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Polymorphism in One Dimension*

By Cecil J. Schneer†

Department of Geology, Cornell University, Ithaca, New York, U.S.A.

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An admissible set of structures is defined to contain all stackings of rigid hexagonal nets at constant vertical interval with the nodes of each net centered on the nodes of the net below. The immediate environment of each net is either cubic or hexagonal. If V is the difference in potential energy between layers in the two environments, the ratio of the number of nets h to the number c is given by $n_h/n_c = \exp[-V/kT]$ (the Boltzmann factor). Setting this equal to $(1-D)/D$, a distribution function D is defined equal to the probability that a given layer is in the state c. By discarding the one-dimensional approximation, V becomes proportional to D and the polymorphism is cooperational with a critical temperature. By assuming a difference in interaction energy between two layers depending on whether the layers are in the same or in different states, the long-period polymorphs are shown to represent potential minima. The 15 observed polymorphs of silicon carbide are characterized by maximum numbers of interaction contacts between layers in unlike states.

The phase transformation proceeds over a temperature range by infinitesimal steps so that density and probability distribution vary continuously across a critical temperature while derivatives of these are discontinuous. An anomalous heat capacity replaces latent heat. Intermediate phases appear at simple proportions of layer types, unaccompanied by discontinuities.

Introduction

Polymorphism in one dimension, or polytypism (Baumhauer, 1915) is here treated as a cooperational phenomenon after the manner of Bragg & Williams (1934, 1935), and Bethe (1935), in their treatment of order–disorder in binary alloys. Fifteen silicon carbide polymorphs in one dimension are known. Seven zinc sulfide structures have been observed with the same periodicities reported for the silicon carbides. The theory implies the existence of other modifications of substances such as AgI and Cu_3AsS_4 already known to crystallize with structures parallel to those of zinc sulfide.

A satisfactory explanation of polymorphism in one dimension must account for the relative energies of the various polymorphs. I have first restricted the problem under consideration to a particular admissible set of structures. This limited set of structures contains closest packings of spheres and also all geometrically similar structures satisfying the condition that they may be related to rigid hexagonal nets stacked at constant vertical interval with the nodes of every net directly above the centers of triangles of the net below. These are true nets of equivalent points until they are stacked together. They are thereafter considered as layers. Ewald & Hermann (1931) observed

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† Present address: Department of Geology and Geography, University of New Hampshire, Durham, New Hampshire, U.S.A.

that any layer in a close-packed sequence could be considered in terms of the layer immediately above and below, as either cubic or hexagonal. Layers in the two possible environments are denominated c and h (Belov, 1939). The two environments are shown in Fig. 1 on $11\bar{2}0$ (110) plane sections. Any structure in the admissible set is described by a linear series in two elements h and c, for example,

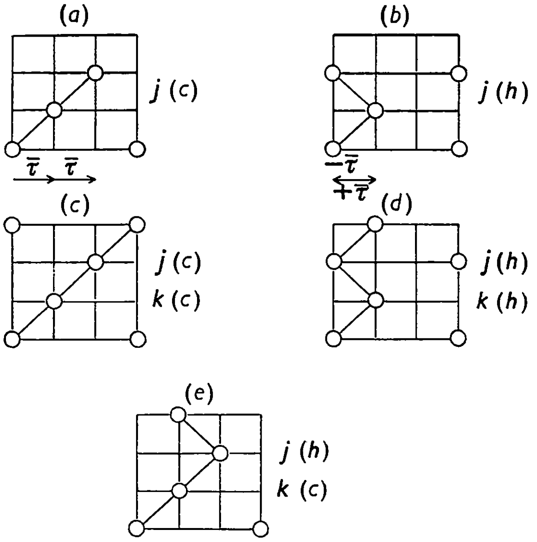

Fig. 1. Environments h and c. $11\bar{2}0$ plane sections showing (a) the jth layer in the environment c; (b) the jth layer in the environment h; (c) two adjacent layers both in environment c; (d) two adjacent layers both in environments h; and (e) two adjacent layers, one c and one h.

