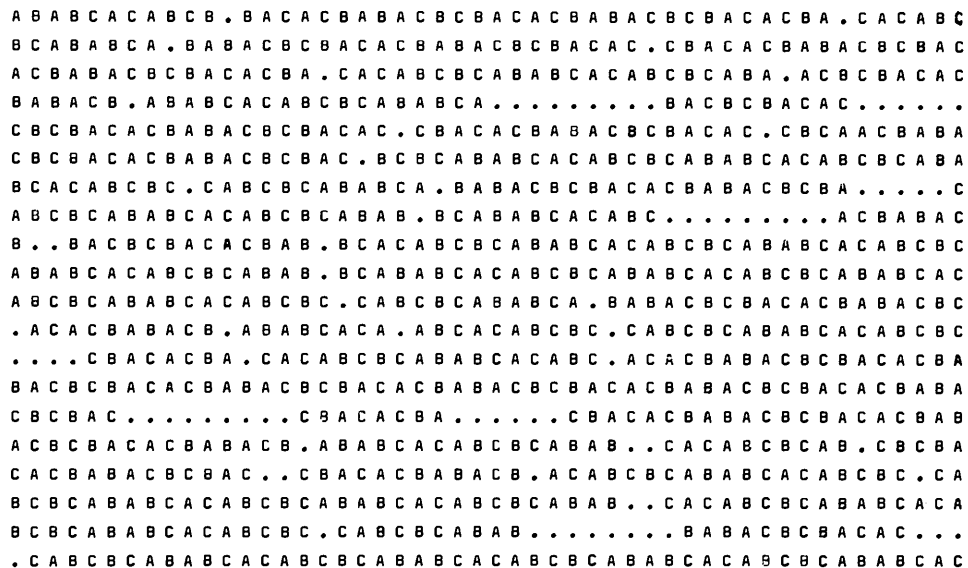
Fig. 1. Display of the $12R$ polytypes formed with a 12-layer $12R$ seed. Interaction strengths are given by no. 2 in Table 1.

V. Origin of short-range interactions

In the Hamiltonian (1) used in the simulation of polytypes, w~ could qualitatively justify the infinite-range interaction term on the basis of elastic interactions (Ramasesha & Rao 1977; Kittel, 1978). However, there was no *a priori* justification for the form of the short-range interaction terms. With a view to justifying the form of short-range interactions in (1), we have attempted a few simple calculations of lattice sums with standard potentials.

The problem of specifying potentials for the layers in a polytype is not simple. The nature of bonding in these compounds is varied and there is no straightforward way of denoting these potentials. However, as a reasonable first guess, the following forms of potentials have been tried.

(i) Lennard-Jones 6–12 potential,

$$\varphi(r) = -A/r^6 + B/r^{12}, \qquad (4)$$

where A and B are constants.

(ii) Kitaigorodski 6: exp potential,

$$\varphi(r) = -A/r^6 + B \exp(-r/\rho), \qquad (5)$$

where A, B and ρ are constants. The parameters in the Lennard-Jones potential were fixed by assuming that the interaction between two neighbouring layers should be attractive with a bond energy of 104·6 kJ/mol. This assumption, coupled with the stability condition

$$\left[\frac{\partial\varphi(r)}{\partial r}\right]_{r=r_0} = 0, \qquad (6)$$

gave unique values of A and B for a given r_0. In the Kitaigorodski potential, a reasonable value of ρ was assumed and the B parameter corresponding to the C—C bond was used (Kitaigorodski, 1973). The parameter A was then evaluated with a reasonable bond distance and a bond energy of 104·6 kJ/mol.

The method employed in these calculations involves the generation of a lattice of several layers in any desired configuration (*e.g. ABCBAC* is a six-layer lattice with a definite configuration) on a computer. Each layer consists of 20 × 20 lattice points. In order to calculate the energy of these configurations by simple lattice summations, a lattice site is located approximately in the middle of a layer and its interactions with all the neighbouring sites lying on other layers is computed.* The series is cut off at a suitable distance to carry out the actual summations. The energies for stackings of layers in different configurations are fitted to (1) to obtain the parameters J, K and H^{ext}. For this purpose, energies of all the different stacking sequences of seven layers are considered. The total number of distinct configuratons in a seven-layer stacking is nineteen and is therefore

