Symmetry–entropy–volume relationships in polymorphism

By R. G. J. Strens

Department of Earth Sciences, The University, Leeds 2

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Summary. Group theoretical analysis of the normal vibrations of isolated molecules and of macroscopic crystals indicates that the principal effect of symmetry reduction is to remove the degeneracy of the normal vibrations, thus reducing the number of microscopic complexions of the phonon distribution, and reducing the entropy. This mechanism is effective only in point groups containing a rotation axis of order 3 or greater, and may play a part in the high–low cordierite transition.

Two other symmetry-related entropy contributions are discussed: the first is the loss of positional degeneracy in systems in which the number of available positions exceeds the number of atoms, as in high–low quartz, vlasovite, and many ferroelectrics. The second is the loss of positional degeneracy in a solid solution, which leads to unmixing, as in high–low albite, microcline–sanidine, and high–low cordierite transitions. These mechanisms are effective in all point groups down to $1 = C_1$, and can proceed even within $C_1$ by a change in the unit cell volume.

Consideration of entropy–volume relationships suggests that the glaucophane I–II transition has less order–disorder character than previously supposed. It is suggested that zoisite–clinozoisite, anthophyllite–cummingtonite and enstatite–clinoenstatite relationships are polytypic rather than polymorphic in the usual sense, and the mechanisms responsible for producing the stacking order are discussed.

The implications of the differences between the behaviour of the classical double oscillator (often used as a model for displacive transitions) and its quantized analogue are discussed.

Two generalizations are commonly made regarding the relationships between symmetry, entropy, and volume changes in polymorphic transitions: first, that the high-temperature high-entropy form has the higher symmetry, and second, that the high-volume form normally has the higher entropy. The first serious attempt to rationalize these observations and to apply them to complex structures appears to have been that of Fyfe, Turner, and Verhoogen (1958), who suspected the existence of a general relationship between entropy and symmetry, and considered that the link would lie in the relationship between the symmetry of the crystal and the number and frequency of its normal vibrations. The analysis was not carried far because of the difficulty at that time of enumerating the vibrational modes of structurally complex structures.
macroscopic crystals, many of them of low symmetry. The same authors
achieved greater success in relating entropy and volume changes.

It will be convenient to adopt Ehrenfest's thermodynamic classifica-
tion of polymorphic transitions according to the order of that derivative
of the Gibbs free energy with respect to pressure or temperature that
first becomes discontinuous in the course of the transition. Thus in first-
order transitions the first derivatives entropy (S) and volume (V) are
discontinuous, and there is a latent heat of transition, whilst in second-
order transitions the thermal expansion (α) and compressibility (χ) but
not S or V are discontinuous, and there is no latent heat (Denbigh, 1961,
p. 206). Few transitions of higher order have been described, and they
will be ignored here. In addition to the thermodynamic criteria Landau
(1937a, b) has laid down symmetry conditions that must be fulfilled if
a transition is to be considered second order, of which the most impor-
tant is that the space group of the low-symmetry form must be a sub-
group of that of the high-symmetry form. Recently, Haas (1965a, b)
has applied the Landau rules to transitions in spinels and certain ferro-
 electrics.

**Origin of the symmetry-related entropy terms in polymorphism**

It will be convenient to consider all entropy terms as configurational
in origin, i.e. as dependent on the number of permissible microscopic
complexions of the system, but to distinguish between the vibrational
entropy (S_{vib}) determined by the distribution of phonons (quantized
lattice vibrations) over the available vibrational levels, and the con-
figurational entropy (S_c) determined in our examples by the distribu-
tion of atoms over the available positions. Derivations of the equations
used are given by MacDonald (1963).

