ORDER AND DISORDER IN FELSPARS

By

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This paper will be concerned with relations between order and disorder from the structural viewpoint, and will draw its evidence almost entirely from the results of X-ray diffraction. Optical properties are left out, partly for lack of room, partly because so little is really known about their interpretation in terms of atomic environments and interatomic forces. Moreover, because the wavelength of light is so much longer than that of X-rays, the effects measured by optical experiments represent averages over very much larger volumes than those which can be resolved by X-rays (cf. § 2). Again, thermodynamic studies, by their nature, represent averages over large enough volumes to treat statistically, and therefore are of limited use for the problems here considered.

The basic ideas underlying this paper are (i) that the *kind* of order is a more fundamental concept than the *degree* of order, and must be given primary consideration, (ii) that there may be regular geometrical differences in the configuration of the framework not dependent on the kind or degree of order (though perhaps modifiable by it), (iii) that, where domain textures exist, the most important characteristic is the nature of the structure *within* a domain, the nature, frequency and disposition of the domain walls being interpretable only in relation to that structure.

These ideas are of general application to all felspars, and probably, more widely, to all three-dimensionally-linked structures. The illustrations and evidence, however, are all drawn from the plagioclase series,

because it is only here that we have enough structural studies to show, even in outline, the effects of varying composition in a "solid-solution series".

1. *Substitution disorder*

The simplest type to consider first is Si/Al substitution disorder. In a felspar, all sites available for Si and Al are chemically-equivalent tetrahedral sites. We may suppose that under certain conditions each site has the same chance of being occupied by Si. When the average of all unit cells in the crystal is taken, the Si:Al ratio at each tetrahedral site is the same. In this case there is complete Si/Al substitution disorder.

If, however, the crystal is partly ordered, the proportion of Si at each crystallographically-independent site may be different. There were several examples quoted by Taylor (this volume). For interpreting such results, it is important to consider the *kind* of ordering to which the crystal tends, as well as the degree of order. Experimentally, there are only two fully ordered distributions known, both very simple: that of microcline and low albite, with a 3:1 Si:Al ratio, and that of anorthite and celsian, with a 1:1 ratio (see Figure 1). But these certainly

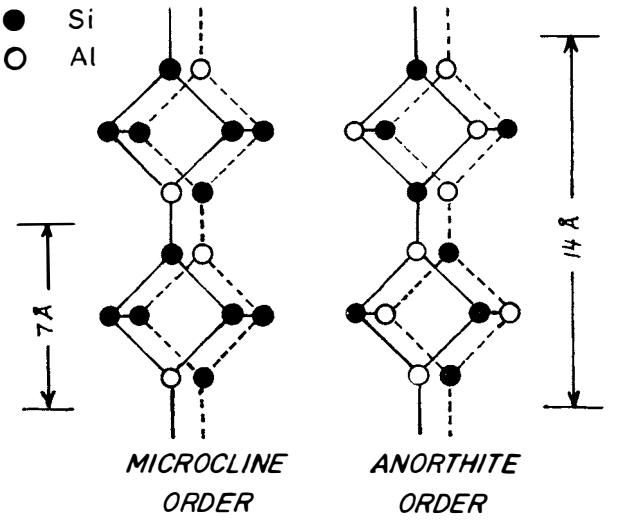

Figure 1. The two observed types of perfect Si/Al order.

do not cover all the possible distributions for other compositions. For example, in a crystal with a 9:7 ratio, do the excess Si atoms go into only one of the 8 original Al sites, or into all 8 at random? Or must we consider quasi-ordered structures in which certain sites admit only Si, others only Al, and others are occupied at random by the remaining atoms? (An example of a quasi-ordered structure, even at a simple composition ratio, is that of ideal orthoclase, with one of its two sites occupied by pure Si, and the other by $Si_{\frac{1}{2}}Al_{\frac{1}{2}}$). We cannot generally answer this kind of question yet, and perhaps never shall be able to, completely (see however § 8 and 12 for further discussion). But it does indicate the complexity of the problem. Moreover, while changes in the *degree* of order occur continuously with temperature and composition, and can be discussed in terms of conventional thermodynamics, changes in the *kind* of order may be discontinuous and need a different approach.

2. *Correlation between adjacent units*

So far, we have assumed that what happens in one unit cell is independent of what happens in its neighbour. This of course cannot be strictly true. If one site contains a particular kind of atom, local stresses are set up which spread outward from its immediate position and inevitably affect the probability of occupation of the next crystallographically-equivalent site by the same kind of atom. However, if the stresses are small and the structure not very rigid, the difference of probabillity may be negligible. In this case, if we pick out any two equivalent sites, the chance that they are alike is independent of the length or direction of their distance apart. This (if applied to every site in the unit cell) is the criterion of homogeneity. If the sites are always alike, the material is perfectly ordered; if they are not, but have a constant ratio of alike to different, it is *homogeneously disordered.*

By contrast, consider what happens if a particular arrangement in one unit cell is strongly correlated with possible arrangements in its neighbours. Suppose for example there are two kinds of unit X and Y. Two cases are to be distinguished.

(i) If each kind of unit has a strong tendency to favour its own kind as neighbour, domains appear consisting of pure X and pure Y. (Figure 2(a)). These may differ in composition, or merely in structure. In either case they represent the beginning of segregation into two

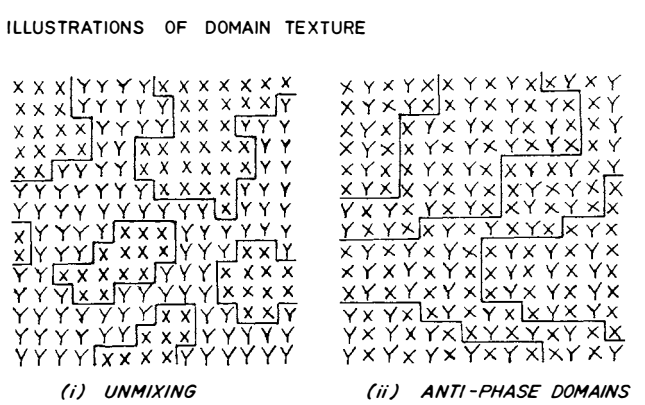

Figure 2. Illustrations of domain texture: (*a*) unmixing, (*b*) antiphase domains. In (*i*), the two different subcells X and Y are unit cells of different structures; in (*ii*), they are not independent but together form the unit cell XY of a single new structure.

phases. Clearly the material is non-homogeneous, except on a much coarser scale than that accessible to X-ray study.

(ii) If each kind of unit has two opposite sides on which it favours the other kind of unit as neighbour, a structure in which they alternate is that of lowest energy. The true unit cell is now double the original, and X and Y are its subcells. If the composition allows for equal numbers of X and Y, a perfectly ordered homogeneous structure (XY) may be formed; or alternatively, in different growth conditions, we may get a domain texture (Figure 2(*b*)) in which each domain is a piece of the same perfect structure, but displaced relative to the next by half the true cell length. These are antiphase [1] domains.

When the composition does not allow equal numbers of X and Y, one of two things may happen: either the excess atoms are absorbed in X and Y, modifying them say to X' and Y'; or there is a tendency to push out the unwanted atoms into the domain boundaries, which thus become two-dimensional regions of composition different from

[1] Unfortunately it is necessary to use the word "phase" in two different senses in this paper. In the term "anti-phase domain" it is used with its physical meaning to name the state of a periodic variation: such a domain is exactly out of phase (180° out of phase) with its neighbour. Elsewhere "phase" is used with its chemical meaning to name a structurally distinct state of a material: thus, different phases exist on either side of a transition. In the first meaning of the word, Figure 2b shows an anti-phase domain texture; in its second meaning, Figure 2a shows a two-phase domain texture.

the bulk of the material. Probably in general both effects will occur simultaneously, but they are discussed separately later.

These arguments apply equally if there are more than two kinds of subcell involved, or if the correlation between them gives rise to a more complicated ordered arrangement than that of Figure 2(*b*). Examples will be given later. However, too great an increase in the complexity of the ordered structure makes it both harder to unravel the evidence for it and harder to assign physical meaning to the results.

Materials showing domain textures are non-homogeneous structurally, whether or not they are homogeneous chemically. Within a domain, however, there is homogeneity. This is true whether the unit cell consists of a single subcell X (or Y) as in Figure 2(*a*), or is a combination of two subcells XY, as in Figure 2(*b*).

Optical investigations necessarily measure average effects over distances comparable with the wavelength of light. Domains with distinguishable X-ray effects may be very much smaller than this (say 1/10th, according to the estimates of § 5). Thus optical homogeneity is compatible with a domain texture and does not imply structural homogeneity; it is the latter which concerns us in this paper.

