MINERALOGICAL MAGAZINE

VOLUME 38 NUMBER 293 MARCH 1971

Hallimond Lecture 1970

Electron-optical study of phase transformations

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SUMMARY. This paper is primarily concerned with the interpretation of phenomena associated with phase transformations in single crystals, as observed by current experiments using electron-optical techniques. An analysis of permissible metastable behaviour in such single crystals, in terms of lattice theory, is provided. The dominant role of symmetry in defining the constraints on permissible behaviour of this kind is explained. The resulting theory indicates that, at low temperatures, permissible thermal fluctuations in local chemical composition, or order, become strongly degenerate and lead to the development of non-Bragg diffraction effects. The theory and practical study of the phenomena by electron microscopy are also described.

The theory of metastable behaviour in a single crystal subject to symmetry constraints is then tested by re-examining the experimental data available for two systems that have been studied recently where such behaviour might be suspected. The first of these concerns the low-temperature behaviour of adularia, and the second deals with incipient exsolution phenomena in the alkali feldspar from a pantellerite. The data in each case appear to be compatible with the general theory proposed. Finally the theory is used to analyse the low-temperature behaviour of the intermediate plagioclase feldspars. In this case the theory indicates that both antiphase phenomena and schiller effects are associated with metastable behaviour in a system subject to strong symmetry constraints at low temperature. The implications of the analysis in relation to peristerite exsolution phenomena are discussed.

A GREAT deal of research in mineralogy is concerned with the study of changes that occur in subsolidus assemblages of crystalline phases. Hence the study of solid state reaction mechanisms is of fundamental importance in many problems of mineral paragenesis. Relevant subsolidus reactions include exsolution, inversion, and the direct reaction between crystalline phases. In the field of applied mineralogy, also, many of the important processes involve the thermal treatment of crystalline material and hence the application of the theory of reaction kinetics, as applied to solid state processes, is particularly relevant.

Recently there has been very considerable interest in the application of the electron microscope to the study of the subsolidus behaviour of minerals and the techniques available have already yielded a considerable amount of new information. In large part this is concerned with fine structure associated with incipient inversion and exsolution phenomena, but to date, no general analysis of the physical principles has been attempted. In the present paper the basic theory appropriate to behaviour of this

kind has been developed. A brief account of the theory and practice of electron microscopy, in this context, has also been included.

Whereas it is possible to define the equilibrium state of a subsolidus system in terms of classical thermodynamics alone, and hence without reference to the ultimate crystalline structure of the individual phases, this approach is generally inadequate in dealing with the mechanism and kinetics of transformations in crystalline phases. This follows from the fact that the properties of the reacting system define certain fundamental constraints, which are related to the ultimate atomic structure and symmetry of the crystalline phases. Such constraints are particularly important in reactions where the high-temperature state is represented by a single homogenous crystalline phase, and exsolution or inversion occurs at lower temperatures. In this case reaction within the single crystal may be dominated by constraints that have their origin in the symmetry properties of the system.

The dominant role of symmetry in defining such constraints may be explained simply as follows. The macroscopic, or point group, symmetry of the single crystal is essentially a statistical property of the whole assembly of atoms or ions present. Consequently, while local departures from the average state, either in terms of composition or structure, are permissible, such fluctuations as a whole must be compatible, statistically, with the point group symmetry of the crystal. Since the progress of a reaction within a single crystal necessarily depends on the existence of local fluctuations, the presence of certain symmetry conditions may constitute a constraint on the behaviour of the system, particularly where the true equilibrium state involves exsolution, or inversion to a structure of lower symmetry.

It is already clear, from the detailed study of a number of transformations in mineralogical systems, that constraints of the type discussed above play an extremely important role in the paragenesis of many common minerals, and that the study of the phenomena in depth is likely to lead to a better appreciation of the nature and origin of metastable phases in nature in general. The role of constraints of this type appears to be particularly relevant in the study of the low-temperature behaviour of the feldspar minerals, although the phenomena are by no means restricted to this particular system. Two examples of metastable behaviour in the feldspars have been described recently by the author (McConnell, 1965, 1969*a*), and deal respectively with inversion phenomena in $KAlSi_3O_8$, and incipient exsolution and inversion phenomena in the alkali feldspars. In each case symmetry constraints appear to operate.

In view of the amount of information already available on behaviour of this type it would seem that, at the present stage in the progress of research, an attempt should be made to provide a general theory appropriate to the phenomena. In what follows, therefore, a general theory of the behaviour of a single crystal under symmetry constraints will be developed and this will be followed by a critical analysis of the data available on a number of the experimental systems that have been studied to date.

The role of fluctuations in defining the behaviour of a single crystal

In attempting analysis of the permissible behaviour of a single crystal it is necessary to deal with the existence of fluctuations since the possibility of change, associated

with inversion or exsolution, is ultimately governed by the probability of local departures from the average state. In general the probability P of a certain fluctuation taking place is related to the minimum work w associated with producing this fluctuation by the relationship $P \approx e^{-w/kT}$, from Boltzmann's principle. In the present analysis it will be convenient to use a wave description of the phenomena associated with the presence of fluctuations in local chemical composition or structure. One practical advantage of this procedure is that it also provides the simplest possible approach to the study of the corresponding diffraction effects. In the study of fluctuations in single crystals, electron diffraction and microscopy, in combination, constitute an extremely powerful experimental tool, and have been used to this end in the examples cited above.

The simple explanation of the origin of symmetry constraints, as outlined above, implies that, in general, one of two types of behaviour may be observed in a single crystal that is required to transform, either by exsolution or inversion, at the temperature considered. Where a symmetry constraint is rigorously imposed on the system, the single crystal may react only by moving towards a structural state that is compatible with the symmetry of the parent state. In these circumstances it is quite legitimate to regard the true equilibrium state of the system as inaccessible and hence irrelevant, implying that permissible thermal fluctuations, on an appropriate time scale, do not lead to the appearance of the stable equilibrium state. The application of equilibrium thermodynamics to a system subject to such constraints is perfectly acceptable and we expect to find that the system, when isolated, behaves reversibly as a function of changes in temperature and pressure.

This argument suggests that it should be possible to define the corresponding metastable equilibrium state rigorously on the basis of symmetry criteria. This is one of the objects of the present analysis.

In the second case considered above, the behaviour of the single crystal is not dominated by constraints due to symmetry, and permissible local fluctuations lead to the appearance of a multiphase system. In the progress of a reaction of this type the system is generally unstable and kinetics alone define the rate of change towards the true equilibrium state. The associated physical phenomena correspond to nucleation and growth.

The definition of symmetry constraints

In the treatment given above it has been tacitly assumed that it is always possible to discriminate between a true single-crystal state and one that involves the coexistence of two or more phases. Since coexistence relationships may be present on a very fine scale, a definition of the properties of a true single crystal is now required that adequately differentiates between fluctuations that are permissible, in terms of the symmetry of the single crystal, and fluctuations appropriate to the development of a multiphase system due to broken symmetry.

