Order and disorder in the feldspars, I.

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Summary. Feldspar structures are classified into small-cell ($c \approx 7$ Å.) and large-cell ($c \approx 14$ Å.) types, as a preliminary to a discussion of the nature of substitution disorder, position disorder, and stacking disorder, and of the relations between them. Diffraction effects characteristic of the different types of disorder are considered and related to experimental observation as far as possible.

THE feldspars comprise a large and extensively-studied group of materials of formula AB_4O_8, where A is a large, low-valent cation (K, Na, Ca, or Ba) and B includes both Si and Al. Between the ideal compositions, in which only one kind of A cation is present, there are large ranges of solid solution, and where these involve A atoms of different valencies there is a corresponding change in the Si:Al ratio to maintain electrical neutrality. An additional complexity consists in the fact that at most compositions 'high' and 'low' forms can be distinguished, which are believed to represent the quenched and annealed conditions respectively.

Much work has been done, by various techniques, to study the relationships between different members of the series, and in particular the nature and extent of the 'ordering' of Si and Al. Though the problem is physically quite different from that of ordering in alloys, the latter has been studied in so much more detail that it has affected much of the thinking about silicates and led to some confusion in terminology. Now that several structure studies on selected feldspars have replaced the vaguer ideas by more exact knowledge, it seems worth while to analyse the problem afresh and clarify our ideas of what we mean by order and disorder.

A list of the feldspars discussed in this paper is given in table I, together with references to recent detailed structure investigations. Names are to be taken, unless otherwise specified, as referring to the pure stoichiometric compound of ideal composition; and where the same name is commonly used for both high and low forms, the low form is meant unless the context makes it clear to the contrary.

TABLE I.

Mineral name	Chemical formula	High or low	Symmetry	Lattice	Cell dimensions (approx.) Å.	References to structure investigation
Microcline	$KAlSi_3O_8$	Low	Triclinic	*C*	8×13×7	Bailey and Taylor (1955)
Orthoclase	$KAlSi_3O_8$	Low	Monoclinic	*C*	8×13×7	Cambridge workers, unpubl.
Sanidine	$KAlSi_3O_8$	High	Monoclinic	*C*	8×13×7	Cole, Sörum, and Kennard (1949)
Albite	$NaAlSi_3O_8$	Low	Triclinic	*C*	8×13×7	Ferguson, Traill, and Taylor (1958)
	$NaAlSi_3O_8$	High	Triclinic	*C*	8×13×7	Ferguson, Traill, and Taylor (1958)
Anorthite	$CaAl_2Si_2O_8$	Low	Triclinic	*P*	8×13×14	Kempster, Radoslovich, and Megaw, unpubl.
	$CaAl_2Si_2O_8$	High	Triclinic	*I*	8×13×14	(Not obtainable in fully quenched condition)
Celsian	$BaAl_2Si_2O_8$		Monoclinic	*I*	8×13×14	Newnham and Megaw (1960)

Unit cells. The known feldspar structures are all built from variants of the same fundamental unit, a parallelepiped of dimensions approximately $a = 8{\cdot}6$ Å., $b = 13{\cdot}0$ Å., $c = 7{\cdot}0$ Å., $\alpha = 90°, \beta = 116°, \gamma = 90°$. Fig. 1 is a perspective diagram of the parallelepiped, and fig. 2 a schematic projection of the atomic arrangement. It forms a three-dimensional *B*-O framework in which every *B* atom is surrounded tetrahedrally by four oxygens, and every O is linked (not collinearly) to two *B* atoms; the *A* atoms occupy large cavities in this framework in which they may have from six to nine oxygen neighbours. The *B* sites are of two kinds, B_1 and B_2, distinguished electrostatically by the fact that the B_1 are linked to the unique O that has two *A* neighbours, the rest having one only.