**Configurational entropy.** The work of Boltzmann and Planck pro-
vided the bridge between classical mechanics and thermodynamics on
the one hand, and statistical mechanics on the other: \( S_c = k \ln \Omega \), where
\( \Omega \) is the number of microscopic complexions of the system and \( k \) is
Boltzmann's constant. For a system containing Avogadro's number
(\( N \)) of molecules: \( R = k \cdot N = 1.986 \text{ eu} \), where \( R \) is the gas constant in
calories per degree per mole (eu is entropy units). For a system in which
\( n \) particles are distributed over \( gn \) degenerate (equal energy) positions:

\[
\Omega = \frac{gn!}{n!(gn-n)!}.
\]

Applying Stirling's approximation for the factorial of a large number,
we arrive at $S_c = R \ln g$. Similarly, the familiar expression for the configurational entropy of a complex solid solution follows:

$$S_c = R \sum_i x_i \ln x_i,$$

where $x_i$ is the mole fraction of the $i_{th}$ component.

Vibrational entropy. The distribution of phonons between the vibrational energy levels of a system is determined by Boltzmann's relation, $n_i/n_0 = \exp(-e_i/RT)$, in which $n_i, n_0$ are the phonon populations of the levels of energy $e_i, e_0$ at a temperature $T$ degrees absolute, with energies measured from $e_0 = 0$. The resultant internal energy contribution ($E$) from all levels is:

$$E = \sum_i n_i e_i g_i$$

where $g_i$ is the degeneracy of the $i_{th}$ level.

If we regard the vibrational energy levels as being filled by a mixture of $p$ phonons and $(1-p) = h$ holes:

$$S_{vib} = R \sum_i g_i (p_i \ln p_i + h_i \ln h_i).$$

The over-all entropy of the substance (ignoring any contribution due to atomic disorder) is then $S = S_{vib} + E/T$. $S_{vib}$ and $\Omega$ are maximized when all $n_i$ are equal, i.e. when all energy levels are degenerate. Provided that the mean energy $e$ of a set of levels remains constant, so that the variation in $E/T$ is negligible, loss of degeneracy leads to unmixing of the phonon-hole distribution, with a resulting decrease in $S_{vib}$. For the case of a pair of degenerate levels of energy $e$ split by an amount $\delta = 0.1e$ to give two levels of energy $e+\delta$ and $e-\delta$, the decrease in $S_{vib}$ is of the order of 30%.

It will now be shown that a reduction of crystal symmetry in classes having rotation axes of order $\geqslant 3$ may lead to a drastic decrease in the proportion of degenerate vibrations, and hence to a decrease in $S_{vib}$, thus establishing one of the links between entropy and symmetry.

Vibrations of an isolated molecule

Methods have long existed for enumerating the normal vibrations of an isolated molecule (Jaffe and Orchin, 1965, p. 107), with no theoretical limit on the number of atoms involved. Similar techniques can be applied to the vibrations of individual structural groups in crystals (e.g. SiO$_4$ groups), but the results are then approximations, although often surprisingly good ones.

An isolated non-linear molecule of $M$ atoms has $3M$ degrees of freedom, of which 6 correspond to 3 rotations and 3 translations of the
molecule as a whole, leaving $3M - 6$ internal degrees of freedom, or normal vibrations, which involve movements of the atoms in the molecule relative to each other. Provided that the point-group symmetry of the molecule is known, the normal vibrations may be classified into symmetry species of known degeneracy with the aid of character tables for each point group (Jaffe and Orchin, 1965; Cotton, 1963).

**Table I. Numbers of general equivalent points and proportions of degenerate vibrations in selected point groups:** for further values see Jaffe and Orchin (1965, Appendix 2)