In attempting to provide a rigorous definition of the single-crystal state in this context it is necessary to examine some of the basic properties of a crystalline lattice. Lattice theory implies that a single crystal can be defined in terms of a distribution of identity points, the lattice points, each of which has identical environment. Theory

also demands that, in order to conserve the translational invariance of the lattice, acceptable perturbations must also be translationally invarient, and thus have the form $A_k e^{ik \cdot R}$, where A_k is an amplitude in general complex, k is a reciprocal wave vector chosen in such a way that it is compatible with the boundary conditions specified for the crystal (cyclic boundary conditions are convenient), and R is a translation vector associated with any two lattice points in the direct lattice. When acceptable lattice perturbations are defined in this way one finds that translational invariance also exists in the corresponding reciprocal lattice, and that it is necessary only to define k vectors in one elementary cell of the reciprocal lattice, i.e. in the first Brillouin zone. Thus k vectors throughout reciprocal space are related by the elementary translation vectors of the reciprocal lattice. In the present context permissible fluctuations in chemical composition or structure must necessarily be subject to these conditions if the system is to be described as a true single crystal.

For any permissible lattice function $F(R)$ which labels the points of the direct lattice and is associated with a particular aspect of the behaviour of the single crystal, we may write $F(R) = \Sigma A_k e^{ik \cdot R}$, where the sum is taken over the whole of the Brillouin zone (Weinreich, 1965). For a crystal of macroscopic dimensions the number of independent k states associated with fluctuations is very large. Hence, in the practical study of fluctuations one normally deals with the average taken over many k states in any small region of reciprocal space. In fig. 1 an attempt has been made to illustrate the relationship that exists between the presence of a single distortion wave on the direct lattice and the associated suite of equivalent k vectors in the reciprocal lattice.

So far we have been concerned only with the translational symmetry of the direct and reciprocal lattices. In most crystals additional symmetry elements are present. Lattice theory, in this context, indicates that the symmetry of the reciprocal lattice accords with the full point-group symmetry of the single crystal (Ziman, 1964, p. 98). From which it follows that certain k states must be related by the symmetry operations of the point group. Thus, in a system of high symmetry, certain k states are degenerate in energy, meaning that they are statistically equivalent, due to the fact that they are related by the symmetry operations of the point group. Fundamentally it is the existence of these symmetry operators that defines the constraints imposed on the behaviour of the single crystal since permissible fluctuations, which as we have already noted govern possible structural changes, are necessarily subject to these primary symmetry conditions.

The ultimate failure of constraints imposed on the behaviour of the single crystal by symmetry conditions can be ascribed to the essentially statistical character of the symmetry operators themselves. Broken symmetry relationships are therefore likely to appear in two quite distinct ways. Failure may occur where very localized fluctuations lead to the development of a viable nucleus of a second phase. It is not easy to deal in a rigorous way with the theory of the behaviour of such fluctuations apart from noting that the corresponding situation is relatively improbable since it involves strong local phase correlations between otherwise uncorrelated fluctuations, each of which probably represents a substantial departure from the normal, or average, state.

Broken symmetry may also appear where there are strong fluctuations of very long

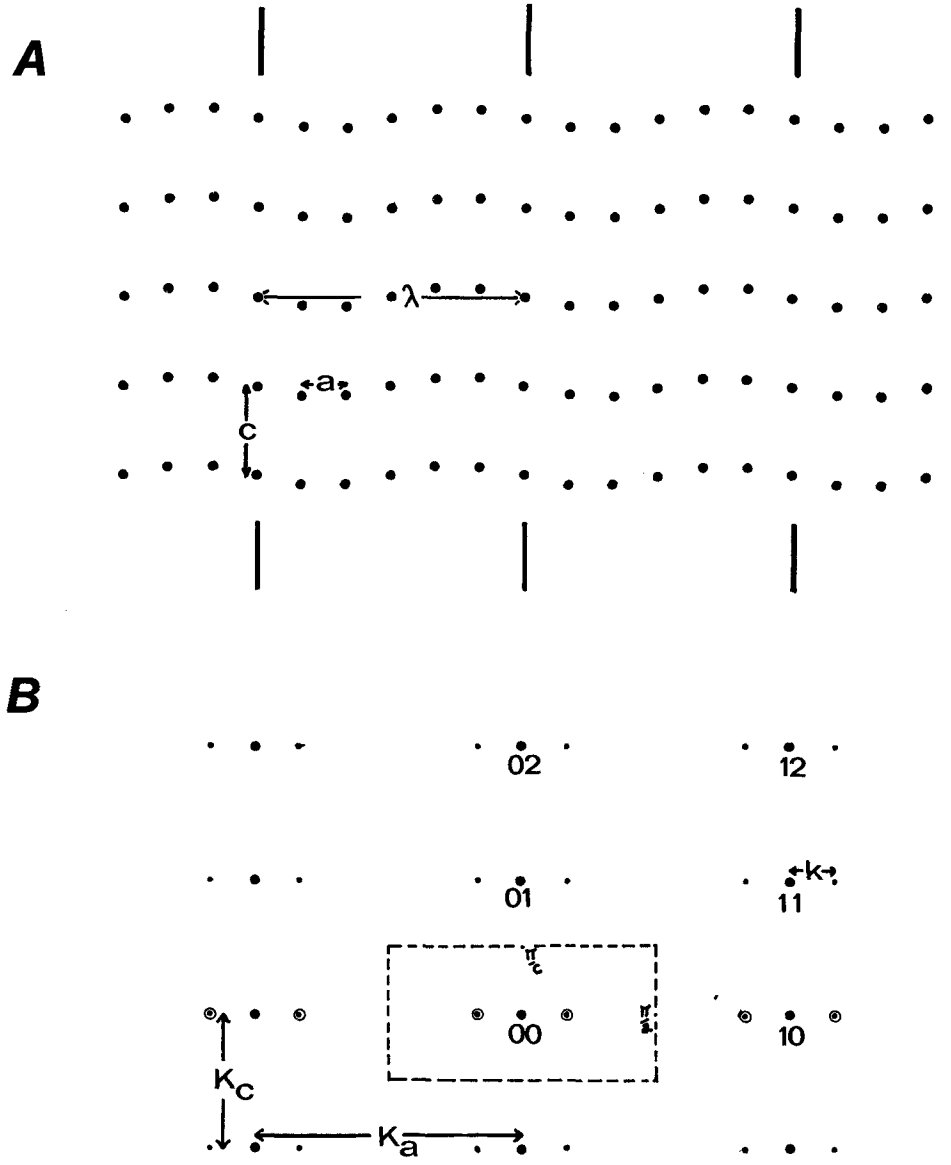

FIG. 1. Schematic diagrams illustrating the relationship between a lattice perturbed by a single transverse wave and its associated diffraction pattern. The translation vectors a and c of the direct lattice in (A) define the corresponding reciprocal lattice vectors K_a and K_c in (B), where $K_a = 2\pi/a$. The positions of the extra, smaller dots in the reciprocal lattice pattern, associated with the presence of the distortion wave, lie at distance k, where $k = 2\pi/\lambda$, from each of the primary reciprocal lattice points. The small vector k defines both the wavelength and wavenormal of the distortion wave. In the present example the extra spectra, ringed, associated with the lattice points $h0$, must have zero intensity, since the wave associated with vector k has amplitude vector A_k normal to these reciprocal lattice vectors, i.e. $K \cdot A_k$ is zero. It should be noted that all the extra points in the reciprocal lattice pattern are related to each other, either by the elementary translation vectors of the reciprocal lattice, K_a and K_c, or by centres of symmetry at or between the reciprocal lattice points. The boundaries of the first Brillouin zone of the reciprocal lattice pattern in (B) have been indicated by dashed lines.

wavelength (small k), or a local concentration of preferred wave vectors at certain critical points on the Brillouin zone boundary. In both cases strong phase correlations occur between certain fluctuation waves, and the simple statistical treatment presented above breaks down. These two cases relate respectively to the existence of very strong tendencies towards clustering and ordering (development of a superlattice) in the parent single crystal. It would seem that, in general, symmetry constraints are likely to be most important where the favoured k states lie well within the Brillouin zone boundary, and, at the same time, are sufficiently far from the origin of the Brillouin zone, thus corresponding to fluctuation waves of intermediate wavelength.