There are differences from one feldspar to another not only in the dimensions of the parallelepiped and the chemical nature of the atoms occupying particular sites, but also in the detailed coordinates of the atomic sites. Further, they differ in the number of such parallelepipeds needed to constitute a true repeat unit. In some feldspars (e.g. albite) the parallelepiped is itself the unit cell, while in others (e.g. celsian) the true unit cell requires two such units, with identical dimensions but slightly different internal arrangements, sharing a common face parallel to (001), and thus giving rise to a doubled *c*-axis. This division into small-cell and large-cell feldspars, or 7 Å. and 14 Å. feldspars, is essential for our discussion. The fact that in some (e.g. sanidine) there is a mirror plane of symmetry within the unit cell, while in others (e.g. albite) there is only a rough approximation to one, is of secondary importance.

In the simpler feldspars, the parallelepiped is face-centred on *C*, so

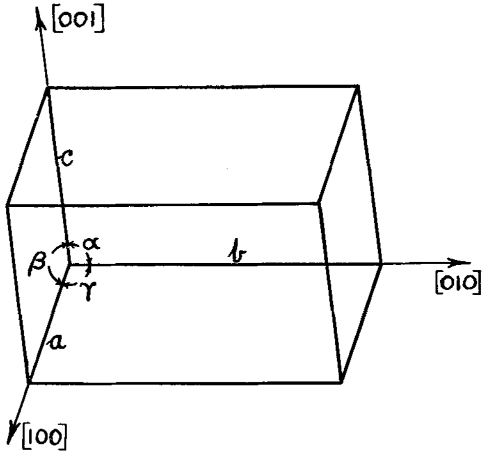

FIG. 1. Unit cell of 7 Å. feldspar, e.g. albite, on conventional axes.

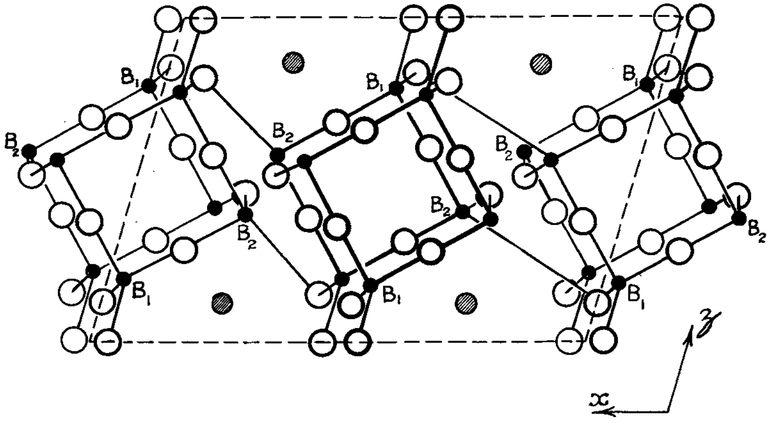

FIG. 2. Stylized diagram of feldspar structure, e.g. albite, projected on (010), to show linkages within the (Si, Al)–O framework. Pairs of atoms related by a pseudo mirror plane have arbitrarily been given a constant relative displacement; linkages to atoms above and below the unit cell shown have been omitted. Small filled circles, Si or Al; large open circles, O; hatched circles, cation *A*.

that a smaller primitive unit cell could have been chosen in various ways, most simply by taking $\frac{1}{2}(\mathbf{a}+\mathbf{b})$ instead of $\mathbf{b}$ for a cell edge. This is shown in fig. 3 by the parallelogram *ORST*, where *OPQR* represents the base of the conventional *C*-centred cell. In anorthite the face-centring has disappeared, and the cell with base *OPQR* is primitive; but we could

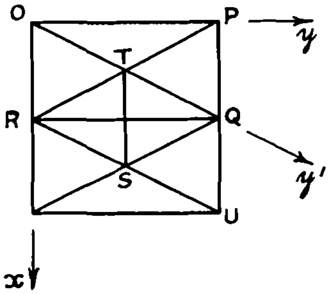

FIG. 3. Base of unit cell of feldspar in (001)-plane. *OPQR*, conventional unit cell of albite (*C*-centred) and anorthite (primitive). *ORST*, primitive unit cell of albite. *OQUR*, alternative choice of primitive unit cell for anorthite.