<table>
<thead>
<tr>
<th>Schoenflies</th>
<th>Hermann-Mauguin</th>
<th>General equivalent positions</th>
<th>Normal vibrational M = 1</th>
<th>Normal vibrational M = 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O_h$</td>
<td>$T_d$</td>
<td>$T$</td>
<td>$D_{4h}$</td>
<td>$C_{4h}$</td>
</tr>
<tr>
<td>$m3m$</td>
<td>$43m$</td>
<td>23</td>
<td>4/$mmm$</td>
<td>4/$m$</td>
</tr>
<tr>
<td>$C_{2}$</td>
<td>$D_{6h}$</td>
<td>$C_{6h}$</td>
<td>$C_{6h}$</td>
<td>$C_{4}$</td>
</tr>
<tr>
<td>$2$</td>
<td>6/$mmm$</td>
<td>6/$m$</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td>$A + B$</td>
<td>$E$</td>
<td>$T$</td>
<td>$M = \infty$</td>
<td>$M = 1$</td>
</tr>
<tr>
<td>12</td>
<td>12</td>
<td>12</td>
<td>12</td>
<td>9/10</td>
</tr>
<tr>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>22</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>4/9</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$M$ is the number of independent sets of points not lying on any symmetry element.

In the most highly symmetrical molecules, a high proportion of the normal vibrations are triply ($T$) or doubly ($E$) degenerate (table I). As symmetry elements are removed, the degenerate species decline in relative importance, until in point groups with no rotation axis of order $\geq 3$, only singly degenerate ($A$, $B$) species remain. This process is illustrated by the data for the [SO$_4$] group in table II.

Study of the vibrations of the idealized Si$_4$Al$_2$O$_6$ ring in cordierite, in which only the 6(Si, Al) and the bridging oxygens are considered, illustrates the use of these methods. In high cordierite the ring is assumed to possess $D_{6h}$ symmetry, with the silicon and aluminium randomly distributed over the six equivalent (Si, Al) positions, whilst in low cordierite (Gibbs, 1966) the symmetry is reduced to $D_{2h}$, with the two aluminium atoms settling into one set of equivalent positions, which
The vibrational spectra of the sulfate group in aqueous solution and in CaSO₄ are presented in Table II.

Table II. Vibrations of the SO₄ group in aqueous solution and in CaSO₄

<table>
<thead>
<tr>
<th>Designation</th>
<th>Solution (av.)</th>
<th>Crystal (obs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>v₁ (3x)</td>
<td>1106 cm⁻¹</td>
<td>1160, 1128, 1108</td>
</tr>
<tr>
<td>v₂ (1x)</td>
<td>983</td>
<td>1018</td>
</tr>
<tr>
<td>v₃ (3x)</td>
<td>622</td>
<td>674, 628, 609</td>
</tr>
<tr>
<td>v₂ (2x)</td>
<td>454</td>
<td>499, 415</td>
</tr>
</tbody>
</table>

(Data of Bhagavantam and Venkatarayudu (1951), from ‘Theory of groups and its application to physical problems’, Andhra University Press, Waltair.)

If the (Si, Al) positions in the high cordierite ring are numbered 1 to 6, the ordering of the Al atoms can clearly proceed in three different ways, i.e. Al can enter 1+4, 2+5, or 3+6, corresponding to three possible orientations of low cordierite developing from a single crystal of the high form. The beautiful and complex inversion twinning that Venkatesh (1954, or see Deer, Howie, and Zussman, 1962, vol. 1, p. 238) found to be characteristic of cordierites cooled from high temperatures can thus be explained. Similar features are, of course, known in many other substances.

Vibrations of a macroscopic crystal

It might be expected that the proportions of vibrations belonging to the various symmetry species would not change greatly as a molecule evolves into a crystal, i.e. as $M \to \infty$, and calculations by Knox (1966) confirm this. Using Knox’s notation, the relative number of normal modes of point symmetry type $\Gamma_\alpha$ is $n_\alpha^2/g$, where $n_\alpha$ is the dimension of $\Gamma_\alpha$ and $g$ is the order of the symmetry group. The order is equal to the number of operations in the group, e.g., for $C_{4v}$:

$$g = 1.I + 2.C_4 + C_4^2 + 2\sigma_v + 2\sigma_d = 8,$$

and the order is also given by the sum of the squares of the degeneracies of the vibrational symmetry types:

$$g = 1^2A_1 + 1^2A_2 + 1^2B_1 + 1^2B_2 + 2^2E = 8.$$
The removal of degeneracies as symmetry is reduced proceeds in the same way as for a molecule, with reduction in entropy (table I).

