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Acta Cryst. (1978). A**34**, 120–123

A Phase Transition in a 3D Growth-Disorder Model

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(*Received* 31 *May* 1977; *accepted* 29 *July* 1977)

It is shown that a model of growth disorder, describing the way in which substitutional disorder can be introduced into binary solid solutions at growth, exhibits a phase transition. In a particular case it is shown that the distribution in 2D sections of the crystal corresponds to the simple pair-interaction Ising model on a triangular lattice.

Introduction

In recent papers (Welberry & Galbraith 1973, 1975; Welberry 1977*a*,*b*) models of the way in which substitutional disorder can be introduced into crystals at growth have been described. So far, however, these models have merely enabled distributions of binary variables (representing two molecular species) to be produced in two dimensions (2D) from given sets of somewhat arbitrary 'growth probabilities'. Our present aim is to put this work on a more realistic footing by extending the models to three dimensions (3D) and in addition to relate the 'growth probabilities' more directly to the forces involved when the molecular species interact at the crystal surface.

It is important at the outset to emphasize the distinction between the disorder produced by the type of growth process described here and a more general type of disorder which we shall refer to as dynamic disorder. In the latter we imagine the crystal to consist of molecules of different species which can rearrange themselves at temperatures below the melting point to achieve a minimum free-energy configuration, while we imagine growth disorder to arise in situations where a molecule once embedded in the crystal surface is subject to energy barriers sufficiently high that the possibility of subsequent rearrangement may be neglected. While the dynamic-disorder situation involves energy equilibrium over the whole 3D crystal, the growth-disorder process only involves equilibrium within the surface layer. A model that has been used extensively for describing systems involving energy equilibrium over the whole crystal is the nearest-neighbour Ising model for which the solution in 2D is known (Onsager, 1944) and for which a considerable amount of information in 3D is available from approximate methods (see Domb, 1974).

It has been shown (Enting, 1977*a*; Welberry, 1977*a*) that the 2D growth-disorder models previously described are equivalent to more general 2D Ising models on which restrictions have been imposed on the values of the parameters in the energy function (Hamiltonian). It has become apparent that these restrictions remove from the particular 2D Ising model just that character of the model essential for the occurrence of a phase transition at a finite temperature. In fact it appears that 2D growth-disorder models give rise to lattice distributions that are little more than compatible 1D distributions in different directions (see Welberry, 1977*a*; Enting, 1977*b*). In extending the growth-disorder models to three dimensions it is of prime interest whether the character of the disorder produced by these models is sufficiently removed from that of the 3D Ising model that a phase transition

does not occur. The present paper is a preliminary report of our investigation of a simple 3D growth-disorder model which does display a phase transition.

The model

The model we consider is the simplest 3D model in which the probability that the (0,1) random variable $x_{i,j,k}$, which represents one or other molecular species and which is associated with the i,j,kth point of a simple cubic lattice, is dependent only on its immediate predecessors in the three crystal directions according to the equation

$$\begin{aligned} P(x_{i,j,k} = 1/x_{i,j,k-1}, x_{i,j-1,k}, x_{i-1,j,k}) \\ = \alpha + \beta(x_{i,j,k-1} + x_{i,j-1,k} + x_{i-1,j,k}) \\ + \gamma(x_{i,j,k-1}x_{i,j-1,k} + x_{i,j-1,k}x_{i-1,j,k} \\ + x_{i-1,j,k}x_{i,j,k-1}) \\ + \delta(x_{i,j,k-1}x_{i,j-1,k}x_{i-1,j,k}). \end{aligned} \quad (1)$$