While it is a relatively simple matter to define the nature of the symmetry constraints imposed on the behaviour of a single crystal, it is in general a much more difficult, if not impossible, task to determine the probability amplitudes of the fluctuation waves in a single crystal under specified conditions of temperature and pressure. In general the values of $|A_k|^2$ are proportional to kT under equilibrium conditions but they also depend, in the case of fluctuations in chemical composition, for example, on the second derivative of the chemical potential with respect to composition, and the elastic properties of the single crystal (Krivoglaz, 1969, p. 19).

Here we are primarily concerned with the qualitative treatment of permissible behaviour in a single crystal under conditions of symmetry constraints at low temperatures. In these circumstances it is reasonable to expect that the normal system of fluctuations appropriate to high-temperature behaviour will become highly degenerate, meaning that certain k states will be strongly favoured at low temperatures due to minor differences in energy. This accords with a physical situation in which the structure locally tends to a lower free energy state, while at the same time such local effects are both defined and correlated by fluctuation waves that preserve the symmetry properties of the lattice as a whole. Since the translational invariance of the lattice must be maintained it is necessary to admit that the local structure of the single crystal must involve alternatives that are statistically equivalent. Statistical equality, in this context, may be described in terms of the concept of parity.

Thus it is essentially in terms of the occurrence of certain highly favoured fluctuation waves, with strongly localized k values, that we may hope to recognize the existence of metastable equilibrium behaviour associated with the existence of symmetry constraints.

Some considerable progress has been made recently in the study of the energy relationships for fluctuation waves of composition that occur in single crystals during spinodal decomposition. A general account of this phenomenon has been presented by Cahn (1968) and a review has been provided very recently in the geological literature by Yund and McCallister (1970). In terms of the present analysis, compositional fluctuations, as observed in spinodal decomposition, represent one possible pattern of behaviour in a single crystal subject to symmetry constraints, although the phenomena have not been approached from quite this point of view previously.

In dealing phenomenologically with the stability of compositional fluctuations in the spinodal context, it has been usual to define[1] the chemical potential in terms of a

[1] It should be pointed out here that there are distinct advantages in dealing with fluctuations in terms of complex functions, since, while it is possible to define the energy in terms of the square of the

local contribution associated with change in concentration and a term that depends on the rate of change of the concentration gradient in the region concerned, $\nabla^2 c$. It is probably not a coincidence that the current treatment of spinodal decomposition leads to a wave solution, since, from our prior definition of permissible lattice functions, fluctuations in which the symmetry of the single crystal is conserved must necessarily have this form.

At this stage we have shown that the characteristics associated with the behaviour of a single crystal under symmetry constraints can be defined in terms of a reciprocal space treatment. It follows naturally that single-crystal diffraction experiments can be used to study the phenomena. The criteria appropriate to true single-crystal behaviour, as observed in the single-crystal diffraction pattern, are particularly simple. In this case the diffraction pattern comprises a single suite of Bragg maxima arranged on a perfect lattice, and the additional intensity, associated with the presence of permissible fluctuations, appears similarly in each unit cell of the reciprocal lattice. Thus the demonstration of true single-crystal behaviour amounts to showing that the distribution of intensity in reciprocal space has certain specific symmetry properties.

Electron diffraction technique

The treatment of electron diffraction technique as applied to the study of lattice fluctuations follows naturally at this point. Since the electron diffraction pattern of a single crystal corresponds to an effectively undistorted section through the reciprocal lattice, the study of additional diffraction effects associated with fluctuation waves is particularly straightforward. In examining the intensity distribution in a single unit cell of the reciprocal lattice each point ideally corresponds to a specific reciprocal wave vector k as defined in relation to the nearest reciprocal lattice point. This has been illustrated in fig. 1. The intensity observed at the point k is proportional to the square of the wave amplitude $|A_k|^2$, but is also proportional to the square of the structure amplitude of the direct cell at this point, and depends on the character and orientation of the wave in relation to the reciprocal lattice vector associated with the adjacent reciprocal lattice point. The origin of the last effect may be explained as follows.

amplitude of the fluctuation waves, $|A_k|^2$, or vice versa, we need make no precise statement about the character of the local situation in the single crystal. In most cases of interest in this connection it can be shown that the statistics, i.e. data derived from the real function $|A_k|^2$, do not readily distinguish between a situation involving a local square waveform for concentration that is slightly irregular, and one involving sinusoidal variation, particularly where the scale of the phenomena is small. In general the appearance of long-range correlations associated with the existence of a particularly preferred k vector of a suite involves the appearance of harmonic terms in the k space representation, implying that, in the phenomenological model, it is no longer permissible to neglect anharmonic terms.

Thus it would appear that, where a local suite of k states are strongly preferred, and at the same time harmonics are not in evidence, the simple phenomenological treatment will give the correct results, since this condition is equivalent to a situation that may be described in terms of fluctuations over a narrow range of k values with statistically uncorrelated phases. It is also relevant to note that it may be quite incorrect to assume that the microstructure observed in a quenched specimen is equivalent to that actually existing at the temperature of equilibration, since anharmonic terms will be more important at low temperatures, and will usually lead to the development of a square wave type of behaviour in any case. At sufficiently low temperatures the energy levels of the k states need not be defined by the relationship $P \approx e^{-w/kT}$, since true equilibrium need not be established.

Since the fluctuation wave may be either primarily longitudinal or transverse in character,[1] its amplitude vector A_k may be either parallel or normal to the reciprocal wave vector k. The phase factor associated with the displacement of a lattice point due to a distortion wave may be written $e^{iK \cdot A_k}$, where K is the reciprocal lattice vector $2\pi/d_{hkl}$ and A_k is the amplitude vector defining the displacement. Clearly no intensity will be observed where, for a given k vector, the amplitude vector for the corresponding wave is normal to the reciprocal lattice vector. The physical explanation of this effect is quite simple since it means that a wave cannot be detected where the displacement of the lattice points is in the corresponding lattice planes, i.e. those associated with the reciprocal lattice vector K. This effect is illustrated in fig. 1 where extra spectra associated with the reciprocal lattice point *h*0 have zero intensity due to the fact that the single wave present is transverse in character with A_k normal to the a axis.