3. *Importance of geometrical configuration of framework*

At this stage it is important to make clear that differences between X and Y need not consist only in their different pattern of Si/Al or Na/Ca occupation; differences in the detailed atomic coordinates may be even more important. It is easiest to illustrate this from anorthite, which has a perfect structure with four different subcells. Figure 3 shows representative parts of the actual structure, projected on (010). Subcells P and S are identical in their Si/Al arrangement, but *not* in their atomic coordinates; the general difference in the shape of the ring of four tetrahedra is quite obvious. On the other hand, P and R, which have exactly reversed Si/Al patterns, have very similar geometrical shapes; the same is true for the pair R and S. It seems that there is something determining the geometrical shape of the framework which is more important than the Si/Al arrangement.

The importance of this geometrical effect is that, because of the rigidity of the structure, it is strongly correlated from one subcell to

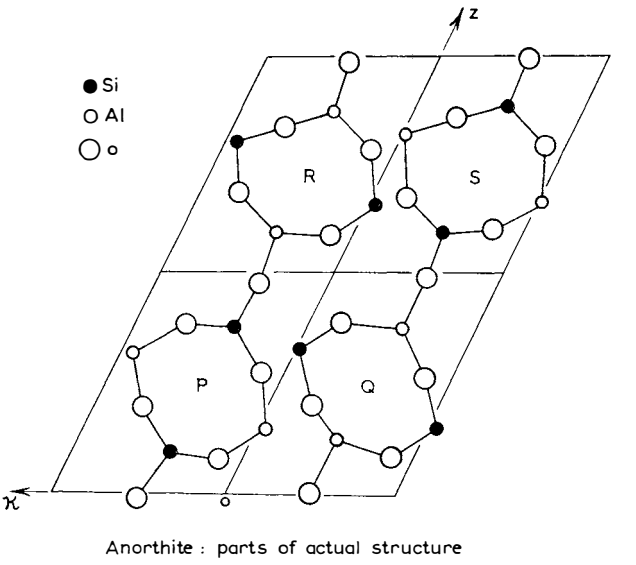

Figure 3. Projection on (010) of corresponding parts of the four subcells of anorthite. (*P* and *R* are displaced sideways relative to Q and S, to make the diagram clearer).

the next. Consider the building of the structure as a problem in statics. If predetermined ideal values are assumed for all the bond lengths and bond angles, the problem will be insoluble, because there are too many constraints. If some tolerance is allowed, say in bond angles, the structure can be built, but there will be local strain energy which must be kept as small as possible. By doubling the repeat period and therefore the number of independent position parameters, the strains may be reduced, and the resulting structure will have a lower potential energy [2].

Evidence for the importance of the detailed geometry comes from a survey of the bond angles at Si and Al in all the felspars, and all the individual tetrahedra within a single felspar, for which information

[2] The equilibrium state of the structure of course depends on the free energy, which includes, in addition to the potential energy, an entropy-dependent term. This latter is likely to increase on doubling the repeat period, because the vibrational entropy is associated with the number of normal modes, which is also doubled. One cannot predict in general whether this increase or the decrease in potential energy will predominate, except to note qualitatively that the relative importance of the latter will be greater in strongly-bonded structures.

was available (Megaw, Kempster and Radoslovich (1962)). The ideal angle is the tetrahedral angle, 109°28′; departures from this may be considered as strains, and may be positive or negative. For the angles with large strains a surprising fact emerges: the sign and approximate magnitude of the strain in a particular angle is always the same in all felspars, and is independent of the type of Si/Al order, of the degree of disorder, and even, in an ordered structure, of whether the atom under consideration is Si or Al. This is illustrated in Table 1 for the atom T_1. The three angles with the largest strain show the effect very conspicuously, and two others show a strong trend of the same sort; only one is indeterminate. Similar results are found for T_2. We must conclude that the general system of linkages in the felspar framework, and the balance of nearest-neighbour directed forces, are responsible for the major part of the potential energy and therefore for the detailed geometry of the equilibrium configuration. From the criterion of bond-angle strains, it is clear that the differences in potential energy between different felspars due to differences in Si/Al arrangement are relatively small. In the same way it is clear that in anorthite the geometrical differences between the subcells are not essentially determined by the Si/Al arrangement. (It can in fact be shown that they are a consequence of the process of packing oxygen atoms of the framework round the moderate-sized Ca ion).

Table 1. Average bond-angle strains.

The letters *A*, *B*, *C*, *D* refer to the oxygen atoms whose bonds to the tetrahedral atom T_1 define the angle. For anorthite, where each value listed is the mean of four independent angles, the R.M.S. deviation from the mean is recorded.

T_1 *tetrahedra*		*AB*	*AC*	*AD*	*BC*	*BD*	*CD*
Anorthite	Si	−6.9 ± 1.3	+5.9 ± 1.2	−6.2 ± 0.9	+2.1 ± 0.8	+3.8 ± 1.1	+0.8 ± 1.0
	Al	−8.4 ± 2.1	+6.7 + 1.7	−8.5 ± 2.5	+3.1 ± 0.7	+4.9 ± 1.2	+1.6 ± 0.5
Albite, low	Si	−3.9	+3.7	−2.9	−0.6	+1.2	+0.8
	Al	−5.9	+5.6	−6.2	+2.1	+0.7	+2.6
Albite, high, Si/Al		−4.8	+2.5	−4.6	−1.5	+3.0	+4.5
Microcline	Si	−4.8	+3.5	−4.3	+3.2	+0.2	+0.9
(intermed.)	Al	−2.2	+3.7	−4.8	+0.7	+0.1	−4.8
Orthoclase, Si/Al		−3.4	+5.1	−3.4	+0.7	+0.5	−0.7
Sanidine, Si/Al		−4.2	+3.5	−3.4	+1.4	+2.4	−0.3
Celsian	Si	−6.5	+6.7	−6.5	+1.8	+4.2	+0.1
	Al	−6.9	+6.4	−8.4	+4.1	+4.3	−0.5

It thefore seems that we must envisage a T–O framework whose detailed shape depends only slightly on Si/Al arrangement. Starting from arbitary initial conditions of Si:Al ratio and degree of disorder, changes in these can cause changes in the detailed atomic coordinates and in the overall dimensions of the framework, but they are small continuous changes which do not destroy its essential shape; they are more closely comparable, geometrically speaking, to the changes normally associated with thermal expansion than to anything usually recognised as a phase transition. However, the framework itself may have at least one discontinuously different configuration, whose energy is differently dependent on the Si:Al ratio and the effects of temperature apart from disorder. If so, there may be conditions in which the new configuration has a lower energy, and a transition will occur. On the phase diagram of temperature versus composition, it is these discontinuous changes in framework configuration rather than changes in degree of order which should be represented by boundary lines.

For a given framework configuration, the potential energy concerned in substitution ordering is of two kinds, (i) that associated with electrostatic charge balance, (ii) that associated with local bond-angle strain or bond-length strain. The electrostatic energy of ordering is fairly insensitive to small changes of geometry, because of the slow variation of electrostatic force with distance; it will be large for departures from a stoichiometrically simple ordered arrangement, but small at compositions where no such simple arrangement is possible. In the latter case the nearly equal potential energies of different arrangements favour cation diffusion and result in a large entropy contribution to the free energy. The part of the ordering energy associated with relief of local strain may depend quite sensitively on the framework geometry, but is not predictable.

The system can be discussed in terms of a free energy surface. Figure 4(*a*) shows schematically the variation of free energy with temperature for a material of given composition; curves *AB* and *CD* refer to two different configurations of the framework, each in its equilibrium state of order. Where they cross at *E* there is a transition. Figure 4(*b*) shows the variation with composition, at a given temperature, again for equilibrium states of order. These curves can have slopes of different sign; consequently sharper discontinuities at a