The $\pm\bar{\tau}$ are the projections of the translations.

$$\ldots h\,c\,c\,h\,c\,h\,c\,c\,h\,c \ldots .$$

The least distance in layers from h to h in a series, is the *packing distance* of Zhdanov (1945*a*, *b*), the combination of packing distances forming his numeral symbol. The admissible condition is that the $(j-1)$th layer is related to the jth layer by a translation $\lambda\bar{\tau}$, where τ is of constant length and restricted to the plane 110, λ is a spinor,

$$\lambda = \pm 1\,, \qquad (1)$$

and (j) is any layer (except the edge).

The jth layer is in the environment c when

$$\lambda_j\bar{\tau}+\lambda_{j+1}\bar{\tau} = \pm 2\bar{\tau}\,. \qquad (2)$$

The jth layer is in the environment h when

$$\lambda_j\bar{\tau}+\lambda_{j+1}\bar{\tau} = 0\,. \qquad (3)$$

For the unit cell of m layers (n is any integer),

$$\sum_{j=1}^{j=m} \lambda_j\bar{\tau} = 3n\bar{\tau}\,. \qquad (4)$$

The energy of the environment and the assembly

Consider a difference in energy V_{ij} between the lattice energies of two layers i and j. We have

$$V_{ij} = \begin{cases} V & \text{(environments as defined in (2, 3) are different)} \\ 0 & \text{(otherwise).} \end{cases} \qquad (5)$$

If the only difference in lattice energies was due to the immediate environment, equation (5) could be rewritten

$$V = V_h - V_c\,. \qquad (6)$$

V_h is the lattice energy of a layer h; V_c is the lattice energy of a layer c. If the relationship $V_h < V_c$ should obtain for any compound, the order of the polymorphs would be exactly opposite to the order of temperature dependence given here.

The polymorphs can be characterized by a proportion between the numbers of layers of each type, and an arrangement of these layers. The partition of energy between the environments may be expressed using the Boltzmann equation. Let ν_j be the state of the jth layer (h or c), n_c the number of layers in the state c, n_h the number of layers in the state h, and N the number of layers in the assembly. The probability that the jth layer is in the state c is

$$P_c(\nu_j) = n_c/N\,. \qquad (7)$$

A distribution function D is chosen equal to P_c. At $D(0)$ all layers are in the state h and the crystal is hexagonal $h\,h\,h \ldots.$ At $D(1)$ all layers are in the state c and the crystal is cubic $c\,c\,c \ldots.$ At $D(\frac{1}{2})$ the layers are half in the state c and the other half in the state h.

The probability that the jth layer is in the state h is

$$P_h(\nu_j) = n_h/N = 1-D\,. \qquad (8)$$

$$\frac{1-D}{D} = \frac{n_h}{n_c} = e^{-V/kT} = e^{X}\,. \qquad (9)$$

T is temperature in degrees Kelvin; k is Boltzmann's constant; X is $-V/kT$.

The plot of $D(V)$ on the D–X plane for any given temperature is an exponential curve. The $D(V)$ curves for different temperatures form a family of isothermals with origins at O and assymptotes at $D(1)$.

Individual layers in the assembly are sensitive to the distribution function D because the distribution decides the probabilities of position of the layers immediately adjacent to the layer under consideration. Assume V directly proportional to D (V_0 is the maximum energy difference between the two states), then

$$V = V_0 D\,. \qquad (10)$$

The intersection of $V(D)$ and $D(V)$ for any given temperature gives the equilibrium D and V at that temperature (Fig. 2). The temperature at which the curves are tangent is the Curie point. In the vicinity of the Curie point, there is a rapid onset of hexagonality. Since D is characteristic of each polymorph, in the stacking. Within any one assembly, the number of systems in each of the two energy states will be fixed by the distribution function D. A very large number of pathways exist for the transmission of the influence of the average state of the assembly to the individual layer.