The use of the $K \cdot A_k$ criteria in the experimental study of the character of lattice waves is particularly important. Normally this demands the study of the actual intensity at equivalent points (k values) throughout a large region of reciprocal space. By using these criteria it was possible to define the character of the distortion waves in adularia (McConnell, 1965) and to show that the fine-scale fluctuations in an alkali feldspar were basically longitudinal in character (McConnell, 1969*a*). Another example of the use of these criteria is provided by the study of additional intensity maxima associated with schiller effects in labradorite by Korekawa and Jagodzinski (1967). In this case it was shown that the fluctuation waves were primarily transverse in character.

Electron microscopy

Direct resolution of the lattice perturbation associated with fluctuation waves, in the electron microscope, is also possible, and explanation of the technique follows directly from treatment of the diffraction phenomena. Electron microscopy yields information on the existence of lattice distortions primarily because of the existence of electron diffraction contrast, which arises in the following manner.

Even thin single crystals in the electron microscope diffract electrons very strongly and hence, if the single crystal is in the correct orientation for diffraction, considerable intensity may be diverted into the diffracted spectra. In normal imaging procedure in the electron microscope this diffracted radiation is prevented from reaching the final image plane because of the presence of a small aperture in the back focal plane of the objective lens. As a result, the image of a crystal that is diffracting strongly appears dark. If the single crystal is slightly bent a dark band will be observed in the image of the crystal corresponding to the locus of positions where the lattice is correctly orientated for diffraction. Such a band is described as an extinction bend contour. Where the single crystal is also perturbed by a distortion wave this also affects the orientation of the lattice planes locally, and contrast associated with the lattice wave will be observed in the extinction bend contour. The presence or absence of contrast in any given case depends on which Bragg maximum is operative through the $K \cdot A_k$ relationship given above.

[1] Purely transverse, or longitudinal, waves are only permissible under special symmetry conditions (Krivoglaz, 1969, p. 67).

It is also possible to produce a dark-field image in the electron microscope by translating the objective aperture in the plane of the diffraction pattern until it permits the passage of the diffraction spectrum desired. In images of this type one is effectively sampling the intensity information in a non-origin Brillouin zone. In the corresponding image the intensity distribution is reversed with respect to the bright-field image. A series of selected area diffraction patterns, and the corresponding bright-field and dark-field images, showing the resolution of the lattice distortion waves in adularia, were presented in McConnell (1967), and may be examined at this point.

In one important respect use of the electron-optical image of a single crystal has advantages over the use of diffraction data alone. This follows from the fact that diffraction data are normally available as intensities, and thus provide only statistical data on the behaviour of the single crystal. Where the diffraction pattern admits of several interpretations, in terms of possible physical models for the microstructure of the single crystal, the electron-optical image is particularly valuable. Thus, in problems of the type considered here, it is possible to determine the phase relationships between different degenerate fluctuation waves, and hence define the true microstructure of the single crystal. Electron microscopy is also particularly important in the study of extremely localized phenomena, such as nucleation, where the corresponding diffraction effects might easily go undetected.

From this brief survey it will be obvious that electron microscopy, when used in conjunction with electron diffraction techniques, provides an extremely powerful technique in the study of problems where the precise local behaviour of the single crystal is in question.

Application of the theory of symmetry constraints

The theory of metastable behaviour in single crystals subject to certain symmetry constraints at low temperatures may now be tested by examining the data available on several experimental systems where such behaviour is suspected. The theory suggests that such behaviour is likely, *a priori*, in situations where a phase transformation is known to exist, but the theory is also relevant in circumstances where a reduction in free energy is possible due to degeneracy associated with local ordering or any similar phenomena, i.e. where the diffraction evidence indicates the presence of highly preferred fluctuation waves of non-zero k values (non-Bragg reflections). In this context, while it is obviously necessary to prove that the high-temperature symmetry constraints are not violated, it is also desirable to define the nature of the structural alternatives that lead to degeneracy.

In the detailed study of the diffraction effects in adularia (McConnell, 1965), it was shown that the symmetry of the distribution of diffracted intensity was compatible with the existence of a single crystal with monoclinic symmetry, i.e. the distribution of intensity had the necessary translational symmetry throughout reciprocal space. In this case it is known that the low-temperature ordered structure (microcline) is triclinic, $C\bar{1}$, and is closely related in structure. The theory of low-temperature behaviour under symmetry constraints therefore suggests that a reduction in free energy in adularia at low temperatures will be possible if alternatives associated with local ordering

and distortion are defined, and, at the same time, the ordering scheme, and the pattern of correlation of the alternatives, preserves the statistical symmetry of the high-temperature state. In this case the dual choice of occupation of the T_1 site by Al defines an appropriate parity condition between the alternatives.

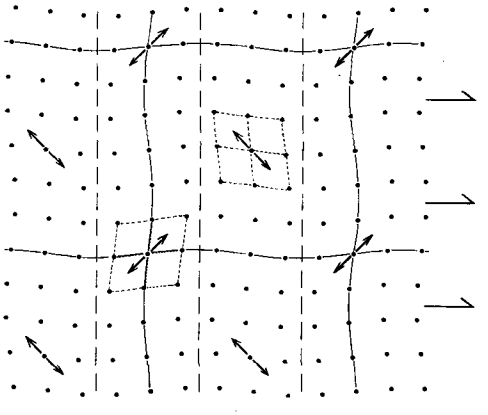

FIG. 2. Schematic diagram illustrating the pattern of distortions due to two orthogonal transverse waves in adularia. The dots represent the positions of the lattice points, and the two types of distortion have been indicated by the system of arrows. In the three dimensional system to which this diagram refers, these alternatives are related, in the ideal case, by screw diads parallel to the original diad axis, and a glide in {010}, parallel to the original mirror plane. In the diagram these symmetry operators have been illustrated in the conventional manner.

Study of the distortion waves present in adularia showed that these corresponded to two sets of transverse waves, which were mutually orthogonal. The wave system as a whole satisfied group symmetry criteria since in one case the wave vectors lay along b^*, i.e. on the diad axis, and in the other case they lay in a general direction in (010), at 18° to a in the obtuse angle β of the direct cell, i.e. in the mirror plane. Using the $K \cdot A_k$ criteria defined earlier it was possible to show that both sets of waves were transverse in character, with amplitude vectors in the plane defined by the two sets of wave vectors, i.e. normal and parallel to the diad axis respectively. Purely transverse waves are permissible in both these cases in point group $2/m$.

Electron microscopy showed that the combined effects of the dual wave system of fluctuations was to produce, at the nodes of a relatively regular repeat pattern, regions of maximum distortion associated with the two alternatives defined above. A schematic diagram illustrating this pattern of distortions is presented in fig. 2, where the alternatives are clearly indicated. This diagram corresponds to a section through the lattice parallel to the plane containing both the wave normals and the amplitude vectors for the distortion waves. Inspection of the diagram shows that the idealized distribution of the two alternatives, in three dimensions, involves the symmetry operators 2_1 and a glide operation in (010). This symmetry, which is appropriate to the highly degenerate state, is compatible with the primary point-group symmetry $2/m$, as required by theory. An electron diffraction contrast pattern that illustrates the phase relationships between the distortion waves in this degenerate state is provided in fig. 3. In this dark field image the alternatives appear with maximum contrast at certain points. An analysis of the contrast pattern is provided in McConnell (1965, p. 1298).