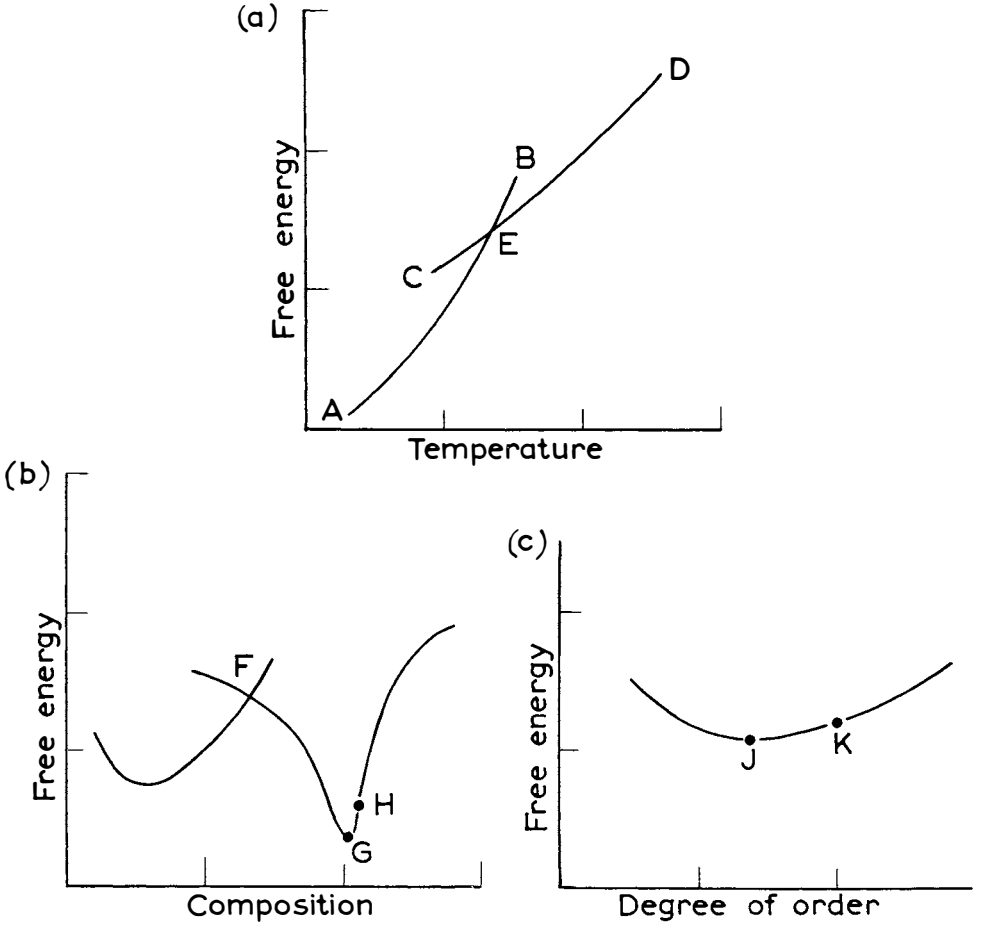

Figure 4. Schematic diagram of free energy. In (*a*) and (*b*) the curves are those for the equilibrium state of order; (*a*) is drawn for a constant composition, (*b*) for a constant temperature, (*c*) for constant composition *and* temperature.

transition are possible, as are minima in the curve for either configuration. The minima correspond to ordered or quasi-ordered arrangements of stoichiometric composition, and may be very deep. Figures 4(*a*) and 4(*b*) may be considered as sections, in planes at right angles, of a three-dimensional representation of the free energy surface for equilibrium states of order; on this surface, the locus of the transition is the line *EF*.

In practice, materials may not always be in equilibrium states of order. Figure 4(*c*) plots free energy against degree of order at a given temperature and composition. The minimum, *J*, is the point used in constructing 4 (*a*) and 4(*b*). Since the minimum is generally shallow, the use of a non-equilibrium state such as *K* will not alter the surface greatly. Deep minima, such as may occur at simple stoichiometric compositions, imply a strong ordering tendency which will normally bring about the equilibrium state. Only where the energy surface is rather flat in the neighbourhood of a transition will the degree of order influence the choice of framework configuration and therefore lead to smearing; elsewhere the ordering follows the choice.

The emphasis is thus on a discontinuous change of framework configuration, unrelated to any ordering effects. The occurence of such a change in an ordered structure is no new idea; an obvious example is the α–β transition in quartz. There is no reason why the presence of substitution disorder should change its character. It is a diffusionless transition, and such transitions cannot normally be quenched in. But if it is accompanied by changes in equilibrium order, and the rate of equilibration is slow, the consequences of the transition may still be detectable in the quenched material.

4. *Anti-phase domains*

Though the above discussion refers to homogeneous structures, it leads on to an explanation of anti-phase domains. Suppose that on one side of the transition the configuration is such that all subcells are alike, i.e., the subcell is identical with the true cell; on the other, the configuration is an alternation of subcells *X* and *Y*, with true cell *XY*. Any cell of the first phase has an equal chance, at the transition, of becoming *X* or *Y*; by doing so it becomes the nucleus of a domain which grows till it meets another domain and either merges with it or forms with it an anti-phase boundary.

Suppose the material is stoichiometric and the domains perfectly ordered. The domain boundaries are then regions of misfit, the atoms in them being displaced relative to those in the perfectly repeating interior; there is thus a surface energy. The material with anti-phase domain texture is in a higher-energy state than if it were a perfect single crystal. Since movement of domain boundaries involves no diffusion of atoms, it may easily be achieved at relatively low tempera-

tures, and the material annealed to a single crystal. (For an example, see § 7).

If on the other hand there is substitution disorder, the boundaries may provide better conditions for one kind of atom than for the other. Figure 5 illustrates this: it shows a hypothetical structure with two fairly rigid chains, (*a*) in correct relative positions, (*b*) with an anti-phase fault. The geometrical relationships of the interstices between the chains are very clearly different in the two cases. If, during the original quenching, atoms of one kind diffuse preferentially to boundary sites, where they lower the potential energy, later movement of the boundaries becomes difficult or impossible. The domain texture of the temperature at which diffusion ceased to be effective is locked in, whether or not it is a truly stable state of the material. (For an example, see § 8).

This can be looked at in another way. Suppose the composition of the material is nearly but not quite that for minimum free energy, (say H in Figure 4(*b*)). It may achieve a lower total energy by building a piece of perfect structure of composition G, and rejecting the unwanted atoms into a boundary region. The boundaries originally formed

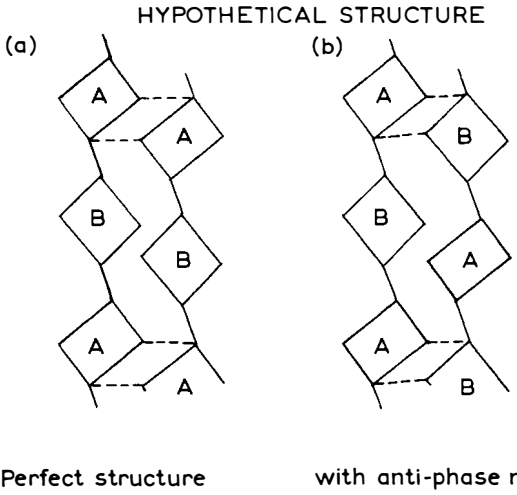

Figure 5. Hypothetical structure with 2 subcells A and B in the unit cell: (*a*) part of perfect structure, (*b*) part of structure with anti-phase mistake. Notice the different shapes of the interstices at the dotted lines.

remain mobile and fuse with one another till they too have a composition of minimum energy appropriate to their different geometry. They can perhaps be regarded as a segregation of a new two-dimensional phase, one unit cell thick or less. (For an example, see § 9).

In discussing anti-phase domains we must notice that there is, on physical grounds, a lower limit to their size. If the surface energy is comparable with the volume energy of the interior, the equilibrium shape of the framework will be deformed from what it would be as part of a large crystal. With decreasing domain size, this effect increases, till in the limit the distinguishing features of the subcells are no longer recognisable. To put the point in another way, there is no meaning in the concept "unit cell" unless it is part of a periodic structure with enough repetitions of the period to make boundary effects negligible. This does not mean that local order in regions smaller than a unit cell cannot occur, but that unless it is effectively periodic it must be dealt with as homogeneous disorder. It is not easy to say *a priori* how many repetitions are needed, for it must depend on the nature and magnitude of the boundary stresses relative to the volume stresses. If the boundary stresses are confined to a layer a fraction of a unit cell thick, perhaps 2 repeat units might suffice.

It is necessary to remember that the actual boundary surface separating physically rigid units will not be a plane, even though its overall direction is that of a rational plane; neither will the form enclosing the unit itself generally be a parallelepiped, though it must be a space-filling repeat. Figure 6 illustrates a possible form enclosing the repeat unit of a hypothetical two-dimensional structure; numerous other examples are found in the drawings of M. C. Escher (1960). In an actual structure, the corrugations of a physically-important boundary plane are not likely to be unduly large.