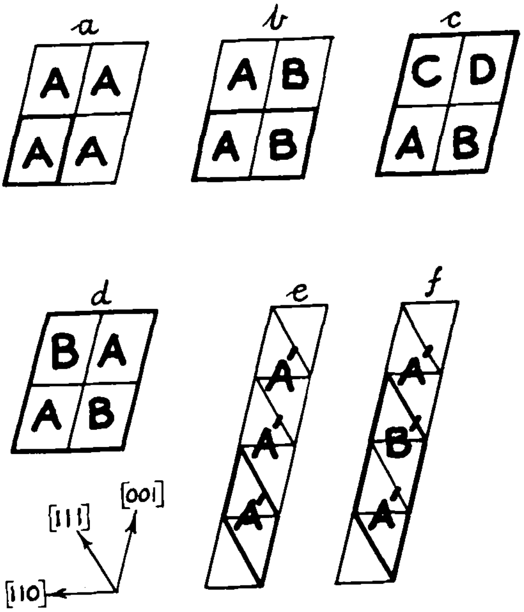

FIG. 4. Relations between true cells and albitoid sub-units for several feldspars: *a*, albite; *b*, hypothetical 7 Å. primitive cell; *c*, anorthite; *d*, celsian; *e*, albite (alternative choice of primitive cell); *f*, celsian (primitive cell). Directions in key are indexed using conventional albite axes.

equally well have chosen the cell with base *OQUR*, which is convenient because its axes are those of a primitive albite cell. Fig. 4 shows comparisons between several feldspar structures in the plane of *OQ* and the

c-axis ($\bar{1}10$) with conventional albite indexing). Fig. 4*a* shows four primitive albite cells, all identical. Fig. 4*b* is a hypothetical structure, of which no actual example is known, where the face-centring has been lost without any change in the c-repeat length; the true cell contains two albitoid sub-cells. Fig. 4*c* shows a primitive cell of anorthite, consisting of four non-identical albitoid sub-cells.

Celsian, when described on conventional axes, has the same cell dimensions as anorthite but is body-centred (Newnham and Megaw, 1960). If we use the primitive-albite axial directions, it can be seen from fig. 3 that it must be described as A-face-centred, and this description allows the comparison with anorthite shown in fig. 4*d*; the unit cell contains four albitoid sub-cells consisting of two identical pairs. If we wish to work with a primitive repeat unit (which is here less convenient) it is most easily described by reference to a differently-chosen primitive albite cell, shown in fig. 4*e*, whose b axis lies along the [111] conventional albite direction. From fig. 4*f* it can be seen that the primitive celsian cell contains two non-identical sub-cells.

Effects in large-cell structures. If the sub-cell instead of the true cell were used to define a lattice for one of these large-cell structures, it would appear that the coordinates of all atoms varied systematically so as to give displacements from a mean position that had equal magnitudes but opposite signs in alternate sub-cells. This description in terms of displacements from mean positions is of course fictitious, though it may be a useful fiction. To understand the effect in physical rather than geometrical terms, it is necessary to realize that the alternation of sub-units is the equilibrium configuration of the whole set of atoms. The stable arrangement does not quite fit a repeat unit with the dimensions of the sub-cell, but the misfit can be compensated when two slightly different arrangements alternate to give the true cell.

Large-cell structures give diffraction maxima at positions determined by the true repeat, but the intensities of these, except when they coincide with small-cell maxima, are due to differences in the positions of the atoms in the sub-cells, and to differences in scattering factor if the chemical contents are not identical; since the differences are, by hypothesis, small, the intensities are small. These *difference reflections* (more commonly, but confusingly, known as 'superlattice reflections') are characteristic of the large cell. In anorthite-like feldspars they have been classified and named 'b', 'c', and 'd' types, the reflections at positions common to the albite and anorthite cells being 'a' (Gay, 1953; Laves and Goldsmith, 1954).

If in any structure investigation the difference reflections are overlooked altogether (as may happen because of their weakness) the resultant electron-density map is an average of those of the sub-cells, and suggests a scatter of the atomic positions about a mean, and hence disorder. If the *difference reflections are included with their correct* sign, or phase, the true structure is displayed. A deliberate omission of the difference reflections for obtaining an average map has been a very useful preliminary step in several structure analyses of feldspars.