This form of the model [*cf.* the 2D models in Welberry & Galbraith (1973, 1975), Welberry (1977*a*,*b*)] already has equivalence of the three crystal directions built in and for the present purposes we further restrict (1) to correspond only to distributions which are invariant to the interchange of 0 and 1 (equivalent to 'zero field' in Ising-model terms). This leaves a two-parameter model for which we conveniently define two transition probabilities:

$$a = P(1/111) = P(0/000) = \alpha + 3\beta + 3\gamma + \delta = 1 - \alpha$$

$$b = P(1/011) = P(0/100) = \alpha + 2\beta + \gamma = 1 - \beta - \alpha.$$

It may be shown in an analogous way to the methods used by Enting (1977*a*) for the two-dimensional models that this growth-disorder model is equivalent to a restricted subset of an Ising model with an energy function (Hamiltonian) given in terms of the usual spin variables $\sigma_{i,j,k}$ ($= \pm 1$) by

$$\begin{aligned} E(\sigma) = -\sum_{\text{all sites}} \sigma_{i,j,k}[J(\sigma_{i-1,j,k} + \sigma_{i,j-1,k} + \sigma_{i,j,k-1}) \\ + K(\sigma_{i-1,j,k-1} + \sigma_{i-1,j+1,k} + \sigma_{i,j,k-1}) \\ + L(\sigma_{i-1,j,k}\sigma_{i,j-1,k}\sigma_{i,j,k-1})], \end{aligned} \quad (2)$$

i.e. a 3D Ising model with pair interactions between points within a trigonal layer, pair interactions between points in adjacent layers, and a four-point interaction only acting on the set of trigonal pyramids which point in the growth direction. Furthermore, following the methods used in 2D by Enting (1977*a*) the values for J, K and L are expressible in terms of the growth transition probabilities:

$$J = \tfrac{1}{8}\ln\frac{b(1-b)}{a(1-a)}$$

$$K = \tfrac{1}{8}\ln\frac{ab}{(1-a)(1-b)}$$

$$L = \tfrac{1}{8}\ln\left[\frac{a}{1-a}\left(\frac{1-b}{b}\right)^3\right]$$

and are thus subject to a constraint in an analogous fashion to the findings in 2D.

Since the Ising model (2) is not soluble in general we proceed by noting that in the absence of the third term the 3D model (2) is symmetric to reflection in the (111) plane and the interactions K can be mapped onto a honeycomb lattice formed by two adjacent trigonal layers. Since J and $-K$ are related by the star–triangle transformation (see Syozi, 1972), the within-layer interactions J are exactly cancelled by the between-layer interactions K connecting the double layer to those immediately above and below. That is, when L is zero 2D sections of the 3D growth model are equivalent to the simple pair-interaction Ising model on the triangular lattice (one layer) or on the honeycomb lattice (two layers). This is a well documented model which has a transition at $K = \pm\frac{1}{2}\cosh^{-1} 2 = 0{\cdot}6585$ or (since $L = 0$ gives $a/(1-a) = [b/(1-b)]^3$) at $a = 0{\cdot}9811$, $b = 0{\cdot}7887$ (ferromagnetic) or $a = 0{\cdot}0189$, $b = 0{\cdot}2113$ (antiferromagnetic).

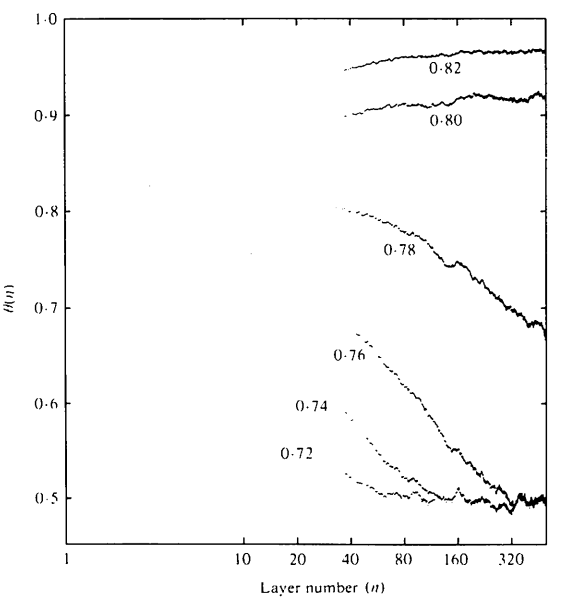

Fig. 1. The concentration of 1's $\theta(n)$ in successive growth layers of a 3D crystal in which the growth probabilities have been constrained to give trigonal layers corresponding to the simple pair-interaction Ising model on a triangular lattice. The value of $b = P(1/110)$ is given on each curve. The critical value of b is 0·7887.