There is no difference in principle between a transition in which all subcells change their geometry in the same way and a transition in which alternate subcells change in different ways. The former will only be recognised as a transition if it is either noticeably discontinuous (no examples of this are known) or it involves a change of symmetry. For a change of symmetry (e.g. monoclinic to triclinic) the domains produced on quenching will be related by twinning, not by anti-phase mistakes. Most of the general discussion about anti-phase domain texture, and the effect of boundary walls on the overall energy, will

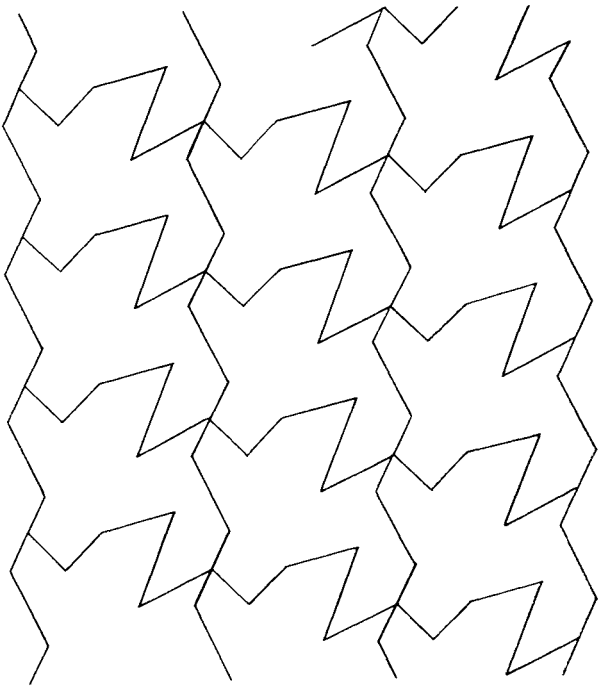

Figure 6. Space-filling repeat units of a hypothetical two-dimensional structure, with outlines chosen so as to avoid cutting any strong bonds. These outlines represent the most likely places for cleavages, or for fault planes.

be equally applicable to twin domain texture, but it is outside the scope of this paper to discuss twinning in any further detail.

5. X-*ray diffraction evidence*

Homogeneous disorder and domain texture are generally distinguishable by their obvious diffraction effects. Homogeneous disorder does not give rise to any diffuseness or streaking of the reflections (we are not here concerned with the general diffuse background). Domain texture, on the other hand, is characterised by such effects (if the domain sizes lie within an appropriate range, which we consider below). For separation into two phases, as in Figure 2(*a*), or two orientations of the same phase (i.e. twinning), the reflections split into double or multiple spots, possibly with some streaking if the domains are very small. Anti-phase domains are only recognisable as

such when they are small, and the effect is a streaking or blurring of the sharp reflections characteristic of the doubled spacing. (Examples are discussed in § 7 and 8). The size and shape of the diffuseness gives information about the size and shape of domains. With decreasing domain size the reflections become broader and weaker; in the limit, when they merge into the background, it is impossible by inspection of photographs to distinguish the case from one of homogeneous disorder.

How small are the domains when they disappear? A theoretical treatment of diffraction by a faulted structure (Megaw (1960a)) relates half-breadths of diffraction maxima to the frequency and slip vectors of faults on planes normal to the direction in which the elongation of the maxima occur. For an anti-phase fault with probability 0.3, the half-breadth is 60°; with higher probabilities, it increases so rapidly that this may be taken as the limit at which detection is possible. It corresponds to an average domain length of 3 unit cells. If there is more than one direction of fault plane, and the reflection is blurred in two or three dimensions, the limiting size for detection is likely to be rather higher.

By contrast, the same treatment shows that diffuseness due to domains larger than about 20 or 30 unit cells may not be noticeable in ordinary single-crystal photographs, and the existence of such domains could remain undetected.

X-ray evidence from intensity measurements of sharp reflections is independent of that from the size and shape of diffuse reflections, and can sometimes take us further. Consider a structure with two subcells, giving strong even-order and weak odd-order reflections, which we may call types "*p*" and "*q*" respectively. The electron density synthesis is the sum of the contributions of "*p*" reflections, which are equal in both subcells, and those of the "*q*" reflections, which are equal in magnitude but opposite in sign. Averaging the electron density in the two subcells is thus equivalent to omitting the "*q*' reflections. Conversely, if we omit the "*q*" reflections, either deliberately in order to simplify the calculation, or unavoidably because they are too diffuse to measure, we obtain a map which has a physical meaning (provided that our trial structure is near enough the true structure to give the correct signs to the "*p*" reflections). Corresponding atoms in the two subcells may appear in the map as resolved half-atom peaks; more

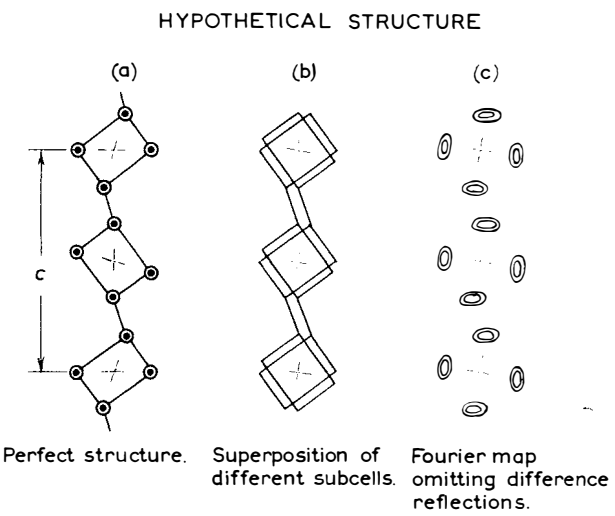

Figure 7. Formation of elongated peaks by superposition of two nearly identical subcells, illustrated with hypothetical structure: (*a*) actual structure, with 2 different subcells, (*b*) superposition of 2 unit cells of structure, displaced relative to one another by $\frac{1}{2}$ cell length, (*c*) sketch of electron density map corresponding to (*b*). (Faint crosses mark corresponding points in each subcell and in each diagram).

commonly, they will overlap to give an elongated peak, or one whose anisotropy is at least detectable by a characteristic anomaly on a difference map. (The formation of elongated peaks is shown diagrammatically in Figure 7, and an actual example is given in Figure 8, from the structure discussed in § 8).

A map in which most of the atomic peaks show this kind of splitting is strong evidence for an anti-phase domain texture. Any alternative explanation suggesting that the paired half-atom sites are occupied at random in adjacent parts of the structure is physically quite unreal. So is the suggestion that, while one atom of each pair belongs to subcell X and the other to subcell Y, the subcells are distributed at random; in strongly-bonded structures, such randomness would destroy the distinctive identities of the subcells.

Of course, this map, taken alone, does not allow us to say which atom of each pair belongs to which subcell. If, however, a good approximation to a possible structure is known from other evidence, the map allows it to be tested and, if correct, refined.

There is a possible ambiguity because elongated peaks on a map

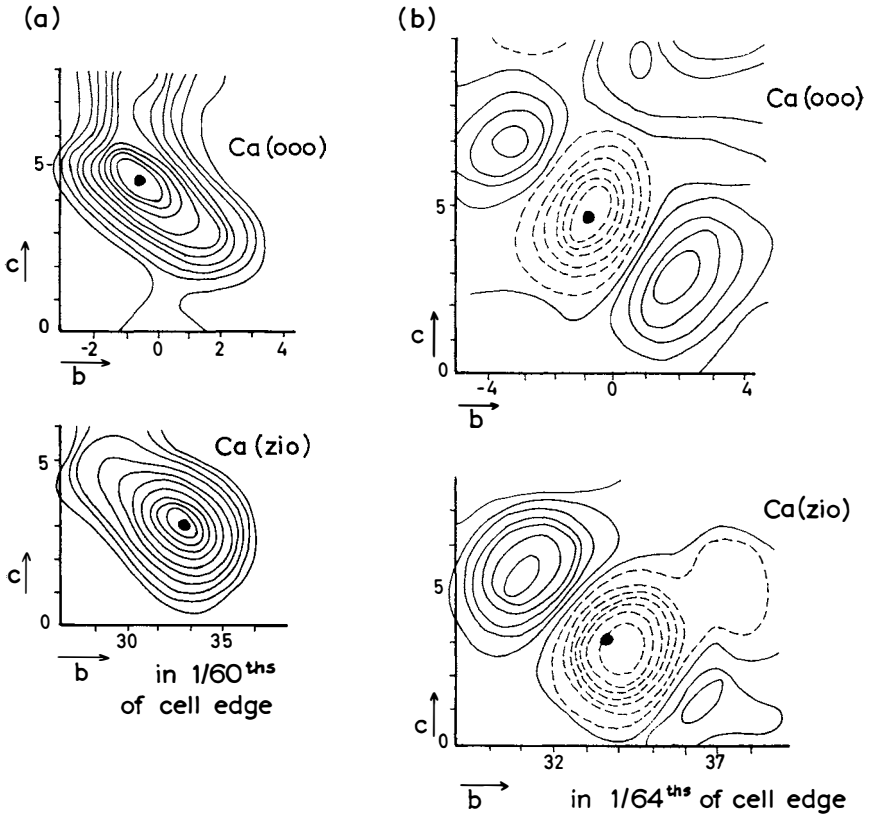

Figure 8. (*a*) Elongated peaks in electron density synthesis of low bytownite, (*b*) corresponding parts of difference map, projected on (100). Dot shows position of Ca/Na atom used in calculation. (Chandrasekhar (1957)).

may often equally well be attributed to anisotropic temperature factors. Some caution is needed, but the physical reasonableness of the model can often serve to discriminate between these two explanations. In the same way, an apparent isotropic temperature factor may actually mask a set of four adjacent unresolved quarter atoms; the absence of observed splitting may not be conclusive in such cases.