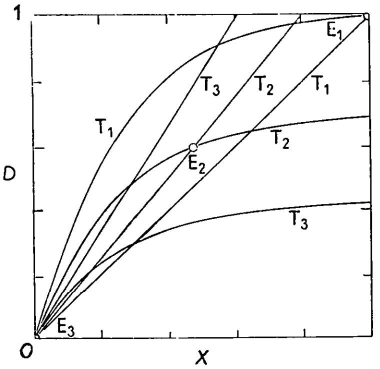

Fig. 2. $D(V)$ and $V(D)$. Isothermals for $D(V)$ and $V(D)$; the intersections (E_n) trace the equilibrium values of D and X with rising temperature. $T_3 > T_2 > T_1$. (After Bragg & Williams, 1934.)

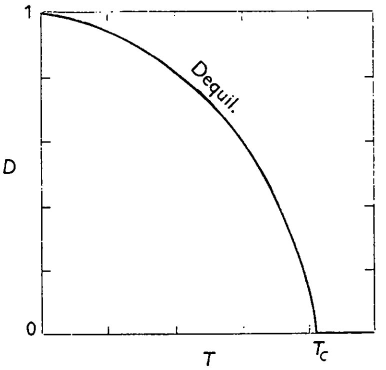

Fig. 3. $D_{\text{equil.}}$ versus T. (After Bragg & Williams, 1934.)

Fig. 3 shows the equilibrium temperatures for the structures of the admissible set (as a first approximation). Without the assumption of the dependence of V upon D, there would be no sharp transition temperature and the assembly could never be completely hexagonal. Bethe has shown that the distinction between a V which depends on D and a V which remains constant, is related to the number of neighbors with which each system may make direct contact. If the systems form a linear chain so that each system has two independent neighbors, then the probability that each is in a given state is unaffected by the average state of the assembly.

The units of structure in the admissible set actually in thermal agitation between energy states are individual atoms rather than layers. If the systems chosen were the units at the nodes of the nets, consisting in zinc sulfide of a vertical pair, zinc–sulfur, assemblies may be considered using one such unit in every layer. The number of distinct assemblies that could be chosen in this way is n^m, where n is the number of nodes per net, and m is the number of nets in the stacking. Within any one assembly, the number of systems in each of the two energy states will be fixed by the distribution function D. A very large number of pathways exist for the transmission of the influence of the average state of the assembly to the individual layer.

The distribution D, is an example of a cooperative phenomenon in physics because it is measured by the proportions of layers in two states, and these layers in turn cooperate to alter the promotional energy V (Nix & Shockley, 1938).

Interaction energy

Once the distribution has been fixed, there are still many possibilities of arrangement of the two kinds of layers. Of these, the structures of the polymorphs which have been observed form a limited set. With one further assumption, it is possible to select the observable structures from the large number of possibilities. Assume a difference in the interaction energy between two adjacent layers, depending on whether the two are in the same states or in different states.

$$\varepsilon_{ij} = \begin{cases} \left.\begin{matrix}\varepsilon_{cc}\\ \varepsilon_{hh}\end{matrix}\right\} \left\{\begin{matrix}\text{the environments as}\\ \text{defined in (2) and (3)}\\ \text{are like:}\end{matrix}\right\} \left\{\begin{matrix}\text{both } c\\ \text{both } h\end{matrix}\right\} & \multirow{2}{*}{} \\ \varepsilon_{ch} \quad \begin{matrix}\text{the environments}\\ \text{differ}\end{matrix} & \Bigg\} \; i, j, \text{ adjacent} \\ 0 \quad \text{otherwise} & \end{cases} \tag{11}$$

$$\varepsilon = \tfrac{1}{2}(\varepsilon_{cc}+\varepsilon_{hh})-\varepsilon_{ch}. \tag{12}$$

Let φ represent the distribution of the interaction contacts. Then

$$\varphi = \frac{n_{ch}-(n_{cc}+n_{hh})}{n_{ch}+(n_{cc}+n_{hh})}; \tag{13}$$

n_{ch} is the number of contacts between layers in the state c and layers in the state h, n_{cc} between c and c, n_{hh} between h and h, $n_{ch}+(n_{cc}+n_{hh}) = N$.