**The configurational entropy contributions**

This paper is not concerned with entropy contributions arising from the ordering of electron spins, which produces symmetry changes undetectable by conventional optical or X-ray methods, or with transitions involving the rotation of anionic groups, which (if rotation is unhindered) should increase the entropy by $R/2$ for each rotational degree of freedom. With these excluded, two important mechanisms remain, both involving the loss of 'positional degeneracy', i.e. a reduction in the number of general equivalent positions as symmetry elements are removed. This reduction in symmetry may involve a change in space group, or simply an increase in unit-cell volume, which decreases the number of symmetry elements per unit volume, and thus reduces the density of equivalent positions. One mechanism operates only in solid solutions, whilst the other may be important whenever there are more equivalent positions than atoms to fill them.

**Removal of positional degeneracy in solid solutions.** In table I, selected point groups have been ranked according to the number of general equivalent positions. It will be seen that the removal of symmetry elements during a polymorphic transition will cause a set of equipoints in the high-symmetry form to split up into 2, 4, 8, ..., or 3, 6, 12, ... sets of equipoints in the low-symmetry form, and these sets, being no longer symmetry-related will now have different structural and energetic characteristics. In the general case, this implies that in a solid solution $A-B$, the original $A:B$ ratio will not be preserved in the several sets of positions, but that unmixing will occur, leading to enrichment of some positions in $A$, of others in $B$. The unmixing of a solid solution when positional degeneracy is lifted is directly analogous to the unmixing of

<table>
<thead>
<tr>
<th>$S_{\text{vib}}$</th>
<th>configurational entropy of the phonon-hole distribution</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta S_{\text{vol}}$</td>
<td>entropy change attributable to a change in volume</td>
</tr>
<tr>
<td>$\Delta S_x$</td>
<td>entropy change attributable to unmixing of a solid solution</td>
</tr>
<tr>
<td>$\Delta S_e$</td>
<td>entropy change on unmixing of atoms and vacant sites</td>
</tr>
<tr>
<td>$S_c$</td>
<td>a configurational entropy</td>
</tr>
<tr>
<td>$S$</td>
<td>entropy $= E/T + S_c + S_{\text{vib}}$</td>
</tr>
<tr>
<td>$E$</td>
<td>internal energy $= \sum n_i \epsilon_i g_i$</td>
</tr>
</tbody>
</table>
the phonon–hole distribution when the degeneracy of the vibrational levels is removed, and produces a similar decrease in entropy. If site occupancies are known, the entropy change can be calculated from (2). This mechanism operates in all classes but $C_1$ by removal of symmetry elements, and can proceed even within $C_1$ by changing the unit cell volume. The most important mineral examples are the high–low albite, sanidine–microcline and high–low cordierite transitions.

In both high-albite and sanidine the (Si, Al) distribution appears to be completely disordered, with $4 \times (\text{Si}_{0.75}\text{Al}_{0.25})$ in the tetrahedral sites (Ferguson et al., 1958; Cole et al., 1949), whilst in low-albite the aluminium contents of the tetrahedra (normalised to 1) are 0.71, 0, 0.20, and 0.09, and in microcline 0.26, 0.59, 0.07, and 0.08 (Ferguson et al., 1958; Bailey and Taylor, 1955). The entropy changes on exsolution are then 2.67 eu and 1.74 eu respectively for these samples, but the figure inevitably depends on the degree of disorder, and would reach 4.47 eu were all aluminium to be concentrated in one site.

The cordierite transition involves not only (Si, Al) ordering in the ring, but also (Si, Al) ordering in the chains that link the rings, and possibly ordering of the Mg also (Gibbs, 1966), for which full data are not yet available. However, the contribution from ordering of the ring is approximately: $\Delta S_z = 6R(\frac{2}{3} \ln \frac{2}{3} + \frac{1}{3} \ln \frac{1}{3}) = 7.7$ eu.