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* Interactions within the layer are neglected because we are interested in the energy differences between different layer stackings. The intralayer interactions are constant and would not contribute to these differences.
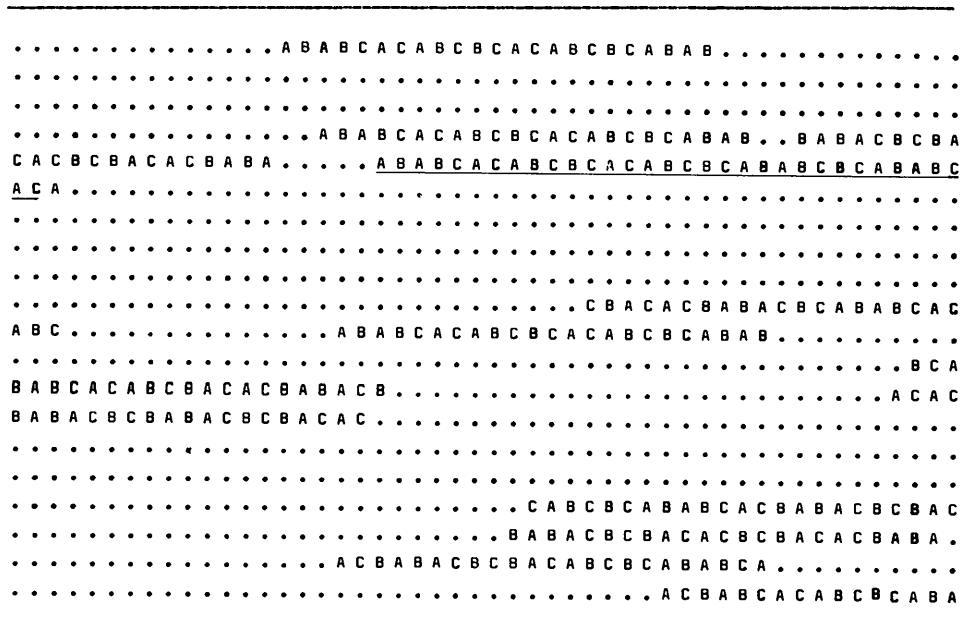

Fig. 2. Stretches of $33R$ polytype formed with a 20-layer $9R$ seed. Interaction strengths correspond to no. 4 in Table 2. A typical $33R$ sequence has been underlined. The order is deciphered in the *hk* sequence of the polytype and corresponds to *hhkkhhkkhhk*.

large enough to give a meaningful fit of the data. The best-fit parameters J, K and H^{ext} give the least variance when the energies of the different seven-layer configurations are fitted to the expression

$$E_{conf} = \Delta + Jp + Kq + H^{ext}r, \qquad (6)$$

where E_{conf} is the energy of the configuration, Δ, a constant, p is the difference between the number of like nearest neighbours and unlike nearest neighbours in the configuration, q is a similar difference for the next-nearest neighbours and r is the number of layers in h configuration minus the number of layers in k configuration.

Table 5. *Configuration energies of non-degenerate seven-layer sequences*

No.	ABC notation	hk notation	Energy for different model potentials (in kJ/mol)	
			6:exp*	6–12†
1	ABABABA	hhhhh	−295·6831	−929·4971
2	ABCBCBC	khhhh	−295·5546	−928·9952
3	ABACACA	hkhhh	−295·6049	−929·1501
4	ABABCBC	hhkhh	−295·5396	−928·9479
5	ABCACAC	kkhhh	−295·5278	−928·8089
6	ABCBABA	khkhh	−295·5412	−928·8504
7	ABCBABC	khhkh	−295·4889	−928·6880
8	ABCBCBA	khhhk	−295·5261	−928·8034
9	ABACBCB	hkkhh	−295·5128	−928·7616
10	ABACABA	hkhkh	−295·5567	−928·8977
11	ABACBAC	hkhhk	−295·4638	−928·4037
12	ABCBACB	khkkk	−295·4403	−928·3301
13	ABCACBA	kkhkk	−295·4776	−928·4456
14	ABABCAB	hhkhh	−295·5010	−928·6222
15	ABACABC	hkhkk	−295·4667	−928·5163
16	ABACBCA	hkkhk	−295·5019	−928·6243
17	ABCBCAB	khhkk	−295·4621	−928·5017
18	ABCABCA	khkhk	−295·4432	−928·4427
19	ABCABCA	kkkkk	−295·4768	−928·3405

* The energies in this column are computed with $r_0 = 2·5$ Å and $\rho = 0·33$.

† The energies in this column are computed with $r_0 = 2·5$ Å.

Table 6. *Best-fit parameters Δ, H^{ext}, J and K for the two potentials with variance for the fit*

No.	Potential	Δ	H^{ext}	J	K	Variance
1	6:exp	−295·4396	−0·0049	−0·0054	+0·0070	2·66
2	6–12	−928·4845	−0·0273	−0·0166	−0·0217	26·26

The energies of the configurations as well as the values of Δ, J, K and H^{ext} and the variance are given in Tables 5 and 6. Two relevant observations can be made from Table 5. Firstly, differences in energies of different configurations are rather small, which is consistent with the similar thermodynamic stabilities of different polytypic forms as well as the number of such forms existing under identical conditions. Secondly, the variation of energy from configuration to configuration depends upon the choice of potential emphasizing the need for a suitable potential to describe interlayer interactions in polytypic substances. While the actual values of parameters in Table 6 may not correspond to real systems, their relative magnitudes and signs are the same for both potentials. We notice, from the negative sign of H^{ext}, that usually a layer in the hexagonal configuration is more stable than a layer in the cubic configuration. This is reasonable since in the h configuration the interatomic distances between atoms in the layers immediately below and above the layer are smaller than those corresponding to the k configuration. The nearest-neighbour interaction between layers is antiferromagnetic, i.e. favouring a hk configuration to either hh or kk configuration. The next-nearest-neighbour interaction is, however, ferromagnetic favouring a like next-nearest neighbour. It appears from these calculations and from the earlier argument of R & R justifying infinite-range interactions that the basic Hamiltonian (1) is suitable for describing interlayer interactions in a polytype.

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