At this point we may note that the microstructure of adularia, as observed, is entirely consistent with the theory of metastable behaviour, in the presence of symmetry constraints, as developed above.

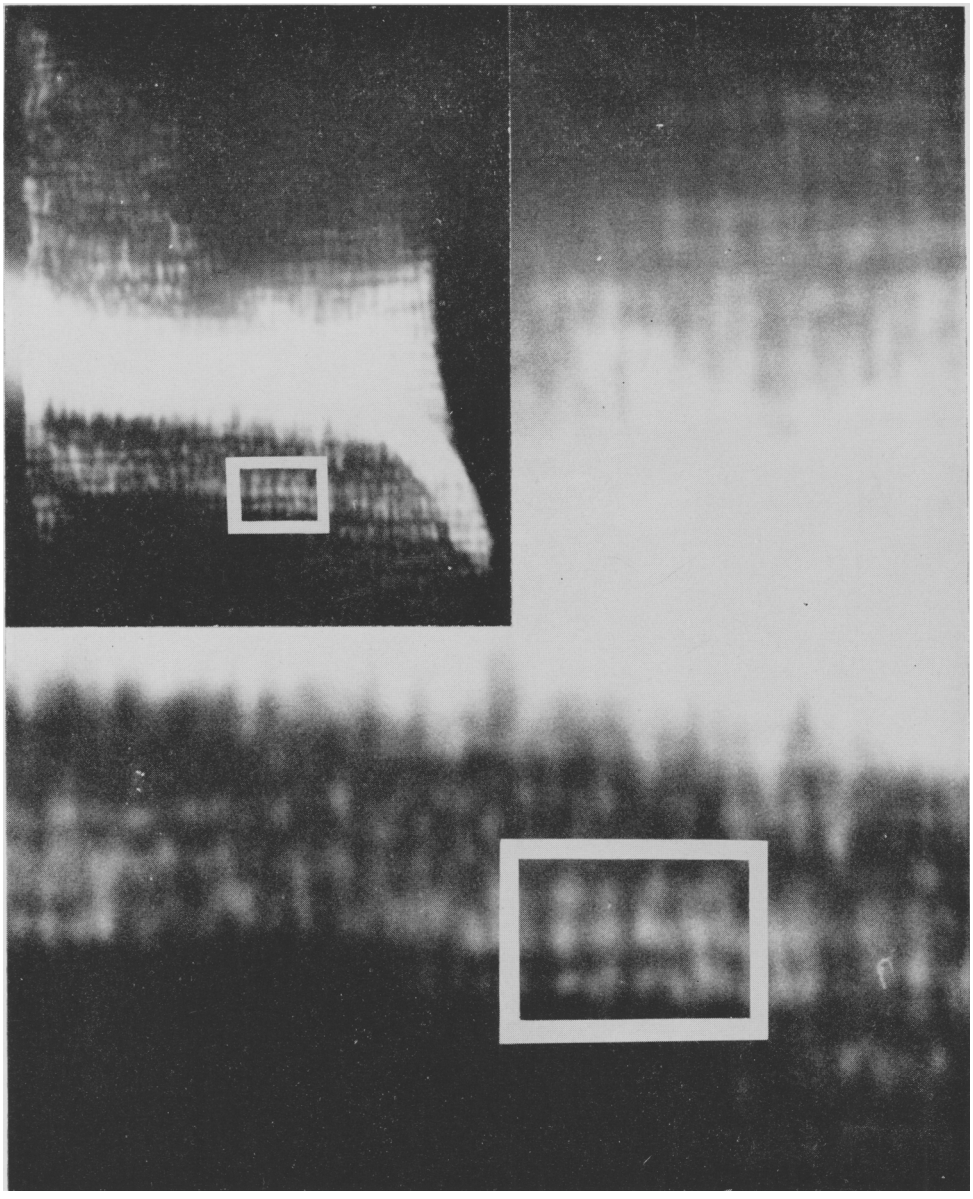

FIG. 3. Electron-optical dark-field image of adularia obtained with the Bragg maximum 24$\bar{1}$. In the enlarged region ($\times$ 550 000) in the lower right the presence of the two transverse waves leads to strong contrast effects. The dark and light regions in this case correspond to the alternatives associated with the two types of distortion illustrated in fig. 2. $\times$ 180 000.

In discussing the mechanism of the monoclinic–triclinic inversion in $KAlSi_3O_8$ previously (McConnell, 1965), it was noted that the scale of the perturbed structure in adularia was uniform in all the single crystals examined, and had a repeat of approximately 100 Å. This accords with a situation in which a true free-energy minimum is likely to exist for the constrained single crystal, associated with a highly preferred suite of k vectors. Clearly if a definite equilibrium state is defined in this way for non-zero k values the symmetry constraint, which impedes the transformation to the low-temperature structure $C\bar{1}$, is likely to be particularly strong since fluctuations associated with the growth, locally, of a single alternative are necessarily extremely improbable.

It is essentially in terms of an analysis on these lines that one may hope to understand why the inversion in $KAlSi_3O_8$ in nature is extremely sluggish. This analysis applies equally well to the occurrence of orthoclase as a metastable phase in nature at low temperatures, since it is known to have a perturbed structure of similar character (McConnell, 1965, p. 1291). Electron-optical data, comparable to those obtained for adularia, have been presented recently for orthoclase by Nissen (1967).

The second example of possible metastable behaviour within the constraints exercised by symmetry to be examined here relates to the fine-scale fluctuations in chemical composition observed recently in an alkali feldspar from a pantellerite (McConnell, 1969*a* and *b*).

In this connection there has been considerable interest shown, in recent mineralogical literature, in the possibility that spinodal decomposition[1] may be a relevant mechanism for exsolution in certain mineral systems. Papers on this topic by Christie (1968, 1969) and Yund and McCallister (1970) deal with the theory of the phenomena as set out by Cahn (1968), and also suggest certain specific mineralogical systems where the effect may be operative. No experimental evidence for the phenomena has been presented, however.

In the present context spinodal behaviour, i.e. fluctuations in chemical composition in a single crystal, can be regarded as one further example of metastable behaviour associated with the existence of symmetry constraints, and the general principles derived above may be applied directly to the analysis of experimental data for systems where such behaviour is suspected. In general, spinodal behaviour corresponds to a situation in which the translational invariance of the lattice is conserved, and degeneracy may be associated with the segregation of atoms of different types.

The diffraction data obtained from single crystal study of the alkali feldspar referred to above are consistent with the translational symmetry of a simple monoclinic lattice with point-group symmetry $2/m$. In this case the diffraction pattern showed intense streaks through the Bragg maxima defining a suite of fluctuation waves with wave normals lying in (010) and at an angle of 22° to a in the obtuse angle β of the direct cell. Use of the $K \cdot A_k$ criteria in this case indicated that the fluctuation waves were primarily longitudinal in character.[2] From this data it was deduced that the intensity

[1] The term decomposition, when used in this context, is particularly unfortunate since a single crystal that is constrained to behave in this way can legitimately be described as a single phase, at least where symmetry constraints dominate the behaviour of the system.