Removal of positional degeneracy other than in solid solution. Many crystals exist in which a given atom has a choice between a number ($g$) of symmetry-related positions. Removal of a symmetry element then produces $n$ sets of $g/n$ equivalent positions, reducing or eliminating the choice, and causing a decrease in $S$ that may in principle be found from (1). This behaviour is essentially the same as that observed in solid solutions if we think of a solid solution of atoms and holes, rather than one involving two types of atom.

The analogy with the behaviour of the phonon–hole distribution is also close. Again, this mechanism will operate in all point groups down to $C_1$ by removal of symmetry elements, and within $C_1$ by a change in the unit cell volume. Most transitions of this type are fast and displacive, including high–low–quartz, $\alpha$–$\beta$–tridymite, $\alpha$–$\beta$–cristobalite, and many ferroelectrics (Kanzig, 1957), and probably high–low–vlasovite (Fleet and Cann, 1967) and albite–monalbite.

Classical and quantized double oscillators

Displacive transitions are frequently treated in terms of the double minimum potential, in which two symmetry-related potential energy
The particle under consideration vibrates over the top of the barrier so long as its thermal energy exceeds \( P \), settling out into \( A \) or \( B \) on cooling: a transition always occurs at \( T > 0 \text{K} \) if \( P \) is finite. In the quantum mechanical formulation of the problem (Powell and Crasemann, 1961), the energy of the particle is restricted to certain well defined values, the lowest of which lies \( h\nu/2 \) above the energy zero, so that the particle retains this 'zero-point energy' even at absolute zero: we now find that no transition occurs unless \( P > h\nu/2 \). The zero-point energy ranges from a few calories to about 5 Kcal/mole, with a value of about \( 1.5 \text{ Kcal/mole} \) for the Si–O stretching vibrations.

In quartz, the diad relating the two minima in the high form is lost on cooling, and inversion twinning develops due to the simultaneous growth of nuclei in which the \( A \) and \( B \) minima are occupied (cf. cordierite). The transition is cooperative in that occupation of one \( A(B) \) position reduces the energy of adjacent \( A(B) \) positions, making their occupation more probable. If it is assumed that the Si–O–Si bending mode which appears in the room-temperature infrared spectrum of quartz at 790 cm\(^{-1} \) is primarily responsible for the transition, \( P \) may be calculated:

\[
P = R \cdot T_e + h\nu/2 = (590 + 790/2) \text{ cm}^{-1} = 985 \text{ cm}^{-1} = 2.8 \text{ Kcal/mole}.
\]

This value should be treated as an order of magnitude estimate only, but it is easy to understand the rapidity of the transition.

**Quantum mechanical tunnelling.** The quantum mechanical treatment of the double oscillator implies that there is a finite probability, not considered in the classical model, that the particle will be found within the potential energy barrier. This quantum mechanical 'tunnel effect' has been shown to be important in reactions involving electrons (Mott and Gurney, 1948) and protons (Brickmann and Zimmermann, 1966), the wave function \( \Psi \) being given by:

\[
\Psi = A \exp(-2\pi\hbar\sqrt{2m(P-E)})x,
\]

where \( A \) is the (vibrational) frequency of the particle, \( m \) its mass, \( (P-E) \) the difference between the energy of the particle and the height of the barrier, and \( x \) the penetration of the barrier. The probability that the particle will penetrate the barrier is given by \( \Psi^2 \). Substitution of appropriate values of \( A \), \( m \), \( (P-E) \), and \( x \) shows that tunnelling will be important only in processes involving electrons (\( x \) up to 50 Å) or, if both \( x \) and \( (P-E) \) are small, protons. A calculation for the Si–Al distribution in feldspars using \( A = 10^{13} \text{ sec}^{-1} \), \( m = 28 \text{ amu} \), \( (P-E) = 74 \text{ Kcal/mole} \) (McKie and McConnell, 1963), and \( x = 3 \text{ Å} \) gives for the
tunnelling frequency: \( \Psi^2 = 10^{-34} \times 10^4 \) sec\(^{-1} \). The persistence of disordered Si–Al distributions in feldspars for periods of the order of \( 10^9 \) years (\( 3 \times 10^{16} \) seconds) is not therefore surprising.