It should be emphasized that large-cell structures are in themselves no indication of disorder; indeed, their occurrence suggests rather that the need for disorder has been eliminated. They warn us, however, that we may need to examine the related small-cell structure for the presence of disorder.

TYPES OF DISORDER.

We define a perfectly-ordered structure, or perfect structure, as one built up by translation-repeat of parallelepipeds identical in size, chemical content, and positions of atoms within the parallelepiped, except for the effect of thermal vibrations. We idealize the situation by neglecting all impurities and mechanical defects.

Three types of disorder may be distinguished: substitution disorder, position disorder, and stacking disorder. Other types that have been recognized in other materials, such as vacant sites or interstitial atoms, are not relevant here; nor are the more complicated effects involving symmetry operations other than translation (the *'OD'* effects described by Dornberger-Schiff, 1956). For the purpose of the present discussion, which is concerned chiefly with the effects of the three types of disorder on the X-ray structure determination, we need make no assumptions as to the mechanism of the processes responsible for the occurrence of disorder; some aspects of these processes will be considered elsewhere in relation to growth and the subsequent thermal history of the feldspar.

Substitution disorder.

This occurs when one crystallographically-equivalent set of sites carries atoms of more than one chemical species distributed at random over the set of sites. It is characteristic of solid solutions (defined as materials in which individual atoms of the 'solvent' or host structure are replaced over a continuous composition range by chemically similar atoms of the 'solute' or guest); but it can also occur in stoichiometric materials containing two very similar atoms, where their disordered distribution between the available sites constitutes a sort of internal solid solution.

It is important here to distinguish between sites which are crystallographically equivalent and those which are merely chemically similar, in the sense that they provide similar environments for the atoms in them. While crystallographic equivalence is an absolute, chemical similarity may show degrees of closeness. Thus, for example, all the B sites in any feldspar are chemically similar to a first approximation, yet there are, as we have seen, differences between B_1 and B_2 which may be important when one comes down to details. It is not often possible to predict whether the chemical similarity between two given sets of sites is sufficient to ensure that they will be equally suitable for guest atoms. In anorthite, for example, there are four independent sets of A sites, and we cannot say *a priori* whether Na will replace Ca in one set only, or in all sets with equal probability, or with a different probability for each set.

When the guest atom differs in size from the host, the coordinates of its nearest neighbours are affected; but if these can adjust themselves easily with respect to their other neighbours the disturbance remains local, and unless the guest atoms are very numerous there is little tendency to order. The consequent random variations of coordinates from one unit cell to the next give rise, on electron-density maps, to a spreading-out of the atoms like that produced by thermal vibrations. If the effect is small, as it usually is, it cannot be distinguished from that of an 'average atom', or mean of the host and guest atoms weighted according to their probability of occurrence, with corresponding average positions for the neighbouring atoms. As far as the intensities of X-ray diffraction maxima are concerned, the structure is a *quasi-perfect* structure of average atoms.

This gives us our standard method of studying Si–Al substitution disorder in the feldspars, a method first used for orthoclase by Chao, Hargreaves, and Taylor (1940). It is assumed that the distance B–O for an average atom varies linearly with its composition. Then exact determination of the B–O distance for each set of sites gives us the composition of the average atom occupying this set.

Evidence from structure determination. The results of structure determination show that in *all* the low feldspars studied (orthoclase, microcline, albite, anorthite, celsian) there is an approach to an idealized perfectly ordered arrangement, except for orthoclase, where there is some evidence (now under re-examination) that while the occupation of the B_2 sites approaches complete order, that of the B_1 sites is random. It is not yet certain whether the residual disorder observed experimentally in some cases is within the limits of experimental error, or is an effect of imperfect annealing, or persists even in the best material; in any event it is not so large as to obscure the idealized picture, and it seems most likely that an understanding of the system as a whole can best be achieved by taking the perfectly ordered structures as starting-points for discussion. In this paper we shall not attempt to go beyond this idealization to the second approximation, which considers residual disorder.