6. *Survey of plagioclases*

Figure 9 is a very rough schematic diagram, intended to show the separate effects of structure type and substitution disorder in the plagioclase system.

The lines represent the boundaries of the different structure types [3]; across them, the changes in geometry are either discontinuous or at least very abrupt. Away from stoichiometric compositions, however, their exact course may be partly smeared out by substitution disorder. No attempt has been made to indicate temperature quantitatively, except at the end compositions, albite and anorthite.

It is important to notice that here, as elsewhere, "structure" means a regularly repeating formation, *not* continuous across domain

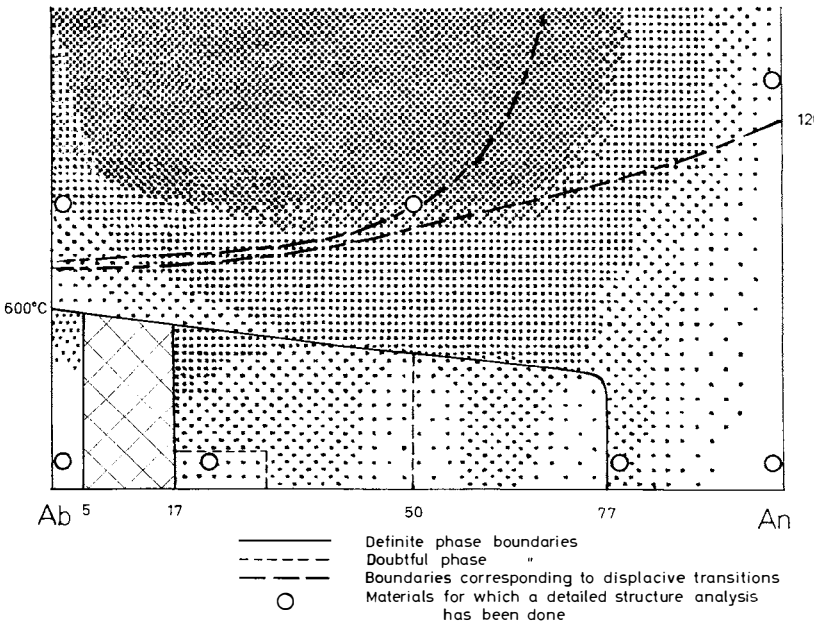

Figure 9. Schematic diagram of plagioclase felspars, showing structure and degree of order as separate features.

Circles mark materials studied. Full lines show phase boundaries; dot-dash lines show transitions believed to be displacive [3]; dashed lines show tentative or doubtful boundaries. Density of dots indicates degree of subsistution disorder. Hatching marks area in which no structure is known to exist.

Note. No significance is to be attached to *detailed* temperature indications except at two points where numerical value is marked.

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[3] The boundary of the displacive transition to monalbite (see Brown (1960) for references) has not been shown, pending further information. It would take the form of a dot-dash line enclosing the top left-hand corner of Figure 9.

boundaries. The diagram is concerned solely with effects *inside* a domain; it does not attempt to show the occurrence or size of domains. Thus, for example, there is a gap in the low-temperature region between about Ab_5 and Ab_{17}, because no structures of this composition range are known to exist in the low form; material of this composition is always unmixed.

Within homogeneous domains, substitution disorder may occur; on the diagram, the equilibrium degree of disorder is indicated schematically by the density of shading with dots. It is greatest at high temperatures; at a given temperature, it is greatest for compositions far from stoichiometric. (Qualitatively, we do not distinguish here between the state of equilibrium disorder *at* high temperatures and the state of disorder quenched *from* high temperatures; this might often need to be taken into account).

X-ray determinations of cell size and atomic coordinates are concerned with homogeneous structures, i.e. with effects not overstepping domain boundaries. If the existence of small domains, say less than 200 Å across, makes it necessary to average the electron density maps over two or more unlike subcells, it becomes difficult or impossible by this method to separate out the true substitution disorder within a domain from the apparent disorder produced by the averaging process. Nevertheless, since the two effects are associated with different causes and can vary independently, the distinction remains important.

The circles in Figure 9 show the approximate composition of materials used for structure analysis, and indicate whether they are "high" or "low", i.e. effectively quenched or annealed. The following sections of the paper deal with these separately.

7. *Transitional anorthite*

Transitional anorthite has the same composition as primitive anorthite, and is effectively pure $CaAl_2Si_2O_8$. It differs in the diffuseness of its "*c*"-type reflections and the absence of "*d*" type [4]. This can be explained by an anti-phase domain texture, as suggested by Laves and Goldsmith (1954) (though their detailed discussion at

[4] The "*d*" reflections are so weak that even moderate diffuseness would make them unobservable. The theoretical assumption that they behave like "*c*" reflections therefore raises no difficulties, and they can be ignored.

that date is not easily reconciled with the modern picture outlined earlier in this paper, or with the structure of primitive anorthite). For both natural and synthetic materials, the sharpness of the reflections can be restored by heating for a few hours at about 1100°C and destroyed by heating for a similar time above 1300° and quenching (Gay (1954); Laves and Goldsmith (1954)). The reversibility and moderate speed of this process is generally taken to imply that no changes in Si/Al order accompany it. It was predicted (Megaw (1961)) that the *structure* at room temperature would be the same as that of primitive anorthite, and only the *texture* (the size and shape of domains, and the necessary misfit at domain boundaries) would be different.

This has now been verified by a structure determination of a transitional anorthite from Miyake, Japan (Ribbe and Megaw (this volume)). A three-dimensional refinement using only the "*a*" and "*b*" reflections gave a synthesis with half-atom peaks. The coordinates, so far as we can yet tell, are indistinguishable from those of two superposed pairs of subcells of primitive anorthite, and the temperature factors of corresponding atoms are very similar. If there are any significant differences, they may perhaps help us to determine the part of the unit cell through which the domain boundaries run.

An attempt to interpret the diffraction effects in terms of anisotropic temperature factors is bound to fail, because, even if the thermal amplitudes required were plausible, the existence of the diffuse "*c*" reflections vould not be explained in this way.

We hope to repeat the work with an extreme high anorthite. Meanwhile we conclude that only the primitive anorthite structure exists at room temperature, and that the true high anorthite structure cannot be quenched in.

What is the true "high anorthite" structure? No structure analyses have been made at high temperatures. The simplest hypothesis is that at a transition near 1200°C the framework alters to make subcells P and S identical, and also Q and R, the Si/Al alternation which distinguishes (P, S) from (Q, R) being retained unaltered. On quenching from above this temperature, anti-phase domains are formed.

This hypothesis can be used to explain the observation of Laves and Goldsmith (1954) that the degree of diffuseness, and therefore the domain size, depends strongly on the quenching temperature but little on the quenching rate (over the range studied). We must postulate

that there are thermal fluctuations distributed uniformly in space with a density which increases with temperature; that their relaxation time is rather long; and that these fluctuations, quenched in from the original temperatures above 1200 °C, provide nuclei for domain growth below 1200 °C.

Laves' own interpretation of the process (Laves (1961)) seems to imply the continued existence of anti-phase domains, and therefore of distinguishable subcells, up to the highest temperatures studied. It would still be necessary to find a reason why, near 1200 °C, the formation of domain walls becomes energetically favourable, and why their area or volume increases with increasing temperature. Possibly a shifting mosaic of domains could be brought into existance by Debye waves, whose wavelength determined the domain size. Perhaps the distinction between this picture and that of the previous paragraph is more apparent than real. The effect at 1200 °C is in any case one concerning the framework, which either adopts a new and simpler configuration above this temperature, or else loses its rigidity and allows subcells to interchange their identity.

On quenching from very high temperatures (Laves and Goldsmith (1955)) weak or diffuse "*b*" reflections are sometimes observed. This effect is interpreted by Laves and Goldsmith as directly due to Si/Al disorder; according to the present author, it is due to formation of a different kind of domain from those giving "*c*" diffuseness, only possible when there is enough Si/Al disorder to destroy the essential continuity of the anorthite alternation. This is considered further in § 10. If It is true that Si/Al disorder can, by extreme thermal treatments, be quenched in (whether or not it ever represents an equilibrium state at any temperature) it seems possible that less extreme treatments may allow a lesser amount of disorder, not enough to destroy the continuity of the alternation, but perhaps enough to provide nuclei for the domains responsible for the "*c*" diffuseness. If so, we must be prepared to find high anorthites with some small amount of substitution disorder at certain sites. This might perhaps explain the small variation of lattice parameter with thermal treatment observed by Goldsmith and Laves (1956).