The distribution energy V was the portion of the potential energy of the layer determined by its immediate environment. The interaction energy ε is a supplement to V, and the parameter φ, which measures the proportions of the kinds of interaction contacts, is a measure of the energy of the assembly after the distribution D has been fixed. The total interaction energy E of an assembly is

$$E = \tfrac{1}{2}(1-\varphi)N\varepsilon. \tag{14}$$

Here $\frac{1}{2}(1-\varphi)N$ is the number of like contacts and the interaction energy for unlike contacts is 0. E is potential energy supplemental to that required to maintain a given distribution D. That arrangement will be most stable which maximizes φ and thereby minimizes E. The assumption $\varepsilon > 0$ is justified. The layers surround themselves with unlike neighbors as far as possible. If $\varepsilon < 0$, each layer would surround itself with like neighbors to achieve a minimum summation of the ε and the assembly would separate into two phases, a cubic and a hexagonal, in the proportions given by D. There is only one other possibility, that ε is negligible or $\varepsilon \sim 0$. In this event, the stacking must be random. There would be no tendency for either spreading the layers of one type among the layers of the other, or for separating the layer types into phases. The X-ray diffraction data would indicate space groups $P6/mmm$ or $P6mm$. Edwards & Lipson (1942) and Wilson (1942, 1949) found that cobalt could have a definite proportion of layers c in random positions along the unique axis of a close-packed assembly of otherwise hexagonal layers. Cobalt would therefore be an example of a substance with $\varepsilon \sim 0$.

Only the assumption $\varepsilon > 0$ has bearing on the observed polymorphs. All of the fifteen silicon carbide structures determined to date are characterized by a maximum value of φ. The maximum value of φ for any assembly is fixed by the distribution

$$\varphi_{\max.} = \begin{cases} 4D-1 \ (D < \frac{1}{2}) \\ 3-4D \ (D > \frac{1}{2}) \, . \end{cases} \tag{15}$$

Equation (15) is a tent function, part of which is plotted on the φ–D plane in Fig. 4. The graph shows several polymorphs with the same values of φ and D, (15R, 10H and 75R), so that, while every polymorph has a unique value of φ and D, these parameters alone are not sufficient to determine the structure. This multiple polymorphism occurs at only one value of φ, D, ($\frac{3}{5}$, $\frac{3}{5}$). The possibility of separate periodicities with the same φ and D arises only in the cases where Ramsdell & Kohn's (1952) separate constituent polymers may be arranged in different ways. In the arrangement 32 32 32 . . . , the unit cell is 15 layers high and rhombohedral. In the arrangement 32 23 32 23 . . . , the unit cell is ten layers high and hexagonal. One 15R cell and one 10H cell can be combined to give 25 layers which would not repeat until three groups had been stacked, making the polymorph 75R. The parameters φ and D, then, determine families of structures where the Zhdanov numeral symbol is polar, and unique structures where the numeral symbol is non-polar as in 4H (22), 6H (33), etc.

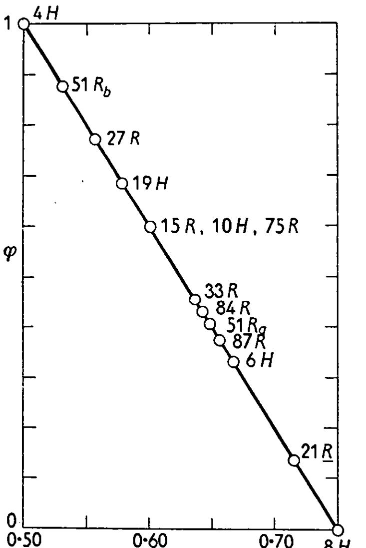

Fig. 4. φ versus D.

Perfectly ordered structures may be conceived with φ less than maximum. One example would be

$$h\,h\,c\,c\,c\,h\,h\,c\,c\,c \ldots ,$$

but it would be difficult to account for the ordering of such a structure since no consistent value for ε may yield this result. The plot of E versus D is a U shaped curve (Fig. 5).

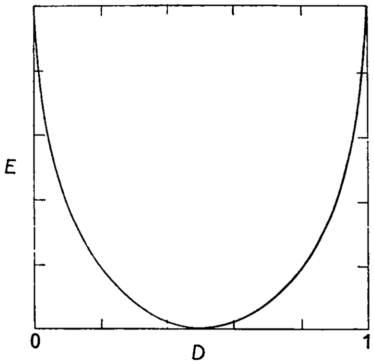

Fig. 5. E versus D.