We have performed computer simulations to confirm these findings for the particular series $a/(1-a) = [b/(1-b)]^3$ and to investigate whether a transition occurs in other regions of the ab plane. Our simulations took the following form. Growth was initiated from a 256×256 random trigonal layer with a specified concentration of 1's (0·75 in Fig. 1). Subsequent layers were added so that points in the new layer occurred only above one of the types of triangle of the preceding layer so forming a simple cubic lattice. Points were added using equation (1) together with a standard pseudo-random number routine and cyclic boundary conditions were imposed on each layer so that the dimension of successive layers did not diminish. A plot of concentration of 1's as a function of layer number (see Fig. 1) indicates the critical behaviour of the model. It is evident from Fig. 1 that a value of $b \simeq 0{\cdot}79$ represents the transition between simulations which tend to converge on a value close to 0 or 1 (1 in this case), corresponding in magnetic terms to regions of 'spontaneous magnetization'. We have also performed simulations when L takes non-zero positive and negative values of $\frac{1}{8}\ln(10)$ and have found similar behaviour along each curve with transitions occurring at approximately $b = 0{\cdot}72$, $a = 0{\cdot}99$ and $b = 0{\cdot}85$, $a = 0{\cdot}95$ respectively. Thus while the presence of the four-point interaction L prevents a solution of the model away from the line $a/(1-a) = [b/(1-b)]^3$ the critical behaviour appears to be maintained. Fig. 2 shows realizations of the distributions reached after 500 layers for the examples given in Fig. 1. The example when $b = 0{\cdot}78$ has still not attained an equilibrium distribution, but nevertheless the sequence of pictures representing only a comparatively small range of probabilities displays the sudden advent of 'spontaneous magnetization'.

Conclusion

We have found that in a special case a 3D growth-disorder model has properties in each of its 2D growth layers identical to those of the 2D nearest-neighbour Ising model on a triangular lattice, which is known to exhibit a phase transition. Our results also indicate that the growth-disorder model exhibits a similar transition in more general cases which do not correspond to known Ising solutions. The results are consistent with a view that while 2D growth models produce lattice distribution with 1D Ising-like properties, 3D growth models produce distributions with 2D Ising-like properties. In this respect it seems that the loss of dimensionality is due to the fact that one of the spatial dimensions plays a role similar to that of time in the normal evolution of an Ising model realization. At the present time it is not clear whether this alternative approach to obtaining realizations of Ising models is of any advantage. However, the present work, simply as