We may sum up by saying that at room temperature the structure of anorthite is always primitive; at 1200 °C it becomes effectively or actually body-centred. This structure cannot be quenched in, but

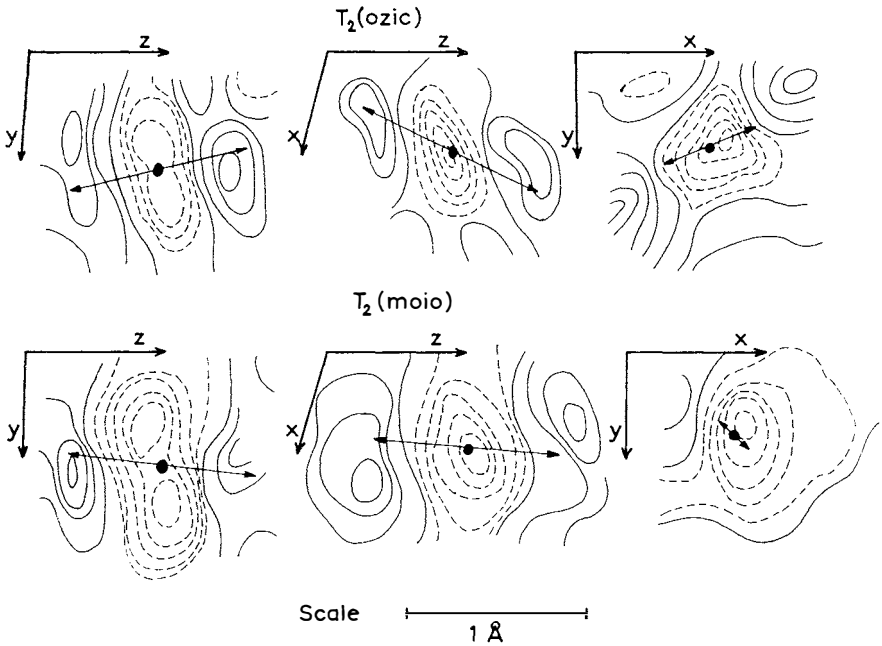

Figure 10. Difference maps (three different projections) showing "splittings" of two T_2 peaks in low bytownite; the trial structure was body-centred except for two half Ca/Na atoms (Fleet (1962)).

leaves clues to its one-time existence in the formation of an anti-phase domain texture, whose details depend on the thermal history. There is no evidence of residual Si/Al substitution disorder, but it could possibly occur in very rapidly quenched materials.

8. *Low bytownite* ("*Body-centred anorthite*")

Just as the "*c*"-type reflections become increasingly diffuse with quenching temperature at the ideal anorthite composition, so they become increasingly diffuse with albite content for material of low-temperature origin (Gay (1953)). Near An_{80} they are no longer observable. If this material alone were known, it would be supposed body-centred. An analysis of the structure assuming this to be true shows very elongated Ca/Na peaks (Figure 8: Chandrasekhar (1957)). When these were treated as half-atom peaks and refinement was continued, similar but smaller splittings were observed on the difference map for

most of the other atoms (Figure 10: Fleet (1962); Chandrasekhar, Fleet and Megaw (in preparation)).

Thereafter, two completely independent methods of refinement using the same observed data were carried out. (i) The single atoms were replaced by pairs of half atoms in accordance with the indications of the map mentioned above, and refinement was carried to completion. (ii) The coordinates of primitive anorthite were used for a trial structure, which was refined to completion, all calculated "*c*" and "*d*" reflections being replaced by zeroes. Both methods gave the same coordinates (within experimental error), and the coordinates were slightly but significantly different from those of primitive anorthite. The attainment of the same result by two independent methods is convincing evidence of its correctness. Hence bytownite has a structure with a primitive unit cell very like that of anorthite; and its texture consists of anti-phase domains.

Some conclusions can be drawn about substitution disorder. Sites which were occupied by Si in anorthite do not acquire any significant Al content in bytownite. Of those occupied by Al in anorthite, there is a slight indication that $T_2(00)$ and $T_1(m0)$ are preferred for the entry of Si, $T_1(0z)$ remaining almost pure Al. There is a tendency for pairs of atoms related by the body-centring vector to behave in a similar way, but there are some differences with may be significant. Comparison with other plagioclases is made in § 12. There is possibly some Ca/Na order. Except for the small amount of substitution disorder the Si/Al sequence continues unchanged across domain boundaries, while the Na/Ca sequence reverses.

The decrease of domain size with increasing albite content in "intermediate anorthites" can be explained very naturally by the considerations put forward in § 4. It seems clear that the anorthite structure with the ideal 1:1 ratio for Si:Al is particularly stable, and that a small change in this ratio will substantially increase the energy, without being enough to break up the overall pattern. A quenched material will hence show anti-phase domains like those of anorthite, with the Si/Al arrangement continuous across boundaries. On annealing, however, the boundaries will only move till they reach regions where the guest atoms have caused local strains of a kind that tend to cancel out the boundary strains; they are then locked in position. (Diffusion of the guest atoms themselves may help this.) Therefore, in the

equilibrium state of the system at the particular temperature, the number of guest atoms will determine the number of domain walls and hence the average domain size. The effect of temperature at a given composition is not easily predictable; according to whether it decreases the strain energy of domain walls more or less than the energy of guest atom substitution, it will lead to a decrease or an increase in the equilibrium size of domains.

9. *Low intermediate plagioclases*

Low plagioclases near An_{77} give new sharp reflections, the "*e*" and "*f*" types. They can be shown to imply a new framework configuration with a much larger unit cell, 9 subcells long and 2 subcells wide (referred to a different set of axes) (Megaw (1960b)). This discontinuous change is the reason for drawing the (approximately) vertical boundary near An_{78} in Figure 9.

The new cell is built mainly out of anorthite-like cells and subcells. The anorthite arrangement of Si/Al is maintained over 8/9 of the length of the unit cell, but in the remaining 1/9 a change of step takes place. The composition at which the new structure appears (2/9 Al, 7/9 An) is exactly right to allow perfect alternation of Si/Al in the 8 pairs of subcells, provided the 9th pair contains Si only. The large unit cell appears less unexpected if it is thought of as a block of 4 anorthite cells, 2 of which have been partly modified geometrically so as to allow the pair of Si-rich subcells to be joined on with little or no strain. It could not easily have been predicted that this particular length of anorthite-like structure would fit well, but the advantage of using blocks of low-energy anorthite structure is obvious. Presumably the Na/Ca ordering will bring Na into or near the Si-rich subcells.

Though this structure has (ideally) no substitution disorder, it must have a domain texture. The extreme diffuseness of the "*c*" reflections can be attributed to faults very like those in the intermediate anorthites. With increasing albite content, a new kind of fault sets in with increasing frequency; it makes the "*e*" and "*f*" reflections move continuously relative to the "*a*" type. A theoretical treatment by Megaw (1960c) gives good agreement with the observations of Gay (1956), as illustrated in Figure 11. (For fuller references to the experimental work, see these papers.)

Though the theory will not be recapitulated here, one or two points

about the domain texture may be mentioned. Between about An_{78} and An_{50}, the slip vector is 2/9 of the cell length, or 2 subcells (hence it cannot be called an anti-phase domain, for which the slip vector must be $\frac{1}{2}$, but it is very similar in effect). This even number

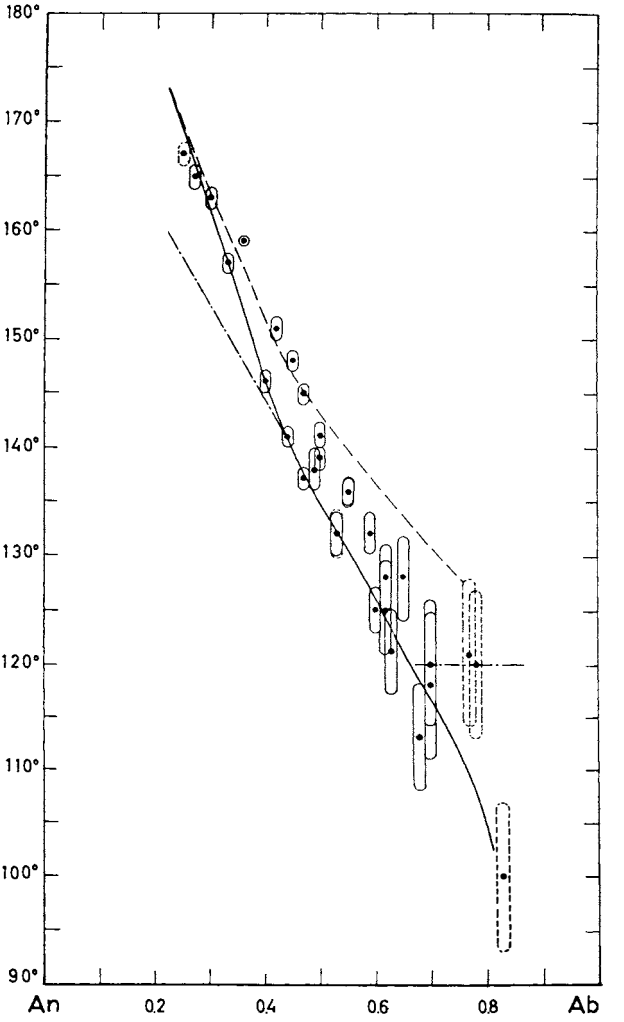

Figure 11. Variation of δc with composition. δc is a reciprocal-space coordinate of "*e*"-type reflections. Observed values shown by dots (with estimated error); theoretical values shown by full line. (Megaw (1960c)).

of subcells has the important consequence that the Si/Al alternation is not interrupted at a fault. Between An_{50} and An_{20}, another kind of fault appears to set in, with slip vector 1 subcell, which *does* break the Si/Al alternation. Each kind of fault may be supposed to have its own causative mechanism in the entry of Si or Na into certain sites. As the domains become smaller, it is hard to say where, if at all, domain texture gives way to homogeneous disorder.