The energies previously discussed can be arranged in the order of range of influence. The first potential energy considered was V, dependent on the positions of the layers immediately adjacent to the layer under consideration. The energy ε is dependent on the positions of the layers once removed. Presumably ε is smaller than V. Potential effects depending on even more remote interaction shells may be conceived. Call these $\varepsilon_2, \varepsilon_3, \varepsilon_4, \ldots$ and define them thus:

$$\varepsilon_n(i, j) = \begin{cases} \left.\begin{array}{l} \varepsilon_{ncc};\ \nu_i(c),\ \nu_j(c) \\ \varepsilon_{nhh};\ \nu_i(h),\ \nu_j(h) \\ \varepsilon_{nch};\ \nu_i(c),\ \nu_j(h) \end{array}\right\} & \left\{\begin{array}{l} \text{the distance from the} \\ i\text{th to the } j\text{th layer is} \\ n \text{ layers} \end{array}\right. \\ 0; & \text{otherwise.} \end{cases} \tag{16}$$

$$|\varepsilon_1| > |\varepsilon_2| > |\varepsilon_3| > \ldots . \tag{17}$$

The major contribution to the lattice energy of a crystal in the admissible set would be the internal energy of the layers, U_i, for example the silicon–carbon bond energies in silicon carbide:

$$U_i = U_0 + \int_0^T C_p dT \, . \tag{18}$$

The lattice energy of the crystal could then be expressed as U_i plus a series of potential terms of rapidly diminishing magnitude:

$$U = U_i + U(\varepsilon_1) + U(\varepsilon_2) + U(\varepsilon_3) + \dots . \qquad (19)$$

By summation, the contributions of the interaction potentials to the lattice energy for various arrangements may be compared. The relationship (17) is replaced by:

$$\varepsilon_n(i,j) = -\varepsilon_0/nr \qquad (20)$$

where r is the distance between i and j.

Differentiating, we have

$$d\varepsilon_n(i,j) = \frac{\varepsilon_0}{nr^2}\,dr = f_n(i,j)\,, \qquad (21)$$

the force between layers. Other assumptions of the rate of falling off of the interaction potential lead to the same qualitative results. Replace equation (12) by

$$\varepsilon = \begin{cases} +\varepsilon_0 = \varepsilon_{cc} = \varepsilon_{hh} \\ -\varepsilon_0 = \varepsilon_{ch} \end{cases} \qquad (22)$$

From (20) and (22), the potential of the ith layer in the assembly $D(\frac{1}{2})$, ... $h\ c\ h\ c$ ... is

$$\begin{aligned} \varepsilon_\alpha(i) &= 2\Sigma -\frac{\varepsilon_0}{r} + \frac{\varepsilon_0}{2r} - \frac{\varepsilon_0}{3r} + \dots \\ &= -2\frac{\varepsilon_0}{r}\Sigma 1 - \tfrac{1}{2} + \tfrac{1}{3} - \dots \\ &= -2\frac{\varepsilon_0}{r}\ln 2\,. \end{aligned} \qquad (23)$$

For a randomly ordered assembly $D(\frac{1}{2})$, the potential of the ith layer is

$$\begin{aligned} \varepsilon_\beta(i) &= 2\frac{\varepsilon_0}{r}\Sigma \tfrac{1}{2} - \tfrac{1}{2} + \tfrac{1}{4} - \tfrac{1}{4} + \tfrac{1}{6} - \tfrac{1}{6} + \dots \\ &= 0\,. \end{aligned} \qquad (24)$$

The difference between the ordered and disordered assemblies with $D(\frac{1}{2})$ is $2(\varepsilon_0/r)\ln 2$.