For the high temperature structures (sanidine, high albite) there is complete disorder, with equal distribution on all sites. It is to be noted that this change from order in the low-temperature form to disorder in the high-temperature form (experimentally irreversible under laboratory conditions at present attained) is in accordance with the evidence from thermal studies, from which in fact it was predicted.

The statement that there is complete order, in the crystallographic sense, does not tell us the whole story; we want to know the relative arrangement of Si and Al in the ordered distribution. (In the literature, the two ideas have sometimes been run together confusingly.) To describe this, we notice that the two independent sets of sites in orthoclase and sanidine, B_1 and B_2, are subdivided into four sets in albite and microcline, $B_1(0)$, $B_1(m)$, $B_2(0)$, $B_2(m)$ (Si_1, Si_1', Si_2, Si_2' in the old notation): and each of these is again subdivided into four sets in anorthite; in the 14 Å. celsian cell the two sets B_1 and B_2 are divided into four in a different way, conforming to body-centred monoclinic symmetry. In albite and microcline, $B_1(0)$ is occupied by Al, the other sites by Si. In anorthite, however, half the four sets derived from *each* of the original four, $B_1(0)$, $B_1(m)$, $B_2(0)$, $B_2(m)$, are occupied by Al and half by Si, and exactly the same distribution is found in celsian, in spite of its different symmetry. This distribution (which is somewhat idealized, since perfection of order is not observed in the actual materials) is characterized by a perfect alternation of Si and Al along any line of B–O bonds. It incorporates the 'aluminium-avoidance' rule suggested by Loewenstein (1954). It can be predicted on electrostatic grounds, as it tends to equalize the electrostatic valence bonds to all oxygens. (See also Goldsmith and Laves, 1955, and De Vore, 1956.) It is satisfactory that it has now been confirmed for anorthite and celsian by direct structure determination. We may note that both the 14 Å. repeat period and the 1:1 ratio of Si:Al are necessary to allow this arrangement.

In solid solutions, of course, perfect order cannot be retained either for the A or for the B sites. If we start from the nearest perfect structure, we expect to find that some but not necessarily all of the sets of sites have become randomly occupied. Little information is yet available experimentally, but there is one known feature of the Si–Al arrangement in the plagioclases that may also be of considerable importance in other feldspars: the arrangement in albite cannot be derived from that of anorthite by continuous replacement of Al by Si, but requires also the replacement of Si on half the $B_1(0)$ sites by Al. This is likely to be a more difficult reorganization, and its onset should therefore be recognizable as corresponding to some break in the continuity of the series. It seems possible that steady replacement of Al by Si on B_2 sites may take place from pure anorthite to about $An_{25}Ab_{75}$, and that the peristeritic effects which then set in, with the formation of two phases, may represent the different kinds of Si–Al arrangements needed on the B_1 sites to secure electrostatic balance at this composition. The orthoclase–microcline relationship may also involve a reorganization of this kind.

Position disorder.

It has been suggested that in the feldspars the A cation may have position disorder. The assumption is that, while the B–O framework repeats perfectly with the periodicity of the small cell, the cavity formed by it allows two (or more) sites for A so nearly equal in energy that they are occupied at random. If their separation in space is small, the electron-density map will look as if A had a large anisotropic temperature factor; if the separation is large, the single elongated peak may be resolved into two half-atoms. As with substitution disorder, the structure is quasi-perfect, but this time it incorporates half-atoms instead of average atoms.

Experimentally, an effect like this has been observed for Na in high-albite by Ferguson, Traill, and Taylor (1958), who suggest that it may represent either position disorder or a true anisotropic temperature factor. A third possible explanation will be mentioned later (p. 239).