What happens near An_{20} is not yet clear. It seems that the "*e*"-plagioclase type of framework has suffered nearly as much distortion as it can stand; there is nowhere to put further Si or Na, except into sites where they would raise the energy greatly. Another stable structure is however available, that of low albite. The Si and Na which are unacceptable in the original structure are segregated and form domains of low albite. This subject is discussed in more detail by Ribbe (this volume). A detailed structural study of oligoclase (Waring (1961)) provides useful evidence.

10. *High plagioclases* [5]

It is here suggested that high plagioclases, examined at room temperature, have essentially the same structure throughout the whole series from anorthite to high albite, the atomic coordinates changing slowly and continuously with composition from those of primitive anorthite to high albite, and also, at a given composition, with degrees of order. Low bytownite and the intermediate anorthites also have this structure.

We consider first the domain texture. This is responsible for the disappearance of "*b*"-type reflections at compositions below about An_{65}; from here to the albite end, there are only "*a*"-type reflections. It can be explained if there is a second kind of fault, coexisting with the kind which occurs in the intermediate and transitional anorthites. The slip vector of the latter was a body-centring vector interchanging P with S, Q with R; the new slip vector must interchange other pairs, for example P with Q, R with S, and thereby break the Si/Al alternation at boundaries. Such a fault implies considerable Si/Al disorder in the homogeneous structure from which the faulted structure is derived,

[5] This discussion does not include the "ultra-high" plagioclases related to monalbite (Brown (1960)), of which no structure determination has yet been made. Their relation to the others is considered in § 12.

likely only to be found at very high temperatures or far from the ideal 1 : 1 ratio.

This kind of fault, like the other, gives rise to anti-phase domains, from which one would expect increasing diffuseness of "*b*" reflections before their disappearance. Diffuseness *is* found (Laves and Goldsmith (1955); Gay (1956); Gay and Bown (1956)), but it is rare; more often thermal treatment weakens them but leaves them sharp. The rarity can be explained if we assume that there is a sharp decrease at a certain Si : Al ratio in the energy associated with disorder. This might correspond, for example, to a state when all favourable sites are already occupied by Si, and the excess Si must be housed in high-energy sites. Then the high energy of faults which break the Si/Al alternation is relatively less important, and they tend to become numerous very rapidly. The weakening of sharp "*b*" reflections suggests a coarser domain texture, too coarse to produce diffraction broadening, such that each domain either remains unaffected by the "diffuse-*b*" faults or is invaded by great numbers of them; its contribution to a "*b*" intensity is either unchanged or blurred out to invisibility.

The dot-dash lines of Figure 9 are meant to illustrate this point. For compositions below about An_{65}, at high temperatures, the subcell is the true unit cell, Si/Al substitution disorder being complete. With decreasing temperature there is a discontinuous (or at least abrupt) change in the framework, making *geometrical* distinctions between subcells. The change from a 1-subcell unit cell to a 4-subcell unit cell may occur in two stages, the intermediate form having a 2-subcell unit cell like (true) high anorthite, and the diagram is drawn on this assumption. On the other hand it may be direct, with no intermediate form, and then the two lines should be merged into one. However, above An_{65} the two stages certainly become distinct. If, at anorthite-rich compositions, the 1-subcell structure ever occurs, it leaves no evidence of its existence on quenching, because the electrostatic ordering tendency is too great to allow formation of domains which do not maintain the Si/Al alternation across boundaries.

Since a synthesis of the "*a*" reflections gives a map which is, according to this hypothesis, an average of 4 anorthite-like subcells, direct evidence may be looked for in the splitting of atomic peaks. At present such evidence is scanty but very suggestive. Split-atom peaks are seen in a high andesine from Linosa (Kempster (1957)) and in high

albite itself. The andesine work (still incomplete) suggests that the Na/Ca peak is best fitted by 4 quarter atoms, with coordinates closely resembling those in anorthite, and there is preliminary evidence for the splitting of other peaks. In high albite, the anomalous Na peak shape was first observed by Ferguson, Traill and Taylor (1958), who considered an explanation in terms of thermal anisotropy, but thought half-atom splitting more probable. This was confirmed by a study (Williams (1961)) at liquid air temperature, where thermal effects should be very much less; a peak of the same anomalous shape appeared. The coordinates of the two half-atom peaks are very like the mean of coordinates of pairs of anorthite peaks. It remains an open question whether they should be further subdivided into four quarter-atom peaks; perhaps three-dimensional work will decide this. So far, there is no evidence for splitting of other peaks, but there is a fairly large "temperature" factor which might mask it.

Indirect evidence for the hypothesis comes from the difficulty of finding any other reasonable explanation of the Na/Ca "splitting". In the fully-ordered anorthite structure, each Ca atom is gripped by its surrounding oxygen atoms, and displacement to a position characteristic of a different sub-cell would lead to impossible interatomic distances. The framework, in fact, provides different sites in the four subcells, but only one site in each subcell. There is no indication of any way in which a change in framework configuration could make a second site appear in each, nor of why, if it did, they should be of exactly equal energy. On the other hand, if it is supposed that the effects of Na/Ca atoms are purely local—that their positions are correlated only with those if nearest oxygen neighbours—they would be spread over a range of positions, and not neatly divided into 2 or 4.

11. *Low albite*

Low albite has a different kind of order from high albite, and it is here suggested that this is associated with, and made possible by, a different configuration of the framework.

Its difference map, like that of high albite, shows split Na peaks which persist at liquid air temperatures and therefore cannot be explained by thermal anisotropy (Williams (1961)). The splitting is rather smaller than for high albite; the difference of coordinates will

be further discussed in § 12. There is doubtful indication, in the two-dimensional work, of the splitting of other peaks; evidence from three-dimensional work is not yet available.

It is tempting to suggest that low albite may have a 2-subcell unit cell, while high albite has a 4-subcell unit cell, but this is very speculative. Alternatively, if they both have 2-subcell units, one might be 14 Å base-centred, the other 14 Å body-centred; or one might be 7 Å primitive.

12. *Comparison of high and low plagioclases*

Three lines of comparison depending on X-ray evidence are of particular interest, (i) lattice parameters, (ii) degree of Si/Al order, (iii) Ca/Na peak position.

Much work has been done on lattice parameter determination (for references and recent work see Brown (1960)). The results divide the plagioclases into a high and a low series, whose parameters vary differently with composition; intermediate states between the two extremes are known. The work will not be surveyed in detail here. According to this classification, of the materials to be discussed, the bytownite, the oligoclase, and the natural albite are low; the andesine and the heattreated and synthetic albites are high.

For degree of Si/Al order, there is now enough information to make comparison worth while. When only "*a*"-type reflections are observed, the results give us only the *average* Al content over corresponding sites in 4 subcells presumed by the present hypothesis to be different. For bytownite and anorthite, the contents of the sites are known separately, but they have to be averaged for comparison with the others. This is done in Table 2, for the 4 groups of sites distinguishable by "*a*" reflections. The ideal anorthite value is 0.50 for each site, representing an average of pure Si and pure Al. Departures from equality at other compositions show preferential entry of Si into certain groups of sites. Before attempting to draw detailed conclusions, it would be necessary to assess the errors rather carefully; but as the determinations were all independent the trends shown appear to be very significant. It is striking that the same two groups, $T_1(m)$ and $T_2(0)$, become Si-rich in all materials. Moreover, $T_1(0)$ retains its 50% Al content for all except albite, where it has still a high value; since in bytownite (as stated in § 8) this is the result of continued perfect order at the four sites of the

Table 2. Average Al contents.