[2] Point-group symmetry indicates that, in this case, the fluctuation waves may have a transverse component.

streaks were associated with the existence of fluctuations in chemical composition and associated lattice repeat in the single crystal. The wavelength of these fluctuation waves was approximately 100 Å. Bright- and dark-field electron-optical images of the fine structure of this specimen have been illustrated in fig. 4, which indicates that the structure is not particularly regular.

In a later paper (McConnell, 1969*b*) direct proof of the existence of chemical variation in this spinodal structure was obtained from degradation structure in the specimen produced during electron bombardment in the electron microscope. Using this technique it proved to be possible to study local variation in the chemical composition of the sample on a scale of less than 20 Å. Using this technique it was shown that the chemical fluctuations in the specimen, at least at low temperatures, were of square-wave character. The true nature of the chemical variation in a spinodal structure has already been discussed on p. 6 of the present paper, where it was noted that it is best to deal with the fluctuation waves in terms of probabilities alone, i.e. in terms of $|A_k|^2$.

It is interesting at this point to note that the orientation of the observed fluctuation waves in this alkali feldspar accord with a situation in which the strain energy of coexistence is likely to be a minimum. This follows from the fact that the major change in cell dimensions of the Na and K feldspars occurs in the *a* direction (McConnell 1969*a*, p. 228). Yund and McCallister (1970) arrived at this conclusion independently and also deduced that, in this case, the coherent spinodal should lie some 80 °C below the solvus in this system. Some preliminary thermal experiments by the present author (1969*a*, p. 227) suggest that this temperature interval may be even smaller, since no change in structure was observed at a temperature of approximately 600 °C. Further, more careful, thermal studies on this problem are in progress, and are likely to be particularly rewarding.

At this point we may conclude, in relation to the central thesis of the present paper, that the experimental data for the alkali feldspars are consistent with the theory of metastable behaviour in a system subject to symmetry constraints. Further, in an even more general context, it would appear that the general concepts developed are likely to be apposite in dealing with a much wider range of phenomena than those previously associated with fluctuations in chemical composition alone, i.e. spinodal phenomena *sensu stricto*. In terms of this broad concept of the nature of metastable behaviour in a single crystal, subject to symmetry constraints at low temperatures, an attempt will now be made to use the theory in the analysis of low-temperature behaviour of the intermediate plagioclase feldspars.[1]

[1] The history of the explanation of the phenomena observed in the intermediate plagioclase feldspars, in the present terms, extends over the period 1962–9, and should be summarized briefly here. A fluctuation-wave theory of the antiphase domain structure of the intermediate plagioclase feldspars was originally derived by the author in 1962. This led to the direct resolution of the antiphase structure in a labradorite in 1963, McConnell and Fleet. Symmetry criteria, appropriate to the existence of metastable states, were defined with reference to the behaviour of adularia and the intermediate plagioclase feldspars in 1966, and a full lattice wave treatment of the antiphase phenomena in the plagioclases was presented in 1969*c*. At a somewhat later date, in private discussion with Professor J. S. Anderson, it transpired that a similar treatment of fluctuations in crystalline solids, in terms of lattice theory, was contained in Krivoglaz (1969), although this author was not directly concerned with the implications of symmetry constraints on the behaviour of single crystals at low temperatures, i.e. strongly degenerate situations.

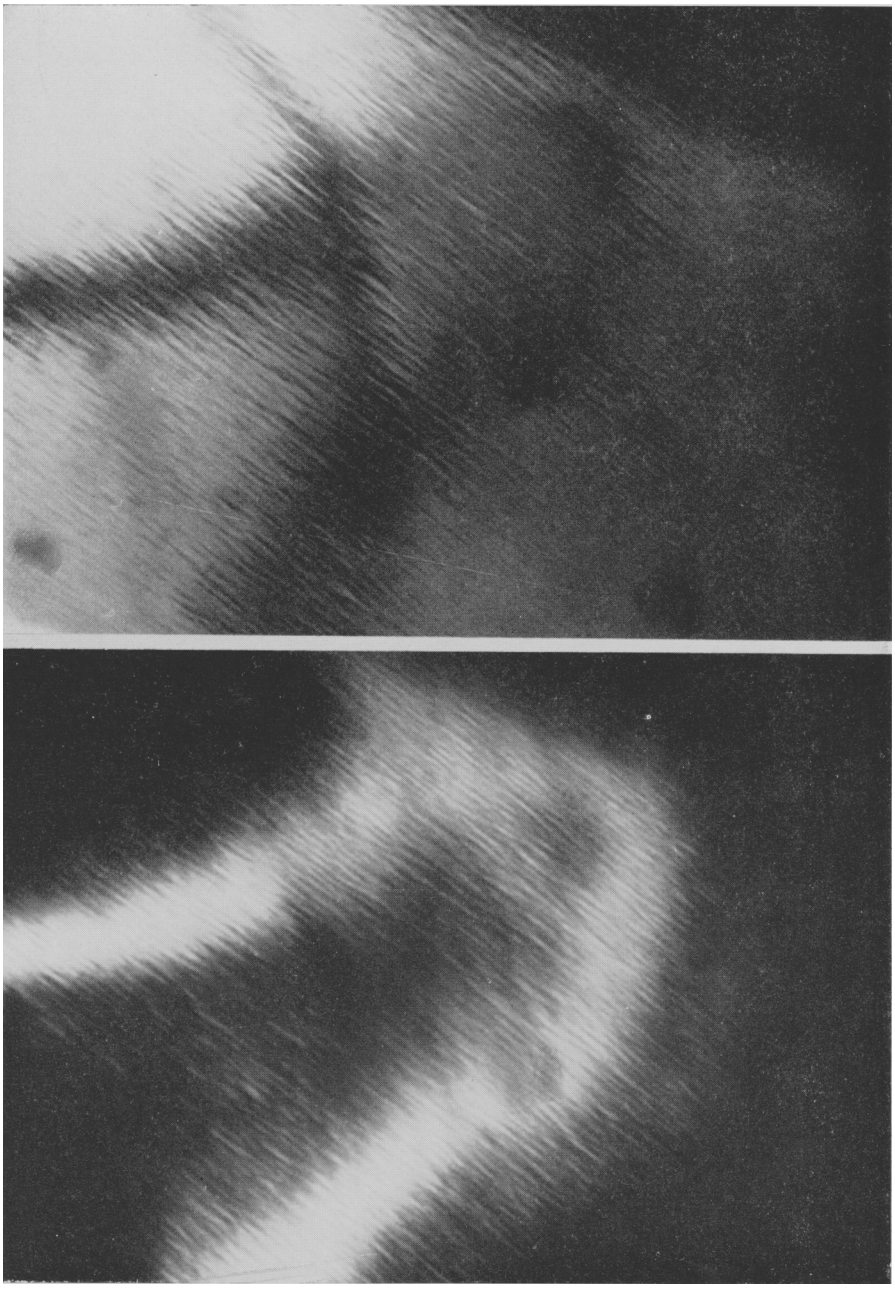

FIG. 4. Light- and dark-field electron-optical images of the spinodal structure observed in the alkali feldspar from a pantellerite. Two extinction bend contours, dark bands, are present in the bright-field image (above). Reversed contrast associated with one of the two Bragg maxima operative in this case, light bands, appears in the dark-field image below. Note that the fine-scale contrast associated with the spinodal structure is best seen in, or near to, the extinction bend contours. × 100 000.