Position disorder has also been invoked (Laves and Goldsmith, 1954, and Goldsmith and Laves, 1955) to explain the low–high transition in anorthite, which involves the reversible disappearance or change of sharpness of certain difference reflections, the c and d types, corresponding to a change of the unit cell from primitive to body-centred. This explanation assumes that the B–O framework is nearly body-centred at all temperatures, and that it contributes negligibly to these reflections, which are in effect entirely due to Ca, ordered on different sites within the cavities in the low form, disordered between the same sites in the high. From our knowledge of the structure of low anorthite (Kempster, 1957) we can now tell that this explanation is neither necessary nor sufficient. The B–O framework is not very close to body-centred, but forms four independent pairs of cavities each occupied at a specified position by Ca: its contributions to the c reflections are not negligible. The transition to a body-centred form necessarily involves a straightening out of the framework, qualitatively of the same kind as occurs in transitions in the perovskite family. If the framework becomes body-centred the set of sites available for Ca becomes body-centred also, and there is no need to postulate disorder while the material remains at the high temperature. When it is quenched, stacking disorder may be introduced; this will be discussed below.

Stacking disorder.

In this we are no longer dealing with individual atoms but with pseudo-translation-repeats or sub-units. Disorder of this kind consists in a break in the ordered sequence of sub-units. We may illustrate the important features with a two-dimensional example where the true unit cell consists of two sub-units P and Q. Two kinds of wrong sequence are possible: in a row of cells in the [001] direction (fig. 5*a*) we may have two consecutive Q's, e.g. ...$PQPQQPQP$... or in a row in the [010] direction (fig. 5*b*) we may change from P to Q, e.g. ...$PPPPQQQ$.... If either kind of mistake happens in the same cells in adjacent rows, we get boundary planes parallel to (001) and (010) respectively, separating two regions of perfect crystal. We call these boundaries *fault planes*.

If we try to introduce either kind of mistake at random, not building up into fault planes, as in fig. 5*c*, we find we have introduced the other as well. An arrangement such as this looks as if it would be smoothed out by annealing. If P and Q differ only in their atomic coordinates and not in their chemical contents—as happens in the rather more complicated example of anorthite, for the sub-cells related by a body-centring translation—a perfect structure should fairly easily be achieved, since the shift needed for any individual atom is small. This may very well be the explanation of the high–low transition in anorthite. But if the sub-cells differ chemically in their contents, the process is more difficult. What happens is that, by diffusion of atoms, the boundaries move until a position of minimum energy is attained. Whether this is like fig. 5*a* or 5*b*, with one type of mistake and one type of fault plane only, like fig. 5*d* with a single stepped boundary in a definite crystallographic direction, or like fig. 5*e* with intersecting fault planes, will depend on the particular nature of the material and perhaps on its thermal history.

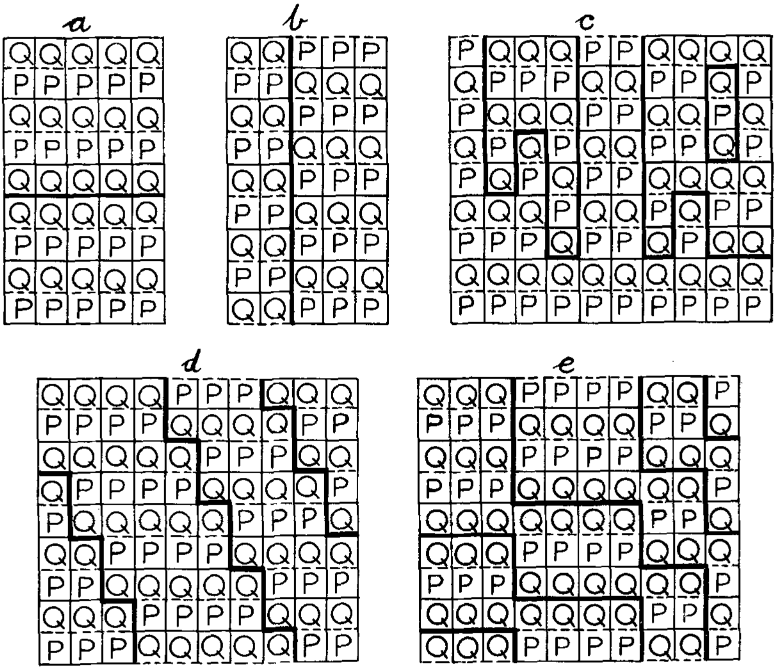

FIG. 5. Different distributions of mistakes in a hypothetical structure *PQ*: *a* and *b*, single fault planes in different directions; *c*, random distribution of mistakes; *d*, combination of two types of fault planes to give effective fault planes parallel to a third direction; *e*, independent occurrence of two types of fault plane.