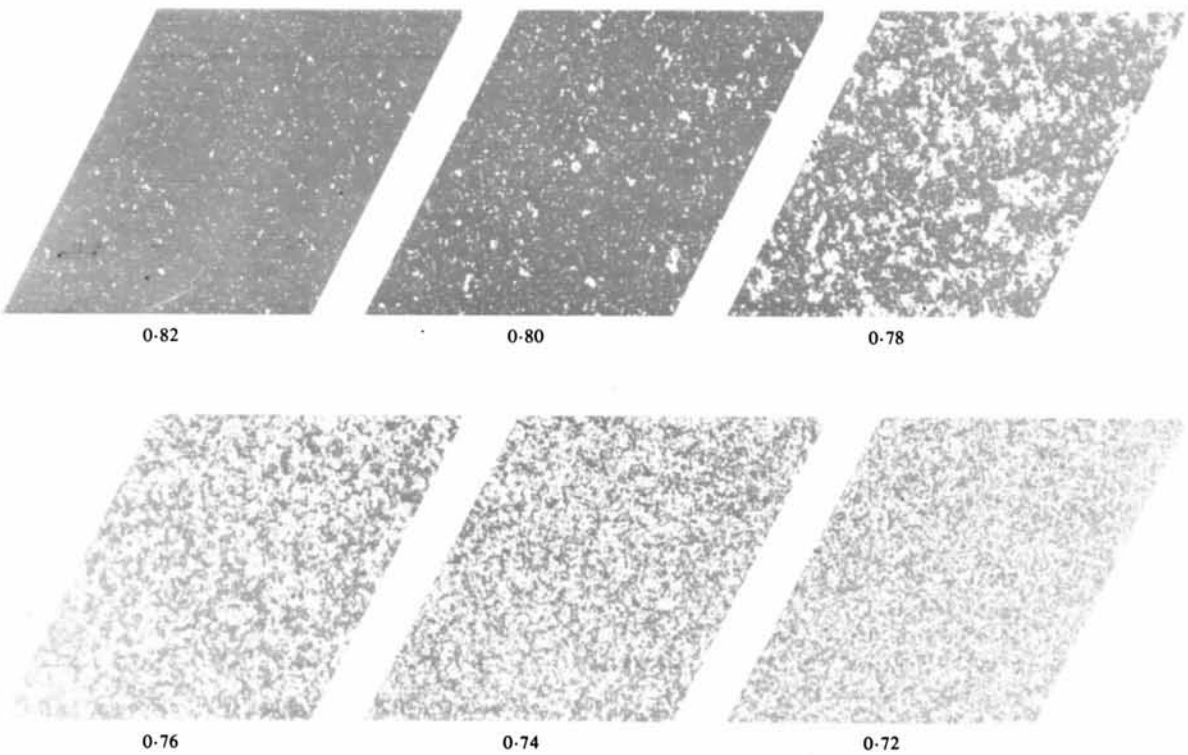

Fig. 2. Realizations of the distribution reached after 500 layers for the examples of Fig. 1. Each example contains 256×256 lattice points.

an alternative way of looking at an old problem, has already lead Enting (1977*c*) to derive the relationship between the single- and triple-spin expectations for the Ising model on the honeycomb and triangular lattices far more simply than the existing derivation of Baxter (1975).

In terms of crystal growth the present findings are significant as they indicate that above a critical temperature we would expect binary systems to crystallize as disordered mixed crystals but below this temperature to tend to crystallize separately. In addition, since it is generally accepted that the critical temperature is dependent primarily on dimensionality (see Domb, 1974), the critical temperature for the introduction of disorder at growth would be expected to be lower than for the same system were it able to rearrange its constituent molecules to achieve energy minimization.

The authors have benefited from numerous discussions with Dr I. G. Enting.

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Acta Cryst. (1978). A**34**, 123–126

The Ordered State of In_3Te_4

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(*Received* 28 *June* 1977; *accepted* 10 *August* 1977)

The composition of In_3Te_4 has been established as a single-phase material. Single crystals of this material have been prepared and its structure has been identified as tetragonal with lattice parameters $a_0 = b_0 = 6{\cdot}173$ and $c_0 = 12{\cdot}438$ Å. The stability of the structure has also been investigated.

Introduction

In a recent study on the ordered phases of In_2Te_3 (Karakostas & Economou, 1975) it was postulated that the high-temperature modification of the cubic phase on cooling separates into hypo- and hyperstoichiometric phases, with different long-range-order arrangements of the vacancies. This segregation occurs by the material passing through a transition state (Bleris, Karakostas, Stoemenos & Economou, 1976) where a short-order arrangement prevails.

The postulated hyperstoichiometric α-In_2Te_3-I, as it was called by Karakostas & Economou (1975), should have a structure within the range of stoichiometry of the compound In_3Te_4. From the electron diffraction patterns it was concluded that the phase should have a one-dimensional long-period superlattice with a tetragonal unit cell. The proposed structure for the In sublattice of α-In_2Te_3-I is given in Fig. 1(*a*), together with the lattice corresponding to the transmission electron diffraction patterns, with cubic cell indexing (Fig. 1*b*) and transformed to a tetragonal cell indexing (Fig. 1*c*).

Since the structure proposed for α-In_2Te_3-I and therefore assumed for In_3Te_4 was based on evidence which was not direct, we considered it important to investigate the In–Te system in the vicinity of the 3:4 composition range to confirm the existence of the tetragonal phase as a single independent stable one.

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