Diffraction data for the intermediate plagioclase feldspars were summarized by Bown and Gay in 1958. Diffraction data related to the development of schiller in a labradorite were presented by Korekawa and Jagodzinski in 1967. In both cases the distribution of additional intensity in the diffraction patterns corresponds to a condition of translational invariance in reciprocal space, from which we may deduce that the criteria appropriate to single-crystal behaviour are satisfied.

The general theory demands that we now deduce the possibilities for degeneracy in this system and thus define the nature of the symmetry constraints that may operate at low temperatures. The high-temperature structure of the intermediate plagioclase feldspars has a disordered Al–Si distribution and may be defined in terms of a small cell (the albite cell). Since the structure of the end-member of the series, anorthite, is fully ordered, and develops a superlattice, the condition exists, *a priori*, that local ordering of the same kind may occur in the intermediate plagioclases at low temperature under conditions of symmetry constraints. The constraint in this case involves statistical equivalence, or parity, between the two alternative origins for the large cell demanded by this ordering scheme. Hence permissible behaviour must preserve the translational invariance of the subcell, which existed at high temperatures. It should be noted here that the alternative origins for the superlattice are related by vector shift $c/2$, as defined in terms of the superlattice repeats.

It is convenient, at this point, to apply lattice statistics to the problem. In terms of a direct lattice appropriate to the large cell we may define a lattice function $F(R)$ that labels the lattice points distinctively as belonging to one or other of the two alternatives. It is convenient to use the terms $+1$ and -1 since these describe the character of the corresponding structure factor for the large cell with different origins, at the superlattice points of the reciprocal lattice pattern.[1] Any permissible distribution of the two types of large cell appropriate to a degenerate situation at low temperatures may now be written

$$F(R) = \sum_{BZ} A_k \, e^{ik \cdot R}$$

where the lattice function describes the labelling pattern applied to the large lattice register. We have already noted that information on $F(R)$ may be obtained directly from the diffraction pattern, where $|A_k|^2$ defines the intensity at appropriate points in k space. Since we chose, of necessity, to define the original lattice function in terms of the large cell, it follows that the intensity distribution appropriate to permissible behaviour of antiphase character will be associated with the true superlattice points, i.e. b maxima positions, of the anorthite structure.[2]

The diffraction data summarized by Bown and Gay indicate the existence of paired maxima (the e maxima) symmetrically disposed about the positions of the superlattice positions (b maxima) in anorthite. The diffraction evidence indicates, therefore, that a member of the intermediate plagioclase series, when dominated by the symmetry

[1] In this case $K \cdot c/2 = \pi$, i.e. the large cells scatter in antiphase.

[2] The advantage associated with dealing with permissible behaviour in terms of complex functions will be apparent at the point, since it is clearly unnecessary to define the real behaviour of the single crystal. All the necessary information may be obtained from the statistics of the distribution, which are uniquely defined by the real functions $|A_k|^2$.

constraint imposed by the translational symmetry of the subcell, succeeds in developing a highly degenerate system of fluctuation waves at low temperatures, which, while they permit the existence of local regions that are ordered on the anorthite scheme, also preserve the fundamental parity relationship, or antisymmetrical condition, demanded by true single-crystal behaviour.

The situation in this case is exactly analogous with that observed in adularia except that in this case the parity relationship involves two possible origins for the large cell, as dictated by the translational symmetry of the subcell. On considering the point-group symmetry in this case, $\bar{1}$, it is obvious that there need be no degeneracies, i.e. special symmetry positions, in the Brillouin zone apart from those associated with centres of symmetry. In consequence the orientation of favoured k vectors in the low-temperature degenerate state need not be subject to any special conditions. This accords with the observations made by Bown and Gay (1958). The behaviour of the favoured k states as a function of changing chemical composition in the intermediate plagioclases is particularly interesting, since the k vectors increase with increasing albite concentration in a regular manner. This may be interpreted in terms of a continuous increase in the energy levels of the favoured degenerate fluctuations with increasing albite content. For compositions corresponding approximately to 75% albite the favoured k states approach the Brillouin boundary appropriate to the anorthite superlattice. Physically this corresponds to a situation where the tendency to order on the anorthite scheme at low temperatures becomes no longer practicable. At the same time the experimental data indicate that the range of k vectors favoured becomes rather large, i.e. the e maxima are very diffuse, indicating that the degree of order in the antiphase structure is low, thus defining a rather large residual configurational entropy term.

So far treatment of the diffraction phenomena in the intermediate plagioclases has been made in terms of a purely statistical model. It is also possible to study the local regularity and character of the degenerate antiphase distribution directly by electron microscopy. Thus, by obtaining a dark-field image with a single pair of e maxima, i.e. by sampling the transform of $F(R)$ directly, the local phase relationships between the degenerate fluctuation waves can be established. That the physical model in this case corresponds to a single, and highly regular, suite of antiphase domains was demonstrated by McConnell and Fleet (1963).

Analysis of the origin of the f type maxima associated with the primary, or a maxima, in the intermediate plagioclases can be treated similarly. In this case that lattice function $F(R)$ used must label the lattice points of the subcell. Since the suite of k vectors associated with the f maxima share the same direction as the e maxima over the whole range of compositions where they occur, and also correspond to half the wavelength of the antiphase structure, it is reasonable to assume that the two effects are strongly correlated statistically. The origin of f maxima may therefore be ascribed to the presence of local distortions of the subcell, or modulation of the contents of the subcell, associated with the basic periodicity of a single antiphase domain. Thus the reciprocal wave vectors for the f maxima are twice as large as those associated with the e maxima. $K \cdot A_k$ criteria, in the case of the f reflections, are capable, in principle, of defining the

nature of the modulation of the subcell, but no experimental data appear to have been obtained on this problem to date. Resolution of the antiphase structure of an intermediate plagioclase (70% mol. An), using 000 and associated *f* maxima, is illustrated in fig. 5.