The tunnelling frequency has been found to decrease markedly when the potential field becomes unsymmetrical (Brickmann and Zimmermann, 1966).

**Entropy–volume relationships**

In first-order polymorphic transitions, the high-temperature high-entropy form commonly has the larger molar volume, and a similar effect characterizes those second-order transitions in which measurable, but continuous, volume changes occur across a transition zone.

The permitted angular frequencies \( \omega \) of a one-dimensional monatomic line of length \( L \) made up of particles of mass \( M \) spaced \( a \) apart, with a force constant \( \beta \) between particles are given (Kittel, 1956) by:

\[
\omega = \pm \sqrt{\frac{4\beta}{M}} \sin \frac{kL}{2},
\]

where \( k \) is the wave vector, possessing values \( n\pi/L \), where \( n \geq 1 \). The force constant \( \beta \) decreases rapidly with increasing \( a \) in real (anharmonic) systems, causing a corresponding reduction in \( \omega \) and hence in the Debye temperature \( \Theta_D \) and the entropy. Analogous relationships hold for three-dimensional polyatomic structures, and imply a general dependence of entropy on molar volume if we take \( V \propto a^3 \).

Wilsdorf (1965), considering melting as a first-order transition between substances having similar structures, and Fyfe, Turner, and Verhoogen (1958), dealing with solid–solid transitions in general, have discussed the relationship between entropy and volume changes. Wilsdorf used an approach based on the Gruneisen equation:

\[
\frac{\Delta \nu}{\nu_0} = -\gamma \frac{\Delta V}{V_0},
\]

where \( \gamma \) is the Gruneisen constant, given by: \( \gamma = \alpha V/\chi C_p \). Development of these equations leads ultimately to the relationship used by Fyfe, Turner, and Verhoogen: \( \Delta S/\varepsilon V \propto \alpha/\chi \). With \( \alpha \), \( \chi \), and \( \Delta V \) in their usual units, the correct numerical value of \( \Delta S_{\text{vol}} \) is given by:

\[
\Delta S_{\text{vol}} = \Delta V \alpha/42 \chi,
\]

where the factor of 42 converts \( \text{cm}^3 \) bars to calories.

This equation should provide a reasonably accurate estimate of the volume-dependent part of the entropy change in second-order transitions of the \( \lambda \)-point type, in which there is a marked but continuous volume change across the transition zone, but only a qualitative estimate of the entropy change can be expected for first-order transitions involving
marked structural changes, or for solid–solid and solid–liquid transitions in general. Recent compilations of thermal expansion and compressibility data (Skinner and Birch in Clark, 1966) show that the ratio $\alpha/\chi$ varies by a factor of 4 between close-packed oxides and framework silicates, and values appropriate to the particular problem must therefore be used.

The application of (4) may be illustrated by the glaucophane I–II transition, which Ernst (1963) considered to be second order with $\Delta V = 6 \text{ cm}^3/\text{mole}$ across a transition zone some 2 Kbar wide. From the $P-T$ slope of the transition zone, $\Delta S = 4.3 \text{ eu}$, and by analogy with hornblende and tremolite $\alpha = 23 \times 10^{-6}$ and $\chi = 1.2 \times 10^{-6}$, whence the volume-dependent part of the entropy change, $\Delta S_{\text{vol}} = 2.8 \text{ eu}$, suggesting that there is considerably less order–disorder character than previously supposed.