By a similar summation procedure, the potential of any layer in any arrangement within the admissible set may be determined. The interaction potential for a layer h in the arrangement $6H$, $D(\frac{2}{3})$, $\varphi(\frac{1}{3})$, ... $h\ c\ c\ h\ c\ c$..., is computed as follows:

$$\varepsilon_h = 2\frac{\varepsilon_0}{r}\Sigma -1 - \tfrac{1}{2} + \tfrac{1}{3} - \tfrac{1}{4} - \tfrac{1}{5} + \tfrac{1}{6} - \dots . \qquad (25)$$

The potential for a layer c in the arrangement $6H$ is

$$\varepsilon_c = \frac{\varepsilon_0}{r}\sum \begin{matrix} -1 + \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \frac{1}{5} + \frac{1}{6} - \\ +1 - \frac{1}{2} + \frac{1}{3} + \frac{1}{4} - \frac{1}{5} + \frac{1}{6} + \dots . \end{matrix} \qquad (26)$$

The sum of the potentials for one layer h and two layers c (the proportion $n_h{:}n_c$ in $6H$) is

$$\varepsilon_\gamma = \varepsilon_h + 2\varepsilon_c = 2\frac{\varepsilon_0}{r}\Sigma -1 - \tfrac{1}{2} + \tfrac{3}{3} - \tfrac{1}{4} - \tfrac{1}{5} + \tfrac{3}{6} - \dots . \qquad (27)$$

The average potential per layer in the arrangement $6H$ is $\varepsilon_\gamma/3$. With the same $D(\frac{2}{3})$, a layer in a random series would have the potential

$$\begin{aligned} \varepsilon_\delta = {} & P_h(\nu_j)2\frac{\varepsilon_0}{r}\Sigma P_h(\nu_{j+1}) - P_c(\nu_{j+1}) + \\ & \qquad P_h(\nu_{j+2})/2 - P_c(\nu_{j+2})/2 + \dots \\ & + P_c(\nu_j)2\frac{\varepsilon_0}{r}\Sigma - P_h(\nu_{j+1}) + P_c(\nu_{j+1}) - \\ & \qquad P_h(\nu_{j+2})/2 + P_c(\nu_{j+2})/2 - \dots \\ = {} & \tfrac{2}{3}\frac{\varepsilon_0}{r}\Sigma - P_h(\nu_{j+1}) + P_c(\nu_{j+1}) - \dots \\ & \qquad P_h(\nu_{j+2})/2 + P_c(\nu_{j+2})/2 - \dots \\ = {} & \tfrac{2}{3}\frac{\varepsilon_0}{r}\Sigma \tfrac{1}{3} + \tfrac{1}{6} + \tfrac{1}{9} + \dots . \end{aligned} \qquad (28)$$

The difference in potential energy between the ordered and disordered $D(\frac{2}{3})$ assemblies is

$$\varepsilon_\delta - \varepsilon_\gamma/3 = \tfrac{2}{3}\frac{\varepsilon_0}{r}\Sigma \tfrac{2}{3} + \tfrac{2}{6} - \tfrac{2}{9} + \tfrac{2}{12} + \dots . \qquad (29)$$

Additions and subtractions of series were made keeping the proper order of the terms so that, although the series are divergent, summations of the first N terms may be compared. The mean interaction energy per layer is always least for the ordered polymorph.

The summation for $15R$, $D(\frac{3}{5})$, $\varphi(\frac{3}{5})$ is

$$\begin{aligned} \varepsilon_{15R} = 2\frac{\varepsilon_0}{r}\Sigma & -\tfrac{3}{5} + \tfrac{1}{10} + \tfrac{1}{15} - \tfrac{3}{20} + \tfrac{5}{25} - \tfrac{3}{30} + \tfrac{1}{35} \\ & + \tfrac{1}{40} - \tfrac{3}{45} + \tfrac{5}{50} - \dots . \end{aligned} \qquad (30)$$

The summation for $10H$, with the same D and φ as $15R$, is

$$\begin{aligned} \varepsilon_{10H} = 2\frac{\varepsilon_0}{r}\Sigma & -\tfrac{3}{5} + \tfrac{1}{10} + \tfrac{1}{15} - \tfrac{1}{20} + \tfrac{1}{25} - \tfrac{1}{30} + \tfrac{1}{35} \\ & + \tfrac{1}{40} - \tfrac{3}{45} + \tfrac{5}{50} - \dots . \end{aligned} \qquad (31)$$