It is of some interest at this point to indicate the nature of the structural information that may be obtained on a member of the intermediate plagioclase series from diffraction studies that utilize all the available information. Earlier it was noted that the absolute intensity associated with a given *k* vector depends on the square of the

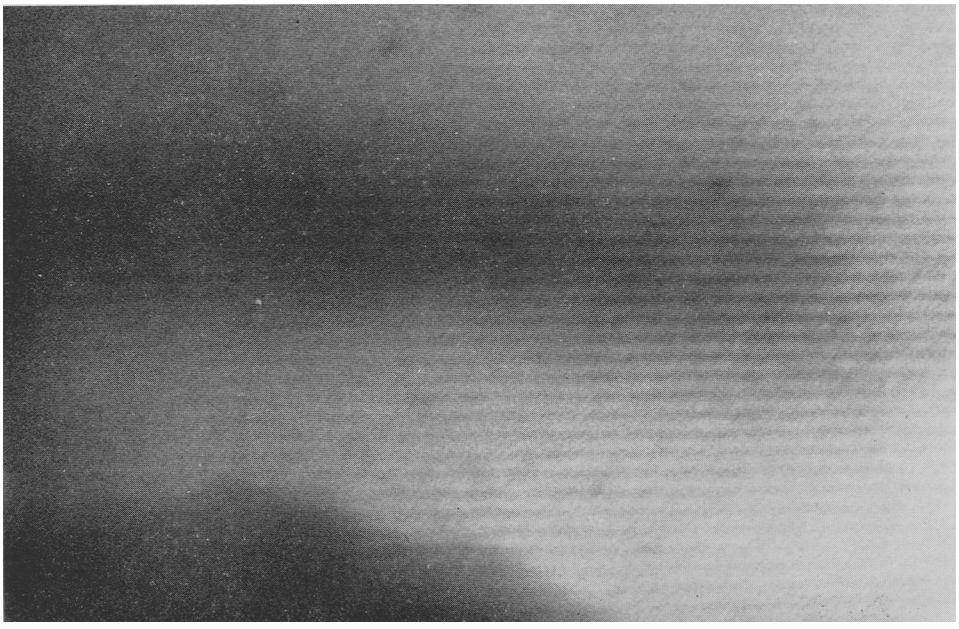

FIG. 5. Direct electron-optical resolution of the antiphase structure in an intermediate plagioclase feldspar. In this case the antiphase domain structure was resolved using the origin spectrum 000 and its associated *f* maxima. The specimen used had composition 70% mol. An, and was previously studied by Gay (1956, table 1, p. 25), where it is referred to as specimen 3. × 530 000.

structure amplitude of the corresponding unit cell at the point in question. Thus, in the present case, while it is permissible to utilize the observed intensity associated with the *a*, *e*, and *f* maxima to derive an average structure for a single large cell of anorthite type, it is not possible to obtain structural information that permits one to distinguish between different large cells within a single domain. The structure amplitudes sampled by the *e* and *f* maxima relate to an average over the appropriate unit cells. In practice it is convenient to consider that the intensity of the *e* maxima are representative of the structure factor at the associated true superlattice point (*b* position) and to proceed with a full structural analysis on this basis.

Having noted that the diffraction data for the intermediate plagioclases, as presented by Bown and Gay, are entirely consistent with strongly degenerate behaviour

due to local ordering under symmetry constraint, we may now examine the evidence for compositional fluctuations in the plagioclases associated with schiller, as set out by Korekawa and Jagodzinski (1967). As already noted the criteria for single-crystal behaviour are also satisfied in this case. Hence the schiller phenomena in labradorite can be explained most easily in terms of spinodal behaviour. This is entirely compatible with the regularity of the schiller structure and the electron-optical observations made by Nissen, Eggmann, and Laves (1967).

It remains to show how the two types of metastable behaviour interact in an intermediate plagioclase showing both antiphase structure and schiller phenomena. A recent, unpublished, electron-optical study of a red schiller labradorite (H.C. 703660, 54·9 wt% An) by the author indicated that, in specimens orientated correctly for the observation of both phenomena simultaneously, the antiphase structure was continuous across the boundaries of the schiller lamellae. At the same time the antiphase lamellae changed both their orientation and spacing gradually across the boundaries and were considerably narrower and less regular in the narrower of the two sets of schiller lamellae. From these observations it was deduced that the schiller boundaries were transitional rather than sharp.

Metastable behaviour in the intermediate plagioclases, and particularly in the labradorites that show schiller phenomena, requires that we consider potential degenerate fluctuations of both order and chemical composition in considering low-temperature, metastable behaviour in this system. While each of these is, *a priori*, permissible, the likely behaviour of the system, as a function of time, involves comparison of the associated free-energy changes and the kinetics of the two basic processes. In each case the rate of development of the degenerate fluctuations must depend on the kinetics of the diffusion of Al and Si. Since local ordering leading to an antiphase structure is likely to be much the faster process in this context, the intermediate plagioclase is likely to move most rapidly, at low temperatures, in the direction of a free energy minimum associated with highly preferred fluctuation waves of antiphase character; at this stage further reduction in free energy may be possible due to the development of fluctuation waves in chemical composition. In this case relatively long-range counter-diffusion of Al and Si is necessary. Thus fluctuation waves involving chemical composition are likely to develop very slowly indeed, since part of the initial driving force, ΔG, has been dissipated during the development of the antiphase structure, and the process of producing degenerate fluctuations of chemical composition now requires the reorientation of the antiphase domains already present.[1]

The present analysis of the low-temperature behaviour of the intermediate plagioclase feldspars, while by no means complete, does provide a logical explanation of the available experimental data, and shows that the theory of symmetry constraints leads to a self-consistent explanation of the phenomena observed. The theory also leads to several additional important conclusions, two of which may be noted here.

[1] Since the energy relationships for subsequent spinodal behaviour depend on the antiphase state of the system it is likely that the favoured k vectors for spinodal behaviour will be strongly dependent on interaction between the two fluctuation wave systems. Thus specimens with different thermal histories may show different schiller planes. Such a phenomenon has in fact been observed (Bøggild, 1924).

The first of these concerns peristerite exsolution phenomena, as studied by electron microscopy by Fleet and Ribbe (1965). Peristerite exsolution structures normally show discrete albite lamellae in a host that, in certain cases, shows antiphase character (*e* maxima). From the present theory it follows that this plagioclase component is metastable and should continue to exsolve albite indefinitely, i.e. the An-rich end of the peristerite field cannot be regarded as the limb of a conventional solvus. That such continuous exsolution is not observed must necessarily be related to the ease of loss of Na and Si from the intermediate plagioclase structure as a function of changing chemical composition. Clearly the continued loss of Na and Si in practice allows the plagioclase to move into the field where behaviour is increasingly dominated by antiphase stability, at which point loss of Na and Si from the antiphase structure becomes a highly cooperative phenomenon, since it must be accompanied by reorientation of a well-established system of regular antiphase lamellae. Thus, on the basis of the present analysis, the nature of the boundary between the field of peristerite exsolution and metastable-intermediate-plagioclase type behaviour must be somewhat diffuse, depending primarily on time-temperature criteria.

It is possible to show, in the same way, that the boundary of the intermediate plagioclase field at high An contents must also be diffuse, since it depends primarily on the probability of permissible fluctuations leading to the development of a true superlattice, i.e. the appearance of true *b* maxima in the diffraction pattern. Electron-optical study of true exsolution phenomena in a bytownite has been described recently by Nissen (1968). In this case also one component corresponds to the metastable antiphase structure and hence similar arguments apply.

Clearly the theory of metastable behaviour associated with symmetry constraints has a wide range of application throughout the plagioclase feldspars. The main advantages of the theory stem from the fact that it is based on a thermodynamic approach that permits one to concentrate on the important features of the problem in hand.

In a more general context the theory is likely to be important in attempting to unravel the behaviour patterns of other non-stoichiometric compounds at low temperatures. It is clear already that it has a large number of possible applications in the field of mineralogy and is immediately relevant in discussing the behaviour of nepheline and mullite, to cite but two examples. It is also clear that, in the experimental study of the associated degenerate fluctuations, the role of the electron microscope will continue to be a very important one.

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[*Manuscript received 24 October 1970*]