Recognition of further examples of polytypism in minerals

Consideration of a number of polymorphic transitions for which adequate data are available indicates that most can be understood in terms of one or more of the mechanisms outlined above, but that three mineralogically important transitions are anomalous, namely zoisite–clinozoisite, enstatite–clinoenstatite, and anthophyllite–cummingtonite. In all cases volume changes are negligible, there is no obvious positional degeneracy, and changes in vibrational entropy should be very small. These transitions have two important features in common: first, to a high degree of approximation the high-symmetry form can be regarded as a modification of the low-symmetry form twinned on the unit-cell scale (Ito, 1950), i.e. as a sequence of layers … $ABAB…$ comparable to a two-layer mica; the ‘twin planes’ are $\{100\}$ in zoisite, enstatite, and anthophyllite, and $\{001\}$ in mica. Second, the stability fields of the various forms show very strong compositional control, but relatively little apparent dependence on temperature or pressure. It is suggested that the orthorhombic varieties are best regarded as two-layer polytypic modifications of their one-layer monoclinic forms, comparable with $2M$ and $1M$ micas.

It has been contended (Buerger, 1945) that the free energy of an $AB$ interface (twin boundary) is necessarily positive relative to that of $AA$ or $BB$ boundaries. Although general structural considerations imply that this will frequently be the case, there does not appear to be any $a \text{ priori}$ reason why negative values should not be encountered occasionally.
Indeed, the observation that such two-layer structures as $2M$ mica are stable implies that the free-energy change $\Delta G_{AB}$ for the reaction: $\frac{1}{2}AA + \frac{1}{2}BB \rightarrow AB$ is negative. The relative numbers of $AA$, $AB$, and $BB$ interfaces will then be defined by the Boltzmann relation, and continuous gradation of properties from a perfectly ordered two-layer structure through two-layer structures with frequent stacking faults and one-layer structures with frequent twin planes to a perfect one-layer structure is to be expected as $\Delta G_{AB}$ varies from $-\infty$ to $+\infty$. Similar conclusions were reached by Schneer (1955) in his derivation of the most convincing theory of polytypism in silicon carbide yet to be advanced.

Factors favouring a small or negative value of $\Delta G_{AB}$ would include the absence of solid solution (which renders adjacent structural units unequal in size), and the presence of either real or false symmetry elements normal to the twin plane. With a single mirror-plane normal to the twin plane, the number of layers in the repeat unit will normally be limited to two ($\ldots ABAB \ldots$), as in most micas, anthophyllite, enstatite, and zoisite.

However, an axis or pseudo-axis of order 3 or 6 permits the formation of much more complex stacking sequences, e.g., $\ldots ABCBA \ldots$ as in silicon carbide (Krishna and Verma, 1966), cadmium iodide, some micas, and a number of close-packed metals and oxides. Increasing solid solution would be predicted to favour the one-layer form, as appears to be the case in micas, and in clinozoisite, clinoenstatite, and cummingtonite, although the frequent twinning observed in the last three minerals indicates that $\Delta G_{AB}$ remains relatively small, of the order of $10kT$. Much lower values, in the region of $kT$, are suggested by the formation of antiphase boundaries in a plagioclase feldspar ($An_n$) at intervals of 30 Å (McConnell and Fleet, 1963).

There is now considerable evidence for the view that the formation of long-range stacking order in metals represents an attempt to minimize the energy of the conduction electrons (Sato, Toth, and Honjo, 1966) and a similar explanation could well hold for covalent substances such as silicon carbide, in which the band gap shows a systematic dependence on the number of layers in the repeat unit (Krishna and Verma, 1966). This is to be expected from the formula for the energy of an electron in a one-dimensional box, if the length of the box is identified with the length of the repeat unit: $E_n = (n^2\hbar^2/8ma^2)$ ($n = 0, 1, 2\ldots$). On this hypothesis, the presence of impurities, by influencing the number of conduction electrons, should have a marked effect on the stability of individual polytypes.
The link between symmetry and entropy is essentially a simple one: increasing the symmetry increases the vibrational and positional degeneracy, and hence $\Omega$, $S_{\text{vib}}$, and $S_c$. Changes in molar volume have little effect on $S_c$, but alter the non-configurational entropy through the $E/T$ term. Multiplication of the unit cell reduces the density of equivalent positions, and through this decreases $\Omega$ and $S_c$.

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