The hypothetical example in fig. 5 is formally like CuAu. Other examples with more than two sub-cells are reminiscent of the 'anti-phase domains' in copper-gold alloys (see, for example, Lipson, 1950), and in fact the same principle underlies both; but the theories of anti-phase domains have been worked out there for the particular case when the sub-cell corresponds to the primitive unit cell of a face-centred cubic lattice, and contains only one atom.

The X-ray diffraction effects from a structure containing stacking faults are no longer those of a perfect or quasi-perfect grating. For the perfect structure whose repeat unit consists of two sub-units, we have seen that the pattern is made up of small-cell reflections and difference reflections. For the faulted structures of fig. 5, if we consider diffracted radiation in the directions which, for a perfect structure, would be first-order maxima, we see that phase differences of π are introduced at the faults. If the faults are numerous, these maxima are wiped out. The same is true for *all* odd-order maxima, i.e. for all the difference reflections. An electron-density map constructed from all the remaining maxima will show the average of sub-cells P and Q, as in the case of substitution disorder, but now, instead of spread-out atoms in the neighbourhood of the average atom only, we expect to find every atomic peak doubled. The distinction between the two is likely to be less marked in practice than in theory, because small separations are hard to detect with certainty.

This, however, is not the whole story. If the faults are in any way systematic, the intensity in directions other than the maxima may build up significantly, and give rise to measurable reflections. (The quasi-perfect structures of course give a background intensity different from that of the perfect structures, but the differences are very much smaller than those with which we are here concerned.) The extra reflections that occur in the intermediate plagioclases, from about $Ab_{25}An_{75}$ to $Ab_{75}An_{25}$, are believed to be due to this effect. They will be discussed more fully elsewhere.

DISCUSSION.

Relations between the three types of disorder.

While the three types can be discussed separately, they are not in fact independent. We assumed, in dealing with substitution disorder, that effects of a guest atom ceased to be felt beyond its near neighbours. This is unlikely to be true, especially if, as in the plagioclase feldspars, the guest atom has a different electrostatic charge from the host. The most important effect of an Na–Ca substitution, for example, is probably not so much on the positions of its nearest O neighbours as on the Si–Al distribution among its second-nearest neighbours, and through them out to distances of the order of magnitude of the sub-cell. In other words, substitution on a particular site tends to produce regions of local order different from the order of the host structure.

Beginning at the other extreme, we notice that changes in the P–Q sequence are likely to be brought about by substitution if the structural difference between the sub-cells is such that one sub-cell can accommodate the guest atom more easily than the other. This suggests that a fault has its origin in a site mistake. If we picture it as arising during growth, and suppose that sub-cell Q can accommodate Na more readily than P can, then when Na is deposited on what should be a Ca site it will affect its surroundings so that Q is built instead of P, giving rise to a fault. During subsequent annealing, Na (and perhaps Si with it) diffuses through the structure, and the fault travels along a row of cells, rather as dislocations do, until it combines with faults in other rows to form a fault plane.

This example is only put forward as a hypothetical one to illustrate the possibilities. The models required to explain actual effects in feldspars have a more complicated set of sub-cells and fault planes.

Probability of site mistakes.

The probability of a site mistake will in general depend on the number of guest atoms available, and on the environment of the site concerned. To obtain a picture of the sort of thing that is happening, it is worth distinguishing certain extreme cases.

In the first, the *simple site mistake,* the probability of a mistake on any permissible site is the same; it is independent of the existence of other mistakes, and is equal to the abundance ratio of the guest atom, i.e. the ratio of the number of guest atoms to the total number of atoms able to enter the site concerned, after atoms required for fully ordered sites have been subtracted. This will be a linear function of the composition.

At the other extreme is the *interchange site mistake.* In this there is a pair of sites such that the guest atom can enter the one normally reserved for the host provided that at the same time the host atom enters the one normally reserved for the guest. The probability of this kind of site mistake is independent of composition, except through the indirect effect of neighbouring mistakes.