The many polymorphs at the same point on the D–φ plane each occupy a potential well. At the exact temperature at which $D_{\text{eq.}}$ is $\frac{3}{5}$, $15R$, with the lowest interaction energy per layer of any of the polymorphs with $D(\frac{3}{5})$, is stable. At a slightly higher temperature, the increment in energy could affect the proportion of layer types leading to a polymorph with $D(\frac{3}{5} - \Delta D)$, or could supply the difference in interaction energy between the $15R$ and the $10H$ or some other $D(\frac{3}{5})$ arrangement. The greater entropy of the $D(\frac{3}{5})$ arrangement than the more complex $D(\frac{3}{5} - \Delta D)$ is evidently sufficient to favor the former. Equations (30) and (31) also show that spreading the layers h as far as possible amongst the layers c lowers the total potential of the arrangement.

Entropy

The entropy is related to the distribution function D. The probability that n_c layers are in the state c is

$$\prod_{j=1}^{j=n_c} P_c(\nu_j) = D^{n_c}\,. \qquad (32)$$

The probability that n_h layers are in the state h is

$$\prod_{k=n_c+1}^{k=n_c+n_h=N} P_h(\nu_k) = (1-D)^{n_h} . \quad (33)$$

The probability that the events n_c layers c and n_h layers h occur together is equal to $W(D)$, the number of ways of arranging the layers of the assembly:

$$W(D) = P_c P_h = D^{n_c}(1-D)^{n_h};$$
$$\ln W(D) = ND \ln D + N(1-D) \ln (1-D) . \quad (34)$$
$$S = -k \ln W ; \text{ (S is entropy)} . \quad (35)$$

From (34) and (35), the entropy of the assembly in the state D is

$$S(D) = -kN[D \ln D + (1-D) \ln (1-D)] . \quad (36)$$

Phase transformation in the admissible set

Following Ehrenfest (1933; see also Tisza, 1951), we classify transformations according to their thermodynamic order. A phase change of the nth order is a phase change in which the first discontinuity of the derivatives of the Gibbs function appears in the nth derivative. Entropy and volume are first derivatives of the Gibbs function.

First- and second-order phase transformations are known; third-order transformations have been proposed (Tisza, 1951). The loss of ferromagnetism at the Curie point and the loss of order in alloys are considered to be second-order phase changes. The idea of second-order phase change is a necessary outgrowth of the theory of cooperational phenomena. It is required that certain units cooperate to produce a common property whose amount is a measure of the degree of cooperation. In this case, the units are layers cooperating to produce hexagonality, measured as $(1-D)$. In passing from the state of no layers h to all layers h, the assembly proceeds by a large number of infinitesimal steps. Each step marks the exchange of a single layer c for a layer h. At any point the process may be halted, and, by quenching, a long period polymorph may be obtained as a record of the degree to which the process had proceeded. Entropy and volume, like the distribution D, change gradually rather than abruptly, and over a range of temperatures rather than at a single temperature. At the transition point, the last layer c inverts to h. Landau (1937*a*, *b*; see also Tisza, 1951) stated the situation in terms of the abrupt appearance of a number of symmetry elements at the transition point, combined with an only slightly different density and probability distribution before and after the transition.

In second-order transformation, each distinct unit inversion from a lower to a higher energy state is accompanied by the absorption of a definite amount of energy. Since the inversions of the units take place over a wide temperature range, the total absorption of energy is spread. In first-order transformation, the inversion from a lower to a higher state is possible only at a single temperature, and all the energy of transformation is absorbed at this temperature. The dispersed 'latent heats' of the large number of unit inversions of the second-order transformation manifest themselves as anomalous heat capacity.