	$T_1(0)$	$T_1(m)$	$T_2(0)$	$T_2(m)$	Total
Anorthite	0.50	0.51	0.49	0.52	2.02
Bytownite	0.51	0.44	0.40	0.45	1.80
Andesine	0.56	0.28	0.27	0.34	1.45
Oligoclase	0.52	0.18	0.16	0.31	1.17
Albite (synthetic)	0.42	0.16	0.20	0.32	1.10
Albite (Amelia, heated)	0.31	0.21	0.24	0.27	1.03

Values for bytownite are calculated from Fleet (1962); all others are from Taylor (this volume). For anorthite and bytownite the averages are over 4 sites, 2 Si-rich and 2 Al-rich, which have been determined separately.

group, it is reasonable to suppose that the same may be at least approximately true for the other materials, i.e. that the $T_1(0z)$ and $T_1(m0)$ sites are particularly unfavourable for the entry of Si [6].

The surprising feature about the table is the way low oligoclase fits naturally into place between high andesine and high albite. From this evidence alone, one could certainly *not* distinguish between the high and low series. Of course oligoclase may have a different choice of Si-rich sites within the groups from that of the high felspars, while giving the same average; but that we have at present no means of knowing. What is certain is that lattice parameters cannot be used as a direct measure of "degree of order", as defined in any observable way.

If the difference between the two high albites us real, as it looks to be, it suggests that thermal treatment can more readily destroy the ordering pattern of low albite than it can restore the equilibrium ordering pattern of high albite—a not very surprising conclusion.

This has a bearing on the work of MacKenzie (1957) on the high-low transition in synthetic albites, and of McConnell and McKie (1960) on the kinetics of the same process. (See also Smith and MacKenzie (1961)). We can no longer take the angle $\theta(131) - \theta(1\bar{3}1)$ as a measure of degree of order across a transition where the *kind* of order changes. Whether

[6] The apparent Al-content of $T_2(m)$ sites may be rather high, because one of these sites is consistently large in felspars which are otherwise ordered, and notably in reedmergnerite, $NaBSi_3O_8$ (Clark and Appleman (1960)) where there is no disorder; hence the size may be due to strain. The error due to this effect is probably not significant, less. (say) than 0.03.

there is actually a small discontinuity in this angle is hard to say, since the accuracy claimed for individual points on the curve is not shown. But in any case the break in the plot of rate constant against temperature, found near 550–650 °C by McConnel and McKie, can only be explained if the ordering on either side of that temperature is directed towards a qualitatively different equilibrium pattern.

The work of Brown (1960) on the lattice parameters of plagioclases on prolonged heating is further evidence for the view that the equilibrium geometry of the lattice is *not* directly a consequence of the state of order, though it can be modified by it. Brown deduced from the evidence of twinning that albite-rich plagioclases, heated at about 1100°C, became monoclinic at the high temperature; the angles α^* and γ^*, measured after return to room temperature, moved towards 90°, and after prolonged heating a specimen which was monoclinic at room temperature—monalbite—was obtained. This shows that the lattice becomes monoclinic, irrespective of the state of order, and thereby demands a different *kind* of order [7] for its equilibrium state. The achievement of this equilibrium state is slow, and until it is reached, or nearly reached, the monoclinic configuration cannot be quenched in; the state of order *is* quenched in, and modifies the geometry of the triclinic configuration. As long as the *kind* of order is unchanged, changes in the lattice parameters help to trace changes in the *degree* of order, but it cannot be assumed that their relation is anything like linear. Brown's results suggest that in fact for the oligoclase with 13% An the equilibrium state of order at 1100°C has been reached in about 50 days, but that it is not capable of stabilising the monoclinic geometry on return to room temperature.

The third feature which may be compared in the series is the set of positions of Ca/Na peaks. Here the coordinates are such that, if plotted in the (100) projection with a common origin for all subcells, all the peaks in all the materials lie close to the same straight line which is approximately that joining $(\bar{1}\cdot96, 0\cdot20)$ and $(0\cdot04, 0\cdot08)$ (using a 7 Å z-axis). The largest peak separations are those in anorthite, but bytownite and high andesine are not very much less, and the mean position of the four peaks (or half-atom or quarter-atom peaks) in each is much the same near $y = 0\cdot015, z = 0\cdot12$. High albite (Williams

[7] "Kind of order" here includes complete substitution disorder as one (but not the only) possibility.

(1961)) falls recognisably into the same series, with a rather smaller splitting and a mean position nearer to $y = 0$. Low albite (Williams (1961)) is distinctly different, with a much smaller splitting, and a mean position with a negative y coordinate. For low oligoclase, though there is some doubt about the detailed character of the splitting (Waring (1961)) the mean position is close to $y = 0$; it can be considered as a member of a series tending towards the low albite configuration.

The y-coordinates of the Ca/Na peaks, both individual and mean values, may perhaps be physically important, because of the important role in the structure of the Ca/Na–Ca/Na repulsive forces across the centres of symmetry (Megaw, Kempster and Radoslovich (1962)). So far this is only a tentative suggestion. It is perhaps worth noting that a zero y coordinate for the mean position of the peak occurs close to a composition where the γ angle is zero. The possible significance for the structural properties when the Ca/Na atom crosses the plane $y = 0$ was first noted by Waring (1957), but more detailed work would be needed before the idea becomes more than speculative.

If we take the classification of plagioclases by their lattice parameters as well established, and consistent with thermal results, we can say that classification by Ca/Na mean peak position is perhaps in agreement with it, but may very well show complexities not brought out by the former; classification by "degree of average order" is almost certainly not in agreement with it. This supports the view put forward in § 1 and § 3, and illustrated in Figure 9, that the *kind* of order is important and that the geometrical configuration is not always dependent in an obvious way on ordering. It is really not surprising that, in a structure with such a complicated bonding-scheme as a felspar, the equilibrium state should be determined by a number of independent variables, differently dependent on temperature and composition.

One conclusion is obvious: that it is not legitimate to talk about "degree of disorder" as an experimentally-known quantity unless it is made quite clear what are the measured quantities from which it is deduced.

Discussion

F. Laves (Zürich)

What does the line mean which starts at the anorthite end in Figure 9 at 1200°C? What are the states above and below this line?

Helen D. Megaw

I think there is a displacive transition near this temperature above which $CaAl_2Si_2O_8$ is truly body-centered. My prediction is therefore that a photograph taken at higher temperatures will show no "*c*"-type reflections. Below it the "*c*"-type reflections will remain sharp. I am not sure of the exact transition temperature, and there may be a smearing over a short range, but I think the reflections will have disappeared above 1300°C.

F. Laves

My prediction is: The diffuseness of the "*c*"-reflections is a continuous function of temperature as observed in the quenched material. However the degree of diffuseness may be somewhat higher if the photographs are taken at the high temperature. No critical temperature in the sense of Dr. Megaw should be observable.

Personal communication by W. L. Brown, W. Hoffmann, and F. Laves, received during press on November 13th, 1962:

Experiments carried out at Zürich in the meantime proved both predictions to be wrong: *c*-reflections of anorthites which are sharp in photographs taken at room temperature are diffuse in photographs taken at higher temperatures. The diffuseness is a continuous and reversible function of temperature up to approximately 350 °C, at which temperature the *c*-reflections virtually disappear. A note on this behaviour with additional information is submitted to the "Naturwissenschaften".

Helen D. Megaw

This result is indeed unexpected and exciting. I think it means (1) that the displacive transition from primitive to body-centred occurs about 350 °C, (2) that whatever happens above 1200 °C provides, on quenching, strain centres which serve a nuclei for antiphase boundaries below 350 °C. I would suggest that 1200 °C is the threshold of a particular kind of disorder, characterised by interchange mistakes of Si and Al on particular sites (cf. Megaw 1959). The number of such mistakes would increase with temperature above 1200 °C, but they would not lead to general Si/Al disorder or a break in the overall Si/Al alternation; when quenched in, they would give rise to localised centres of strain, which the formation of antiphase domain boundaries could help to relieve.

MEGAW (1959): Min. Mag. 32, 226.

Fritz Laves

It may be a question of semantics how to call this sort of transformation. In my opinion, it has only in part the characteristics of a displacive transformation (as visualized today) but also in part the characteristics of a "distortional disorder" as introduced by Buerger (1949). It seems to be a transformation not yet "classified" having characteristics of both (1) a displacive transformation and (2) a temperature dependent distortional disorder, leading to a temperature dependent "Domain-size". As the temperature dependent "domain size" of the quenched material comes to an equilibrium state so rapidly I doubt that Al/Si-exchanges could play any decisive role at temperatures between 1100 °C and 1500 °C. I still prefer an influence of the Ca ion positions. More experimental work using several approaches will be necessary for a final understanding of this new kind of transformation (districtal transformation might not be a bad word to characterize this sort of transformation, indicating that temperature dependent district sizes are formed within a morphological unit).

Cf. F. LAVES and J. R. GOLDSMITH: Acta Cryst. 7, 1954, 465–472; Z. Kristallogr. 106, 1955, 213–226; Cursillos y Conferencias, Instituto Lucas Mallada, Madrid, 8, 1961, 155–157.
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