We may also consider the possibility of *paired site mistakes.* These will occur if the sites are grouped in pairs so that a mistake must occur on both if it occurs on either; if all sites are in pairs, the probability is exactly the same as for a simple site mistake.

This list is not meant to be exhaustive, and is put forward merely to clarify the possibilities; it is not known yet what actual examples occur.

Probability of faults.

If faults have their origin in site mistakes, the probability of occurrence of a fault is linked through them with the composition. It may be that one site mistake on a particular site is sufficient to nucleate a fault; it may be that several specified site mistakes are required; on many sites, perhaps on most sites, mistakes will be ineffective. In general, the probability of a fault is thus some function of the composition.

The 'fault' boundary is in fact a region of perfect two-dimensional order (except where it is intersected by other faults), of thickness about one unit cell. Each half is continuous with the perfect structure on that side of it, but the two halves together constitute something new, and have a different chemical composition from the rest. When a nucleus is laid down, annealing gives rise to lateral growth, by diffusion of ions from the immediate environment to sites of lower energy in the boundary structure.

Character of disorder in feldspars.

We must return to the question whether, in the high-temperature feldspars, the occupation of B_1 and B_2 sites by Al and Si is completely random, or whether there is local order based on a large unit cell with faults. It seems very improbable that there should be no sort of local order. On the other hand, if the faults exist they are not organized so as to give extra maxima, and hence the only information available to us is the electron-density map of the average sub-cell. If, on this, it were possible to recognize each peak as the combination of some small number of nearly coincident peaks—say two or four—and if these could be sorted out so as to give two or four B–O networks each with reasonable interatomic distances, it would be a strong argument in favour of the large-cell description with stacking faults. (The problem of sorting out the set of multiple peaks into separate networks is like that solved by Carlisle and Crowfoot (1945) for more widely separated peaks in cholesteryl iodide.) Practically, however, it is unlikely that a structure analysis of sufficiently high resolution could be achieved. The most that might be expected is that a few multiple peaks could be detected which were consistent with such an hypothesis.

The limited amount of information available rather favours the hypothesis. It was mentioned above, p. 234, that high albite has an elongated peak for Na, which may be interpreted as due to anisotropic temperature factor or to position disorder. It may equally well mean that the observed unit cell is an average of two sub-units of a large cell in which only Na has conspicuously different coordinates. If the more detailed examination now in progress should reveal separation of peaks of neighbouring atoms it would be evidence for this point of view.

The difference between orthoclase and microcline may be discussed in terms of stacking disorder. As a first approximation, the Al atoms in a maximum microcline may be supposed completely ordered in the $B_1(0)$ sites of a 7 Å. cell, while those in orthoclase appear to be distributed at random between the $B_1(0)$ and $B_1(m)$ sites (which are indistinguishable in monoclinic symmetry) of the same size of cell. Suppose, however, that we had a 14 Å. structure in which Al was ordered on half the B_1 sites in the same way as in anorthite, while all B_2 sites were occupied by Si, and suppose that this structure had a random set of faults on planes with zone axis [001], whose slip vector had a component $c/2$: this would be indistinguishable from orthoclase, within the limits of accuracy so far achieved. It is an essentially different picture from that of submicroscopic twinning put forward (Laves, 1950; Goldsmith and Laves, 1954) to explain orthoclase. A refinement of the orthoclase structure, now in progress in this laboratory, may perhaps throw light on this question.

CONCLUSION.

This paper attempts to set out the important physical features of a complex problem in which much confusion has arisen, partly from a tendency to assume that concepts developed for application to order–disorder phenomena in alloys can be used fairly directly in relation to effects observed in feldspars. As far as possible the discussion is based on factual information, much of it derived from recent accurate analyses of type structures in the feldspar group; where speculative suggestions are advanced, they are clearly distinguished as such, and their eventual confirmation or disproof will leave the main account unaffected.

It is worth while to point out that although the present treatment is confined to the feldspars, a more detailed development of some of the fundamental ideas, to be published elsewhere, makes it clear that they may be of considerable importance in their application to other minerals.

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