In first-order transformation, inversion occurs for all units of structure at a single temperature. Regardless of the fact that this temperature may vary from experiment to experiment or even in the heating and cooling of the same specimen (as in the case of quartz), any given transformation has been accomplished at a specific temperature. The crystal cannot be held in the state half-high, half-low; it is all or nothing. By contrast, a second-order transformation proceeds by infinitesimal steps. At any given temperature below the critical temperature the specimen in equilibrium consists of a number of units inverting from a lower to a higher energy state, and an equal number reverting from a higher to a lower energy state. At any one instant, a definite proportion of the units are in each energy state. If the temperature is raised, the higher thermal energy supports more units in the higher energy state. This extra energy must be supplied to raise the temperature. The required heat is the anomalous heat capacity. At all temperatures below the transition point, the partition of the units into two energy states is a function of temperature, and holding the specimen at a given temperature for long periods of time will not accomplish a total transformation. The rate of attainment of equilibrium will depend upon the activation energy required and available, and hysteresis effects might be marked.

Order of transformation

There is no discontinuity in the curve D–T (Fig. 3) at the critical point, T_c. The distribution before T_c differs from the distribution after T_c by an infinitesimal amount:

$$D_{T_c-\delta} \sim D_{T_c+\delta} \quad (37)$$

(δ is arbitrarily small).

By contrast, the rate of change of the distribution is markedly discontinuous:

$$\left|\frac{\partial D}{\partial T}\right| > 0 . \quad (38)$$

At the critical temperature, the same relationship holds for volume and entropy. Equation (36) shows that D is of the same order as volume and entropy (first derivatives of G, the Gibbs function), and therefore

$$\frac{\partial D}{\partial T} = \frac{\partial^2 G}{(\partial T)^2} . \quad (39)$$

The transformations from polymorph to polymorph within the admissible set, other than the complete transformation from cubic to hexagonal, must be considered as third or higher order because, for these transformations, even the rate of change of D is constant. There is no discontinuity in either the first or the second derivatives of the Gibbs function:

$$\left|\frac{\partial D}{\partial T}\right|_{T-\delta} \sim \left|\frac{\partial D}{\partial T}\right|_{T+\delta} . \tag{40}$$

One further transformation type occurs in the admissible set, the transformations between polymorphs of the same D and φ, $15R$, $10H$, and $75R$. Since, for these transformations, D is constant, all derivatives of D vanish and the transformations are borderline between polymorphism and homogeneous deformation.

Considering one-dimensional polymorphic transformations as transformations of second order with intermediate transformations of higher order, predictions of the behaviour of the properties of the polymorphs can be made. The specific volumes, entropies, and probability distributions vary continuously across the critical temperature. All derivatives of these—heat capacity, thermal expansion, resistivity, compressibility, etc.—may rise anomalously in the vicinity of the critical temperature. Minute differences in temperature or in the degree of approach to equilibrium may bring about major differences in periodicity. These differences in periodicity modulate the resonance characteristics of the structures for X-rays and possibly for other portions of the electromagnetic spectrum. It may be of significance that substances crystallizing in the admissible set, silicon carbide and zinc sulfide, are also of interest for their electroluminescent behaviour.

Conclusions

The theory of polymorphism in one dimension arranges the observed structures in the order of their energy dependence. Polymorphism in one dimension is a cooperational phenomenon analogous to order–disorder in alloys, and ferromagnetism. Restrictions on the occurrence of possible structures have been outlined. The behaviour of a substance in one-dimensional polymorphism can be predicted. Specifically, the order of transformation (second), the existence of a transition point, a hysteresis effect, an anomalous heat capacity, and anomalous behaviour of other functions are predicted.

The theory implies that sharp discontinuities within the earth's crust may be of the second order. For example, a transition from olivine (with oxygen in approximate hexagonal close-packed positions) to a magnesium silicate spinel (with oxygen in approximate cubic close-packed positions) would be accompanied by anomalies in the elastic properties at a critical temperature, but by only continuous variation of density and entropy.

Other problems in mineralogy appear related: the problem of intermediate phases in isomorphous series, the problem of diadochy and the partition of constituents of magma between phases, and the problem of twinning. Temperature determines the partition of particles among energy states while potential energy and entropy affect the nature of those energy states. The concept of order is one of degree.

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* This article, containing a parallel formulation of the distribution function, was called to my attention shortly after the original preparation of this paper.